

# Développement d'alliages métalliques à gradient de composition pour l'exploration combinatoire des microstructures

Imed-Eddine Benrabah

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# THÈSE

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préparée au sein du Laboratoire SIMaP dans l'École Doctorale I-MEP2

## Développement d'alliages métalliques à gradient de composition pour l'exploration combinatoire des microstructures

## Development of compositional-gradient metallic alloys for combinatorial investigation of microstructures

Thèse soutenue publiquement le **08 janvier 2021**, devant le jury composé de :

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# À vous deux.

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Nomenclature	
N	density of potential atomic sites $(m^{-3})$
$\beta^*$	attachement rate, $(s^{-1})$
Ζ	non-equilibrium Zeldovich factor
$\Delta G^*$	activation energy barrier for nucleation $(J)$
au	incubation time $(s)$
t	isothermal transformation time $(s)$
$k_B$	Boltzmann constant (1.38 $10^{-23} J.K^{-1}$ )
T	absolute temperature $(K)$
M	interface mobility $m.mol.J_{-1}.s_{-1}$
$x_c^{lpha}$	carbon content in ferrite $(at.\%)$
$x_c^{\gamma}$	carbon content in austenite $(at.\%)$
Q	activation energy $(J.mol^{-1})$
R	gas constant $(J.K^{-1}.mol^{-1})$
v	interface velocity $(m.s^{-1})$
$V_m$	molar volume of austenite and ferrite $(m^3.mol^{-1})$
$x_k^{i,\gamma}$	k mole fraction on the austenite side of the interface
$x_k^{i,lpha}$	k mole fraction on the ferrite side of the interface
$J^k_{lpha}$	flux of k atoms in ferrite close to the interface $(mol.m^{-2}.s^{-1})$
$J_{\gamma}^k$	flux of k atoms in austenite close to the interface $(mol.m^{-2}.s^{-1})$
$x_c^{i,lpha}$	mole fraction at the ferrite interface
$x_c^{i,\gamma}$	mole fraction at the austenite interface
$D_c^{\gamma}$	carbon diffusion coefficient in austenite $(m^2.s^{-1})$
z	distance (m)
$\mu_C^\gamma$	chemical potential of carbon in austenite $(J.mol^{-1})$
$\mu^{lpha}_C$	chemical potential of carbon in ferrite $(J.mol^{-1})$
$\mu_X^\gamma$	chemical potential of element X in austenite $(J.mol^{-1})$
$\mu_X^{lpha}$	chemical potential of element in ferrite $(J.mol^{-1})$
$\mu_X^{\gamma,i}$	chemical potential of element at the austenite side of the interface $(J.mol^{-1})$
$\mu_X^{lpha,i}$	chemical potential of element at the ferrite side of the interface $(J.mol^{-1})$
$x_k$	mole fraction of $k$ element
E	free energy of attraction of the solute with the boundary $(J.mol^{-1})$
$C_X$	X element concentration
$\delta$	half width of the interface (m)
$\Delta G_m^{chem}$	molar gibbs energy available as chemical driving force $(J.mol^{-1})$
$\Delta G_m^{fric}$	molar gibbs energy dissipated due to interface friction $(J.mol^{-1})$
$\Delta G_m^{diss}$	molar gibbs energy dissipated due to X diffusion across the interface $(J.mol^{-1})$
$u_X = \frac{x_X}{1 - x_c}$	molar U-fraction of element X
$u_X^0$	alloy nominal U-fraction

# Résumé étendu

This is a long version of french abstract of the manuscript.

#### Introduction

Les innombrables applications des aciers dans le domaine industriel et dans la vie moderne sont dues à la variété des microstructures et des propriétés mécaniques qui peuvent être obtenues par les traitements thermomécaniques ce cet alliage. Les transformations de phase sont le levier principale pour contrôler les propriétés mécaniques des aciers. Les éléments d'alliage jouent un rôle important dans la détermination des microstructures des aciers et donc indirectement sur leurs propriétés mécaniques. Parmi les nombreuses transformations de phases solide-solide, la décomposition de l'austénite en ferrite est certainement la transformation la plus répandue lors de l'élaboration des aciers. Par conséquent, une étude scientifique des mécanismes mis en jeu au cours de cette réaction, ainsi que l'effet des éléments d'alliage et des paramètres des traitements thermique sur l'issue de cette réaction, apparaît donc comme une nécessité pour obtenir les caractéristiques mécaniques désirées et assurer une mise en service fiable des pièces en aciers [1-3]. D'un point de vue théorique, la transformation de l'austénite en ferrite comporte deux étapes, la germination et la croissance. Deux processus interviennent au cours de la croissance de la ferrite à partir de l'austénite, un réarrangement structurel (de fcc à bcc) à l'interface et un processus de diffusion des éléments interstitiels et substitutionels. La cinétique de croissance de la ferrite est fortement conditionnée par le partitionnement des éléments d'alliage de substitution entre les phases parent (austénite) et la phase produit (la ferrite). Ceci est dû à l'écart de diffusivité de plusieurs ordres de grandeur entre l'élément interstitiel rapide (C, N) et les solutés de substitution lents (tels que Si, Cr, Mn, Ni, Mo...). En raison de cette différence de mobilité, la transformation austénite-ferrite peut se faire soit par partitionnement des éléments de substitution et la cinétique de croissance est donc contrôlée par la diffusion lente de ces éléments, soit par un partitionnement négligeable des éléments de substitution entre l'austénite mère et la ferrite en croissance.

Dans ce dernier cas, la réaction est principalement contrôlée par la diffusion du carbone dans l'austénite.

Deux modèles représentant les limites thermodynamiques de la transformation austénite-

ferrite sans partitionnement ont été proposés pour décrire la cinétique de croissance de la ferrite. La différence entre les deux modèles réside dans les considérations thermodynamiques des conditions aux interfaces. Le modèle para-équilibre (PE) considère que seul l'élément interstitiel est en équilibre à l'interface. Le modèle équilibre locale avec partitionnement négligeable (LENP, local equilibrium negligible partitioning) considère que les deux éléments, interstitiel et substitutionel, sont à l'équilibre locale à l'interface en mouvement. L'équilibre de l'élément substitutionel est assuré par un pic (ou spike en anglais) de sa concentration du côté austénite de l'interface de transformation. Les deux modèles ont été utilisés avec succès pour prédire la croissance de la ferrite dans les systèmes ternaires Fe-C-X dans des conditions particulières de température et de composition [4–7]. Cependant, des observations expérimentales ont montré un comportement plus complexe des conditions aux interfaces pendant la croissance de la ferrite dans certains systèmes où ces modèles ont échoué pour prédire la cinétique mesurée. L'un des mécanismes proposés pour expliquer ces observations est que l'interaction des éléments solutés avec l'interface en mouvement  $(\gamma/\alpha)$ , ignorée dans les deux modèles susmentionnés, conduit à une dissipation de la force motrice de transformation et donc à un retardement de la cinétique de la précipitation de la ferrite [8,9]. Cet effet a été appelé « Solute Drag effect » et a été intégré dans une variété de modèles qui ont montré une meilleure aptitude à prédire la cinétique pour de larges gammes de composition et de température dans les systèmes ternaires [10, 11].

La validation des modèles existants décrivant la croissance de la ferrite nécessite une étude expérimentale large et approfondie de l'effet de la composition et de la température. Bien que l'étude de l'effet de la température soit relativement simple, l'évaluation de l'effet de la composition peut être longue et coûteuse, car elle nécessite la fabrication de multiples échantillons avec différentes compositions.

Les approches combinatoires ont été souvent présentées comme une méthodologie efficace pour étudier l'effet de la composition sur les propriétés des matériaux. Les matériaux à gradient de composition ont été utilisés avec succès pour étudier l'effet de la concentration sur les propriétés fonctionnelles (propriétés mécaniques [12,13], conductivités thermique et électrique [14,15]), les évaluations des diagrammes de phase [16], les mesures des coefficients de diffusion [17], et les études de l'effet des solutés sur la cinétique de précipitation dans les alliages d'aluminium [18–20]. De manière occasionnelle, des matériaux à gradient de composition ont également été utilisés pour étudier les transformations de phase dans les aciers [21–23].

Les techniques de caractérisation à haut débit jouent un rôle important dans l'accélération de l'acquisition de données et dans l'optimisation des matériaux [24]. La diffraction des rayons X offre plusieurs caractéristiques intéressantes pour la caractérisation à haut débit, telles que la mesure in situ de l'évolution microstructurale et les caractérisations à haute résolution spatiale [25, 26]. Le couplage de cette technique avec des couches minces à

gradient de composition a permis de cartographier les diagrammes de phase sur une grande partie de l'espace de composition [27]. Récemment, la diffraction des rayons X aux petits angles (SAXS) a été utilisée sur des échantillons à gradient de composition pour étudier la cinétique de précipitation en fonction de la composition [18, 19, 28].

Dans la présente étude, nous proposons une méthodologie complète pour étudier l'effet de la composition sur la cinétique de croissance de la ferrite pendant la transformation austénite-ferrite dans les systèmes ternaires Fe-C-X et quaternaires Fe-C-X<sub>1</sub>-X<sub>2</sub>, où (X, X<sub>1</sub> , X<sub>2</sub> sont des solutés de substitution). La première étape de cette méthodologie consiste à réaliser des couples de diffusion contenant des gradients de X<sub>1</sub> et/ou X<sub>2</sub>. La deuxième étape consiste à effectuer des mesures *in situ* aux rayons X synchrotron pour mesurer les cinétiques de croissance de la ferrite dans les différents systèmes en fonction du temps et de la composition.

#### Procédure expérimentale

Le processus de fabrication des couples de diffusion a été décrit dans le chapitre 3 et comprend trois étapes, comme le montre la figure 1 :

Le soudage par diffusion à l'état solide utilisant la compression uniaxiale à chaud, la décarburation/diffusion à haute température pour générer les gradients de composition des éléments substitutionels, la re-carburation, et enfin, le raffinement de la taille des grains. Puisque cette étude vise à explorer l'effet des éléments de substitution sur la croissance de ferrite intercritique dans les aciers, les couples de diffusion doivent contenir des gradients de composition pour les éléments de substitution avec (idéalement) une teneur en carbone constante. En utilisant les alliages de base énumérés dans le tableau 1, des couples de diffusion contenant un gradient d'éléments substitutionels ont été créés en assemblant un alliage Fe-C binaire avec un alliage Fe-C-X ternaire. Des couples de diffusion contenant des gradients de composition opposés peuvent également être générés en couplant Fe-C-X<sub>1</sub> et Fe-C-X<sub>2</sub>, où X<sub>1</sub> et X<sub>2</sub> sont deux solutés de substitution différents.

Table 1: Composition chimique (en poids %) des différents alliages utilisés pour réaliser les couples de diffusion

Composition %massique	С	Si	Mn	Мо	Cr	Ni	Al	Autres
Fe-C	0.26	0.03	0.004	< 0.002	< 0.002	< 0.002	0.003	< 0.002
Fe-C-Ni	0.26	0.03	0.02	< 0.002	< 0.002	< 0.002	0.003	0.98
Fe-C-Mn	0.26	0.03	0.3	< 0.002	< 0.002	< 0.002	0.003	< 0.002
Fe-C-Mo	0.26	0.02	0.004	0.21	< 0.002	< 0.002	0.003	< 0.002
Fe-C-Cr	0.26	0.02	0.004	< 0.002	1.0	< 0.002	0.003	< 0.002
Fe-C-Si	0.26	1.54	0.004	< 0.002	< 0.002	< 0.002	0.006	< 0.002



Figure 1: Illustration schématique des différentes étapes de fabrication de matériaux à gradients de composition. 1- compression uniaxiale à chaud. 2- Décarburation et traitements de diffusion à haute température. 3- Traitement de re-carburation. 4- Raffinement de la taille des grains.

Le soudage à l'état solide entre les différents alliages a été réalisé par compression uniaxiale à chaud, au cours de laquelle les échantillons ont été maintenus ensemble sous une contrainte de compression de 20 MPa à 900°C pendant 1 h, dans une atmosphère d'Ar/2%  $H_2$  à 5 mbar, en utilisant un dispositif de compression fabriqué au sein du laboratoire SIMaP. Au cours de cette étape, les couples ont été enveloppés dans une feuille de tantale pour les protéger de l'oxygène résiduel.

L'étape suivante consiste à générer des gradients de composition des éléments substitutionels par diffusion à haute température. Le traitement doit être effectué à une température où l'alliage est monophasé et où les éléments de substitution ont une mobilité suffisante pour former des gradients de taille millimétrique. Ces conditions sont remplies dans le domaine ferrite delta monophasée à haute température. Étant donné la teneur initiale en carbone des alliages de cette étude (0,26 % en poids), ils ne peuvent être entièrement ferritisés avant que le liquide ne commence à se former. Pour contourner cet obstacle, le traitement de diffusion a été effectué dans une atmosphère décarburante, ce qui a permis d'obtenir des échantillons sans carbone avec des gradients de composition en éléments substitutionnels d'échelle millimétrique. Par la suite, le carbone a été réintroduit dans ces échantillons en utilisant un traitement de carburation dans un mélange  $CO/CO_2$ .

Les traitements de décarburation/diffusion ont été effectués à des températures comprises entre 1400°C et 1460 °C selon la composition des alliages de base, pendant 72 h sous un flux d'Ar/2% H<sub>2</sub> à une pression de 1,3 bar. Les échantillons ont ensuite été carburés à 0,2 %C à 1100 °C pendant 72 h dans une atmosphère de carburation au CO/CO<sub>2</sub>, à une pression de 1 bar. Les échantillons re-carburés ont été traités à 1300 °C pendant 2 h dans de l'Ar sec pour homogénéiser la teneur en carbone sur l'ensemble de l'échantillon. La figure 2 montre un exemple des profils de composition obtenus après les traitements de décarburation et de recarburation d'un couple de diffusion entre deux alliages ternaires Fe-C-1Ni et Fe-C-1Cr. Les résultats montrent des profils de concentration de 5 mm pour le Cr et le Ni et une teneur en carbone homogène d'environ 0,2 %.



Figure 2: Profils de composition mesurés à l'aide de la microsonde de Castaing sur l'interface Fe-0.26C-1Ni/Fe-0.26C-1Cr (% en poids) après les traitements de décarburation et de recarburation.

Toutefois, l'utilisation des traitements prolongés à haute température (72h à 1400  $^{\circ}C$  + 72h à 1100 °C) sans déformation a rendu le contrôle de la taille des grains particulièrement difficile avec cette méthode. La taille moyenne des grains obtenue après ces deux traitements était de 4-7 mm, ce qui ne convient pas aux expériences de diffraction des rayons X. La déformation plastique doit être utilisée avec précaution pour affiner la microstructure par recristallisation, car une distribution inhomogène de la déformation à travers l'épaisseur peut provoquer une perturbation du gradient de concentration, comme observé durant cette étude. Une façon d'affiner la taille des grains sans déformation plastique consiste à utiliser des traitements thermiques à cycle rapide, comme le montre la figure 3. À cette fin, les échantillons ont d'abord été austénitisés au 880°C pendant 1 minute dans un bain de sel, puis trempés à l'eau pour obtenir une structure entièrement martensitique. Ensuite, les échantillons ont été traités à 880°C pendant 7 secondes, puis trempés à l'eau, et l'opération a été répétée 5 fois, comme le montre la figure 3. Les traitements thermiques à cycle rapide ont permis de réduire la taille moyenne des grains des couples de diffusion à 200 - 250  $\mu$ m. Pour affiner d'avantage la microstructure, les couples de diffusion ont été laminés à froid de manière à ce que la direction de laminage soit perpendiculaire au gradient de composition. Avant l'étape de laminage à froid, les échantillons ont été trempés à 660 °C pendant 5h pour générer une microstructure ductile. Pour éviter l'inhomogénéité de la déformation, seulement 20% de réduction a été appliquée sur les couples de diffusion. A la fin, les échantillons ont été traités à 900 °C pendant 1 min pour recristalliser la microstructure. En conséquence, la nouvelle taille moyenne des grains après traitements thermiques cycliques rapides et laminage à froid était d'environ 50-80  $\mu$ m ce qui est bien adapté aux expériences de diffraction des rayons X.



Figure 3: Illustration schématique des différentes étapes utilisées pour le raffinement de la taille des grains, les traitements thermiques cycliques, la trempe, le laminage à froid et la recristallisation.

Les expériences in situ de diffraction des rayons X à haute énergie (DRXHE) ont été réalisées sur la ligne de faisceaux P21.2 du synchrotron DESY PETRA III à Hambourg, en Allemagne, en utilisant une énergie de 82 keV ( $\lambda = 0.1512$  Å). Pour maximiser le nombre de grains dans le volume diffractant, une taille de faisceau de  $1 \ge 0.08 \text{ mm}^2$  (80  $\mu m$  le long du gradient de concentration, 1 mm perpendiculairement) a été utilisée. Des échantillons cylindriques, de 30 mm de longueur et de 3 mm de diamètre, ont été usinés à partir des couples de diffusion. Les couples de diffusion ont été chauffés à l'aide d'un four à rayonnement spécialement conçu pour effectuer des traitements thermiques avec une rotation contrôlée de l'échantillon (Fig.4). Le chauffage est obtenu par un ensemble de lampes entourant l'échantillon. Le porte-échantillon rotatif minimise les effets potentiels de la texture et de la taille de grains sur les clichés de diffraction. Un flux d'argon de haute pureté a été utilisé pour protéger l'échantillon et empêcher la décarburation et l'oxydation pendant les expériences. Pour une mesure résolue dans le temps et dans l'espace de la cinétique de croissance de la ferrite pendant les traitements thermiques, les couples de diffusion ont été scannés le long du gradient de composition sur 3 à 11 mm en utilisant le moteur vertical de la ligne.



Figure 4: Dispositif expérimental utilisé pour les expériences DRXHE.. Le couple de diffusion a été déplacé le long de son gradient de composition dans la direction Z et un système de rotation a été utilisé pour maximiser le nombre d'orientations analysées dans le volume diffractant.

Les détails des traitements thermiques pour les expériences DRXHE *in-situ* étaient les suivants. Les échantillons à gradient de composition ont été chauffés à 910°C (970°C pour les échantillons contenant du Si) à 10°C/s et maintenus 30 s à cette température pour atteindre une austénitisation complète. Les échantillons ont ensuite été rapidement refroidis à  $60^{\circ}$ C/s à une température inter-critique (730°C, 750°C, et 775°C) et maintenus 15 min à cette température pour suivre la transformation de phase austénite-ferrite. Enfin, les échantillons ont été trempés à la température ambiante à  $60^{\circ}$ C/s. Les anneaux de diffraction de Debye-Scherer obtenus ont été convertis en clichés de diffraction 1D par intégration circulaire à l'aide du logiciel pyFAI. Le raffinement de Rietveld a été utilisé pour calculer les fractions de phase à l'aide du logiciel FullProf.

# Cinétiques de transformations de phase pour des compositions fixes

Le chapitre 4 présente un aperçu des mesures de cinétiques de croissance de la ferrite réalisées par DRXHE *in-situ* sur des alliages Fe-C-X (X: 0.3Mn, 0.7Mn, 1Mn, 1Ni, 0,2Mo et 1Cr) et un Fe-C-1Mn-1Cr de composition fixe. Ces résultats ont été ensuite comparés aux prédictions des modèles classiques LE et PE ainsi qu'une version modifiée du modèle *solute drag* initialement développé par Zurob et al. [11] pour décrire la cinétique

de croissance de la ferrite en fonction de la teneur en éléments solutés. Les modifications apportées à la version originale du modèle concernent essentiellement la description thermodynamique de l'interface. D'une part, la ségrégation du carbone à l'interface a été prise en compte pour répondre aux observations expérimentales rapportées dans la littérature [29]. Ceci a été réalisé en modifiant le paramètre d'interaction Fe-C dans l'interface. D'autre part, l'interaction entre le carbone et les éléments substitutionels, ainsi que l'interaction mutuelle entre les deux éléments substitutionels ont été fixées à des valeurs similaires à celles de l'austénite. Le modèle comporte un paramètre d'ajustement, le Fe-X qui représente l'interaction entre l'élément substitionel et l'interface. Le tableau 2 résume les différents systèmes étudiés, leurs composition, température de traitement isotherme, taille de grain ainsi que les fractions finales mesurées et celles prédites par les différents modèles.

Système	T(°C)	f(Exp.)	f(LE)	f(PE)	f(SD)	Taille de grain $(\mu m)$
Fe0.26C0.3Mn	730	58	58	64	60	50
Fe0.26C0.3Mn	750	49	47	55	48	80
Fe0.26C0.3Mn	775	27	28	38	28	120
Fe0.26C0.7Mn	730	47	41	59	47	120
Fe0.26C0.7Mn	750	27	27	47	27	120
Fe0.26C0.7Mn	775	10	0.5	25	2	120
Fe0.26C1Mn	730	26	25	52	25	120
Fe0.26C1Mn	750	9	8	38	8	120
Fe0.26C1Mn	775	<2	1	13	1	120
Fe0.22C1Ni	730	57	60	67	56	40
Fe0.22C1Ni	750	40	44	53	41	40
Fe0.22C1Ni	775	2	12	21	7	70
Fe0.26C1Cr	750	48	52	55	48	50
Fe0.26C1Cr	775	23	30	39	22	120
Fe0.26C02Mo	730	62	65	65	62	50
Fe0.26C02Mo	750	55	60	60	56	50
Fe0.26C02Mo	775	40	46	46	40	60
Fe0.26C1Mn1Cr	730	31	11	50	30	30

Table 2: Comparaison entre la fraction finale mesurée (%) et celles prédites à l'aide des modèles LE, PE et SD pour l'ensemble des systèmes étudiés.

Ces résultats sont résumés et commentés par système dans le texte suivant.

Le système Fe-C-Mn : L'effet du manganèse sur la cinétique de la transformation austénite-ferrite a été étudier en utilisant trois compositions différentes du manganèse, 0.3 %, 0.7 % et 1 % (toutes les compositions sont en poids) et à trois températures

différentes, 730°C, 750°C et 775°C. Pour toutes les conditions étudiées, le modèle LE été en mesure de prédire les résultats expérimentaux en termes de cinétiques et de fraction finale atteinte à la fin du maintien isotherme. Le modèle PE, par contre, a prédit des cinétiques plus rapides que celles mesurées et des fractions finales supérieures à celles observées. Le modèle 'solute drag' arrivait bien à prédire les cinétiques expérimentales en utilisant un même paramètre d'ajustement (Fe-Mn) pour toutes les températures et les concentrations en manganèse. Les facteurs d'enrichissement en manganèse à l'interface calculés par le modèle ont été comparables avec les mesures expérimentales réalisées à la sonde atomique [30]. Le calcul de l'énergie de ségrégation intrinsèque du manganèse a montré que cet élément ségrège peu à l'interface austénite/ferrite et que son affinité à l'interface est accentuée par la présence du carbone.

Le système Fe-C-Ni : La cinétique de croissance de la ferrite dans le système Fe-C-Ni a été étudié en utilisant un échantillon de composition Fe-0.22C-1Ni et à trois températures, 730°C, 750°C et 775°C. La comparaison avec les modèles a montré que le modèle LE prédit des cinétiques plus rapides que celles mesurées expérimentalement et que la différence entre le calcul et les mesures augmente avec la température. Le modèle 'solute drag' a été capable de reproduire les mesures expérimentales à deux températures, 730°C et 750°C en utilisant aussi un seul paramètre d'ajustement (Fe-Ni). Cependant, les paramètres utilisés dans la modélisation prédisent une ségrégation élevée du nickel à l'interface contrairement à ce qui est reporté dans la littérature où cet élément est connu pour ne pas ségréger à ce type d'interface.

Le système Fe-C-Mo : Les cinétiques mesurées pendant la transformation austénite ferrite dans le système Fe-C-0.2-Mo à trois températures différentes, 730°c, 750°C et 775°C ont été aussi comparées aux prédictions des différents modèles. La cinétique observée expérimentalement était plus lente que celle prédite par les deux modèles PE/LE. Ceci indique la présence d'une énergie dissipée supplémentaire liée à la diffusion du molybdène à travers l'interface. La comparaison avec les prédictions du modèle 'solute drag' montrent un accord parfait entre ces deux résultats. Les prédictions du modèle montrent une ségrégation forte du molybdène à l'interface due à la fois à son énergie intrinsèque de ségrégation et à son interaction forte avec le carbone.

Le systeme Fe-C-Cr : La transformation austénite ferrite a été étudiée dans le système ternaire Fe-C-1Cr à deux températures, 750°C et 775°C. Encore une fois, le modèle 'solute drag' a bien prédit les cinétiques mesurées contrairement au deux autres modèles, PE et LE. Les résultats du modèle montrent que le chrome ségrège à l'interface essentiellement due à la présence du carbone et que sa ségrégation intrinsèque à l'interface est faible.

Le système Fe-C-1Mn-1Cr : La cinétique de transformation austénite-ferrite dans le système quaternaire Fe-C-1Mn-1Cr a été étudiée à 730°C. La version quaternaire du modèle 'solute drag' a été utilisée pour prédire la cinétique de transformation dans ce système. Les paramètres d'interaction Fe-Mn et Fe-Cr ont été tirés des résultats de la modélisation dans les systèmes ternaires Fe-C-Mn et Fe-C-Cr, respectivement. Un bon accord a été trouvé entre les résultats de la modélisation et les mesures expérimentales. Les valeurs de ségrégations des deux éléments à l'interface montrent une similitude pour le manganèse avec le cas ternaire et une ségrégation plus faible que celle calculée pour le chrome dans le système ternaire.

### Cinétique de précipitation de la ferrite dans les alliages ternaires Fe-C-X et quaternaires Fe-C- $X_1$ - $X_2$ à gradient de composition

La méthodologie combinatoire développée a été utilisée pour étudier la cinétique de croissance de ferrite dans 5 systèmes Fe-C-X ternaires (X : Ni, Mn, Si, Mo et Cr) ainsi que dans 3 systèmes Fe-C-X<sub>1</sub>-X<sub>2</sub> quaternaires (X<sub>1</sub>, X<sub>2</sub> : Ni, Cr et Mo) en fonction de la composition du soluté et à différentes températures. Les résultats obtenus sont présentés dans les chapitres V et VI. De la même manière, les résultats ont été comparés aux prédictions des modèles cités plus haut.

#### Système Fe-C-Ni

Un exemple des résultats obtenus pour un couple de diffusion Fe-C-Ni est donné dans la suite pour montrer l'importance de l'utilisation de la méthode combinatoire dans l'étude des transformations de phase.

Un couple de diffusion entre Fe-C et Fe-C-1Ni a été utilisé pour étudier l'effet de la teneur en nickel sur la cinétique de précipitation de la ferrite à trois températures différentes : 730 °C, 750 °C et 775 °C. Pour cela, le couple de diffusion a été austénitisé à 910 °C, trempé à la température intercritique (730 °C, 750 °C ou 775 °C) et maintenu à cette température pendant 15 min. La teneur en nickel mesurée à l'aide de la microsonde varie de 0 à 1 (% en poids) sur une distance de 6 mm. Une teneur constante en carbone de 0,22% a été mesurée à travers le couple de diffusion. Un exemple de l'évolution de la fraction de ferrite obtenue en fonction du temps à travers le couple de diffusion traité à 730 °C est présenté sur la figure 5-a. Les oscillations observées sur la fraction de ferrite correspondent à la translation de l'échantillon le long du gradient de nickel. Pour avoir une meilleure lecture des données, les fractions de ferrite obtenues sont triées en fonction de la composition.

Dans une première étape, l'évolution des fractions en fonction du temps à chaque position du moteur est extraite en combinant la figure 5-a et la figure 5-b. Ensuite, chaque position du moteur est liée à ses teneurs en carbone et en nickel correspondantes à l'aide de mesures EPMA (figure 5-c). Sur la figure 5-d, chaque courbe correspond à l'évolution de la fraction de ferrite en fonction du temps d'une seule composition de nickel. Compte tenu de la taille



Figure 5: Évolution de la fraction volumique de la ferrite en fonction du temps pendant le maintien isotherme du couple de diffusion Fe-C/Fe-C-Ni à 730 °C. Les oscillations représentent la translation de l'échantillon le long du gradient de composition. b) Position du moteur en fonction du temps pendant le maintien isotherme. c) Teneur en nickel et en carbone dans le couple de diffusion en fonction de la position du moteur. d) Évolution de la fraction de ferrite en fonction du temps et de la teneur en nickel pendant le maintien isotherme.

du faisceau de 80  $\mu$ m utilisée lors de ces expériences DRXHE, la variation maximale de la composition du nickel dans le faisceau est 0,018 (% en poids). Ce résultat illustre l'effet de la teneur en nickel sur la croissance de la ferrite. Les cinétiques mesurées, ainsi que la fraction de ferrite atteinte au plateau, diminuent avec l'augmentation de la teneur en nickel. Cette dépendance de cinétique de transformation par rapport au nickel a été obtenue à l'aide d'une seule expérience illustrant l'efficacité du couplage entre les couples de diffusion et la DRXHE pour fournir des bases de données riches qui peuvent être utilisées pour comprendre les transformations de phases dans les aciers.

Les résultats obtenus ont été comparés aux prédictions des différents modèles en fonction de la teneur en nickel et la température et en termes de la fraction atteinte après 15 min du maintien mais aussi en termes de cinétique. La figure 6 montre une carte thermique montrant l'évolution de la ferrite en fonction du temps et de la composition en nickel, mesurée expérimentalement à 730°C et calculée par les trois modèles, LE, PE et SD à la même température. Les résultats montrent bien que les deux modèles classiques, LE et PE prédisent des cinétiques plus rapides que celles mesurées expérimentalement. Le modèle SD prédit assez bien les cinétiques observées sur toute la plage de composition comme montré sur la figure 6 mais aussi sur la figure 7 qui représente la fraction de ferrite mesurée et calculée après 15 min du maintien isotherme à 730 °C. Sur toute la plage de composition, le même paramètre d'ajustement Fe-Ni a été utilisé pour modéliser la croissance de la ferrite durant le maintien isotherme à 730°C mais aussi pour 750°C. Pour 775°C, il a été remarqué que le modèle surestime les fractions mesurées à des taux en nickel supérieur à 0.7 % indiquant une limitation du modèle solute drag pour la prédiction des cinétiques dans les cas où une faible force motrice de transformation est disponible.



Figure 6: Cartes thermiques représentant l'évolution de la fraction de ferrite en fonction du temps et de la composition du nickel à 730°C, telle que mesurée par des mesures de diffraction des rayons X aux hautes énergies (Exp.) et celles modélisées par des calculs de solute drag (SD), des modèles de para-équilibre (PE) et l'équilibre local avec partitionnement négligeable (LENP).

Les résultats du calcul 'solute drag' ont encore une fois prédit que le nickel ségrège considérablement à l'interface contrairement aux mesures sonde atomique rapportées dans la littérature. En revanche, une mesure à la sonde atomique a été réalisée sur un échantillon étudié durant ce travail et les résultats ont montrés la présence d'un pic de nickel à une



Figure 7: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en nickel à 730°C.

interface ferrite/perlite. Même si l'interface ne représente pas les conditions réelles de transformation austenite ferrite, ce résultat indique la nécessité d'étudier la ségrégation du nickel aux interfaces formées pendant les traitements de précipitation.

#### Système Fe-C-Mn



Figure 8: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en manganèse à 730°C.

L'effet de la composition en manganèse sur la cinétique de transformation austénite-ferrite a été étudié en utilisant un couple de diffusion contenant un gradient de manganèse entre 0 % et 1 %. La comparaison entre les cinétiques mesurées à deux températures, 730°C et 750°C et celles calculées par les modèles montre que le modèle LE arrive à bien prédire les cinétiques expérimentales contrairement au modèle PE qui surestime les mesures sur toute la plage de composition et pour les deux températures. Un exemple de cette comparaison est montré sur la figure 8 pour la température 730°C. Les cinétiques calculées par le modèle SD ont été aussi en bon accord avec les mesures. Le paramètre d'ajustement, Fe-Mn était le même sur toute la plage de composition en manganèse et pour les deux températures. Les calculs des énergies intrinsèques de ségrégation du manganèse à l'interface montrent encore une fois que cet élément ségrège à l'interface, principalement en raison de la présence du carbone.

#### Système Fe-C-Si

L'effet du silicium sur la décomposition de l'austénite en ferrite a été étudiée en utilisant un couple de diffusion contenant un gradient du silicium allant de 0 % jusqu'à 1.2 % sur une distance de 12 mm couplé avec un gradient de carbone allant de 0.24 % jusqu'à 0.18 % sur la même distance. Ces résultats ont été comparés aux prédictions des différents modèles. Un exemple de cette comparaison est montré sur la figure 9 pour la température 730°C. Les deux modèles classiques, LE et PE prédisent des cinétiques plus rapides que celles mesurées expérimentalement ainsi que des fractions finales plus élevées que celles enregistrées pour les trois températures et sur toute la plage de composition en silicium. Le paramètre d'ajustement Fe-Si qui a permit d'avoir un bon accord entre les calculs 'solute drag' et les mesures était indépendant de la composition en silicium, mais il diminue en diminuant la température. La ségrégation de silicium à l'interface diminue en augmentant la température. L'énergie de ségrégation intrinsèque du silicium calculée à partir des résultats de la modélisation indique que cet élément a une forte ségrégation à l'interface austénite ferrite, mais que cette ségrégation est diminuée par la présence du carbone à l'interface due à l'interaction répulsive entre le silicium et le carbone.

#### Système Fe-C-Mo

L'effet d'un autre élément alphagène, le molybdène, sur la cinétique de transformation a été étudié à trois températures différentes, 730°C, 750°C et 780°C en utilisant un échantillon à gradient de composition en molybdène allant de 0 % à 0.2 % sur une distance de 1.5 mm. De la même manière que le système Fe-C-Si, les cinétiques prédites par les deux modèles PE et LE ont été plus rapides que celles mesurées expérimentalement. La comparaison entre les fractions finales mesurées et calculées avec les différents modèles est montrée sur la figure 10 pour la trois températures. Un bon accord entre les cinétiques calculées par le modèle SD et les résultats de la DRXHE a été obtenu en utilisant le même paramètre d'interaction Fe-Mo pour toute la plage de composition et aux trois températures. Contrairement au silicium, le molybdène a une interaction attractive avec



Figure 9: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en silicium à 730°C.

le carbone et la ségrégation élevée de cet élément à l'interface austénite ferrite obtenue par les calculs SD est due à la fois à son énergie de ségrégation intrinsèque aux interfaces  $\alpha/\gamma$  couplée à son affinité élevée pur le carbone.



Figure 10: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en molybdène à 730°C (noir), 750°C (bleu) et 780°C (rouge).

#### Système Fe-C-Cr

Le dernier élément étudié est le chrome. Ceci a été effectué en utilisant un couple de diffusion comportant un gradient du chrome allant de 0 % à 1 % sur une distance de 6.5 mm et traité à 750°C. Le modèle LE prédit avec un bon accord les fractions mesurées en

fin du traitement isotherme mais surestime les cinétiques de transformations enregistrées à des taux de chrome supérieur à 0.5 %. Le modèle solute drag a réussi à prédire à la fois les cinétiques mesurées ainsi que les fractions finales (Fig.11) en utilisant le même paramètre d'ajustement pour toute la plage de composition en chrome. Les calculs SD suggèrent que cet élément ségrège à l'interface austénite-ferrite due principalement à la présence du carbone et que son énergie intrinsèque de ségrégation à l'interface est faible.



Figure 11: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en silicium à 750°C.

En conclusion de chapitre, il a été intéressant de rappeler l'intérêt de la méthodologie combinatoire développée durant ce travail dans l'étude des transformations de phase dans les aciers. Il a été montré que le modèle solute drag été capable de prédire les cinétiques mesurées sur toute une plage de composition de l'élément X en utilisant un seul paramètre d'ajustement, le paramètre d'interaction Fe-X à l'interface.

#### Système Fe-C-Ni-Mo

La même méthodologie a été utilisée pour étudier la cinétique de transformation austénite ferrite dans les systèmes quaternaires Fe-C-X<sub>1</sub>-X<sub>2</sub>. Pour ceci, des couples de diffusion contenant des gradients de compositions opposés des élément X<sub>1</sub> et X<sub>2</sub> ont été utilisés. L'effet des éléments nickel et molybdène sur la cinétique de croissance de la ferrite a été étudié à trois températures, 730°C, 750°C et 775°C en utilisant un échantillon à gradient de composition du nickel et du molybdène allant de 0%Ni (Resp. 0.2%Mo) à 1%Ni (Resp. 0%Mo). Les résultats ont été, comme pour les systèmes ternaires, comparés aux prédictions des modèles PE, LE et SD. Un exemple de cette comparaison est montré sur la figure 12 pour la température 730°C. Le modèle PE prédit des cinétiques plus rapides que celles mesurées expérimentalement sur l'ensemble du gradient du nickel et molybdène et aux trois températures. Un bon accord a été trouvé entre les résultats de la modélisation LE et les mesures à 750°C en termes de fractions finales. Le modèle cependant prédit des cinétiques plus rapides que celles enregistrées. Pour les deux autres températures, le modèle (LE) échoue à prédire et les cinétiques et les fractions finales atteintes à la fin du traitement isotherme.



Figure 12: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en nickel et molybdène à 730°C.

Pour la modélisation solute drag, les paramètres d'interaction Fe-Ni et Fe-Mo ont été tirés dans un premier temps des résultats de la modélisation des systèmes ternaires Fe-C-Ni et Fe-C-Mo à des températures similaires. Ces paramètres ont été utilisés pour modéliser les cinétiques obtenues aux extrémités du couple de diffusion Fe-C-Ni-Mo qui sont aussi des compositions ternaires avant d'être utilisé sur l'ensemble du gradient de composition du couple de diffusion à condition que le modèle arrive à bien prédire les cinétiques expérimentales pour les compositions ternaires du couple quaternaire. Dans le cas contraire, une nouvelle calibration de ces paramètres a été effectuée sur ces compositions avant d'être généralisée sur l'ensemble du couple de diffusion. Cette méthode de calibration reste valable pour tous les autres systèmes étudiés.

Pour le système Fe-C-Ni-Mo, un bon accord a été trouvé entre les résultats de la modélisation solute drag et les mesures expérimentales en termes de cinétiques et aussi les fractions finales, en utilisant les mêmes paramètres d'interaction Fe-Ni et Fe-Mo que ceux utilisés dans les systèmes ternaires pour deux températures, 730°C et 775°C. Cependant, le paramètre Fe-Ni qui a donné le meilleur accord avec l'expérience à 750°C était différent de celui utilisé pour le système ternaire à la même température.

Les calculs des facteurs d'enrichissement des deux éléments montrent des niveaux de ségrégations similaires à ceux calculés pour les systèmes ternaires pour les deux éléments et

pour les deux températures 730 °C et 775 °C. De la même manière les énergies intrinsèques de ségrégation des deux éléments étaient comparables à celles obtenues pour les ternaires. Cependant, des niveaux de ségrégation différents ont été calculés pour le nickel à 750°C comparé aux résultats du système ternaire à la même température. Ceci est dû à la différence du paramètre d'interaction Fe-Ni utilisé dans les deux systèmes, Fe-C-Ni-Mo et Fe-C-Ni à 750°C.

#### Système Fe-C-Ni-Cr

L'effet des concentrations du nickel et chrome sur la cinétique de transformation austénite ferrite a été étudié à deux températures, 750 °C et 775 °C en utilisant un couple de diffusion contenant des gradients opposés de nickel et chrome allant de 0%Ni (Resp. 1%Cr) à 1%Ni (Resp. 0%Cr). La comparaison des résultats avec les prédictions des différents modèles a montré que le modèle PE échoue complètement à prédire l'évolution de le cinétique en fonctions de la composition en nickel et en chrome, pareillement que pour tout les autres systèmes étudiés durant cette thèse. Le modèle LE prédit assez bien les cinétiques obtenues pour le côté riche en chrome (surtout à 775 °C), mais ses prédictions commencent à diverger des mesures en augmentant le taux du nickel. Un exemple de cette comparaison est montré sur la figure 13 pour la température 750°C. Les mesures expérimentales ont été en bon accord avec les prédictions du modèle SD



Figure 13: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en nickel et chrome à 750°C.

sur toute la plage de composition et pour les deux températures. Le paramètre Fe-Ni utilisé dans la modélisation était le même que celui utilisé pour les ternaires. Pour le paramètre Fe-Cr, la même valeur utilisée dans le système Fe-C-Cr à 750°C a été utilisé pour le système quaternaire à la même température. A 775°C, un ajustement de ce paramètre était nécessaire due à l'absence de données concernant ce paramètre à cette température. Les niveaux de ségrégation ainsi que les énergies intrinsèques de ségrégation à l'interface des deux éléments, le nickel et le chrome, étaient similaires à ceux calculés pour les ternaires.

#### Système Fe-C-Cr-Mo

Pour finir, l'effet de la composition des éléments chrome et molybdène a été étudié à 750°C et 775°C en utilisant un échantillon à gradient de composition en chrome et en molybdène allant de 0%Cr (Resp. 0.2%Mo) à 1%Cr (Resp. 0%Mo) sur une distance de 1.5 mm. La comparaison entre ces résultats et les prédictions des différents modèles a montré que le modèle LE, contrairement au cas précédent (FeCNiCr) échoue à prédire les cinétiques mesurées expérimentalement sur toute la plage de composition en chrome et en molybdène et pour les deux températures. Ceci semble lié à la différence en teneur en carbone entre les deux systèmes (0.26 % pour le cas présent et 0.2 pour le cas précédent FeCNiCr). Un exemple de cette comparaison est montré sur la figure 14 pour la température 750°C. De la même manière que pour les autres systèmes, le modèle solute drag prédisait assez bien les mesures de cinétiques et les fractions finales. Le paramètre d'interaction Fe-Mo était le même que celui utilisé pour le système ternaire Fe-C-Mo ainsi que pour le système quaternaire Fe-C-Ni-Mo et pour les deux températures. Le paramètre interaction Fe-Cr était le même utilisé pour le système Fe-C-Cr et aussi le système Fe-C-Ni-Cr à 750°C. Cependant, une différente valeur de ce paramètre était nécessaire pour modéliser la cinétique de croissance de la ferrite à 775°C que celle utilisé pour le système Fe-C-Ni-Cr à la même température. Ce dernier résultat suggère un effet du carbone important sur la cinétique qui n'est pas bien pris en compte par le modèle solute drag. Une piste serait de bien calibrer le paramètre d'interaction Fe-C à l'interface en se basant sur des mesures expérimentales de ségrégation du carbone à l'interface dans différents systèmes Fe-C-X et idéalement à différente températures.

En conclusion de ce chapitre, ces résultats ont encore une fois bien exposé l'efficacité de la méthodologie développée durant ce travail pour la génération rapide et large des données sur les cinétiques de transformation de phase en utilisant un nombre très limité d'expériences. L'extension du modèle solute drag pour les systèmes quaternaires a montré une efficacité prometteuse de ce modèle pour la prédiction des cinétiques de précipitation de ferrite même dans des systèmes plus complexes en utilisant les paramètres d'ajustement calculés à partir des systèmes plus simples, les ternaires. Cependant certains points doivent être étudiés plus en profondeur concernant l'effet du carbone sur la ségrégation des éléments à l'interface comme cela a été remarqué pour le chrome.



Figure 14: Comparaison entre les fractions de ferrite mesurées après 900 s (cercles ouverts) et les prédictions des modèles PE (triangles), LE (cercles remplis) et solute drag (croix) en fonction de la teneur en chrome et molybdène à 750°C.

#### Conclusion

En fin de ce manuscrit, le lecteur peut noter que la méthodologie combinatoire développée durant ce travail a permis de générer un nombre très important de données de transformation de phase austénite-ferrite, qui est probablement plus important que le nombre de toutes les cinétiques rapportées déjà dans la littérature et ceci en utilisant un nombre très limité d'échantillons et d'expériences. La comparaison entre ces résultats et les prédictions des différents modèles a permis de noter quelques points importants. Il a été montré que le modèle PE échouait à prédire les cinétiques de transformations pour toutes les conditions étudiées. Nous avons aussi vu que le modèle LE ne peut pas être utilisé pour décrire entièrement la cinétique de transformation austénite ferrite sur l'ensemble de gradient de composition dans les systèmes Fe-C-Ni et Fe-C-Mn, où il est généralement indiqué que le modèle LE peut être considéré comme un état naturel de précipitation de la ferrite. La version modifiée du modèle solute drag a été utilisée avec succès pour prédire les cinétiques de transformation dans les différents systèmes étudiés. Les calculs ont montré que le paramètre d'interaction Fe-X est indépendant de la composition mais peut changer avec la température. Dans les systèmes quaternaires, le modèle arrive aussi à bien prédire les cinétiques mesurées en utilisant les paramètres d'ajustement calibrés à partir des systèmes ternaires.

En perspective de ce travail, il serait intéressant de reprendre la même méthodologie pour étudier la cinétique de précipitation de la ferrite dans d'autres systèmes. De plus, la même procédure peut être utilisée pour étudier d'autres transformation de phases dans les aciers, comme la transformation bainitique mais aussi pour étudier toutes autres transformations de phase dans d'autres systèmes métalliques. Pour le côté modélisation, il serait maintenant indispensable de développer les présents modèles pour arriver à suivre le nombre croissant de données expérimentales. Une solution intéressante serait peut-être l'utilisation d'approches d'apprentissage automatique couplé avec les riches bibliothèques expérimentales générées par la présente méthodologie pour étudier de nouvelles plages de paramètres.

# Introduction

Steel has had an important impact on human history from ancient times where iron replaced bronze in weaponry to modern steel industry (after 1856, the invention of the Bessemer process) where steel is exploited in almost every domain, from buildings and infrastructures to automotive and aircrafts. Additionally, since the Bessemer process, steel has a very low production cost, when compared to other metallic alloys. As an indication of the importance of steel in industry, the world steel production is more than a billion tons every year when the second most produced metal, aluminum has a production of 70 million tons per year [3, 31, 32]. For these reasons, steel is the most widely used but also the most recycled metallic material on Earth, due to its inherent magnetism and its endless life cycle. One reason that made steel dominant in the modern industry is the large variety of microstructures and properties that can be obtained using thermo-mechanical treatments. Alloyed steels allow obtaining more advanced properties by adding specific alloying elements at appropriate levels. Depending on the chemical composition and temperature, alloyed steels can exhibit different mixtures of phases. Tailoring microstructures by means of solid-solid phase transformations is by far the main tuning parameter to control mechanical properties in steels. Among a large variety of solid-solid phase transformations, austenite-to-ferrite (and its related products martensite and bainite) is usually the most encountered reaction when processing steels and a better understanding of the mechanisms of this transformation is a key element towards controlling microstructures and thus mechanical properties [1-3]. It is thus not surprising that the austenite-to-ferrite phase transformation has been the most studied reaction from both technological and scientific perspectives.

From a theoretical point of view, the transformation involves two stages, nucleation and growth. Two processes are involved during ferrite growth, a structural rearrangement (from fcc to bcc) at the interface and a diffusion process of interstitial and substitutional elements. Ferrite growth kinetics is highly conditioned by the partitioning behavior of substitutional alloying elements between the parent and child phases. This is due to the diffusivity gap of several orders of magnitude between the fast interstitial solutes (C, N) and slow substitutional solutes (such as Si, Cr, Mn, Ni, Mo...). Due to this difference in mobility, the transformation can proceed with either partitioning or negligible partitioning of the substitutional element between the growing ferrite and austenite. In the former case,

the transformation kinetics is controlled by the slow diffusion of these elements, whereas in the latter, the growth of the product phase is mainly controlled by carbon (or nitrogen) diffusion. Two models representing the limit cases of partitionless transformation known as para-equilibrium (PE) and local equilibrium with negligible partitioning (LENP) were used in the numerous attempts to predict the rate of this transformation in ternary and higher order systems. Both models were successfully used to predict ferrite growth in ternary Fe-C-X systems under particular conditions of temperature and composition. However, experimental observations showed a more complex behavior of the interface conditions during ferrite growth in some systems where those models failed to predict the measured growth kinetics. In attempts to explain such observations, it has been proposed that interactions of solute elements with the moving  $(\alpha/\gamma)$  interface, while ignored in the two aforementioned models, lead to a dissipation of the available transformation driving force and thus to a retardation of ferrite precipitation. This effect was named 'Solute Drag effect' and it was integrated in a variety of models that displayed a better aptitude at predicting kinetics for broad ranges of composition and temperature in ternary systems.

Validating the existing models describing ferrite growth requires an extensive experimental investigation of the effect of composition and temperature. While studying the effect of temperature is relatively simple, evaluating the effect of composition can be time-consuming and costly since it requires multiple castings with different compositions. Combinatorial experiments were actively reported as an effective methodology to study the effect of composition on materials properties. Compositionally graded materials were successfully used to investigate the effect of composition on functional properties (mechanical properties [12, 13], thermal and electrical conductivities [14, 15]), phase diagram assessments [16], diffusion coefficient measurements [17], and investigations of the effect of solutes on precipitation kinetics in aluminum alloys [18–20]. Occasionally, compositionally graded materials were also used to study phase transformations in steels [21–23].

High-throughput characterization techniques play a significant role in accelerating data acquisition and advancing the field of materials optimization [24]. X-Ray diffraction provides several attractive features for high-throughput screening such as *in situ* monitoring of microstroctural evolution and space resolved characterization [25, 26]. Coupling this technique with compositionally graded thin films allowed phase diagram mapping over a large portion of composition space [27]. Recently, small angle X-ray scattering (SAXS) was used on compositionally graded samples to study the dependence of precipitation kinetics on composition [18, 19, 28].

In the present study we propose a complete methodology to study the effect of composition on ferrite growth kinetics during austenite to ferrite phase transformation in ternary Fe-C-X and quaternary Fe-C-X<sub>1</sub>-X<sub>2</sub> systems, where (X, X<sub>1</sub>, X<sub>2</sub>) are substitutional solutes. The first stage of this methodology consists in making diffusion couples containing gradients of X<sub>1</sub> and/or X<sub>2</sub>. The second step is to perform *in situ* synchrotron X-ray measurements to gather ferrite growth kinetics in the different systems as a function of time and composition.

This thesis is structured as follows. In the first chapter, a literature review about the austenite-to-ferrite phase transformation from both theoretical and experimental standpoints is given. In the same chapter, the use of combinatorial approaches in studying microstructure dependency on composition is detailed. The different steps followed during this thesis to develop of the combinatorial approach are detailed in chapters II and III. Chapter IV presents an overview of the ferrite growth kinetics measured using *in-situ* HEXRD on Fe-C-X and Fe-C-X<sub>1</sub>-X<sub>2</sub> alloys of fixed composition. These results are compared with the predictions of the classical PE and LE models as well as a new version of the three-jump solute drag model [11]. The developed high-throughput methodology has been used to study ferrite growth kinetics in graded ternary Fe-C-X systems as well as quaternary Fe-C-X<sub>1</sub>-X<sub>2</sub> systems and results are presented in chapter V and VI, respectively. The measured ferrite growth kinetics are compared with the predictions of the different models in the same chapters.

# Chapter I

# Literature review

### I.1 Austenite-to-ferrite phase transformation

Austenite is the starting structure for almost all the solid-solid phase transformations in alloyed steels [2, 33]. This face-centered cubic (fcc) phase is stable between 910°C and 1392°C in pure iron but forms between 723°C and 910°C in iron-carbon alloys. In hypoeutectoid steels and during cooling from austenitic state the first phase to form is proeutectoid ferrite. At equilibrium conditions, this phase forms below the  $Ae_3$  temperature and above  $Ae_1$  eutectoid temperature [34]. These temperatures of transformation depend on the steel composition.



Figure I.1: Schematic Fe-C phase diagram.

The body centered cubic phase (ferrite) forms predominatly at the austenite grain boundaries which are energetically favorable nucleation sites. The most reported crystallographic orientation relationships between ferrite and austenite are Kurdjumov–Sachs (K- S) and Nishiyama–Wassermann (N-W) expressed as [34] :

$$\begin{array}{ll} (K-S): & (111)_{\gamma} || (110)_{\alpha} & [\overline{1}11]_{\gamma} || [\overline{1}11]_{\alpha} \\ (N-W): & (112)_{\gamma} || (110)_{\alpha} & [\overline{1}01]_{\gamma} || [001]_{\alpha} \end{array}$$
 (I.1.1)



Figure I.2: Optical micrographies showing pro-eutectoied morphologies of ferrite. a) grain boundary allotriomorphs [35]. b) Widmanstätten ferrite plates [36].

Depending on the crystallography and the temperature of transformation different morphologies of proeutectoid ferrite are observed [37]. Dubé et al. [38] proposed a classification of ferrite morphologies which occur as a result of the isothermal austenite to ferrite phase transformation. The Dubé classification system was based on many single twodimensional observations using optical microscopy. The two most common morphologies reported in a large variety of alloyed steels are :

- Grain boundary allotriomorphs (Fig.I.2a) form at high temperatures on the austenite grain boundaries and quickly grow preferentially along them. The ferrite precipitates grow into the austenite with an approximately planar interface. Grain boundary allotriomorphs are the first morphology to appear during austenite to ferrite phase transformation.
- Widmanstätten sideplates (Fig.I.2b) are formed at lower temperatures (at temperatures close to  $Ae_1$ ) either directly on austenite grain boundaries (primary Widmanstätten) or on existing grain boundary allotriomorphs (secondary Widmanstätten).

The austenite-to-ferrite phase transformation involves two processes, nucleation and growth. In the following sections a brief description of nucleation is given followed by a more comprehensive focus on growth.

#### I.1.1 Nucleation

The chemical driving force of a first order phase transformation as the austenite-to-ferrite transformation, is the difference between the free energies of the parent and the formed phase. Upon cooling below  $Ae_3$  temperature, a number of clusters of atoms arranged in a bcc-structure (Ferrite) emerge inside the fcc-parent phase (austenite) [7, 33]. Some of these clusters, that are larger than a critical radius form a stable nucleus of ferrite and grow by the diffusion process. Nucleation of ferrite is reported generally to start at the three grain boundary preferred sites, i.e. at grain corners followed by edges and then at grain boundary faces (Fig.I.3) [39]. The applied thermal path has an important role in determining the type of nucleation sites. Enomoto et al. [40] reported that grain faces nucleation becomes dominant over grain edge nucleation when increasing undercooling. This can be explained by the energy barrier for nucleation which is higher at grain faces then in grain edges followed by grain corners.



Figure I.3: Different ferrite nucleation sites. a) grain boundary faces. b) grain edges. c) grain corners. modified from [41]

The nucleation rate of ferrite formation from austenite is estimated by the classical nucleation theory [42].

$$J = N\beta^* Zexp(\frac{-\Delta G^*}{k_b T})exp(\frac{-\tau}{t})$$
(I.1.2)

To apply the classical theory of nucleation, it is important to well describe the activation energy of nucleation. This term depends on several parameters such as the driving force of nucleation, interface energies and the shape of the critical nuclei. Determining the nucleus shape is one of the most challenging questions as it has an enormous effect on the nucleation rate. A variety of nucleus shapes were considered in the literature ranging from spherical caps to disk shaped 'pillboxes' [40, 43–45]. Another parameter that plays an important role in the nucleation rate, is the interfacial energy. Again, this parameter is hard to determine experimentally and depends strongly on the coherency of the  $\gamma/\alpha$ interface [39, 41]. It can also be noticed that the rate of nucleation depends on the density of potential nucleation sites (N), which is related to the shape and size of the
former austenite grains in the case of nucleation at the grain boundaries (allotriomorph ferrite) [41].

Several studies on the nucleation rate of proeutectoid ferrite at austenite grain boundaries have been conducted in the past 40 years and compared to the predictions of nucleation rate theory. In the Fe-C system, Lange et al. [43] showed that the measured nucleation rates were well described assuming a pillbox-type nucleus shape with a very low interfacial energy ( $\sim 10 \ mJ.m^{-2}$  for edge nucleation). Enomoto and Aaronson [46] applied the same model to study nucleation of ferrite in Fe-C-X systems and Tanaka and Aaronson [47] extended it to quaternary Fe-C-X-Y systems. An additional effect must be considered in studying ternary and higher order systems concerning the partition of substitutional element between austenite and ferrite. Two assumptions are generally applied, the first being ortho-equilibrium where the nuclei achieve their equilibrium composition and thus mass transfer of X controls the nucleation rate. The other is the para-equilibrium assumption where only carbon is diffusing and the nuclei inherit the parent phase substitutional composition [47].

Lange et al. [43] used *ex-situ* observations to determine the nucleation rate by polishing the surface of heat treated samples. They were able to distinguish nucleation sites using etching techniques to separate former austenite grains and the newly formed ferrite. However, this method can introduce some errors on the measured nucleation rates since the parent austenite is never the same for the different experiments [41]. The development of X-ray diffraction methods opened new possibilities in measuring the nucleation rate *in-situ* and studying the transformation kinetics at the level of individual grains [48,49]. In their study, Offerman et al. [48,49] used 3-D X-ray diffraction technique to investigate ferrite nucleation in a Fe-C-Mn-Si steel, and one of their major findings was that the activation energy for nucleation is two orders of magnitude less than the reported one from earlier studies and that was used in modeling using the classical theory of nucleation. However, this finding was subject to other discussions [50] due to limitations of the diffraction technique.

Clearly, the understanding of the mechanisms underlying ferrite nucleation from austenite grain boundaries is still limited.

## I.1.2 Growth kinetics during the austenite-to-ferrite phase transformation

Ferrite growth from austenite involves two mechanisms, structural change (from fccaustenite to bcc-ferrite) and redistribution of carbon and/or alloying elements by diffusion [6,7,33,39]. Attempts at modeling growth kinetics of ferrite depend strongly on the assumption on whether the driving force of transformation is consumed by the structural change at the migrating interface (interface-controlled mode) or by diffusion (diffusioncontrolled mode) [6,7,33]. In the former case, the velocity of the interface between ferrite and austenite is proportional to the driving force of phase transformation and is given by Eq.I.1.3 [42] :

$$v = M\Delta G = M\chi(x_c^{\gamma} - x_c^{\alpha}) \tag{I.1.3}$$

 $\chi$  is a proportionality term and  $(x_c^{\gamma} - x_c^{\alpha})$  is the difference in carbon concentration between austenite and ferrite. *M* is considered as an effective mobility accounting for a number of factors such as the inter-atomic interactions at the interface and the segregation of solutes at the migrating interface. The interface mobility can be written as :

$$M = M_0 exp(\frac{-Q}{RT}) \tag{I.1.4}$$

Determining an accurate value of the interface mobility M and its dependence on composition is an ongoing endeavor [51, 52]. Several studies were carried to investigate the mobilities in binary systems Fe-X (X is a substitutional element) and its dependence on temperature and composition [51, 53].

The interface-controlled model describes well the kinetics of massive growth of ferrite in substitutional iron alloys and the proeutectoid ferrite growth in some binary Fe-X alloys as in Fe-Mn with low manganese content and large undercooling [53].

In diffusional growth mode, the structural change at the interface is supposed to be an infinitely fast process. The available driving force of transformation is dissipated by long-range diffusion of carbon and/or substitutional elements. During isothermal growth of ferrite from austenite under one-dimensional diffusion, the flux  $J_k$  of atoms k transferred across the migrating interface can be expressed as follows [6,54]

$$J_k = J_{\gamma}^k - v \frac{x_k^{i,\gamma}}{V_m} \tag{I.1.5}$$

It is assumed that both phases have the same molar volume  $V_m$  and it is independent of concentration.

Since the same amount of atoms k taken from the forming ferrite must be transferred to austenite and if we consider no sidewise diffusion, the same flux  $J_k$  can be expressed as follows :

$$J_k = J_\alpha^k - v \frac{x_k^{i,\alpha}}{V_m} \tag{I.1.6}$$

Eq.I.1.5 and Eq.I.1.6 yield to mass balance equation relating the interface velocity to the net flux of atoms transferred across the interface (Eq.I.1.7).

$$\frac{v}{V_m}(x_k^{i,\gamma} - x_k^{i,\alpha}) = J_k^{\gamma} - J_k^{\alpha}$$
(I.1.7)

For a multicomponent system with N elements, the mass balance equation (Eq.I.1.7) generates N-1 independent equations. Using Fick's second law to define the flux densities in both phases and the two relations,  $\sum_{k}^{N} J_{k} = 0$  and  $\sum_{k}^{N} x_{k} = 1$ , one ends up with 2N+2 additional equations and 4N + 1 unknown variables. N more equations are needed to determine a unique solution for the system of equations in (Eq.I.1.7). The assumption of local equilibrium at the interface  $\gamma/\alpha$  yields to N more equations of equality of chemical potentials (Eq.I.1.8):

$$\mu_k^{\gamma} - \mu_k^{\alpha} = 0(k = 1, ...., N) \tag{I.1.8}$$

In the Fe-C binary system, the assumption of local equilibrium at the interface is a good approximation due to the high diffusivity of carbon. In higher order systems containing substitutional elements with slow diffusivities compared to carbon diffusivity, this assumption can be questionable [6,7].

Recently, mixed-mode models taking into account both interface mobility and volume diffusion process have been proposed [52,55–57]. These models suggest that grain boundary ferrite formation is interface controlled at the early stage of the transformation and shifts towards a diffusion controlled character as the transformation proceeds [55]. Both diffusion-controlled and interface-controlled modes can be considered as extreme cases of the mixed-mode model [6]. In the mixed-mode phase transformation, the flux of the diffusing element into the austenite is not fully compensated by the structural change at the migrating interface due to its finite mobility. As a result, the local concentration at the austenite interface side  $x_k^{i,\gamma}$  is different from the equilibrium value  $x_k^{e,\gamma}$  giving rise to a driving energy  $\Delta G$ . In case of the Fe-C system, the interface velocity that is proportional to the driving energy can be expressed as follows :

$$v = M\Delta G = M\chi(x_c^{e,\gamma} - x_c^{i,\gamma}) \tag{I.1.9}$$

Assuming no accumulation of carbon at the interface, the flux of carbon due to the fininte interface movement (Eq.I.1.9) is balanced by the carbon diffusion in the austenite bulk (using Fick's Law).

$$(x_c^{e,\gamma} - x_c^{i,\gamma}).v = -D_c^{\gamma} (\frac{dx_c^{\gamma}}{dz})_{z=z_{int}}$$
(I.1.10)

The interfacial carbon contents in this case are not constant as a result of a non-zero net flux at the interface. The carbon concentration at the interface is determined using both diffusive flux and interface mobility.

## I.1.2.1 Growth kinetics in Fe-C system

Ferrite formation in Fe-C alloys is in most cases modeled assuming that volume diffusion in austenite is rate limiting for the growth kinetics [7,33,58,59]. Fig.I.4 shows the carbon concentration profiles in both ferrite and austenite in a binary Fe-C system during the precipitation of ferrite from austenite at a given temperature and time. The carbon flux in ferrite is approximated to zero due the fast diffusion of carbon in ferrite compared to austenite (two orders of magnitude). As a consequence, ferrite growth is mainly controlled by carbon diffusion in austenite.



Figure I.4: Carbon profiles in ferrite and austenite during isothermal precipitation of ferrite in Fe-C system

Local conditions at the interface defining the equilibrium state (Eq.I.1.8) can be obtained from the molar Gibbs free energy diagram by constructing the common tangent as shown in Fig.I.5. One can notice that in Fe-C binary system, the local equilibrium (LE) condition defines one unique set of interfacial compositions at given temperature and pressure [6]. The obtained carbon concentrations at the interface are then used to solve Fick's equations and determine the velocity from Eq.I.1.7. Zener's model is one of the classical diffusion controlled models describing ferrite growth kinetics in binary alloys Fe-C. Zener showed that the thickening of ferrite (x) proceeds parabolically with time (Eq.I.1.11), where  $D_C^{\gamma}$  is the carbon diffusivity in  $\gamma$  and  $\alpha_c$  is a dimensionless coefficient (also called growth factor) that depends on carbon contents at the migrating interface, the bulk carbon concentration and grain geometry assumption.

$$x = \alpha_c \sqrt{D_C^{\gamma} t} \tag{I.1.11}$$

Several experimental studies were conducted to investigate the ferrite growth kinetics for different carbon contents and at different temperatures [60–63]. Parabolic rate constants were determined from experimental results and compared with theoretically calculated values using Zener's model [64]. In Atkinson [62] and Kinsman [61] works, the measured growth kinetics were found to exceed the calculated ones using Zener's approximation.



Figure I.5: Schematic molar gibbs energy diagram showing boundary conditions at the  $\alpha/\gamma$  interface in the case of a binary Fe-C system.  $x_C^{\alpha}$  and  $x_C^{\gamma}$  are the carbon contents at the ferrite and austenite interfaces respectively,  $x_0$  is the nominal carbon content of the alloy.  $\mu_{Fe}$  and  $\mu_C$  are the equilibrium chemical potentials of iron and carbon respectively.

Atkinson [62] modified the Zener model [64] to describe the carbon diffusivity in austenite taking into account the variation of carbon composition due the rejection of carbon from the growing ferrite. The same author changed the assumption of a planar austenite ferrite boundary and assumed an oblate ellipsoid shape instead.

Bradley et al. [60] used optical microscopy to measure growth constants in Fe-C alloys with different carbon contents and at different temperatures, and compared the obtained parabolic rates with the calculated growth constants using the Atkinson's model [62](Fig.I.6). Results showed that for all cases, the calculated growth kinetics were faster than the observed ones. This discrepancy was attributed to a structural effect related to the presence of partially coherent facets within the ferrite austenite interfaces, which tend to reduce the growth rate, rather than just a disordered interface as assumed by the Atkinson's model [33, 58, 60]. This discrepancy can also be attributed to statistical error in the conventional metallographic approach used by Bradely [60] as suggested by Crusius [65].

In an ingenious approach, Purdy et al. [66] used a macroscopic two-phase (austenite and ferrite) diffusion couple to investigate ferrite growth in an Fe-C system. A binary ferriteaustenite diffusion couple with a planar interface was created using the decarburization technique. The interface motion was followed by metallographically measuring the layer of ferrite after different treatment time at a given temperature. The use of this technique



Figure I.6: Comparison between experimental  $\alpha(exp)$  and calculated  $\alpha(calc)$  growth constants as function of temperatures in a) Fe-0.11wt. pct C and b) Fe-0.23wt. pct C. [60]

has the advantage to suppress the nucleation effect on the measured growth kinetics and avoid the difficulties inherent to statistical metallography. The comparison between the obtained growth rates and the calculated ones using LE assumption showed an excellent agreement (Fig.I.7) and provided a strong evidence that ferrite growth in Fe-C system with an incoherent interface is volume diffusion controlled.

Krielaart et al. [63] developed a mixed-model to predict ferrite growth kinetics in Fe-C system and compared the calculated kinetics with experimental results from Bradley et al [60]. The mixed-model was found to describe the experimental results well, suggesting that the finite mobility of the interface plays a role during ferrite growth in Fe-C. Nevertheless, it should be mentioned that the choice of the mobility parameter (M) in the mixed-model is questionable and is used as a fitting parameter. In Krielaart study, authors used mobility parameters obtained for Fe-Mn alloys [63]. However, experimental evidences exist, that the  $\alpha/\gamma$  interface moves in different modes during ferrite growth under isothermal conditions [67] and that the interface velocity is not constant and shows accelerations and decelerations during austenite to ferrite phase transformation. This indicates that the interface does not behave only as highly disordered interface as suggested in equilibrium models [63].



Figure I.7: Comparison between measured  $\gamma/\alpha$  interface positions (dots) in a diffusion couple and the calculated interface positions using LE conditions (dashed line) [66].

## I.1.3 Growth kinetics in ternary systems

Predicting growth kinetics in ternary Fe-C-X (where X is a substitutional element) systems is more complex than in the Fe-C binary system. The difficulty originates from the large difference in volume diffusivity between the interstitial element C and the substitutional element X (a factor of  $10^6$ ). As a result, substitutional alloying elements modify the kinetics of the austenite-to-ferrite transformation. On the other hand, alloying elements influence the thermodynamic properties of the system. It was observed that with the presence of substitutional elements, growth of proeutectoid ferrite can be either accompanied by a redistribution of both C and the alloying element X or only bulk partitioning of the C [68]. Two approaches were proposed to describe ferrite growth in these systems, the local equilibrium (LE) model and para-equilibrium (PE) model [5–7, 33, 69–71]. In the following sections, a description of both models is given.

#### Equilibrium with and without partitioning (LEP and LENP)

As for the binary Fe-C system, assuming local equilibrium between austenite and ferrite in Fe-C-X ternary systems can be described using Eq.I.1.8 of equality of chemical potentials

$$\mu_C^{\gamma} = \mu_C^{\alpha}$$

$$\mu_X^{\gamma} = \mu_X^{\alpha}$$
(I.1.12)



Figure I.8: Isothermal section of the Fe-C-Mn phase diagram at 730°C. LE tie lines are represented in green and the equilibrium tie-line passing through the nominal content (black circle) is represented in red line.

Contrary to the Fe-C system, an infinite number of tie lines can be chosen to satisfy the LE assumption at a givent temperature [6,7]. This is illustrated for a ternary Fe-C-Mn system as shown in Fig.I.8. At the end of transformation, or when final equilibrium has been reached, this tie-line can be obtained by considering the tie-line passing by the nominal composition (Fig.I.8). However, the operative tie-line changes during phase transformation and it is not necessarily the one passing by the nominal composition [5, 6, 69]. This is due to the large difference in mobilities between C and X element. Determining the operative tie-line must satisfy LE conditions and mass conservation condition (Eq.I.1.7, I.1.12). Coates [5,69,70] demonstrated that the interface compositions (or the operative tie-line) can be defined using the so-called interface composition contours (IC) for a given nominal composition. Coates also demonstrated that if  $D_C/D_X$  is too large, that growth is shape-preserving and that inter-diffusion coefficients are approximated to zero, the operative tie-line can be considered time-independent and thus can be determined directly from phase diagram. Using this approach, two types of transformations can occur depending on the bulk composition. It is thus possible to divide the two region  $(\alpha + \gamma)$ phase diagram for a ternary system into two regions as shown in Fig.I.8. The line that separates the two regions is called the zero partition line.

Let us consider an alloy with a bulk composition above the zero partition line (at low

supersaturation). Using the construction shown in Fig.I.9a it can be seen that carbon gradient in austenite is negligible while the X element is redistributed in the matrix. The transformation in this case is considered to proceed with X partition between austenite and ferrite and ferrite is considered to grow under local equilibrium with partitioning (LEP). In the case of an alloy with a bulk composition below the zero partition line (at high supersaturation), ferrite growth can proceed without bulk partitioning of element X and only carbon is redistributed. A spike of X concentration is developed at the interface to satisfy LE conditions (Fi.I.9b). Growth in this case is controlled by carbon diffusion in austenite and is termed a transformation under Local Equilibrium with Negligible Partitioning (LENP) [5,6,69].



Figure I.9: a) Schematic isothermal section of Fe-C-Mn showing the construction of Mn and C concentration profiles in ferrite and austenite during growth of an alloy (1) with a bulk composition above the zero partition line (LEP condition). b) Mn and C profiles during growth of an alloy (2) with a bulk composition below the zero partition line (LENP condition).

#### ParaEquilibrium (PE)

Hultgren [68] introduced the term 'paraequilibrium' to describe transformations proceeding without partitioning of alloying elements that he observed in some Fe-C-X alloys. Hillert [72], analyzed theoretically the assumption of 'para-equilibrium' and concluded that under high supersaturation, ferrite can form and grow with the same substitutional alloy content as that of austenite. Under para-equilibrium, the ratio of substitutional element X to Fe atoms (X/Fe) is assumed to be constant across the interface but local equilibrium is established for C. Thus, transformation rate is considered to be controlled by carbon diffusion only. Substitutional elements in this case influence growth kinetics by changing the carbon content at the interface compared to a binary Fe-C system. Thus, in para-equilibrium growth conditions, the rate of ferrite precipitation can be calculated using the same approach as in Fe-C system. Para-equilibrium can be expressed using the set of Eq.I.1.13 :

ŀ

$$\mu_C^{\gamma} = \mu_C^{\alpha}$$

$$\mu_X^{\gamma} - \mu_X^{\alpha} = -\frac{x_{Fe}}{x_X} (\mu_{Fe}^{\gamma} - \mu_{Fe}^{\alpha})$$
(I.1.13)



Figure I.10: Isothermal section of the Fe-C-Mn phase diagram at 730°C. Para-equilibrium diagram is plotted with the equilibrium diagram showing the different growth modes LE, LENP and PE. The dashed line represents the zero partition line.

A para-equilibrium phase diagram can be constructed using the set of Eq.I.1.13 as shown in Fig.I.10 with tie-lines plotted in red defining the paraequilibrium interface conditions. The resulting 'paraequilibrium tie-lines' are almost parallel to the interstitial element axis and perpendicular to the X concentration axis due to the assumed immobility of X. Hillert [72] showed that the paraequilibrium phase boundaries always lie within the  $\alpha + \gamma$ equilibrium phase boundaries.

The PE and LENP models describe growth in non-partitioned austenite to ferrite phase transformation [6]. In both models, ferrite growth is controlled by carbon diffusion in

austenite but with different assumptions concerning the effect of element X on the kinetics. In LENP mode, a full equilibrium of element X at the interface is maintained by the formation of a spike of X at the interface. On the other hand, PE mode assumes that X elements are completely immobile and the interface is under constrained equilibrium. LENP and PE modes represent thermodynamic limits of unpartitioned growth.

## I.1.3.1 Experimental investigation of ferrite growth in Fe-C-X alloys

A considerable amount of data is available on growth kinetics in ternary Fe-C-X systems. Enomoto [73] compared the measured growth rates for several Fe-C-X (X : Ni, Mn, Si, Cr) at different temperatures with the calculated growth constants using LENP and PE assumptions. Fig.I.11a shows an example on Fe-C-Ni where dots represent the experimentally determined constant growth rates and lines are the calculated ones by assuming LENP and PE conditions. A faceting correction of measured kinetics was made to take into account the effect of low energy facets on the retardation of growth. Growth kinetics in this alloy is well described by LENP mode. Bradley [74] reported the same behavior in a Fe-0.12C-3.18Ni system. Phillion [22] used controlled decarburization method to investigate growth behavior in Fe-C-Ni system with different nickel contents and at different temperatures. In Decarburization method, as mentioned before, permits the minimization of the effects of interface structure on growth kinetics as well as the suppression of nucleation effects. Results showed good agreement between the measured kinetics and the modeled ones using LENP conditions.

This was confirmed in another study by Hutchinson [35], Fig.I.11b. In the same study, Hutchinson et al. performed a series of precipitation experiments on different Fe-C-Ni alloys with different nickel contents (Fig.I.12). Hutchinson [35] reported that the measured growth kinetics are well described by PE conditions at the early stage of transformation (Fig.I.12a). By contrast, the final volume fraction is closer to LENP predictions and overestimated by the PE model (Fig.I.12b). Hutchinson suggested a transition in growth behavior during austenite to ferrite phase transformation in Fe-C-Ni system. This transition in behavior in Fe-C-X alloys was already mentioned and discussed by Hillert [4]. Several attempts were made to develop models describing the transition behavior. A description of these models will be provided later in the present study.

Fig.I.13a compares the measured growth rates for a Fe-C-Mn system during precipitation experiments with the calculated ones using LENP and PE modes [73]. The measured kinetics are faster than kinetics under LENP assumptions and slower than those calculated using PE conditions. Other studies reported the same growth behavior in Fe-C-Mn systems [74–76]. Enomoto and Aaronson [75], suggested that Mn segregation at the interface can be a source of the observed discrepancies between measured growth rates and LENP/PE ones. In decarburization experiments, Purdy et al. [66] reported that the measured kinetics for Fe-C-Mn alloys were in good agreement with LENP predicted ones.



Figure I.11: a) Comparison between measured ferrite growth constants of a Fe-0.51C-3.11Ni (at pct) and calculation using LENP (solide line) and PE (dashed line) assumptions in function of temperature [73].b) Comparison between experimentally measured ferrite layer thickening kinetic and the predictions of LENP/PE models during decarburization of a Fe-0.5C-0.97Ni (wt pct) at 775°C. [35]



Figure I.12: Comparison between the experimentally measured allotriomorph half-thicknesses in a range of Ni containing alloys at 700°C and a) predictions of PE model [35]. b) predictions of LENP model [35].

Zurob et al. [77, 78] performed decarburization experiments on different Fe-C-Mn alloys with different contents and at different temperatures. The authors reported a transition from LENP kinetics at lower temperatures to PE kinetics when increasing temperature. This was a surprising result since PE is more likely to occur at low temperatures where high supersaturations can be obtained. The results also showed a long-lived state with constant interfacial conditions that lies between LENP and PE limits during the austenite to ferrite phase transformation at certain temperatures as shown in Fig.I.13b. Based on the mentioned studies, a completely different behavior is observed during growth of ferrite in Fe-C-Ni and Fe-C-Mn alloys. Zurob et al. attributed this difference to the behavior of both element with the interface. Manganese is known to have a tendency to segregate at the interface [79]. By contrast, nickel is reported to have no strong interaction with the interface [80].



Figure I.13: a) Comparison between measured ferrite growth constants of a Fe-0.56C-3.12Mn (at pct) and calculation using LENP and PE assumptions in function of temperature [73].b) Comparison between experimentally measured ferrite layer thickening kinetic and the predictions of LENP/PE models during decarburization of a Fe-0.56C-1.96Mn (at pct) at 806°C [77].

Before discussing the different suggestions proposed to explain the observed growth kinetic transitions and the different effects of substitutional elements on growth kinetics, kinetics in other ternary Fe-C-X systems will be reviewed. G.Inden [81] compared measured growth rates obtained by [74] of a Fe-C-Si system to the calculated ones using LENP and PE modes for different temperatures (Fig. I.14a). It can be noticed that growth kinetics follow a PE mode. In another study, Inden showed that for a different silicon content, LENP is more likely to describe the measured growth [81]. In decarburization experiments, Zurob reported that measured growth kinetics in Fe-C-Si systems were always slower than both PE and LENP modes (Fig.I.14b). The authors estimated a dissipation energy that can bring the LENP kinetics to be in agreement with the measurements. They also reported that the dissipated energy is larger of lower temperatures [83].

In the case of Fe-C-Cr, decarburization experiments conducted by Béché et al. [84] showed also that the growth kinetic was slower than both LENP and PE predicted kinetics (Fig.I.15a). The estimated dissipated energy to bring LENP to the measured kinetics



Figure I.14: a) Comparison between measured ferrite growth constants of a Fe-0.4C-1.73Si (wt pct) and calculations using LENP and PE assumptions in function of temperature. b) Comparison between experimentally measured ferrite layer thickening kinetic and the predictions of LENP/PE models during decarburization of a Fe-0.58C-0.88Si (at pct) at 775°C.

increased with decreasing temperature indicating also an existing effect of interaction between chromium and the interface. In precipitation experiments, Bradley et al. [74] also reported that the measured kinetics are slower than both PE and LENP (Fig.I.15b).



Figure I.15: a) Comparison between experimentally measured ferrite layer thickening kinetic and the predictions of LENP/PE models during decarburization of a Fe-0.58C-2.0Cr (wt pct) at 775°C [74]. b) Comparison between measured ferrite growth constants of a Fe-0.6C-3.2Cr (at pct) and calculation using LENP and PE assumptions in function of temperature [84].

Another element reported to have a considerable effect on growth kinetics is Mo. Hutchin-

son et al. [85] measured growth kinetics in a Fe-C-Mo system during both precipitation and decarburization experiments at different temperatures. The authors observed that growth rate is slower than PE and LENP for all studied temperatures and for both experiments (Fig.I.16). The molybdenum content was chosen to identify experimental conditions where PE and LENP give the same kinetics. In these conditions, the observed deviation between experimental kinetics and LENP/PE predicted ones is an indication of an interaction of molybdenum with the moving interface.



Figure I.16: Comparison between experimentally measured ferrite growth kinetics and the predictions of LENP/PE model [85] a) in a Fe-0.1C-0.1Mo (wt pct) alloy transformed at 775°C and b) a Fe-0.54C-0.51Mo (wt pct) alloy decarburized at 775°C

## I.1.4 Solute Drag effect

It is clear now that ferrite growth in Fe-C-X systems can not be fully described by the classical thermodynamic models considering local equilibrium (LE) or constrained equilibrium (PE) at the interface. One of the theories generally invoked to explain the mentioned discrepancies between calculated kinetics and measured ones is the solute drag theory [9,86]. During ferrite growth, solutes can segregate at the mobile  $\alpha/\gamma$  interface reducing its velocity. Solute drag was first observed by Lücke et al. [87] when studying the effect of alloying elements on recrystallization kinetics in aluminum alloys. They concluded that the presence of foreign atoms can affect the grain boundary motion causing a retardation of recrystallization. Lücke et al. [87] attempted to develop a theoretical model to describe the solute drag effect, they supposed that during interface migration the segregated atoms are left behind, which leads to an attraction force applied by the interface on these atoms. As a result, the grain boundary velocity is decreased. Cahn [86] also developed its theoretical model based on the same approach of force attraction between the center of the grain boundary and solute atoms. Hillert [9], in a different approach, studied the effect

of atoms segregation on phase transformation by estimating the dissipated energy due to the solute-interface interaction. Later, different numerical calculations have been developed to describe solute drag in Fe-C-X systems based on either the force approach or the dissipation approach. In the following sections, a brief overview is given on the different models.

#### I.1.4.1 Models based on Cahn's force approach

Purdy and Brechet [88] presented their solute drag model (PB model) to describe phase transformations in Fe-C-X alloys. The authors used the Cahn force approach [86] to describe the attraction of solutes to the interface. A potential well is assumed to describe the X solute attraction energy profile across the interface (Fig.I.17a). The sign of potential is chosen to be negative in case of attraction and positive in case of repulsion between solute elements and the interface. In order to evaluate the drag force acting on the interface, the solute concentration profile across the interface must be defined first [86]. The equilibrium potential of element X in Cahn's approach is defined as :

$$\mu_X(z) = kT ln C_X(z) + E(z) \tag{I.1.14}$$

Where E is the free energy of attraction of the solute with the boundary,  $C_X$  is the X element concentration. The diffusion flux of atoms across the interface is expressed as :

$$J = -D\frac{\partial C_X}{\partial z} - \frac{DC_X}{kT}\frac{\partial E}{\partial z}$$
(I.1.15)

Assuming a steady velocity state, Eq.I.1.15 is written :

$$0 = \frac{\partial}{\partial x} \left[ D \frac{\partial D}{\partial z} + \frac{C_X D}{kT} \frac{\partial E}{\partial z} + v C_X \right]$$
(I.1.16)

D is the interfacial diffusion coefficient of X, assumed to be constant throughout the boundary and v is the interface velocity. It worth mentioning that both the interaction energy profile E(z) and interface diffusivity D are two unknown parameters and are generally estimated using different assumptions. Solving the flux equation for different velocities gives the solute distribution across the interface as plotted in Fig.I.17b.

Cahn then estimated the force exerted by solutes on the interface by summing the force of individual atoms as shown by Eq.I.1.17.

$$P = \int_{-\delta}^{+\delta} \frac{(C_0 - C_X)}{V_m} \frac{\partial E}{\partial z} dz$$
(I.1.17)

 $\frac{\partial E}{\partial z}$  is the force exerted by one atom on the interface and  $\delta$  is the half width of the interface. Due to the asymmetry of the concentration profiles across the interface, the net force is not zero and it is called the net solute drag. Cahn reported that the calculated drag reaches a maximum at intermediate velocities and tends toward zero at high velocities.



Figure I.17: a) A schematic description of interaction energy profile of solute element around the interface as assumed by Cahn [88] b) A series of solute composition profiles calculated for various interface velocities [88].

Using the balance force criterion (Eq.I.1.18) the available driving force  $\Delta G^{chem}$  is balanced by the dissipated force due to the solute drag effect P and the friction force due to the finite mobility of the interface M.

$$\frac{\Delta G^{chem}}{V_m} = P + \frac{v}{M} \tag{I.1.18}$$

It should be mentioned that the transformation is assumed to be controlled by carbon diffusion only. The carbon content at the interface is an unknown variable. Using the criterion of force balance, instantaneous velocities and thus interfacial carbon contents can be obtained for a given precipitate thickness. Once the interfacial carbon contents are defined, the new thickness of the precipitate can be calculated using Fick's law and mass balance equations, same as in the Fe-C system (section I.1.2.1). The same procedure is then repeated for the new precipitate thickness. The major artefact in Purdy-Brechet model is that when applied to a stationary interface, it predicts a non-zero drag force as demonstrated by [89]. The authors also argued that in the PB model [88], the dissipation energy is calculated over a region including the interface and the spike of solute in the shrinking phase and thus should be compared with the driving force calculated over the same region [89]. This is not the case in PB model, where the driving force is estimated over the interface only without including the spike.

Fazeli et al. [90] modified the PB model by introducing a new term in the potential well description to remove the obtained artifact of non-zero solute drag at zero interface velocity. The model predictions were compared with experimental results in a Fe-C-Mn



Figure I.18: a) Comparison between measured kinetics in a Fe-0.17C-0.74Mn (wt.%) at different temperatures and the PB modified solute drage model [90]. b)Comparison between measured kinetics for different Mn content in a Fe-C-Mn system at 700°C and the GEB calculated kinetics [91].

system (Fig.I.18a). Good agreement was obtained between the measured kinetics and the predicted ones using the PB modified model.

Based on a similar approach, Chen et al. [91] developed their GEB (Gibbs energy balance) model with a difference in the estimation of the chemical driving force. Chen et al. evaluated the driving force over the interface as well as the spike ahead of the interface. The comparison between the measured ferrite fractions during isothermal austenite-toferrite transformation in the Fe-C-Mn and the predicted values using GEB model is showed in Fig.I.18b. The predicted kinetics are in good agreement with the measured ones for the different manganese contents. Chen et al. argued that their GEB model predicts the transition between non-partitionned, negligible partitioning and partitioned growth in a natural way. The thermodynamic properties of the interface such as the binding energy and the interface diffusion coefficient of the substitutional element were chosen as fitting parameters. The interface diffusion coefficient in austenite, manganese diffusion coefficient in ferrite and manganese diffusion coefficient in grain boundaries.

## I.1.4.2 Models based on Hillert's dissipated energy approach

Odqvist's model [92] used the dissipation approach developed by Hillert and Sundman [9] to model the observed deviation from equilibrium in case of phase transformation of Fe-C-X alloy. Hillert's approach differs from Cahn's approach by considering the dissipated energy by solute drag as the free energy due to diffusion of solutes across the moving interface Eq.I.1.19. Hillert argued that the energy needed for the interface to overcome the solute drag must be dissipated by the diffusion of solutes when the interface is moving.

$$\Delta G_m^{diss} = -\int_{-\infty}^{+\infty} (u_X - u_X^0) \frac{\partial \mu}{\partial z} dz \tag{I.1.19}$$

It can be noticed that the dissipation energy is evaluated over the whole interface as well as the region ahead of the interface containing the solute spike. Odqvist considered a thick interface between austenite and ferrite within which thermodynamic properties vary continuously from those of ferrite to those of austenite. An atomic flux of solutes atoms is thus generated within the interface due to the chemical potential gradient and the dissipated energy is evaluated from the atomic flux by Eq.I.1.19. Again the local energy balance (Eq.I.1.20) across the interface is used to determine the interface velocities and the interface carbon concentrations.

$$\Delta G_m^{chem} = \Delta G_m^{diss} + \Delta G_m^{fric} \tag{I.1.20}$$

 $\Delta G_m^{fric} = \frac{v}{M}$  is the energy dissipated by interface friction. The chemical driving  $\Delta G_m^{chim}$  force is evaluated using Eq.I.1.21 :

$$\Delta G_m^{chem} = u_{Fe}^0 (\mu_{Fe}^\gamma - \mu_{Fe}^\alpha) + u_X^0 (\mu_X^\gamma - \mu_X^\alpha)$$
(I.1.21)

Where  $u_{Fe}^0$  and  $u_X^0$  are initial contents of substitutional elements (Fe and X respectively). Similar to the solute drag energy, the driving force is evaluated over both the interface and the spike regions. This is different from the force based model (PB model) as stated before, where the driving force is evaluated without the solute spike.

Again parameters as the binding energy  $E_b$  of the solute at the interface, interface diffusion coefficient  $D_X$  and the thickness of the interface region are unknown and must be chosen based on assumptions. PE is considered as the initial mode to describe interfacial conditions and growth is considered to be controlled by carbon diffusion in austenite only. This means that growth under LEP mode is not considered by this model. Odqvist applied his model to a Fe-C-Ni system, where he considered a three zone interface with a thickness of 0.5 nm. The interface diffusivity of nickel was estimated as the nickel grain boundary diffusion coefficient (which is several orders of magnitude higher than the solute diffusivity in  $\alpha$  ( $D_{\alpha}$ ) and  $\gamma$  ( $D_{\gamma}$ )). The thermodynamic properties of the interface (the binding energy  $E_b$ ) were chosen as fitting parameters to obtain the desired segregation. A series of calculations of the dissipation energy were carried as function of the velocity, added to the dissipated energy by friction and compared to the chemical driving force as shown in fig.I.19.

The intersection points represent the possible velocities for growth under steady state. In fig.I.19 the intersection point at high velocity is due to the interface friction and the intersection point at low velocity is due to diffusion in the interface. By considering only intersections at low velocities, the austenite interfacial conditions were determined and plotted as function of velocity as shown in fig.I.20a. This result shows how the spike of



Figure I.19: Gibbs energy dissipation as a function of interface velocity for a Fe-C-Ni alloy calculated using Odqvist et al. model, the intersection points between total driving force and energy dissipation curve represent the possible steady-state growth velocities [92].



Figure I.20: a) Carbon and nickel u-fractions as function of velocity obtained from intersections in Fig.I.19. The marked velocity represents the highest interfacial carbon content that ferrite can inherit [92]. b) The interfacial conditions plotted on a Fe-C-Ni phase diagram at 720°C showing the path of transition from paraequilibrium (point P) to equilibrium conditions (point F) [92].

nickel in this example is built at the interface when interface velocity decreases during growth. In fig.I.20b, the interfacial conditions are plotted on a phase diagram showing the path of transition from Paraequilibrium (point P) when the interface velocity is high to equilibrium conditions when interface velocity approaches zero (point F). This result illustrates how the solute drag theory can predict transition from PE during early stages of transformation to LENP mode when the transformation proceeds. The results of Odqvist's model [92] were compared to the experimental measurements of Oi et al. [93], where different austenite to ferrite transformation experiments were conducted on a Fe-0.29C-2.42Ni (wt.%) at two different temperatures 700°C and 720°C. Oi et al. reported that a transition between slow partitioned growth (at 720°C) to fast non-partitioned growth (700°C) was observed experimentaly. Odqvist model failed to predict this transition and predicted a much faster growth in case of 720°C. Odqvist stated that a larger binding energy  $E_b$  (-20kJ/mol instead of -1kJ/mol considered in Odqvist modeling) of nickel at the interface must be considered to reproduce the experimentally observed transition. This value implies a significant tendency of nickel to segregate at the interface, which is not reported experimentally [79]. Odqvist stated that this result means that the present modeling must be modified radically in order to predict such conditions [92].

Zurob et al. [11] proposed a discrete model to describe growth kinetics in Fe-C-X systems. Zurob's model was inspired from Odqvist et al. treatment as well as the approach of Hutchinson [35] to describe the interface and the chemical driving energy. A brief description of the Hutchinson approach is needed here before introducing Zurob's model. In his treatment, Hutchinson, as in Odqvist's model, used a local energy balance at the interface to calculate the interfacial conditions during ferrite growth (Eq.I.1.20). The main difference is that, Hutchinson neglected the dissipated energy by solute drag  $\Delta G_m^{diss}$  as well as the friction energy  $\Delta G_m^{fric}$ . As a result, the driving free energy  $\Delta G_m^{chem}$  is dissipated only by the bulk diffusion and local balance energy is written as :

$$\Delta G_m^{chem} = \Delta G_m^{diss} + \Delta G_m^{fric} = 0 \tag{I.1.22}$$

The other difference in Hutchinson's model is the choice of the local driving energy and the description of the interface. Hutchinson considered a discrete interface and its velocity proportional to the net flux of the substitutional elements across the interface. The driving force was expressed only in terms of substitutional elements as follows :

$$\Delta G_m^{chem} = \frac{(u_X^{\alpha} + u_X^{\gamma})}{2} (\mu_X^{\gamma,i} - \mu_X^{\alpha,i}) + \frac{(u_{Fe}^{\alpha} + u_{Fe}^{\gamma})}{2} (\mu_{Fe}^{\gamma,i} - \mu_{Fe}^{\alpha,i})$$
(I.1.23)

It can be seen from EqI.1.23 that the driving force is zero under equilibrium conditions (same solute chemical potentials in both austenite and ferrite). Further, PE conditions (Eq.I.1.13) are obtained from Eq.I.1.23 by setting the driving froce to zero and the ratio of substitutional elements is the same in austenite and ferrite. During growth, solute elements will diffuse across the interface creating a build-up spike of element X at the austenite interface. The variable X content at the interface results in a variation of C concentration to satisfy Eq.I.1.22. It should be mentioned that Hutchinson's model predicted the measured kinetics well in the Fe-C-Ni system where the dissipation energy due to the solute drag was assumed negligible. Zurob [11] stated that not considering the solute drag dissipation energy in Hutchinson's model limited its application to systems

where no segregation of solutes at the interface is expected. This type of models are called dissipation-free transition models [6].

Zurob et al. [11] used the same local energy balance as in Odqvist's model (Eq.I.1.20) but neglected dissipation energy due to interface friction  $\Delta G_m^{fric}$ . Moreover, Zurob's model ignores the dissipation energy due to solute diffusion in the spike, hence the driving force is evaluated across the interface only. Qiu et al. [94] considered these assumptions as reasonable since the interface friction effect mainly contribute at very high (>  $10^{-6}m/s$ ) and solute diffusion in the spike at very low velocities (<  $10^{-11} m/s$ ), which are not the operating velocities during decarburization experiments. The driving force  $\Delta G_m^{chem}$  was calculated as in Hutchinson's model Eq.I.1.23. The dissipation energy due to diffusion of solutes across the interface (solute drag) was evaluated from Hillert's [9] expression (Eq.I.1.19).

$$\Delta G_m^{diss} = -\frac{V_m}{v} \int_{-\infty}^{+\infty} J_X \frac{\partial \mu}{\partial z} dz \tag{I.1.24}$$

The difference from Odqvist's model, is that Zurob considered a discrete interface consisting of two atomic layers (fig.I.21) and that diffusion across the interface involves 3 jumps from ferrite to austenite. Alloying element content at each atomic plane is estimated using mass balance equation :

$$dx_X^i \frac{\delta}{V_m dt} = J_X^i - J_X^{i+1} + \frac{v}{V_m} (x_X^{i+1} - x_X^i)$$
(I.1.25)

 $J_i$  is the flux of solute element from plane i-1 to plane i and is expressed as follows :

$$J_X^i = -\frac{D_X^i}{V_m R T} x_{Fe}^{i-1} x_X^{i-1} \frac{(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})}{\delta}$$
(I.1.26)

 $\mu^i$  is the chemical potential of X and Fe at plane  $i, \delta$  is the interface thickness,  $V_m$  is the molar volume, R is the gas constant, T is temperature and  $D_i$  is the diffusion coefficient of X element from plane i-1 to plane i. Assuming a steady state, the X content at each plane can be evaluated from Eq.I.1.25 and I.1.26. The dissipated energy due to diffusion is then estimated by discretizing of EqI.1.24 :

$$\Delta G_m^{diss} = \sum_{i=1}^{i=3} -\frac{V_m}{v} J_X^i [(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})]$$
(I.1.27)

The PE conditions are considered as the initial interfacial state and growth kinetics of ferrite are evaluated from carbon diffusion in bulk phases (ferrite and austenite in decarburization and austenite only in precipitation). It is thus necessary to evaluate the carbon concentration variation at the austenite and ferrite interfaces as function of the velocity. This can easily be evaluated using the energy balance equation by adjusting the interfacial conditions that give the same velocity evaluated from mass balance equation and the velocity satisfying the local energy balance.



Figure I.21: A schematic description of the interface as used in Zurob's three jump model [11].

Zurob et al. used an approach developed by Hillert [11, 95] to describe the thermodynamical properties of the interface. The interface properties were modified from those of austenite by shifting the reference state for the free energy by 3.5kJ/mol. This value was chosen to capture an interfacial energy of  $0.5J/m^2$ . The interaction parameter of Fe-X at the interface was modified to express the segregation behavior of element X at the interface. This term is decreased for elements with high segregation tendency and increased for elements with tendency to desegregate from the interface. Diffusion coefficients for the different jumps were chosen as  $D_{\alpha}$  for  $D_1$ ,  $D_{\gamma}$  as  $D_3$  and the geometrical average as  $D_2$ . As a result, the interaction parameter is the only fitting parameter used in Zurob's model. A detailed numerical description of Zurob's model is given in Appendix A.

As showed before, Odqvist's model [92] failed to predict the transition temperature between partitioned and un-partitioned growth measured in Oi's [93] study on the Fe-C-Ni system [93]. Zurob's model on the other hand predicted accurately this temperature by choosing a weak interaction parameter of nickel with the interface ( $E_b = +1.5kJ/mol$ ) contrary to Odqvist suggestion that a large interaction parameter should be used to predict the observed results in Oi's work [93].

Zurob's model was also applied on the obtained data from decarburization experiments of a Fe-C-Mn. As stated before, intermediate kinetics between LENP and PE limits were measured suggesting a different behavior of Mn compared to nickel on the interface. These data were compared with new calculations using a modified thermocalc database [11]. The new results showed that the measured kinetics are closer to LENP mode and no transition to PE at high temperature was recorded (Fig.I.22). By choosing an appropriate binding energy for manganese at the interface, good agreement was obtained between predicted kinetics using Zurob's model and the measured ones. Zurob defined a parameter  $P_{spike}$  (Eq.I.1.28) representing the fraction of the spike formed at the austenite interface.  $X_{interface}$  is the X concentration at the interface at a given time,  $X_{LENP}$  and  $X_{PE}$  are the X contents on the austenite side of the interface under LENP and PE conditions. The parameter varies from 0 at PE conditions to 1 when a full spike is formed at the interface. It can be seen from fig.I.22 that Zurob's model predicts a LENP kinetic with only a partial spike of manganese at the interface.

 $P_{spike} = \frac{X_{interface} - X_{PE}}{X_{LENP} - X_{PE}}$ 

(I.1.28)

Figure I.22: Comparison between the measured growth kinetics during decarburization of Fe-0.94%Mn-0.57%C alloy at 806°C and the predictions of LENP, PE and Zurob's model kinetics. The evolution of the spike's fraction is also represented in the secondary axis [11].

It is now clear that models considering a dissipation due to solute drag describe in a good way the measured kinetics in Fe-C-Mn and Fe-C-Ni systems. However, it should be mentioned that in both systems, the measured kinetics were close to LENP in decarburization experiments. Zurob's model was able to describe the measured kinetics by choosing the appropriate binding energy Eb. Huctchinson's model neglected the dissipation energy due to diffusion within the interface and it succeeded as well to describe the kinetics in the Fe-C-Ni system as well as the PE/LENP transition temperature in Oi's precipitation experiments. The fitting parameters in this model are the diffusivity of solute elements at the interface only. It has to be noted that the same diffusivities were used in Hutchinson's model and Zurob's model. An important point is highlighted : in Hutchinson's approach, the spike of nickel on the austenite side of the interface built up by diffusion of nickel through the interface is the only source of interfacial condition deviation from PE to LENP conditions. In Zurob's approach the LENP kinetics are obtained by combining just the correct magnitude of dissipated energy due to trans-interface diffusion with a partial spike of solute elements at the austenite interface. In other words, solute drag models should not predict exactly LENP kinetics since it is a state that exists only with a zero interface velocity. The amount of experimental data showing excellent agreement with LENP mode give rise to an important question whether the LENP mode is a natural regime of phase transformation.

Qiu [94] conducted other decarburization experiments on Fe-C-Ni to test if the LENP is always the mode of growth in this system as it was reported in previous decarburization experiments. As shown in fig.I.23 the kinetics measured at 775°C in a Fe-0.74C-1.46Ni (wt.%) lie between PE and LENP limits. This deviation was successfully reproduced using Zurob's model. Qiu argued that this result shows that both dissipation due to diffusion through the interface and the solute spike at the austenite interface play a role in the growth behavior of Fe-C-Ni system. One must note that the binding energy used to fit the data is different from that used for another Fe-C-Ni system approximately the same nickel content and at the same temperature. Qiu argued that this may be caused by the different carbon contents in the two systems or to an oxidation effect suspected to occur in one of the experiments.



Figure I.23: Comparison between the measured growth kinetics during decarburization of Fe-0.74%C-1.46%Ni (wt.) alloy at 775°C and the predictions of LENP, PE and Zurob's model kinetics. modified from [94]

Kinetics slower than LENP were observed in Fe-C-Si, Fe-C-Mo and Fe-C-Cr during pre-

cipitation and decarburization experiments. The dissipation-free transition models are not able to predict kinetics slower than LENP and it is a major limitation given this experimental evidence.

On the other hand, Zurob's model was extended to many other ternary Fe-C-X systems (X : Mo, Cr, Si, Al, Cu...) and excellent agreement was achieved by choosing the appropriate binding energies and trans-interface diffusivities. Three cases are illustrated in Fig.I.24 for Fe-C-Si (a), Fe-C-Cr (b) and Fe-C-Mo (c). The obtained results can be considered as strong evidence that PE (as an initial state) combined to a dissipation due to solute drag is a good description of ferrite growth in Fe-C-X systems [94, 96].



Figure I.24: Comparison between the measured growth kinetics during decarburization of a) Fe-0.74%C-0.45%Si (wt.), b) Fe-0.58%C-2%Cr (wt.) and c) Fe-0.54%C-0.51%Mo (wt.) alloys at 775°C and the predictions of LENP, PE and zurob's model kinetics [94,96].

## I.1.4.3 Growth kinetics in Fe-C-X-Y systems

It is now a necessary step to extend Zurob's model to more complex systems with more than one substitutional element. An overview of ferrite growth kinetics in quaternary Fe-C-X-Y systems is given as well as the comparison with solute drag models. In multicomponent systems, the segregation behavior of solute elements at the interface becomes more complex. Co-existing of solutes at the interface may affect the interaction behavior of each element with the moving interface. Beside the solute-interface interaction of each solute element, a solute-solute interaction must be considered when modeling growth kinetics in Fe-C-X-Y systems. This is called the Coupled-Solute drag effect [97–99]. The apparent segregation is modified by the mutual interactions of solute atoms at the interface. It was shown by Guo and Enomoto, that taking into account an interaction parameter between manganese and silicon (Mn-Si interaction is attractive) enhances the dissipated drag energy in a Fe-C-Mn-Si resulting in even slower growth kinetics of ferrite [79]. In case of a repulsive interaction between the two solutes, this can result in a lower dissipated energy for both solutes and thus a lower effect on growth kinetics [100].

Moreover, carbon is reported to segregate at the interface [80]. Thus, it is also important to consider the solute-carbon interaction that can be different between the two X-Y solutes resulting in a more complex segregation behavior. This is the case in Fe-C-Mn-Si, where manganese has an attractive interaction with carbon in contrast to silicon which has strongly repulsive interaction with carbon [97]. As a consequence, the segregation of manganese leads to an increased carbon content at the interface and thus can affect the segregation of silicon. The potentially important role of C has been previously highlighted by Enomoto [101]. Tanaka et al. [102] measured the ferrite growth rates in Fe-C-Mn-X (X : Ni, Si) and compared the obtained results with the measured growth rates in a ternary system Fe-C-Mn with comparable carbon and manganese concentrations. The comparison showed that adding silicon, a ferrite stabilizer, increases the growth rate. On the other hand, adding nickel, an austenite stabilizer, induced a considerable decrease in the measured growth rate. Further et al. [103] studied the effect of molybdenum addition on bainite/ferrite growth kinetics in Fe-C-Mn system. Results showed that adding molybdenum delays the transformation onset and result in a stasis phenomenon where the transformation stops before reaching the equilibrium fraction and continues after a prolonged holding time (Fig.I.25). Xia et al. [104, 105] reported the same behavior at low temperatures  $(550^{\circ}C)$  but no stasis was observed at higher temperature  $(650^{\circ}C)$ .

Solute drag was proposed as one possible cause of the transformation stasis [106, 107]. During the transformation, solute segregation becomes large enough causing a large dissipated energy. As a result, the transformation becomes sluggish or stops completely. Furuhara investigated the solute segregation at the interface at the onset of transformation stasis and results showed only small segregation of manganese and no segregation of Mo. This result is in complete opposition with the solute drag predictions. An alternative explanation was provided by Sun et al. [108] to describe the stasis phenomenon using solute drag theory. If the dissipated energy increases rapidly with decreasing velocity, the carbon interfacial content decreases rapidly, which can lead to a local inversion of the carbon profile. In their study, Zurob's model was used to model ferrite growth under the experimental conditions reported by Furuhara et al. [103]. The authors argued that the



Figure I.25: Ferrite growth kinetics during isothermal holding at 823 K (550°C) of Fe-0.15C-1.49Mn (wt.%) with and without 0.5 wt. % Mo addition [103].

stasis onset is due to an inversion of the carbon profile at the interface. The inversion is caused by a rapid decrease of interfacial carbon content that can not be adjusted by longrange distribution in austenite. This means that the stasis phenomenon is related to the rate of change of the dissipated energy with velocity and not to the absolute magnitude of solute drag energy. Sun et al. [108] reported that the predicted solute segregations using Zurob's model were consistent with the measured ones by Furuhara et al. [103].

Qiu [94,97] used Zurob's model to predict ferrite growth kinetics in the Fe-C-Mn-Si quaternary system during decarburization experiments at different temperatures. The binding energies used for manganese and silicon, as well as the diffusion coefficients, were the same used to successfully predict the growth kinetics in Fe-C-Mn and Fe-C-Si systems [94]. In contrast to previous model applications in ternary system where  $E_b$  and trans-interface diffusion coefficients were fitted to obtain the best agreement with experimental results, no fitting parameters were used in this case. The Mn-Si interaction in the interface was assumed to be the same as in austenite. Under all the studied conditions (different manganese and silicon contents and different temperatures), the predicted ferrite growth kinetics were slower than the measured ones. This means that the estimated net solute drag was overestimated using Zurob's model (Fig.I.26-a). A more surprising result was that a good agreement with experimental results was obtained when the Mn-Si interaction at the interface was set to zero (Fig.I.26-b). This result is the opposite of what was reported in the literature about the coupled solute drag effect (CSDE) observed in Fe-C-Mn-Si [79, 102]. One of the suggested possibilities to explain the apparent absence of CSDE is the role of carbon on the segregation behavior of silicon at the interface as mentioned above. The used binding energies  $E_b$  extracted from the ternary Fe-C-Mn

and Fe-C-Si systems are 'effective' binding energies and include the solute carbon interaction. In Fe-C-Mn-Si, this effective binding energy may change due to different Mn-C (attractive) and Si-C (repulsive) interaction behavior. This can result in a lower effective binding energy of silicon in the quaternary Fe-C-Mn-Si system than that reported in Fe-C-Si ternary system [97].



Figure I.26: Comparison between the measured growth kinetics during decarburization of Fe-0.68C-1.58Mn-1.33Si (wt. %) alloy at 775°C and the predictions of LENP, PE and Zurob's model kinetics in case (a) when Mn-Si interaction in the interface is the same as in austenite and (b) when Mn-Si interaction in the interface is set to zero [97].

Sun et al. [108] suggested that if this was the origin of the observed discrepancies in growth kinetics between experimental results and modeling in the Fe-C-Mn-Si system, this effect would be much less in a system where both X and Y have attractive interactions with carbon. Sun et al. [108] used a Fe-C-Mn-Mo system to investigate this effect. Using the same procedure, the authors used the same binding energies and interface diffusivities already used to successfully predict ferrite growth kinetics in ternary Fe-C-Mn and Fe-C-Mo systems. Good agreement was obtained between the measured and the predicted growth kinetics (Fig.I.27). Sun et al. argued that the obtained result is a strong evidence of the important role of carbon on the segregation behavior of solute elements at the interface. However, the complex interaction between the three elements (Mn,Si,C) is not intuitive. One can assume that silicon should segregate more in the Fe-C-Mn-Si system then in the Fe-C-Si ternary system by considering the Mn-Si attractive interaction. On the other hand, the attractive interaction between manganese and carbon leads to an increase of carbon content at the interface. As a result, one can presume a desegregation of silicon at the interface seen the repulsive interaction between carbon and silicon.

Song et al. [109] used the GEB model to predict growth kinetics in a Fe-C-Mn-Si system at different temperatures. As mentioned before, the GEB model uses Cahn's approach to evaluate the dissipated energy due to solute interaction with the interface. The used



Figure I.27: Comparison between the measured growth kinetics during decarburization of Fe-0.42C-0.49Mn-0.42Mo (wt. %) alloy at 775°C and the predictions of LENP, PE and Zurob's model kinetics [108].

binding energies were extracted from Chen's work [91] on modeling ferrite growth in Fe-C-Mn and Fe-C-Si systems. The Mn-Si interaction at the interface was assumed to be the same as in austenite. The obtained results showed good agreement with experimental measurements for all temperatures (Fig.I.28). This result confirms the coupled solute drag effect in Fe-C-Mn-Si system as already reported in previous experiments [79].



Figure I.28: Ferrite volume fractions from dilatation measurements (scatters) as a function of time for the isothermal transformation of Fe-0.17C-0.91Mn-1.03Si (wt.%) alloy at different temperatures compared to the predictions of GEB model (lines) [109].

Qiu et al. [97] and Sun et al. [108] reported an apparent absence of CSDE in Fe-0.66C-Mn-Si system and argued that carbon interaction with solutes at the interface may play an important role in this effect. On the other hand, Song et al. [109] reported that the coupled solute drag effect was effectively apparent in the Fe-0.17C-Mn-Si system and succeeded to predict the ferrite growth kinetics using their approach. One of the reasons that may explain this difference is the carbon content in both systems. The low carbon content used in Song's experiment can lead to lower segregation of carbon at the interface and thus affects less the effective binding energy of silicon with the interface. As a result, a higher silicon segregation is expected at the interface in Song's system and the dissipated energy due to solute drag is more important than in Qiu's system. An application of Zurob's model to the Song's Fe-C-Mn-Si system can be a good test to validate one more time the important role of carbon in solute segregation at the interface.

An et al. [110] used a modified GEB approach to model the ferrite-to-austenite phase transformation in a Fe-0.07C-1.2Mn-0.45Si (wt.%). The authors neglected the dissipated energy due to silicon diffusion in the interface but also modified the half chemical potential difference of manganese ( $\Delta E = \frac{\mu_{Mn}^{\gamma} - \mu_{Mn}^{\alpha}}{2}$ ), which has a considerable effect on the dissipated energy. This modification was based on APT observations showing that some manganese partitioning took place during phase transformation, which will reduce the chemical potential difference between austenite and ferrite. The obtained results were in good agreement with experimental measurements. However, neglecting the dissipated energy due to silicon diffusion must be examined more carefully in regard to the reported high dissipated energy due to silicon diffusion through the interface at the same temperature in Song's work [109].

# I.1.5 Experimental investigation of solute segregation at the interface

As shown in the previous sections, solute drag and coupled solute drag theories are now largely discussed in the literature due to their success in predicting ferrite growth kinetics in a wide range of ternary Fe-C-X systems and also quaternary Fe-C-X-Y systems. It was shown that in systems as Fe-C-Si, Fe-C-Cr and Fe-C-Mo, the measured kinetics are slower than the predicted ones using LENP and PE models. This was an indirect evidence of the existence of a dissipated energy by solute diffusion across the interface. On the other hand, in systems as Fe-C-Mn and Fe-C-Ni, the measured kinetics were in perfect agreement with LENP measurements (in most decarburization experiments) and under other conditions, a transition PE-to-LENP was observed during ferrite growth in these systems. Moreover, the calculated dissipated energies with respect to PE state for different Fe-C-Mn systems at different temperatures showed similar trends for different manganese contents. As an example, the same dissipated energy was estimated for Fe-C-1Mn and Fe-C-2Mn at a same temperature,  $100 \ J/mol$  at  $775^{\circ}C$  and  $70 \ J/mol$  at  $755^{\circ}C$  [6]. The dissipation theory predicts an increase in dissipation energy with increasing solute concentration which is in contrast with the observed trend. So the question that solute drag is the operating mechanism in all systems remains open.

Recently, Chen et al. [111,112] proposed a cyclic phase transformation concept to study ferrite growth kinetics during austenite-to-ferrite phase transformation. The concept consists in thermally cycling the sample between two temperatures T1 and T2 in the  $\gamma + \alpha$ two phases domain (Fig.I.29). One major advantage of the technique is that it allows following ferrite growth without the uncertainties related to nucleation process.



Figure I.29: The heat treatment procedure used in cylic phase transformations [112].

Chen et al. [112] cycled a Fe-0.023C-0.17Mn (%wt.) alloy between 860°C and 885°C as presented in fig.I.29. The obtained results showed two interesting behaviors of ferrite growth during cycling (Fig.I.30a), a stagnant stage where no phase transformation occurs  $(A_1 - A_2, A_4 - A_5 \text{ and } A_7 - A_8)$ ; and an inverse stage where the phase transformation proceeds in the opposite direction of the heat treatment  $(A_3 - A_4 \text{ and } A_6 - A_7)$ . Comparison with both LE and PE (Fig.I.30b) models gave some details of the observed behaviors. The LE model predicted with a good accuracy the observed kinetics where the PE model failed completely to capture the stagnant stage and predicts a very short inverse transformation stage. It worth mentioning that isothermal modeling of ferrite growth in the same system predict the same kinetics using LE and PE modes. Using the cyclic phase transformation approach, it is clear that PE is not the operating mode during phase transformation in the studied Fe-C-Mn system. The LE modeling was used to explain the stagnant stage and the inverse phase transformation.

Simulations results showed that manganese partitioning at the interface is the main cause of the stagnant stage. During this stage, the transformation switches from LENP mode to LEP mode. On the other hand, the inverse phase transformation was due to the equilibrium not being reached at the transition temperature. The cyclic phase transformation



Figure I.30: a) Dilation as function of temperature during cyclic experiments of a Fe–0.023C–0.17Mn (wt. %) cycled between 885 and 860°C. b)  $\gamma/\alpha$  nuterface position as function of temperature during cycling experiments between 885 and 860°C simulated using LE (blue) and PE (red) modes [112].



Figure I.31: Dilation as function of temperature during final cooling (red) after cyclic experiments of a Fe–0.023C–0.17Mn (wt. %) between 885 and 860°C showing the growth retardation due to interaction between interface and manganese spike [113].

highlighted, in an indirect way, the presence of a spike of manganese at the interface and that it plays an important role in controlling phase transformation kinetics. The LE model predicts that a spike of manganese is left behind the migrating interface in the bulk phase during cycling experiments. This was proven experimentally by Chen et al. [113] by noticing a growth retardation during the final cooling stage to room temperature after a set of cycling transformations (Fig.I.31). This retardation is due to the interaction between the interface and the manganese spike already formed during cycling. The growth retardation was not observed in Fe-C system cycled under the same conditions. This result is another indirect evidence of the existence of a solute spike at the interface during ferrite growth. Despite the good prediction of the observed austenite-to-ferrite phase transformation using the LE model, it is not evident if the observed kinetics are only due to a LEP/LENP transition or to the solute drag effect. Moreover, the LE predicted kinetics were faster than the measured ones and the interface appears to be completely immobile in the observed stagnant stages, in contrast to the LE predictions were the interface has a sluggish velocity but not zero.

Discriminating LENP from solute drag effect requires informations about the chemistry at the interface. Solute drag, as stated before, results from interactions between solutes and interface constituted of few atomic planes. Despite the accuracy of these solute drag models in predicting growth kinetics during austenite-to-ferrite phase transformation, little direct evidence of solute segregation at the interface due to solute drag effect is available in the literature. One main reason is the nano-scale where these solute segregations take place, which requires high resolution characterization methods. Fortunately, in the last 20 years, new advanced experimental techniques were developed and allowed such nano-scale investigations. However, most of the available techniques fail in quantifying carbon due to either its low atomic number (using EDX) or to the contamination effect. This problem can now be limited by using FIB preparation, plasma cleaning or liquid nitrogen cooling trap [6]. Another complexity is the differentiation between the predicted LENP spike and solute segregation due to solute drag. This requires choosing experimental conditions were the predicted solute contents at the interface highly differ between both modes (LENP and solute drag).



Figure I.32: Measurements of manganese (a) and carbon (b) concentration profiles by APT accross the  $\gamma/\alpha$  interface of a Fe-C-Mn treated at 680°C for 3 hours [29].

Danoix et al. [29] used atom probe tomography (APT) and scanning transmission electron microscopy (STEM-EDX) to investigate the co-segregation of manganese and carbon in a Fe-C-Mn treated at 680°C during 10800s (3hours) and quenched to room temperature (Fig.I.32). The Fe-C-Mn composition was chosen so that a competition between LENP and PE growth modes is expected. Results showed a high carbon segregation at the interface that largely exceeded the predicted carbon contents by both classical modes LENP and PE. This carbon segregation was attributed to the presence of manganese at the interface inducing co-segregation of carbon and manganese. The high content of carbon at the interface excluded the PE to LENP transition as a possible mode of transformation in the investigated alloy. The authors concluded that their result is a strong evidence that solute drag is the operating mode during ferrite growth. However, carbon profiles measured at room temperature by APT should be interpreted carefully due to the auto-tempering of martensite, which can result in a redistribution of carbon after quench [6, 29].

A set of atom probe tomography (APT) experiments were conducted by Van Landeghem et al. [30, 114] to investigate solute segregation at the interface in different Fe-C-X (X : Mn, Ni, Mo, Cr, Si) systems. Decarburization experiments were used to create incoherent planar interfaces with well-known velocities. Results showed a strong segregation of molybdenum and chromium at the interface and no segregation was observed in case of Ni. One interesting result was the observation of a depletion of silicon at the  $\alpha/\gamma$ interface where an attractive interaction is reported between silicon and the interface I.33. The observed depletion was attributed to the repulsive interaction between carbon and silicon. This result highlights the importance of accounting for C/X interactions in modeling ferrite growth as discussed by Qiu et al. [97]. Van Landeghem et al. [114] compared the manganese segregation in two systems Fe-C-Mn and Fe-N-Mn under the same experimental conditions. The authors reported a higher manganese segregation in Fe-C-Mn accompanied by an important presence of carbon at the interface in contrast to the Fe-N-Mn where minor segregation of nitrogen and no manganese were observed. The obtained results reinforced the idea that C/Mn attractive interaction is responsible in enhancing the segregation of manganese at the interface.



Figure I.33: Composition profiles of C and Si across the ferrite/martensite interface from decarburization experiments of a Fe-C-Si alloy treated at 775°C for 16min [114].

In a recent study, Zurob's team compared the segregation behavior in Fe-C-Mn, Fe-C-Si and Fe-C-Mn-Si in an attempt to investigate the observed results in Qiu's attempt to model growth kinetics in Fe-C-Mn-Si system [97]. Qiu concluded that the repulsive interaction between carbon and silicon at the interface may be the reason of the discrepancies observed between measured kinetics and modeling. APT results showed nearly the same segregation of manganese in the ternary and quaternary systems. On the other hand, silicon showed a minor segregation in the quaternary system opposed to a desegregation in the Fe-C-Si ternary system. Comparison between the excess area under the segregation profiles in the three systems (Fe-C-Mn, Fe-C-Si and Fe-C-Mn-Si) showed that the dissipated energy in the quaternary system should be less than the addition of the two dissipated energies in the ternary systems Fe-C-Mn and Fe-C-Si. Moreover, the silicon segregation in the Fe-C-Mn-Si system suggests a strong Mn-Si attractive interaction at the interface in contrast to the predicted no interaction by Qiu's modeling. The observations made by Zurob's team highlight the complex relationship between Mn-C, Si-C and Si-Mn at the interface and emphasize the importance of an accurate description of these parameters toward a proper modeling of ferrite growth in multi-component systems that show co-segregation.

# I.2 High throughput approach to study ferrite growth kinetics

Developing new and advanced materials is now more than ever, a key fetool to meet the growing economical and environmental concerns [115]. The remarkable advances made in computational tools to accelerate predicting materials properties with a high accuracy [116–119] coupled with the increase of existing empirical data [120] created new possibilities in discovering new materials or optimizing existing ones to fulfill the desired high and sometimes antagonist properties [115, 121]. However, screening materials properties in relation to their composition, morphology, microstructure and other nano scale parameters is still particularly challenging [24]. Moreover, gathering empirical informations using classical experimental methods based on discrete, repetitive experiments and characterization loops is time-consuming and can also be costly. High throughput experimental techniques is a good alternative to rapidly explore a large set of parameters and accelerate materials development.

Compositionally-graded alloys generated using diffusion couples were used to investigate and explore the composition-dependence of microstructures [16, 18–20]. In steels, it has been used in conjunction with optical microscopy to characterize the effect of composition on recrystallization and on austenite-to-ferrite transformation [21, 22, 122].

High-throughput characterization techniques such as X-ray diffraction experiments are
the second important lever for rapid screening of materials properties dependence on composition. For studying phase transformation kinetics, synchrotron X-ray techniques (such as HEXRD and SAXS) offer important tools to monitor such reactions in-situ. Coupling this technique with compositionally graded materials enables gathering growth kinetics with simultaneous high time- and space-resolutions [18, 19].

#### I.2.1 Compositionally graded materials (CGM)

Compositionally graded materials provide significant advantages for investigating compositiondependent phenomena such as phase transformations. The classical approach for studying such phenomena is to fabricate a large set of individual alloys of different compositions. Obviously, this method can be time- and ressource-consuming and further, it does not allow continuous scanning of the composition space. There are several preparation methods to create compositionally graded materials [121]. For phase transformation investigation, continuous composition gradients are generally created using a diffusion couple approach. A diffusion couple or multiple consists in two or multiple samples of different compositions joined together and heat treated to generate composition gradients [12, 123]. Interfacial contact between the different samples are classically formed at high temperature using high isostatic pressure or thermomechanical simulators (Gleeble system) [21, 122, 123]. The advantage of this method is the possibility of joining multiple pieces simultaneously. However, the initial interfaces must be well prepared to avoid defects at the bonding interface that can alter the diffusion process. Moreover, a good control of the atmosphere during pressing at high temperature is required to avoid forming oxides at the interface. Another method for solid state joining is linear friction welding (LFW) which allows rapid joining of dissimilar alloys without prior interface preparation [19]. One limitation of this method is the limited number of samples that can be joined (two samples at one time). Once the diffusion couple or multiple is created, gradients of composition are generated using inter-diffusion treatment. For phase transformation investigations, the generated gradient length should be several orders of magnitude larger than the characteristic distance of the microstucture (grain size, precipitate size...) so that the local concentration at the phase transformation scale can be considered as constant [19, 21]. Besides, the inter-diffusion treatment should be carried in a single-phase domain to avoid composition discontinuities in the generated gradients [121]. In some cases where the obtained gradient length using diffusion treatment is not large enough, it can be enlarged using further plastic deformation such as rolling [19, 21].

Diffusion couples are used in phase diagram mapping where different samples of pure elements are joined together and treated at high temperature to cause interdiffusion. Using electron probe microanalysis, the compositions across phase interfaces and three-phase junctions are measured to obtain tie-lines and construct the different isothermal sections of phase diagrams. An example of a Fe–Cr–Ni–Co–Mo diffusion multiple made by as-



Figure I.34: Fe–Cr–Ni–Co–Mo diffusion multiple used by [124] to investigate phase diagrams.

sembling pure Fe, Co, Cr, Mo and Ni samples using hot isostatic pressing is shown in figure I.34. The diffusion multiple was annealed at 1200°C for 500 h to generate wide composition gradients. Several slices were cut from the multiple and treated at intermediate temperatures (700-800°C) for long times (1000h) to induce phase transformation and reach equilibrium. Electron microscopy images were used to identify the existing phases and EPMA was used to identify interfacial compositions and construct the phase diagram [124].

In phase transformations, De Geuser et al. [18] used Small-Angle X-ray Scattering (SAXS) to study the effect of Co content on precipitation kinetics in a Cu-Co system. The diffusion couple was fabricated using pure Cu and Cu-2%Co, and treated at 1000°C for 15 days to generate Co gradient of 500-600  $\mu m$ . To further expand the composition gradient, the diffusion couple was hot compressed in a channel die resulting in a 3 mm concentration profile length. The diffusion couple was then heat-treated in-situ and continuously scanned using X-ray beam. The large dataset obtained by this approach in a single experiment allowed the authors to compare the obtained results to a precipitation model and thus test the robustness of the model since it should cover a large concentration range and over the complete precipitation sequence (nucleation, growth and coalescence).

In steels, Sinclair et al. [122] studied the effect of Nb in solid solution on recrystallization and grain growth of a ferritic iron alloy. The diffusion couple was created by joining a Fe-0.095Nb sample between two pure Fe blocks using high temperature pressing and the gradient was formed by annealing at 1450°C for 20min. To simultaneously investigate the effect of composition and temperature on recrystallization, the diffusion couple containing the Nb gradient was cold rolled and then treated in a temperature gradient placed perpendiculary to the composition gradient. Scanning electron microscope (SEM) observations were used to quantify recrystallization and grain growth within the composition and temperature gradient. Results showed that the measured grain sizes were in good agreement with the predicted ones using solute drag models.



Figure I.35: Ferrite precipitation under isothermal conditions - 700°C for 2 min - in a sample containing gradient of Ni. The dashed lines mark the calculated boundary separating the LEP/LENP regimes [21].

Hutchinson et al. [21] used the diffusion couple approach to study the effect of nickel content on the austenite-to-ferrite growth kinetics. The diffusion couple was created from two binary alloys Fe-1Ni (wt.%) and Fe-5Ni (wt.%) using pressing at high temperature. The nickel composition gradient was generated at 1400°C for 72h. The obtained gradient length being not sufficient to quantitatively studying phase transformation, the composition gradient was extended using cold rolling resulting in a 10mm gradient length. Carburization under a  $CO_2/CO$  gas mixture was used to add the desired carbon content of 0.1 C (wt.%). The carburized diffusion couple was annealed at 1100°C for 5 min to fully austenitise the microstructure, quenched to 700°C for various times before quenching into water. Fig.I.35 shows the formed ferrite within the nickel composition gradient of the diffusion couple after 2min at 700°C. Hutchinson et al. reported a smooth transition from the LENP regime at low nickel contents where low ferrite fractions are observed. The transition LENP/LEP is predicted to occur at 2.9 (wt.%) Ni using the classical LE model. However, notable ferrite formation was observed at contents higher than 2.9% and

the transition was reported to occur at 3.5% (wt.). Using a diffusion couple approach, the authors were able to identify the critical composition that separates sluggish from fast ferrite growth in a single experiment.

#### I.2.2 Ferrite growth kinetics measurements

Experimental investigation of the austenite to ferrite phase transformation in steels is generally carried out using two main approaches, precipitation and controlled decarburization (Fig.I.37). Precipitation is the most used technique since it is more representative of the microstructural evolution in industrial conditions. A precipitation experiment involves generally three steps. First, austenization, where the alloy is heated above the  $Ae_3$  temperature to form a fully austenitic microstructure. Second, rapid cooling and holding at an inter-critical temperature in the two phase region  $\alpha + \gamma$  where ferrite starts precipitating at the austenitic grain boundaries [7]. Finally, water quenching to freeze the formed microstructure during the isothermal hold. The main drawback of this technique in measuring growth kinetics is the overlap of nucleation and growth processes that can affect the effective time of growth [6]. Moreover, the growth of individual precipitates is highly dependent on the crystallographical orientation between the parent and the formed phase [22]. Thus, statistical errors may be produced when using metallographical techniques to determine the ferrite fraction.



Figure I.36: Schematic description of precipitation and decarburization techniques generally used for ferrite growth investigation.

The decarburization technique consists in heating the sample into the austenite one phase region and exposing the sample to wet-hydrogen atmosphere to remove carbon from the surface [11, 22, 84, 94, 108]. As a result, a uniform ferrite layer is formed at the surface when the carbon concentration at the surface drops to zero. Ferrite growth in this case



Figure I.37: Optical micrographs showing the obtained martensite (former austenite) and ferrite microstructure in : a) precipitation experiments [35] and b) decarburization experiments [85].

is controlled by carbon diffusion in both ferrite and austenite [11]. The advantage of this technique is the possibility to accurately measure ferrite growth kinetics with a limited contribution from nucleation, since it only occurs at the beginning of the experiment and completes in a negligible time. The effect of crystallography can be neglected since the interface between ferrite and austenite progress through different austenite grains with different orientations. The interface position is easily followed using metallography due to the planar geometry of the interface [11, 22]. However, some limitations are noted when using decarburization in studying ferrite growth kinetics. The range of measured interface velocities is approximately one order of magnitude slower than those encountered in classical precipitation experiments and is not relevant in the industrial conditions [11, 85, 94]. Another disadvantage is the limited range of temperatures at which ferrite growth can be studied. For a given carbon content, decarburization can only be performed at temperatures where the alloy is initially fully austenitic [94].

Traditionally, the most common technique used to investigate ferrite growth kinetics is post-mortem optical metallography. After the isothermal treatment, either by precipitation or decarburization, the quenched sample is polished and etched to reveal the formed microstructure. Optical microscopy is used to measure ferrite volume fraction or thickness. Growth kinetics are obtained from a series of ex-situ measurements on samples treated isothermally for different times. This method can generate some statistical errors when measuring growth kinetics from precipitation experiments due to stereological and sectioning effects [22,85]. Observations are made on the cutting plane and since this plane does not pass through the center of all the observed grains, the measured grain sizes are not representative of the 3D microstructure [125]. This sterological effect made the comparison between the different measured ferrite growth kinetics and the predictions of modeling very difficult [74,75].

Dilatometry is another experimental technique used to investigate phase transformations in steels [112, 126–128]. In this case, the relative change in length that occurs during the applied heat treatment is measured as a function of time. Due to the difference in atomic volumes of ferrite-bcc and austenite-fcc, austenite to ferrite phase transformation is accompanied by volume change of the sample. This method allows an *in situ* measurement of the growth kinetics. However, to obtain quantitative informations about the formed volume fraction of ferrite, assumptions must be made on some unknown parameters such as austenite and ferrite lattice parameters and their evolutions during phase transformation [126].

High energy X-ray diffraction (HEXRD) is a less commonly used technique in the characterization of phase transformations in steels [25,128–130]. This method however, gives accurate quantitative data regarding structural parameters such as lattice parameters [131], strain [132] as well as phasesvolume fractions and their natures [128]. Coupling this method with heating devices, *in situ* investigations of microstructural developments can be accurately performed with a high time resolution of few seconds or less. However, HEXRD requires access to a high energy X-ray facility such as a synchrotron beamline, which is in high demand. Another important feature of HEXRD technique is the high spatial resolution which is typically of 100  $\mu m$  in a synchrotron beam [25,121]. This characteristic coupled with a high time resolution and recent technological developments that improved the acquisition speed [121] and allowed the automation of the technique [26], made of HEXRD a perfect tool for high-throughput characterizations.

Coupling in-situ experiments such as HEXRD SAXS with compositionally graded samples can provide a powerful tool for studying phase transformation dependence on composition and generating large kinetic databases. However, some experimental requirements need to be taken on consideration for a successful characterization.

- The spatial extension of the composition gradient must be large enough so that the probed volume using X-ray (100-200  $\mu m$ ) techniques can be considered approximately homogeneous in composition. Thus, many alloy compositions can be measured in a single experiment [18, 121].
- In HEXRD experiments, the probed volume must be chosen to cover a sufficient number of grains to ensure quantitative and statistic characterization of the phase transformation from the HEXRD data. This requirement depends, for a given X-Ray beam size, highly on the grain size [25].
- The scanning time across the entire gradient must be adjusted for the time scale of transformation kinetics. For example, in ferrite precipitation experiments, if the composition gradient is too long so that every alloy composition is scanned every

60s or more, fast precipitation growth kinetics can be passed over [121]. Moreover, for continuous scanning, translation motors must be available with desired speed.

• Finally, specific equipments can be required for the in-situ experiments such as furnaces that ensure uniform temperature distribution across the full composition gradients. Moreover, the furnace should adapted the used technique (HEXRD or SAXS), notably in terms of holes for the beam path [18].

## Chapter II

## Experimental methods

#### **II.1** Materials and characterization techniques

The samples used in this study were cast, hot-rolled and homogenized at 1200°C for 18h at ArcelorMittal, Maizieres-les-Metz, France, and their precise initial compositions are provided in Table 1.

Since the aim of this study is to explore the effect of substitutional elements on ferrite growth in steels, the diffusion couples should contain gradients of composition for the substitutional elements with (ideally) a constant carbon content. Using the different samples listed in Table 3, diffusion couples containing one substitutional element gradient can be created by joining one binary Fe-C alloy and one ternary Fe-C-X alloy. Diffusion couples containing opposite gradients of composition can also be generated by coupling Fe-C-X<sub>1</sub> and Fe-C-X<sub>2</sub>, where X<sub>1</sub> and X<sub>2</sub> are two different substitutional elements.

Composition %wt	C	Si	Mn	Mo	Cr	Ni	Al	Other alloying elements			
Fe-C	0.26	0.03	0.004	< 0.002	< 0.002	< 0.002	0.003	< 0.002			
Fe-C-Ni	0.26	0.03	0.002	< 0.002	< 0.002	< 0.002	0.003	< 0.002			
Fe-C-Mn	0.26	0.03	0.3	< 0.002	< 0.002	< 0.002	0.003	0.98			
Fe-C-Mo	0.26	0.02	0.004	0.21	< 0.002	< 0.002	0.003	< 0.002			
Fe-C-Cr	0.26	0.02	0.004	< 0.002	1.0	< 0.002	0.003	< 0.002			
Fe-C-Si	0.26	1.54	0.004	< 0.002	< 0.002	< 0.002	0.006	< 0.002			

Table 3: Chemical compositions (wt. %) of the different alloys used to make diffusion couples, realized by Spark-OES method.

Optical microscopy and scanning electron microscopy (SEM) were used to characterize the microstructure. The observed samples were polished to 1  $\mu m$  using standard metallographic techniques and etched using either Nital (5% solution of  $HNO_3$  in ethanol) for standard microstructure observations or 4% metabisulfite (100 ml  $H_2O + 4$  ml  $Na_2O_5$ ) for ferrite quantification. Metabisulfite reagent was chosen for phase quantification because it often gives a good contrast between the as quenched martensite and ferrite (Fig.II.1). To estimate phases fractions, several gray-scale images were taken along the sample surface using a Zeiss Axiovision optical microscope. Ferrite and martensite fractions were measured by image processing using Image J software. The same preparation procedure was used to measure the austenite parent grain size. Sevral gray-scale images were taken along the sample surface and the grain size was calculated assuming a spherical grain shape.



Figure II.1: Optical micrograph showing a microstructure after quenching consisting of ferrite (in white) and martensite (dark), revealed using 4% metabisulfite etching.

Composition profiles were measured using electron probe microanalysis (EPMA). This technique is used in identification of elements, their concentrations and distribution in solid specimens at the micrometer scale [133]. The other advantage of EPMA is its sensitivity to detect and quantify light elements like carbon. This method involves focusing an electron beam on the analyzed sample and analyzing the emitted X-rays according to their wavelength. In the present study, measurements were carried out using a CAMECA SX50 electron microprobe with an accelerating voltage of 15 kV and a beam current of 900 nA. Samples were polished to 1  $\mu$ m using standard metallographic techniques and finished using an alumina suspension. To avoid surface contamination, which can affect carbon content measurements, carbon standards were polished along with the samples using the same recipe and cleaned together, right before their introduction into the analysis chamber. Furthermore, a liquid nitrogen cooling trap and a low-pressure oxygen jet were used to reduce carbon contamination. An EPMA quantification procedure consists in measurements

ing the peak and background intensities on the analyzed sample and comparing them to the measured intensities on the standards for each of the analyzed elements [134]. An analytical procedure based on the calibration curve method was used for the quantification of carbon [135]. This method consists in measuring the C K $\alpha$  intensity at the maximum of the peak as a function of carbon content for different standards. The used carbon standards in this study consisted in fully martensite steels containing different carbon contents (wt%): pure iron, 0.2 C (20NiCrMo2), 0.42 C (42CrMo4), 0.98 C (100Cr6), and 0.99 C (100Cr6). For the samples to be analyzed, carbon content is determined assuming a linear relationship between the measured C K $\alpha$  intensity and carbon concentration [135].

#### II.2 High energy X-ray diffraction data processing

In situ high-energy X-ray diffraction (HEXRD) experiments provide a large amount of data and analyzing all this data requires using automated tools. In the present study, time- and space-resolved measurements were gathered by coupling compositionally graded samples with *in-situ* HEXRD. As an example, for a 20 min heat treatment with a 0.1 s acquisition time, a total of 12000 measurements are obtained for one sample. Moreover, these measurements are taken at different positions of the sample, thus corresponding to different compositions. Besides extracting information (such as phase fractions) from all the available data (approximately 100 experiments), it was essential to establish the link between each measurement and its space coordinate (and thus its composition).

#### II.2.1 Rietveld refinement method

As a first step, the obtained Debye-Scherer diffraction rings were converted to classical intensity vs.  $2\theta$  diffraction spectra by circular integration using pyFAI software (python library). The diffraction patterns were then analyzed by Rietveld refinement using the FullProf software. The concept of the Rietveld refinement method consists in minimizing the difference between the calculated and the observed powder diffraction patterns using least squares refinement. The adjustment is realized by varying instrumental and structural parameters such as lattice parameters, shape and temperature factors. For a successful Rietveld refinement, prior knowledge of the approximate crystal structure of the present phases in the specimen is required. The shapes of the peaks were described using a pseudo-Voigt function, which is a result of an analytical convolution of a Gaussian and Lorentzian.

Rietveld refinement was conducted using FullProf.2k software, which uses a cyclic refinement of a single diffraction pattern by adjusting the parameters set as free by the user. On every step, the root-mean-square error between the actual and simulated pattern is calculated and the best fit is determined when this value is at its minimum. Before starting the refinement procedure, a text file containing a description of the present phases in the sample is created. In the present study, this file contains two phases, ferrite and austenite. For each phase, several parameters are defined and set to be either fixed, meaning that their value will not be changed during the refinement procedure, or free meaning that this value can be adjusted during the refinement.

In the present study, the fitted parameters were:

- Background contribution parameters
- Lattice parameters of ferrite and austenite
- Scale and shape factors
- Full Width at Half Maximum (FWHM) parameters U and V
- Temperature factor

For each experiment, a starting model was generated using the best refinement parameters obtained by adjusting manually a diffraction pattern where both austenite and ferrite phases are expected to be present (ex. the end of the isothermal holding). The rest of the diffraction patterns were automatically refined using a batch analysis where each diffraction pattern of a same experiment is individually processed using the same refinement template. Ferrite and austenite fractions are then extracted from the output files of each treated diffraction pattern.

As it will be shown in the present study, due to some experimental difficulties, some of the obtained diffraction patterns contained shouldered peaks. This artefact made Rietveld refinement more difficult and resulted in errors on the calculated phase fractions. Fig.II.2 shows an example of a shouldered peak and the calculated peak using Rietveld refinement. In addition, Rietveld refinement is not suitable for low volume fractions (<10%) such as encountered at the beginning or at the end of the transformation.

As an alternative, an integration method was used in order to evaluate the area of isolated peaks corresponding to the two phases, fcc-austenite (200, 211 and 321) and bcc-ferrite (200, 211, 211). A linear interpolation was used to extract the background noise and the individual peaks were integrated using the trapezoidal method. The volume fraction of ferrite  $f_{\alpha}$  was estimated from the integrated intensity of the monitored austenite  $(I_{\gamma}, i)$ and ferrite  $(I_{\alpha}, i)$ :

$$f_{\alpha} = \frac{\frac{1}{N} \sum_{i=1}^{N} \left(\frac{I_{\alpha,i}}{R_{\alpha,i}}\right)}{\frac{1}{N} \sum_{i=1}^{N} \left(\frac{I_{\alpha,i}}{R_{\alpha,i}}\right) + \frac{1}{M} \sum_{i=1}^{M} \left(\frac{I_{\gamma,i}}{R_{\gamma,i}}\right)}$$
(II.2.1)

where N and M are the number of considered ferrite and austenite reflections, respectively. The index i refers to the h k l reflection of interest. The normalization factors



Figure II.2: Integrated 1D diffractogram (intensity vs  $2\theta$ ) showing the shouldered peaks and the resulting error on the Rietveld refinement.



Figure II.3: Ferrite fraction evolution as function of time calculated using Rietveld refinement (black line) and the integration method (red line).

for the austenite  $R_{\gamma,i}$  and ferrite  $R_{\alpha,i}$  peak intensities were extracted from the ICCD files (international centre for diffraction data).

In order to test the validity of the numerical method, a comparison between the calculated ferrite fraction using Rietveld refinement and the numerical integration was carried out on samples where the obtained diffraction patterns were free of shouldered peaks. Figure II.3 shows a comparison between the calculated ferrite fractions using both Rietveld refinement method and the integration method. Good agreement was found between the predicted ferrite fraction using the two methods, as the absolute measurement discrepancy on the ferrite fraction was 10% in the worst case.

## II.2.2 Synchronization between diffraction patterns and motor positions

During the second set of HEXRD experiments at DESY, Hamburg, Germany, the positions of the heat-treated sample during its translation was separately recorded and a later synchronization with the corresponding diffraction pattern was necessary. To this end, the calculated ferrite fraction is plotted as a function of its recorded time as shown in Fig.II.4. On the same plot, the motor position as function of its recorded time is also represented. The synchronization was made by mateching the maxima of the position oscillation with either the minima or the maxima of the ferrite fraction depending on the studied gradient (the dashed line in Fig.II.4). In some cases, some abrupt changes were noticed on the calculated ferrite fractions. This was related to a lag during recording of diffraction patterns either caused by a saturation of the detector server or a bug in the python script used by the beamline technical support team. To deal with this issue, the whole oscillation containing this artefact was deleted and an oscillation period time was added systematically at the next oscillation to account for the missing measurements. At the end, an algorithm written in the PYTHON programming language was used to get the ferrite fraction evolution for defined positions and thus for defined compositions.



Figure II.4: a) An example showing the synchronization procedure between the ferrite fraction (black line) and the sample position (blue line). b) An example showing abrupt changes in ferrite fractions (dashed line) observed during some experiments. The corresponding time of the artefact (15 s in this case) is deleted from the overall kinetics.

## Chapter III

# Development of the combinatorial approach

This chapter is based on a published paper: I.-E. Benrabah, H.P.Van Landeghem, F. Bonnet, F. Robaut, A. Deschamps, Use of Space-Resolved in-Situ High Energy X-ray Diffraction for The Characterization of The Compositional Dependence of The Austenite-to-Ferrite Transformation Kinetics in Steels, Quantum Beam Science. 4 (2020) 1. https://doi.org/10.3390/qubs4010001.

The paper is reproduced below, with additions for providing more details when necessary. The aim of the present chapter is to describe the development of the combinatorial methodology that was leveraged in the present work to investigate ferrite growth kinetics in ternary and quaternary systems. The first part concerns the fabrication of samples with composition gradients of several substitutional species (X and Y, achieving graded quaternary Fe-C-X-Y alloys). Then, in situ high-energy X-ray diffraction (HEXRD) is used to gather ferrite growth kinetics with simultaneous time- and space-resolution. In order to provide a detailed description covering the entire steps followed during this thesis in the development of the combinatorial methodology to investigate ferrite growth kinetics, the experimental procedure is divided into two parts. A first methodology for fabricating compositionally graded steels, followed by a preliminary set of HEXRD experiments conducted at the European synchrotron ESRF will be first presented in this chapter. Based on this first attempt, artefacts affecting the interpretation of the obtained results were identified and several modifications were suggested to improve the developed methodology. This improved methodology, followed by a second set of HEXRD experiments conducted at the DESY synchrotron will be detailed in the present chapter.

### III.1 Fabrication of compositionally graded samples (diffusion couples)

The workflow of diffusion multiple fabrication consists of three steps as shown in Fig.1: solid state diffusion bonding using uniaxial hot compression, high temperature diffusion to generate gradients of composition and finally cold rolling to extend the composition profiles. Since the aim of this study is to explore the effect of substitutional elements on ferrite growth in steels, the diffusion multiples should contain gradients of composition for the substitutional elements with (ideally) a constant carbon content.



Figure III.1: Schematic illustration of the different steps for making materials with macroscopic gradients of composition (First approach). 1- uniaxial hot compression. 2- hightemperature diffusion treatment. 3- cold rolling. 4- recrystallization treatment.

#### **III.1.1** Hot compression experiment

To create solid bonds between different alloys, samples of dimensions 15 mm x 15 mm x 7 mm were prepared from one binary alloy Fe–0.26C (all compositions are given in wt. %) and five ternary alloys Fe–0.26C–X (X : 1.0Mn, 1.0Ni, 1.0Cr or 0.2Mo) using standard metallographic techniques, then held together under a pressure of 20 MPa at 900°C for 1 hour using a custom-made compression device (Fig.III.2). The hot compression device consists in a vertical furnace that allows performing controlled heat treatments up to 1100°C. Compression was performed using a simple lever setup linking an external applied weight to the sample grips inside the furnace. To avoid high temperature oxidation, the samples were wrapped in tantalum foil and the joining operation was conducted under a controlled atmosphere using  $Ar/2\%H_2$  gas at reduced pressure (5 mbar). The same procedure can be used to create diffusion multiples of 3, 6 and 9 samples.

Examples of diffusion multiples made of 3 samples (Fe-C-Ni, Fe-C-Mo and Fe-C-Mn), 6 samples (Fe-C, 2xFe-C-Mo, 2xFe-C-Si and Fe-C-Mn) and 9 samples (Fe-C, 2xFe-C-Mo, 2xFe-C-Mn, 2xFe-C-Cr and 2xFe-C-Ni) are shown in Fig.III.3-a, III.3-b and III.3-c.



Figure III.2: a) A picture of the hot compression device showing the furnace in the upper part and the applied weight in the lower part. b) the grips used to apply compression. c) an example of a diffusion couple before compression.



Figure III.3: Diffusion multiple between a) three ternary alloys, a Fe-C-Ni, a Fe-C-Mo and a Fe-C-Mn. b) one binary Fe-C alloy and three ternay alloys, 2xFe-C-Si, x2Fe-C-Mo and a Fe-C-Mn. c) one binary Fe-C alloy and four ternary alloys, 2xFe-C-Mo, 2xFe-C-Mn, 2xFe-C-Cr and 2xFe-C-Ni

At the end of the compression experiments, the interfaces between different alloys were observed using optical microscopy and scanning electron microscopy (SEM). An example of an optical micrograph showing interfaces of a diffusion multiple between Fe-C, Fe-C- Mo, Fe-C-Si and Fe-C-Mn is presented in Fig.III.4. Fig. III.5-a shows an example of SEM micrograph of the interfaces of a multiple between 2 different ternary alloys, of composition Fe-C-Mn and Fe-C-Mo. The observations show that the interfaces are free of porosities or secondary phases such as oxides or nitrides. In certain cases, grains grow across the interface to the point that it can no longer be distinguished in the microstructure, as shown in Fig.III.5-b between a binary Fe-C and a ternary Fe-C-Mo interface.



Figure III.4: Optical micrograph of a junction between Fe-C, Fe-C-Mo, Fe-C-Si and Fe-C-Mn alloys of an as-joined diffusion multiple.



Figure III.5: Secondary electron micrograph of a junction between: a) two ternary Fe-C-Mn and Fe-C-Mo alloys. b) one binary Fe-C and one ternary Fe-C-Mo alloys. The interfaces are free of pores and secondary phases. In the case of the Fe-C/Fe-Mo-C interface, the austenite grains have grown across the interface, which is no longer visible using secondary electrons.

#### **III.1.2** High temperature diffusion treatment

The next step consists in generating gradients of composition using diffusion at high temperature. In order to avoid composition discontinuities, diffusion should be performed in a single-phase domain. Calculations using the Mob2 database from Thermocalc software [136] suggested that a treatment at 1380°C ( $\gamma$  phase) during 72h should result in gradient lengths between 600  $\mu$ m and 900  $\mu$ m depending on the diffusing element. Controlling the atmosphere during this step is of paramount importance to prevent oxidation or decarburization of the sample. One of the challenges of this methodology was to find a suitable atmosphere for high temperature diffusion treatments. Major efforts were targeted at refining the conditions of this critical step during the first year of the study.

To limit oxidation, a cleanup cycle was performed before the diffusion treatments by flushing the furnace tube multiple times at low temperature (100-200°C) with argon containing 2% of hydrogen. At higher temperature, argon 2%-hydrogen is not a suitable atmosphere for steels due to decarburization caused by the reaction between carbon and hydrogen to form methane  $CH_4$ .

In a first attempt to avoid decarburization, diffusion couples were treated under a lowpressure inert gas (Argon - 99.99% purity) atmosphere. The pressure of the furnace chamber was 2.5 mbar with an argon flow of 1 L.min<sup>-1</sup>. Electron probe microanalysis (EPMA) measurements showed a pronounced decrease in carbon content in the treated samples. Our assumption is that the purity of the inert gas (Argon) was not high enough to avoid decarburization.



Figure III.6: a) a picture of an as assembled diffusion multiple. b) a picture of the same sample after diffusion treatment under high vacuum  $(10^{-5} \text{ mbar})$  showing the material loss due to sublimation.

In a second attempt, high vacuum  $(10^{-5} \text{ mbar})$  was used to assure a very low oxygen content in the atmosphere. The results showed that no decarburization occurred during diffusion treatment. Unfortunately, this atmosphere has some drawbacks related to the vapor pressure of some alloying elements used in the treated specimens (Fig.III.6). When the pressure of the furnace is lower than the vapor pressure of an element, the element evaporates. Since the used samples are a mixture of 3 to 4 elements, the vapor pressure of the alloy is changed following the ideal gas mixture law (Raoult's law). As an example, manganese (Mn) has a vapor pressure of  $10^{-2}$  mbar at  $1380^{\circ}$ C as a pure element. An Fe-C-Mn alloy with 1%wt Mn has a vapor pressure of  $10^{-4}$  mbar which is higher than the chamber pressure causing the sublimation of the sample.

The alternative solution was to use a controlled atmosphere with a given carbon activity similar to that of the specimens. Diffusion treatments were conducted under primary vacuum with a continuous flow of carbon monoxide (4 to 8 ml/min) and argon (0.1L/min) creating a total pressure of 0.5 mbar inside the furnace. The results showed a more limited decarburization compared to the low-pressure argon atmosphere and even no decarburization was observed for some samples. This result, however, was not reproducible across different samples.

The last set of conditions that gave the best results consisted in using a reduced atmosphere with a continuous flow of high purity argon. Argon was passed through a purification system to ensure high purity of the gas. The purification system consists of an oxygen trap filled with active oxygen adsorbant that binds covalently with oxygen. The oxygen content after purification is expected to be less than 1 ppb as indicated on the purification system. The pressure of the furnace chamber was 0.5 mbar with an argon flow of 0.5 L/min. Measurements using EPMA showed no carbon loss across the sample. This atmosphere was chosen over carbon monoxide for its reproducibility. After the diffusion treatment (1380°C during 72h), diffusion multiples were cooled in the furnace and held at 650°C for 8h to obtain a sufficiently ductile microstructure for the subsequent plastic deformation step

Electron probe microanalysis (EPMA) measurements were used to characterize the obtained concentration profiles. Figure III.7-a shows an example of composition profiles between Fe-C-Mn and Fe-C-Mo before and after high temperature treatment. Results show concentration profiles of 950  $\mu m$  (for Mn) and 700  $\mu m$  (for Mo) after diffusion. Composition gradients were generated for all the possible ternary systems (using Fe-C and Fe-C-X couples) and quaternary systems (using Fe-C-X<sub>1</sub> and Fe-C-X<sub>2</sub>).

#### III.1.3 Plastic deformation using cold-rolling

The main target of making diffusion multiples in the present case is to measure the austenite-to-ferrite transformation kinetics as a function of composition using in situ synchrotron X-ray diffraction. Since the characteristic dimension of ferrite growth reaction is 10 to 100  $\mu m$ , a 600-900  $\mu m$  diffusion zone is not suitable to achieve accurate investigation of composition effect on austenite-to-ferrite phase transformation. For this reason, the composition profiles were extended above the millimeter scale using cold rolling. In order to obtain a homogeneous deformation, diffusion multiples were mounted into a block of low-carbon steel (Fig.III.8) and the whole assembly was cold-rolled with multiple small passes to avoid sample damage. The thickness of diffusion couples was reduced by 85%,



Figure III.7: Measured composition profiles using EPMA for substitutional alloying element across Fe-0.26C-1Mn/Fe-0.26C-0.2Mo (wt.%) interface as assembled (line) and after the diffusion treatment (circles).

from 7 mm to 1 mm. This step was followed by a heat treatment at 900°C for 5min followed by water quench to homogenize the carbon distribution in the microstructure and to recrystallize the sample and obtain small grains, so that the diffraction patterns obtained using X-ray experiments would approach continuous Debye–Scherrer rings.



Figure III.8: The low-carbon steel block used as a sample holder to perform cold rolling.

After the cold rolling step, the new composition profiles were measured using EPMA. Fig.III.9-a compares the composition gradients after diffusion treatment and after cold rolling for a diffusion couple between Fe-C-Mn and Fe-C-Mo. The concentration profiles



Figure III.9: a) Measured composition profiles using EPMA for substitutional alloying elements across Fe-0.26C-1Mn/Fe-0.26C-0.2Mo (wt.%) interface as assembled (line), after the diffusion treatment (circles) and after cold rolling (dashed lines).b) Carbon and nickel weight contents as function of distance measured after cold rolling in a Fe-0.26C/Fe-0.26C-1Ni (wt.%) diffusion couple

went from 950  $\mu m$  for Mn to 6.6 mm and from 600  $\mu m$  for Mo to 4.2 mm after cold rolling. Another example of diffusion couple between Fe-C and Fe-C-Ni is shown in Fig.III.9-b. One can notice that the carbon content is constant across the diffusion couple. In some cases, due to the influence of substitutional content on the chemical potential of carbon, a gradient of carbon concentration exists, however it remains of small magnitude, at most  $0.02\% wt.mm^{-1}$  in case of Cr/Si containing couples. This gradient does not interfere with the interpretation of the data since any further modelling compared against experimental data will take into account the carbon content measured locally by EPMA.

#### **III.2** High energy X-ray diffraction experiments

The in-situ High energy X-ray diffraction experiments were performed at the beamline ID11 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using an energy of 87 keV ( $\lambda = 0.4125$  Å). The high-energy beam allows working in transmission diffraction mode. To maximize the number of grains in the illuminated volume, a beam size of  $0.6 \times 0.2 \ mm^2$  (0.2mm in the direction of the concentration gradient, 0.6mm in the perpendicular direction) was used. The austenite grain size after the heat treatment of 5 min at 900°C was measured to be about 50  $\mu m$ . The Debye-Scherrer diffraction rings were collected using a high-resolution 2D FReLoN CCD detector with a high acquisition rate (5 Hz) placed 0.260 m away from the sample. Diffusion couples with dimensions of 10 mm x (6 to 8) mm x 1 mm were heated using an INSTRON electro-thermal mechanical set-up (ETMT), Fig.III.10. Heating was performed by passing a current through the sample (Ohmic heating) and the temperature was regulated using a spot-welded type-S thermocouple. Since temperature gradients exist within the sample due to the watercooled grips holding them, samples were mounted so that the composition gradient was perpendicular to the temperature gradient induced by the water cooled grips, as shown in Fig.III.11. From thermal modelling, we expect a maximum temperature deviation within the beam size of  $3^{\circ}$ C.



Figure III.10: a) A picture of the experimental setup used for HEXRD experiments. b) a picture of the heating system in the ETMT device.

An argon flow was used to limit the decarburization and oxidation during the experiments. Prior to each experiment, the top surface of the sample was scanned horizontally by the X-ray beam to precisely find the location of the control thermocouple and thus ensure that the control temperature is effectively that of the sample location hit by the X-rays. In order to gather time- and space-resolved ferrite growth kinetics during heat treatments, the compositionally graded samples were translated along the composition gradient. The samples were translated over 3 to 8 mm (depending on the gradient length of each sample) using the vertical motor of the beamline that allows a maximum speed of 0.385  $mm.s^{-1}$ . The acquisition time was 0.156 s and diffraction patterns were recorded every 75  $\mu m$ .



Figure III.11: Sketch of the experimental setup used for HEXRD experiments. The compositionally graded sample was translated along the composition gradient in direction z to avoid the temperature gradient caused by the water cooled clamps.

Using this configuration, we were able to record diffraction patterns for each composition along the gradient every 10 to 30 s, depending on the gradient length.

The details of the heat treatments for in-situ HEXRD experiments were as follows. The compositionally graded samples were heated to 910°C at 30°C/s and held 10 s at this temperature to reach full austenitization, which was checked using the diffraction patterns recorded during this step. Samples were then rapidly cooled at 80°C/s, down to an intercritical temperature (730°C, 750°C, 762°C and 775°C) and held 20 min at this temperature to follow austenite-to-ferrite phase transformation. Finally, samples were quenched to room temperature at 80°C/s.

As already explained, the obtained Debye-Scherer diffraction rings (Fig.III.12-a) were converted to classical intensity -  $2\theta$  diffraction spectra (Fig.III.12-b) by circular integration using pyFAI software. Rietveld refinement was used to calculate phase fractions using the FullProf software. A pseudo-Voigt function was used to model the experimental diffraction peaks and a total of 22 parameters were used for Rietveld refinement, such as scale and shape factors, temperature effect, lattice parameters and asymmetry factors.

The obtained 2D diffraction patterns contained some saturated pixels due to the presence of some coarse grains in the microstructure. As a result, some intensity was lost due to saturation close to the peak maxima, resulting in a comparatively higher intensity in the peak tails, so that the measured diffraction peaks appeared shouldered. Fig.III.13-a shows an example of an azimutal map of a diffraction dataset (angular sector on y-axis versus 2-theta diffraction angle) containing saturated pixels. When the radial integration



Figure III.12: a) Debye-Scherer diffraction rings obtained from HEXRD experiments. b) Integrated 1D diffractogram (intensity vs  $2\theta$ ).

is made, the high intensity of the saturated peaks is lost as shown in fig.III.13-b and the resulting peak contains shoulders (Fig.III.13-c). This artefact made Rietveld refinement more difficult and resulted in errors on the calculated phase fractions. In addition, Rietveld refinement is not suitable for low volume fractions such as these encountered at the beginning or at the end of the transformation. As an alternative, we used an integration method in order to evaluate the area of isolated peaks corresponding to the two phases austenite and ferrite as explained in section II.2.



Figure III.13: a) A partial azimuthal map of a diffraction dataset showing saturated pixels. b) Schematic illustration of the radial integration with or without the presence of saturated pixels. c) Schematic illustration of the obtained peak when both saturated and not saturated pixels are integrated.

#### III.2.1 Results

A list of the investigated systems during the first set of HEXRD experiments is shown in Table 4.

Composition	Temperature (°C)					
gradients	775°C	$762^{\circ}\mathrm{C}$	$750^{\circ}\mathrm{C}$	730°C		
Fe-C - Fe-C-1%wtNi	х	х	х			
Fe-C - Fe-C-0.2%wtMo	х	х	х			
Fe-C - Fe-C-1%wtCr	х	х	х			
Fe-C - Fe-C-1%wtMn	х	х	х			
Fe-C-1%wtMn - Fe-C-0.2%wtMo	х	х	х	х		
Fe-C-1%wtMn - Fe-C-1%wtNi	x	х	х			
Fe-C-1%wtMn - Fe-C-1%wtCr	х	х	х			
Fe-C-1%wtNi - Fe-C-0.2%wtMo	х	х	х			
Fe-C-1%wtNi - Fe-C-1%wtCr	x	X	X			
Fe-C-0.2%wtMo - Fe-C-1%wtCr	X	х				

Table 4: Diffusion couples investigated using HEXRD and the corresponding transformation temperatures

Fig.III.14 shows an example of the evolution of diffraction patterns for one composition (0.15C-0.65Mn-0.06Mo (wt.%)) of the diffusion couple Fe-0.16C-1Mn/Fe-0.16C-0.2Mo during different steps of the thermal cycle. At room temperature, before the *in-situ* experiment, the microstructure is fully martensitic and only bcc-phase peaks are present on diffraction patterns. At 910°C, only fcc-phase peaks corresponding to austenite are observed, which confirm the complete austenitization of the material microstructure at this temperature. After cooling to the inter-critical temperature (730°C), both phases are observed on diffraction patterns with variable intensities during holding. Monitoring the integrated intensities of ferrite and austenite peaks during the holding step provides the evolution of the phase volume fraction.

The data obtained for the special case of a gradient in Mn at constant carbon content will now be presented in more detail. A diffusion couple between Fe-0.16C/Fe-0.16C-1Mn (wt.%) was austenitized at 910°C, quenched to 760°C and held at this temperature for 20 min. Fig.III.15 shows the Mn profile as function of position superposed to the corresponding measured ferrite fraction by HEXRD at the end of the isothermal step (i.e. after 20 min). The Mn content varies from 0 % to 1 % over a distance of 8 mm. If we consider a beam size of  $200\mu$ m as used in the HEXRD experiments, the variation of composition within the beam is of 0.025Mn (%wt.). The corresponding formed ferrite fraction shows a transition from high fractions (~80%) at low Mn content to low ferrite fractions (~ 20%) at high Mn content (1%). Fig.III.16 illustrates an isothermal section of the Fe-C-Mn



Figure III.14: Evolution of diffraction patterns during a thermal treatment at different times, corresponding to one composition of a diffusion couple Fe-0.16C-1Mn/Fe-0.16C-0.2Mo.  $t_1$ : room temperature.  $t_1$ : austenization at 910°C.  $t_2$ : beginning of isothermal holding at 730°C.  $t_3$ : at the end of isothermal holding.

phase diagram at 760°C calculated using the TCFE9 database of ThermoCalc, showing the different growth modes for the composition range of the diffusion couple. It can be seen that for the whole composition gradient, both LENP or PE are theoretically possible transformation modes. The predicted ferrite fraction using PE and LENP modes after 20 min at 760°C are represented in Fig.III.15. LENP and PE calculations were carried using DICTRA software, TCFE9 and MOB2 databases. A spherical, 50  $\mu$ m grain size was used, which is representative of the real microstructure.

At low Mn content, the measured ferrite fraction is comparable to the predicted one using both PE and LENP models, which differs little from the equilibrium fraction. As Mn concentration increases, the measured ferrite fraction gets lower than both PE and LENP predictions. Both PE and LENP modes consider that ferrite formation is controlled by carbon diffusion in austenite but with different assumptions at the interface. They represent the thermodynamic limits of non-partitioned growth. In LENP, local equilibrium of the substitutional element is maintained at the interface by a solute spike. PE on the other hand, considers that substitutional elements are completely immobile and equilibrium is satisfied for carbon only as explained in section I.1.2.

Another example illustrating the effect of Mn and Mo content on the formed ferrite fraction is shown in fig.III.17. In this case, the diffusion couple between Fe-C-Mn/Fe-C-Mo was austenitized at 900°C, quenched at 730°C and held at this temperature during 20 min. The profile gradients of Mn and Mo as well as the corresponding measured ferrite fraction at the end of the isothermal step are plotted in fig.III.17. Mn and Mo contents vary from 1% to 0% and 0% to 0.2% (wt.%) respectively, over a distance of 6mm with a constant carbon concentration of 0.16%. A low ferrite fraction (~35%) is measured at low Mo/ high Mn content (1%Mn and 0%Mo); the ferrite fraction increases



Figure III.15: Measured ferrite fractions using HEXRD experiments (solid line) within the Mn concentration gradient of the diffusion couple austenized at 900°C for 10min and quenched to 760°C for 20min. The plotted fractions correspond to the end of the isothermal step at 760°C. The calculated ferrite fractions using LENP (black circles) and PE (gray circles) models for different Mn compositions are superimposed. The error bars represent the local fluctuation of ferrite fraction.



Figure III.16: Isothermal section of the Fe-C-Mn at 760°C showing the different growth modes (LEP-LENP and PE) for the composition range of the diffusion couple (gray circles).



Figure III.17: Measured ferrite fractions using HEXRD experiments (solid line) along the diffusion couple Fe-C-Mn/Fe-C-Mo austenitized at 900°C for 10 min then quenched to 730°C for 20min. The calculated ferrite fractions using LENP (black circles) and PE (gray circles) models for different Mn and Mo compositions are superimposed.

with increasing Mo content and decreasing Mn content to reach ~75% at the Mo rich/ Mn lean side of the diffusion couple (0.2%Mo - 0%Mn). Ferrite fraction evolution shows some irregularities due to the presence of some coarse grains that affect the diffraction patterns and thus introduce an error on the integrated peaks. This error can also originate from a decarburization process during isothermal holding. In fact, a layer of ferrite was observed at the surface of the sample after the HEXRD experiments (Fig.III.18). However, the large size of the observed ferrite grains due to decarburization (>100 $\mu$ m) means that these large volumes are less likely to contribute to the diffraction pattern given the requirement for them to be in Bragg position. If they happen to be in such a position, they contribute spots that saturate the detector locally, leading in turn to shouldering on the integrated profiles.

The last two examples illustrate the effect of composition on the formed ferrite fraction at a given temperature and time. The use of HEXRD gives access to time- and space-resolved kinetics of ferrite growth during precipitation experiments. Fig.III.19 shows the evolution of ferrite fraction measured using HEXRD as a function of time and position (composition) along a diffusion couple between Fe-0.16C-1Mn and Fe-0.16C-0.2Mo (%wt.). The composition variation within the X-ray beam in this case was  $\pm 0.02$ Mn and  $\pm 0.004$ Mo (%wt.). The effects of Mn and Mo content on ferrite growth kinetics are clearly illustrated by the obtained dataset using HEXRD experiments. Ferrite growth rates, as well as the ferrite fraction reached at the plateau, increase with the combination of increasing Mo content. This dependence of ferrite growth rate on Mn and Mo



Figure III.18: An optical micrograph showing the decarburization layer formed during the in situ HEXRD experiments on the Fe-C-Mn/Fe-C-Mo diffusion couple.



Figure III.19: Evolution of ferrite fraction measured using HEXRD as a function of time and distance (composition) along a diffusion couple between Fe-0.16C-1Mn and Fe-0.16C-0.2Mo (%wt.). The diffusion couple was austenitized at 900°C for 10 s then quenched to 730°C for 20 min. The Mn and Mo content evolution as a function of distance is shown in figure III.17.

compositions was obtained using one single experiment, which illustrates the importance of high-throughput methods on providing rich databases that can be used to understand phase transformation kinetics in steels.

In order to have a better understanding of the effect of Mn and Mo contents on ferrite growth kinetics, comparisons were made between the measured fractions using HEXRD



Figure III.20: Experimental ferrite growth kinetics measured using HEXRD experiments for different compositions of the diffusion couple Fe-C-Mn/Fe-C-Mo during the holding step at 760°C for 20min. a) Fe-0.14C-0.15Mn-0.18Mo (%wt.). b) Fe-0.15C-0.3Mn-0.14Mo (%wt.). c) Fe-0.16C-0.65Mn-0.06Mo (%wt.). d) Fe-0.16C-0.88Mn-0.015Mo (%wt.). The calculated kinetics using LENP and PE models are shown for the different compositions.

and the predicted kinetics using both PE and LENP models for a series of compositions (figure III.20 a to d). The following compositions were selected: Fe-0.16C-0.3Mn-0.14Mo, Fe-0.16C-0.65Mn-0.06Mo, Fe-0.16C-0.88Mn-0.015Mo and Fe-0.16C-0.96Mn-0.001Mo (%wt.).

The time t = 0 s corresponds to the beginning of the isothermal step at 730°C. The ferrite growth rate is parabolic at the beginning and tends toward a plateau of practically constant ferrite fraction. The predicted kinetics using both PE and LENP models for the same compositions are superimposed on the same figures (Fig.III.20 a to d). For all compositions, the measured transformation rates are slower than both LENP and PE predictions and the plateau fractions are smaller than the calculated ones. In case of high Mo content and low Mn content (Fe-0.14C-0.15Mn-0.18Mo, Fig.III.20-a), measured kinetics are comparable to the calculated ones using PE and LENP at short times (up to 80 s) and get slower and diverge from PE and LENP at longer times. The predicted ferrite fractions (PE (82%) and LENP (81%)) at the plateau are higher than the measured

one (65%). With increasing Mn content and decreasing Mo content (Fe-0.15C-0.3Mn-0.14Mo, Fig.III.20-b), the measured transformation rate deviates from the predicted kinetics (LENP (20%) or PE (78%)) after 30 s and the gap between the predicted fraction at the plateau and the measured one increases (59%). The same trend is observed in Fig.III.20-c (Fe-0.16C-0.65Mn-0.06Mo) and Fig.III.20-d (Fe-0.16C-0.88Mn-0.015Mo), the difference between the measured and the predicted kinetics becomes more pronounced, as is the case for the final ferrite fraction.

#### **III.3** Discussion

The use of HEXRD technique on compositionally graded materials allowed obtaining time and space-resolved austenite-to-ferrite transformation kinetics. To illustrate the effect of composition on ferrite growth kinetics, experimental results were compared with calculations using LENP and PE models.

#### III.3.1 Effect of Mn on ferrite growth

The comparison between the ferrite fractions reached at the stasis of transformation at  $760^{\circ}$ C, in a ternary alloy Fe-C-Mn with a gradient of Mn content (0 to 1% wt) and the predicted ones using LENP and PE models showed that for low Mn contents (up to (0.3%), the measured fractions are in agreement with the predicted values. At higher Mn contents, the measured fractions become lower than both LENP and PE predictions but closer to LENP calculations. To illustrate this effect, Fig. III.21 shows the evolution of the degree of non-complete transformation with Mn content calculated from using the formula  $\frac{f(PE/LENP)-f(EX)}{f(PE/LENP)}$ , where f(PE/LENP) is the obtained ferrite fraction using PE or LENP conditions and f(EX) is the measured ferrite fraction at the stasis stage, as introduced by Chen et al. [137]. The incomplete (IC) transformation degree increases with Mn content. Using LENP conditions, the degree of IC transformation reaches a plateau at 0.65% of Mn, while the PE corresponding IC transformation degree increases linearly with Mn content. This effect of non-complete transformation was already observed in Fe-C-Mn alloys by Chen et al. [91, 137]. This phenomenon was explained by the segregation of Mn atoms at the moving interface causing a dissipation of the available driving force. The dissipation energy increases with Mn content and when it gets higher than the available driving energy, the transformation stops or becomes too sluggish. During this 'stasis stage', the interface is stationary or moving very slowly.



Figure III.21: The degree of incomplete transformation as function of Mn content at 760°C.

#### **III.3.2** Effect of Mn and Mo on ferrite growth kinetics

In Fig.III.17, the measured ferrite growth kinetics for different compositions of Mo and Mn in quaternary Fe-C-Mn-Mo is compared to the predicted kinetics using PE and LENP approaches. Results showed that with increasing Mn content and decreasing Mo content, the transformation gets slower compared to PE and LENP calculations and the ferrite fraction at the stasis stage gets lower. The incomplete transformation phenomenon is again observed in this system and it intensifies with increasing Mn content and decreasing Mo content. In quaternary Fe-C-X-Y and higher order systems, the effect of substitutional elements on phase transformation kinetics becomes more complex due to the possible solute-solute interaction at the interface and its effect on the segregation behavior of substitutional elements [97]. In austenite to ferrite phase transformation, this effect is known as coupled solute drag effect [97, 108]. In Fe-C-Mn-Mo system, the incomplete transformation was already observed in previous studies [104, 105]. Xia et al. [104] showed that adding 0.3Mo to a Fe-0.1C-1.5Mn (%wt) induced a transformation stasis at 550–600°C but not at 500°C where Mo showed no effect on the plateau of transformation. They also showed that adding Mo could affect the kinetics by retarding the transformation. In another study, the same authors [105] conducted a series of ferrite/bainite precipitation experiments on Fe-0.12C-1.49Mn-xMo (wt. %) with different Mo contents at 550°C. Results showed that adding Mo does not affect the kinetics but it clearly has an effect on the plateau volume fraction. In the present study, the first results indicate an effect of Mo (and Mn) on both kinetics and stasis volume fraction.

#### **III.4** Artefacts and possible solutions

The first approach used in this study to create diffusion couples showed that coupling high temperature diffusion and cold rolling enables obtaining composition profiles at a millimeter scale compatible with the requirements to accurately investigate austenite-toferrite phase transformation. However, some experimental difficulties were encountered during the development of the methodology, making the interpretation of the obtained results more difficult, even impossible in certain cases.

The major artefact was related to the through-thickness gradient of composition generated during cold rolling, due to a deformation disparity between the surfaces and the center of samples, which prevented measuring the transformation at constant composition for a given X-ray beam position. Fig.III.22 shows an example of the through-thickness gradient measured using EPMA in a diffusion couple between Fe-0.26C and Fe-0.26C-1Mn. Most of the gradient samples had to be discarded due to this artefact.



Figure III.22: Mn weight content as function of distance along the thickness of a diffusion couple after cold rolling.

The many low-reduction passes are suspected to have amplified the through-thickness inhomogeneity of deformation normally expected from rolling [138, 139]. Another reason would be the block/sample geometry and the position of the sample in the block used as an assembly for cold rolling. The sample being placed on the top part of the low-carbon block may have enhanced the deformation inhomogeneity, which is known to be higher at the surfaces of the deformed samples using rolling [140]. One of the proposed solutions was to use higher reductions to promote a more homogeneous deformation. To achieve this without damaging the sample, hot rolling can be used with a minimal number of highreductions. Moreover, different block-sample geometries were tried in order to limit the observed inhomogeneity such as centering the sample in low-carbon block (Fig.III.23-a) or using the same thickness for both the sample and the block so that the sample surfaces are in direct contact with the rolls (Fig.III.23-c). Unfortunately, none of the proposed solutions gave satisfying results.



Figure III.23: Different block sample geometries used to limit deformation inhomogeneity during cold rolling. a-b) the sample is placed at the center of the low carbon block. c) the sample and the block have the same thickness.

Alternatively, hot channel-die compression was used instead of rolling to ensure a plane strain deformation mode. This test consists of compressing a preheated thick sample by means of a punching tool. However, the obtained results showed again a heterogeneous deformation between the surfaces and the center of the sample. This was probably due to the used parameters in the hot channel die test which were not adapted for the used samples and more experiments should have been done to find the best conditions for a plan strain deformation mode. Unfortunately, this was not possible within the time frame of this study.

As a last resort, plastic deformation step could to be skipped altogether so that the long composition gradients would be generated using thermal treatments only. As it will be described in detail on the next chapter, we have achieved this using decarburization and re-carburization treatments.

Besides the first problem concerning through-thickness composition gradients, HEXRD

experiments highlighted two other important artefacts that had to be resolved. The first one concerns the relatively coarse grain size of the compositionally graded samples, which resulted in discontinuous 2D diffraction patterns and subsequent shouldered peaks, making the Rietveld adjustment more difficult and resulting in errors on the calculated phase fractions. It should be mentioned that the average grain size of the diffusion couples used in the first set of HEXRD experiments was 50-100  $\mu m$ . The solution to overcome this problem was to use a newly developed furnace with a rotating sample holder. The last problem encountered during the first set of HEXRD experiments. A layer of ferrite was observed on samples surface at the end of HEXRD experiments. This artefact may have caused errors in the measured ferrite fraction. The furnace mentioned above also features superior atmosphere control and should solve this issue as well.

# III.5 The second attempt in the development of the combinatorial approach

#### III.5.1 Fabrication of compositionally graded samples (decarburization and re-carburization)

As it was shown above, the plastic deformation step created undesirable through-thickness gradients of composition. As a proposed solution, the composition gradients should be created using high temperature diffusion treatments only. To this end, diffusion should be carried out in the delta ferrite range where the diffusion of substitutional elements is 10 times faster than in austenite. However, this is possible only samples with very low carbon content. With the initial carbon content of the alloys of this study (0.26% wt.), the ferritic domain cannot be reached without forming liquid. Therefore, the new proposed approach for diffusion couples fabrication consists in four steps as shown in Fig.III.24 : the same first step, uniaxial hot compression for solid state diffusion bonding, decarburizing the diffusion couples at high temperature to generate millimeter scale composition gradient, re-caburization treatment to reintroduce the required amount of carbon, and finally grain size refinement using cyclic heat treatements and limited cold rolling. (Fig.III.25).

Decarburization and diffusion treatments were carried together at high temperature (between 1400°C abd 1460°C, depending on the elements) during 72h under  $Ar - 2\% H_2$ atmosphere (Fig.III.25). The temperature was chosen based on the diffusion couple composition to guarantee diffusion in the ferrite single phase domain. The pressure in the furnace chamber was 1.3 bar with an  $Ar - 2\% H_2$  flow of 11/min. The high pressure was used to prevent oxygen leaks in the furnace chamber and avoid oxidation. It should be mentioned that samples containing Mn could not be treated under these conditions due to Mn evaporation. This was probably caused by the high continuous flow of  $Ar - 2\% H_2$  and



Figure III.24: Schematic illustration of the different steps for making materials with macroscopic gradients of composition (Second approach). 1- uniaxial hot compression. 2- Decarburization and high temperature diffusion treatments. 3- Re-carburization treatment. 4- Grain size refinement.



Figure III.25: Schematic illustration of the different heat treatments used to create gradients of composition in the second approach. a- decarburization treatment to generate large gradients of composition, b- re-carburization treatment to introduce the required amount of carbon and c-homogenization of carbon across the sample.

the low vapor pressure of Mn ( $10^{-2}$  mbar). In a second step, the samples were treated at 1100°C for 72h under a carburizing atmosphere using a  $CO_2/CO$  gas mixture (Fig.III.25). The samples were carburized to 0.2wt.%C under a continuous flow of 98%CO (200ml) and 2% $CO_2$  (4ml). The re-carburized samples were then treated at 1300°C for 2h to homogenize the carbon content over the whole sample (Fig.III.25).

Fig.III.26 shows an example of the obtained composition profiles after the decarburization and re-carburization treatments of a diffusion couple between two ternary alloys Fe-C-1Ni and Fe-C-1Cr (wt.%). Results show concentration profiles of 5 mm for both Cr and Ni and an approximate carbon content of 0.2(wt%). One can notice that the carbon content is


Figure III.26: Measured composition profiles using EPMA across Fe-0.26C-1Ni/Fe-0.26C-1Cr (wt.%) interface after decarburization and recarburization treatments.

constant across the diffusion couple, due to the limited influence of substitutional elements on the chemical potential of carbon at the high temperature of the carburization and homogenization treatments. In some cases, a gradient of carbon concentration exists, however it remains of small magnitude, at most  $0.025\% wt.mm^{-1}$  in case of chromium containing couples. This gradient does not interfere with the interpretation of the data since any further modelling compared against experiments can take into account the carbon content measured locally by EPMA. The obtained gradient lengths are sufficiently extended to allow recording time-resolved measurements at many compositions over the gradient using a synchrotron beam size of  $200\mu m$ . Moreover, the composition profiles are continuous and without local fluctuations, which is necessary to obtain accurate HEXRD measurements.

However, the use of prolonged high temperature treatments (72h at 1400°C + 72h at 1100°C) without deformation made grain size control particularly challenging with this method. The obtained average grain size after these two treatments was 4-7 mm, which is not suitable for X-ray diffraction experiments (Fig.III.27). One way to refine the grain size without plastic deformation is using rapid cycling heat treatments as shown in Fig.III.28. To this end, samples were first austenitized at 880°C for 1min in a salt bath then water quenched to obtain a fully martensitic structure. Then, the samples were treated at 880°C for 7 seconds followed by water quenching and the operation was repeated 5 times as shown in Fig.III.28. The rapid cycling heat treatments allowed reducing the average grain size of the diffusion couples to  $200 - 250\mu m$ .

To further refine the microstructure, diffusion couples were cold rolled in a way that the rolling direction is perpendicular to the composition gradient. Prior to the cold rolling step, samples were tempered at 660°C during 5h to generate a ductile microstructure. To avoid inhomogeneity of deformation, only 20% of reduction was applied on the diffusion couples. At the end, samples were treated at 900°C for 1 min to recrystallize the microstructure. As a result, the new average grain size after rapid cyclic heat treatments and cold rolling was about 50-80  $\mu m$  which is well suited for the X-ray diffraction experiments as it will be shown in the next section.



Figure III.27: Grain size visible with the naked eye after the prolonged high temperature treatments, decarburization and re-carburization.



Figure III.28: Schematic illustration of the different steps used for grain size refinement, cyclic heat treatments, tempering, cold rolling and recrystallization.

To summarize, large gradients of composition were successfully generated using only high temperature treatments and without subsequent large plastic deformation that caused through-thickness gradients of composition as shown in the first methodology. The challenge in this approach was to refine the grain size to fulfill the X-ray diffraction requirements. This was handled using rapid cyclic heat treatments coupled with small reductions using cold rolling in a perpendicular direction of the composition gradient.

#### III.5.2 High energy X-ray diffraction experiments

A second set of in-situ High energy X-ray diffraction experiments were performed at the beamline P21.2 of the DESY PETRA III synchrotron in Hamburg, Germany, using an energy of 82 keV ( $\lambda = 0.1512$  Å). The high-energy beam allows working in transmission mode. To maximize the number of grains in the illuminated volume, a beam size of 1 x 0.08  $mm^2$  (80  $\mu m$  in the direction of the concentration gradient, 1 mm in the perpendicular direction) was used. The Debye-Scherrer diffraction rings were collected using a high-resolution 2D VAREX 4343CT detector with a high acquisition rate (10Hz) placed at 1 m from the sample. Cylindrical samples with a 30 mm length and a 3 mm diameter were cut from the diffusion couples and were heated using a radiation furnace specially developed to perform thermal treatments with a controlled rotation of the sample (Fig.III.30). The used rotation speed was 5 rotations/s. Heating is achieved by a set of lamps surrounding the sample and the temperature is regulated using a spot-welded type-s thermocouple.



Figure III.29: The new furnace developed by Denand et al The furnace allows performing thermal treatments with a controlled rotation of the sample.

The sample and furnace configuration ensured minimizing the temperature gradient over the scanned composition profile of the diffusion couple. Prior tests were conducted to measure this gradient using two thermocouples separated by 10 mm on the sample. Results showed a gradient of temperature of  $1^{\circ}C/mm$ . This gradient will be taken into account



Figure III.30: Diagram of the experimental setup used for HEXRD experiments. The composionally graded sample was translated along the composition gradient in Z direction and a rotation system was used to maximize the number of analyzed grains in the diffracted volume.

when modeling phase transformations. An argon flow was used to limit the decarburization and oxidation during the experiments. In order to gather time- and space-resolved ferrite growth kinetics during heat treatments, the compositionally graded samples were translated along the composition gradient. The samples were translated over 3 to 11 mm (depending on the gradient length of each sample) using the vertical motor of the beamline. Over the course of the experiment, two motors were used, with respective scanning speeds of 0.5 mm/s and 1 mm/s. Due to some technical difficulties, two acquisition times were used, 0.067 s and 0.1 s and diffraction patterns were recorded continuously. Using this configuration, diffraction patterns were recorded every 8 to 20 s (depending on the gradient length and the used scan speed) for each composition along the gradient.

The details of the heat treatments for in-situ HEXRD experiments were as follows. The compositionally graded samples were heated to 910°C (970°C for Si containing samples) at 10°C/s and held 30 s at this temperature to reach full austenitization, which was checked using the diffraction patterns recorded during this step. Samples were then rapidly cooled down at 60°C/s to an inter-critical temperature (730°C, 750°C, and 775°C) and held 15 min at this temperature to follow austenite-to-ferrite phase transformation. Finally, samples were quenched to room temperature at 60°C/s. The obtainedDebye-Scherer diffraction rings (Fig.III.31-a) were converted to classical intensity-2 $\theta$  diffraction spectra (Fig.III.31-b) by circular integration using pyFAI software. Rietveld refinement was used

to calculate phase fractions using the FullProf software. A pseudo-Voigt function was used to model the experimental diffraction peaks and a total of 18 parameters were used for Rietveld adjustment, such as scale and shape factors, temperature effect and lattice parameters. For small fractions (<10%), an integration method was used to calculate ferrite and austenite fractions as described in section II.2.



Figure III.31: a) Debye-Scherer diffraction rings obtained from HEXRD experiments. b) Integrated 1D diffractogram (intensity vs  $2\theta$ ).

# Chapter IV

# Solute drag modeling of ferrite growth kinetics

This chapter reports the investigation of ferrite precipitation kinetics using HEXRD in ternary Fe-C-X and quaternary Fe-C- $X_1X_2$  systems at fixed, discrete compositions. Different substitutional elements were considered, in order to outline their interaction behavior with the moving interface. Variation of temperature and solute content enabled to evaluate their effect on the kinetics. The experimental results were compared to the predictions of a modified version of the solute drag model developed by Zurob et al. [11]. The new version highlights the importance of considering the different interaction parameters when modeling the austenite to ferrite phase transformation.

### **IV.1** Experimental procedure

The samples used in this study were cast, homogenized at 1200°C for 18h and hot-rolled at ArcelorMittal, Maizieres-les-Metz, France, and their precise initial composition is provided in Table 5. Six ternary alloys Fe-0.26C-X (where X: Mn, Ni, Mo and Cr) and one quaternary alloy Fe-0.26C-1Mn-1Cr (%wt.) were used to study the effect of alloying elements on ferrite growth kinetics. To investigate the effect of composition, three Mn compositions were chosen, 0.3%, 0.7% and 1%. The isothermal transformations were conducted at three different temperatures, 730°C, 750°C and 775°C.

In-situ High energy X-ray diffraction experiments were performed at the beamline P21.2 of the DESY PETRA III synchrotron in Hamburg, Germany, using an energy of 82 KeV  $(\lambda = 0.1512 \text{ Å})$ . The high-energy beam allows working in transmission diffraction mode. To maximize the number of grains in the illuminated volume, a beam size of 0.5 x 0.5 mm<sup>2</sup> was used. The Debye-Scherrer diffraction rings were collected using a high-resolution 2D VAREX 4343CT detector with a 10Hz acquisition rate placed 1 m away from the sample. Cylindrical samples with a 30 mm length and a 3 mm diameter were cut from the diffusion

growth kinetics using HEARD experiments, realize by spark-OES method.								
Composition $\%$ wt	С	Si	Mn	Mo	$\operatorname{Cr}$	Ni	Al	Other alloying elements
Fe-C-1Mn	0.26	0.029	0.98	< 0.002	< 0.002	< 0.002	0.003	< 0.002
Fe-C-0.7Mn	0.26	0.03	0.7	< 0.002	< 0.002	< 0.002	0.003	< 0.002
Fe-C-0.3Mn	0.26	0.03	0.3	< 0.002	< 0.002	< 0.002	0.003	< 0.002
Fe-C-0.2Mo	0.26	0.019	0.004	0.21	< 0.002	< 0.002	0.003	< 0.002
Fe-C-1Ni	0.22	0.02	0.004	< 0.002	< 0.002	1.05	0.003	< 0.002
Fe-C-1Cr	0.26	0.027	0.004	< 0.002	0.98	< 0.002	0.003	< 0.002
Fe-C-1Mn-1Cr	0.26	0.02	0.98	< 0.002	1.01	< 0.002	0.006	< 0.002

Table 5: Chemical compositions (wt. %) of the different alloys used to investigate ferrite growth kinetics using HEXRD experiments, realize by Spark-OES method.

couples and were heated using a radiation furnace specially developed to perform thermal treatments with a controlled rotation of the sample (Fig.IV.1). The rotation speed was set at 5 rotations/s. Heating is achieved by a set of lamps surrounding the sample and the temperature is regulated using a spot-welded type-S thermocouple. An argon flow of  $0.4 \text{ l.min}^{-1}$  was used to limit the decarburization and oxidation during the experiments.



Figure IV.1: Diagram of the experimental setup used for HEXRD experiments. A rotation system was used to maximize the number of analyzed grains in the diffracted volume.

The details of the heat treatments for *in-situ* HEXRD experiments were as follows. The samples were heated to 910°C at 10°C/s and held for 30 s at this temperature to reach full austenitization, which was checked using the diffraction patterns recorded during this step. Samples were then rapidly cooled down at 60°C/s to an inter-critical temperature (730°C, 750°C, and 775°C) and held 15 min at this temperature to follow austenite-to-ferrite phase transformation. Finally, samples were quenched to room temperature



Figure IV.2: a) Debye-Scherer diffraction rings obtained from HEXRD experiments. b) Integrated 1D diffractogram (intensity vs  $2\theta$ ).

at 60°C/s. The obtained Debye-Scherer diffraction rings (Fig.IV.2-a) were converted to classical intensity-2  $\theta$  diffraction diagram (Fig.IV.2-b) by circular integration using the pyFAI software package [141]. Rietveld refinement was used to calculate phase fractions using the FullProf software package [142]. A pseudo-Voigt function was used to model the experimental diffraction peaks and a total of 18 parameters were used for Rietveld refinement, including as scale and shape factors, temperature effect and lattice parameters.

## IV.2 Solute drag modeling

We developed a modified version of the three-jump solute drag model proposed by Zurob et al. [11] to predict the effect of composition and temperature on ferrite growth kinetics. Zurob et al. [11] used Hillert's [9] approach tto develop a discrete model of mass transport across the interface to evaluate solute drag during ferrite growth in Fe-C-X systems. In this model, the austenite-ferrite interface is considered as a two atomic layer thick discrete interface. During ferrite growth, diffusion of substitutional elements across the interface involves three jumps across the interface, from ferrite to the first atomic layer, a second jump within the interface and a final jump to austenite. As a result, an atomic flux of solute atoms is generated due to the difference of thermodynamic properties across the interface. The composition of alloying elements in each of these atomic planes is estimated using a mass balance equation:

$$dx_X^i \frac{\delta}{V_m dt} = J_X^i - J_X^{i+1} + \frac{v}{V_m} (x_X^{i+1} - x_X^i)$$
(IV.2.1)

where v is the interface velocity and  $J^i$  is the flux of the solute element from plane i-1

to plane i and is expressed as follows :

$$J_X^i = -\frac{D_X^i}{V_m RT} x_{Fe}^{i-1} x_X^{i-1} \frac{(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})}{\delta}$$
(IV.2.2)

where  $\mu_X^i$  and  $\mu_{Fe}^i$  are the respective chemical potentials of X and Fe at plane *i*,  $\delta$  is the interface thickness,  $V_m$  is the molar volume, *R* is the gas constant, *T* is temperature and  $D_i$  is the diffusion coefficient of element X from plane i-1 to plane *i*. Assuming a steady state, the composition of X in each plane can be evaluated from Eq.IV.2.1 and IV.2.2. The dissipated energy due to diffusion is then estimated using Hillert's approach [9]:

$$\Delta G_m^{diss,X} = \sum_{i=1}^{i=3} -\frac{V_m}{v} J_X^i [(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})]$$
(IV.2.3)

and the total dissipated energy due to diffusion of all substitutional elements is given by :

$$\Delta G_m^{diss} = \sum_{k=1}^{X} \Delta G_m^{diss,X} \tag{IV.2.4}$$

The local energy balance at the interface is used to calculate the interfacial conditions during ferrite growth.

$$\Delta G_m^{chem} = \Delta G_m^{diss} + \Delta G_m^{fric} = 0 \tag{IV.2.5}$$

The interface mobility is considered large enough for the dissipated energy due to interface friction to be neglected in the present model [35,94]. Moreover, interface friction mainly contributes at very high (>  $10e^{-6} m.s^{-1}$ ) and very low velocities (<  $10e^{-11} m.s^{-1}$ ), which are not the operating velocities during precipitation or decarburization experiments [94]. The driving force is expressed in terms of substitutional elements as follows:

$$\Delta G_m^{chem} = \sum_{k=1}^{X} \left\{ \frac{(u_X^{\alpha} + u_X^{\gamma})}{2} (\mu_X^{\gamma,i} - \mu_X^{\alpha,i}) \right\} + \frac{(u_{Fe}^{\alpha} + u_{Fe}^{\gamma})}{2} (\mu_{Fe}^{\gamma,i} - \mu_{Fe}^{\alpha,i})$$
(IV.2.6)

Where  $u_{Fe} = \frac{X_{Fe}}{1-X_C}$  and  $u_X == \frac{X_X}{1-X_C}$  are the molar fraction of X and Fe elements at the austenite and ferrite interface sides. The interface is considered to be initially in PE mode and the interface velocity is evaluated from carbon diffusion in bulk phases (ferrite and austenite in decarburization and austenite only in precipitation):

$$v = \frac{J_C^{\gamma} - J_C^{\alpha}}{x_C^{i,\gamma} - x_C^{i,\alpha}} \tag{IV.2.7}$$

The thermodynamic properties of the interface are described using an approach developed by Hillert [11,95]. The interface properties are modified from those of austenite by shifting the reference state for the free energy by  $3.5kJ.mol^{-1}$ . This value was chosen to capture an interfacial energy of  $0.5 \text{ J.m}^{-2}$ . In the present study, and in order to capture the significant segregation of carbon at the interface observed using atom probe experiments [29,30], the

'L' interaction parameter between carbon and iron at the interface was adjusted from -34  $kJ.mol^{-1}$  (as in austenite) to -50  $kJ.mol^{-1}$ . This parameter is explained further in the text. A key feature of Zurob's model is the choice of two parameters: the binding energy of the substitutional element at the interface and the trans-interface diffusion coefficient of the solute element. These two parameters are not known experimentally and generally used as fitting parameters. The binding energy is generally defined as the difference between the chemical potential of X at the interface and the average chemical potentials of X in ferrite and austenite as shown in figure IV.3 [11, 91, 96].  $\Delta E$  is the average of the solute chemical potential difference between austenite and ferrite,  $\mu_X^{\alpha}$  and  $\mu_X^{\gamma}$  are the chemical potential of the substitutional solute in ferrite and austenite, respectively. The binding energy parameter has been used to express the segregation behavior of the substitutional element at the interface [11, 78, 91, 94, 97, 143]. However, this parameter as calculated with this approach depends on the conditions under which the calculations are made. Carbon segregation and thus interface velocity highly impacts the calculated binding energy. Moreover, taking the average chemical potentials of element X in ferrite and austenite as a reference to calculate the binding energy is questionable.



Figure IV.3: Schematic illustration of the potential well for (a) ferrite stabilizer and (b) austenite stabilizer inside the interface and the calculation of the binding energy in solute drag models.

This issue can explain the troubling feature that different binding energies are sometimes found in the literature for the same element. Zurob et al. [11] and Chen et al. [91] both studied ferrite growth kinetics in the Fe-C-Mn system using solute drag based models. The binding energy of manganese was reported to be around -2.5  $kJ.mol^{-1}$  in Zurob's calculations [11] and -9.9  $kJ.mol^{-1}$  in Chen's [91] study. However, when comparing the enrichment factor of manganese ( $K_{max} = \frac{x_{X,max}}{x_{X,0}}$ ), which is defined as the ratio of the maximal Mn segregation at the interface ( $x_{Mn,max}$ ) and the Mn bulk content ( $x_{Mn,0}$ ), of the two models, one find similar values, 3.3 at 755°C in Zurob's study and 3.4 at the same temperature in Chen's study. This difference in the calculated binding energies can originate from the considered conditions in the calculations. In Zurob's [11] approach, the binding energy is calculated at the initial PE conditions, i.e. high interface velocity and no carbon segregation. This value can be highly different from the calculated one at the local equilibrium conditions. In Chen's approach, it is not clear under which conditions the binding energy was calculated. Moreover, the predicted binding energies ( $E_0$ ) using solute drag models as shown in figure IV.3 are compared to the calculated ones from APT measurements, which are derived from the enrichment factor [29, 86] using Eq.IV.2.8.

$$K_{max} = \frac{x_{X,max}}{x_{X,0}} = \exp(\frac{E_0 - \Delta E}{RT})$$
(IV.2.8)

where  $\Delta E$  is the half difference between chemical potentials of element X in austenite and ferrite. It has to be noted that the effect of carbon co-segregation is not considered in these calculations (Eq.IV.2.8). As already mentioned, carbon can have a considerable effect on the segregation behavior of element X and thus its intrinsic binding energy can be different form the calculated one using Eq.IV.2.8.

In order to overcome this ambiguity in the present study, the segregation behavior will be discussed in terms of enrichment factor calculated at slow velocities (when equilibrium conditions are approached). Sometimes, the binding energy will be given in comparison with other studies when the conditions of calculations are known. To differentiate between the two calculated binding energies, namely that shown in figure IV.3 and the one calculated using Eq.IV.2.8, the latter will be called the effective binding energy.

In the present study, diffusion coefficients for the different jumps were chosen as: the diffusion coefficient of element X in ferrite  $D_{\alpha}$  for  $D_1$ , the diffusion coefficient in austenite  $D_{\gamma}$  as  $D_3$  and the geometrical average of  $D_{\alpha}$  and  $D_{\gamma}$  as  $D_2$ . It is important to note that this assumption was used for all the studied systems. As a result, interface diffusion is not a fitting parameter as in previous studies [96]. The only fitting parameter used in the present study is the interaction parameter between Fe and X element at the interface. It has to be noted that this parameter does not express directly the segregation behavior of element X at the interface. The segregation behavior of element X at the interface depends on a set of interaction parameters, namely those for Fe-X, Fe-C, X-C and  $X_1-X_2$ (in case of two substitutional solutes). For example, an element with a high affinity to carbon such as molybdenum will highly segregate at the interface due to the presence of carbon [85]. The interaction between Fe and X element is expressed using the  $L_{Fe,X:Va}$ thermodynamic parameter in the ThermoCalc database and the Fe-C interaction parameter is expressed using  $L_{Fe,C:Va}$  parameter. The interaction parameter between X and C at the interface is estimated using the Wagner interaction parameter as function of the different L parameters as shown by Eq. IV.2.9 [144]

$$\epsilon_{XC} = -\left\{ \left( {}^{0}L_{Fe,X:Va} + {}^{1}L_{Fe,X:Va} + {}^{2}L_{Fe,X:Va} \right) + \left( {}^{0}L_{Fe,C:Va} - {}^{1}L_{Fe,C:Va} + {}^{2}L_{Fe,C:Va} \right) - \left( {}^{0}L_{X,C:Va} - {}^{1}L_{X,C:Va} + {}^{2}L_{X,C:Va} \right) - \left( {}^{0}L_{Fe,X:C} + {}^{1}L_{Fe,X:C} + {}^{1}L_{Fe,X:C} \right) + {}^{2}L_{Fe,X:C} - L_{Fe,X:C,Va} \right\} / RT$$

$$(IV.2.9)$$

where  $\epsilon_{XC}$  is the Wagner interaction parameter between X and C elements, expressed in the two-sublattice model [145], where one sublattice is occupied by the substitutional solute elements and the second one by the interstitial elements (carbon). The thermodynamic parameters L describe the mutual interaction between two elements.  $L_{Fe,X:Va}$ and  $L_{Fe,X:C}$  express the interaction between Fe and X elements when the first sub-lattice is occupied by Fe and X elements and the second sub-lattice by interstitial vacancies  $V_a$  and carbon, respectively. The left side superscripts on the L parameters express the coefficients of the Redlich-Kister polynomial order.

As it is shown by Eq.IV.2.9, the Wagner interaction parameter  $\epsilon_{XC}$  is affected by the Fe-X and Fe-C interaction parameters ( $L_{Fe,X:Va}$  and  $L_{Fe,C:Va}$ , respectively). Consequently, changing these two parameters, Fe-X (to fit the experimental results) and Fe-C (to express the high carbon segregation at the interface) results in a modification of the interaction behavior between carbon and the solute element at the interface. In the present study, the interaction between X and C at the interface was considered to have the same value as in austenite [80]. To this end, the Wagner interaction parameter ( $\epsilon_{XC}$ ) is calculated both in austenite and at the interface using Eq.IV.2.9 and the difference is adjusted by modifying the  $L_{Fe,X:C,Va}$  parameter of the interface.

In quaternary systems, the Wagner interaction between the two solutes  $X_1$  and  $X_2$  ( $\epsilon_{X_1X_2}$ ) at the interface is expressed using Eq.IV.2.10. This parameter is impacted by the Fe-X1 and Fe-X2 interaction parameters. Again, the  $X_1$ - $X_2$  interaction parameter in the interface is assumed similar to the one in austenite [80]. Once the Fe- $X_1$  and Fe- $X_2$ interaction parameters are adjusted, the Wagner interaction parameter between  $X_1$  and  $X_2$  is calculated in both austenite and the interface and the  $L_{X1,X2:Va}$  parameter of the interface is adjusted to capture the same  $X_1$ - $X_2$  Wagner parameter as in austenite.

$$\epsilon_{X1X2} = -\left\{ \left( {}^{0}L_{Fe,X1:Va} + 2\left( {}^{1}L_{Fe,X1:Va} \right) + 3\left( {}^{2}L_{Fe,X1:Va} \right) \right) + \left( {}^{0}L_{Fe,X2:Va} + 2\left( {}^{1}L_{Fe,X2:Va} \right) + 3\left( {}^{2}L_{Fe,X2:Va} \right) \right) - \left( {}^{0}L_{X1,X2:Va} \right) - \left( {}^{L}L_{Fe,X1:Xa} \right) \right\} / RT$$
(IV.2.10)

# IV.3 Experimental results and modelling according to PE and LE

#### IV.3.1 Fe-C-Mn system

Three different manganese compositions, 0.3, 0.7 and 1% (all compositions are in %wt.) were examined at three different temperatures 730°C, 750°C and 775°C. Figure IV.4 a, b and c show the isothermal sections of the Fe-C-Mn system calculated using TCFE9 database of ThermoCalc, at 730°C, 750°C and 775°C, respectively. At 730°C and 750°C, the three studied compositions are located below the zero partition line, where both LENP and PE growth modes are expected. At 775°C, the 0.3%-Mn containing alloy (Fe-C-0.3Mn) is located below the zero partition line, Fe-C-0.7Mn lies on the zero partition line and Fe-C-1Mn is located above the LENP/LEP boundary.



Figure IV.4: Isothermal section of the Fe-C-Mn at a) 730°C, b) 750°C and c) 775°C showing the different growth modes (LEP-LENP and PE) for the studied compositions (grey circles).

The measured ferrite fraction as a function of time in the Fe-0.26C-0.3Mn, Fe-0.26C-0.7Mn and Fe-0.26C-1Mn systems are shown in figures IV.5 and IV.6, for the three temperatures 730°C, 750°C and 775°C. Experimental results were compared with the predicted ferrite growth kinetics using LE and PE calculations carried using DICTRA software, TCFE9 and MOB2 databases. Calculations were performed using an initial spherical microstructure parent grain. The grain size was measured by metallography techniques for each sample. Ferrite is assumed to nucleate at the boundary of austenite and grow into the spherical grain. An initial ferrite nucleus of thickness 100 nm is considered at the start of modeling, and thus nucleation is not taken into account in modeling. Table 6 summarizes the measured ferrite fractions at the end of the isothermal holding and the ones obtained using the different models as well as the measured grain sizes. In the following section, the obtained HEXRD results are compared with the LE and PE predictions. The comparison with solute drag calculations is discussed later in section IV.4.



Figure IV.5: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of PE (dashed blue line), LE (dashed green line) and solute drag (dashed red line) models for the : a) Fe-0.26C-0.3Mn at 730°C, b) Fe-0.26C-0.3Mn at 750°C, c) Fe-0.26C-0.3Mn at 775°C, d) Fe-0.26C-0.7Mn at 730°C, e) Fe-0.26C-0.7Mn at 775°C



Figure IV.6: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of PE (dashed blue line), LE (dashed green line) and solute drag (dashed black line) models for the : a) Fe-0.26C-1Mn at 730°C, b) Fe-0.26C-1Mn at 750°C, c) Fe-0.26C-1Mn at 775°C

Table 6: Comparison between the measured final fraction (%) and the predicted ones using LE, PE and SD models for the Fe-C-Mn system.

Fe-C-Mn	T(°C)	f(Exp.)	f(LE)	f(PE)	f(SD)	Grain size( $\mu$ m)
Fe0.26C0.3Mn	730	58	58	64	60	50
Fe0.26C0.3Mn	750	49	47	55	48	80
Fe0.26C0.3Mn	775	27	28	38	28	120
Fe0.26C0.7Mn	730	47	41	59	47	120
Fe0.26C0.7Mn	750	27	27	47	27	120
Fe0.26C0.7Mn	775	10	0.5	25	2	120
Fe0.26C1Mn	730	26	25	52	25	120
Fe0.26C1Mn	750	9	8	38	8	120
Fe0.26C1Mn	775	<2	1	13	1	120

In the Fe-0.26C-0.3Mn alloy and for the three temperatures, the experimental ferrite growth rate is parabolic and tends toward a plateau where ferrite fraction is nearly constant. As the transformation temperature increases, the measured kinetics becomes slower and the final ferrite volume fraction reached at the plateau is lower (table 6). The predicted growth kinetics using the PE model is faster than the experimental measurements for all temperatures and the calculated ferrite fractions at the end of the transformation are overestimated by the PE model. For the three temperatures, the measured growth kinetics as well as the reached ferrite fractions at the plateau are well described by the LE calculations.

For the 0.7-Mn containing system, the measured ferrite growth kinetics are slower than PE and faster than LE model at the 730°C and 775°C as shown in Fig.IV.5. The final ferrite volume fractions obtained at the end of the transformation lie between the two predicted ones using LE and PE models. At 750°C, the experimental measured kinetics as well as the final ferrite fraction are well described by the LE model. Finally, the obtained experimental results for the Fe-0.26C-1Mn alloy are slower than the PE calculations at the three temperatures. The LE model describes well the measured kinetics at 730°C and 750°C. Concerning the measured ferrite fraction at 775°C, results show a very low formed ferrite fraction (0.5%) which is very close to the predicted fraction using LE mode (1%). One must mention that quantification of low ferrite fractions (<5%) using Rietveld refinement has a low precision and thus should be treated with caution.

#### IV.3.2 Fe-C-Ni system

The isothermal sections of the Fe-0.22C-1Ni (%.wt.) system at the three examined temperatures 730°C, 750°C and 775°C respectively are shown in figure IV.7. The studied composition is located below the zero partition line for 730°C and 755°C temperatures, and on the partition boundary at 775°C.



Figure IV.7: Isothermal section of the Fe-C-Ni at a) 730°C, b) 750°C and c) 775°C showing the different growth modes (LEP-LENP and PE) for the studied compositions (grey circles).

The measured ferrite fractions as function of time for the Fe-C-Ni alloys are shown in figure IV.8 for the three temperatures 730°C, 755°C and 775°C, respectively. At 730°C and 755°C, the measured kinetics is parabolic at the beginning of transformation and tends towards a plateau with a constant ferrite fraction (57% and 41%, respectively). At 775°C, the growth kinetics is very slow and the final fraction at the end of the isothermal holding is (<1%). The comparison with the predicted ferrite growth kinetics using LE and PE models shows that the experimental results are slower than both modelled kinetics.



Figure IV.8: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of PE (dashed blue line), LE (dashed green line) and solute drag (dashed red line) models for the : a) Fe-0.22C-1Ni at 730°C, b) Fe-0.22C-1Ni at 750°C, c) Fe-0.22C-1Ni at 775°C

Table 7: Comparison between the measured final fraction (%) and the predicted ones using LE, PE and SD models for the Fe-C-Ni system.

/				v		
Fe-C-X	$T(^{\circ}C)$	f(Exp.)	f(LE)	f(PE)	f(SD)	Grain size $(\mu m)$
Fe0.22C1Ni	730	57	60	67	56	40
Fe0.22C1Ni	750	40	44	53	41	40
Fe0.22C1Ni	775	2	12	21	7	70

PE fails at predicting both the growth kinetics and the final fractions (table 7). The LE calculations predict closer final fractions at 730°C and 750°C. At 775°C, the measured ferrite fraction (2%) is much lower than the predicted one using LE calculations (12%) as well as the PE model (32%). Again, low quantified ferrite fractions using the Rietveld refinement must be treated with caution.

#### IV.3.3 Fe-C-Cr and Fe-C-Mo systems

Both molybdenum and chromium are ferrite-stabilizing elements and hence it is interesting to compare ferrite growth in these systems with that obtained in systems containing austenite stabilizers such as nickel and manganese. Moreover, chromium and molybdenum are known to have a strong interaction with the interface when compared to that of nickel and manganese [85, 99]. The measured ferrite growth kinetics for the Fe-C-Cr system is shown in figure IV.9 for the two temperatures 750°C and 775°C. The data obtained at 730°C are not shown here due to the formation of pearlite during the isothermal holding. At both temperatures, the measured ferrite growth kinetics are slower than those obtained using LE and PE models. The measured ferrite fractions at the end of the isothermal holding are compared to the predicted ones using the different models in table 8.



Figure IV.9: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of PE (dashed blue line), LE (dashed green line) and solute drag (dashed red line) models for the : a) Fe-0.26C-1Cr at 750°C, b) Fe-0.26C-1Cr at 775°C

Table 8: Comparison between the measured final fraction (%) and the predicted ones using LE, PE and SD models for the Fe-C-Cr and the Fe-C-Mo systems.

Fe-C-X	$T(^{\circ}C)$	f(Exp.)	f(LE)	f(PE)	f(SD)	Grain size( $\mu$ m)
Fe0.26C1Cr	750	48	52	55	48	50
Fe0.26C1Cr	775	23	30	39	22	120
Fe0.26C02Mo	730	62	65	65	62	50
Fe0.26C02Mo	750	55	60	60	56	50
Fe0.26C02Mo	775	40	46	46	40	60



Figure IV.10: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of PE (dashed blue line), LE (dashed green line) and solute drag (dashed red line) models for the : a) Fe-0.26C-02Mo at 730°C, b) Fe-0.26C-02Mo at 750°C, c) Fe-0.26C-02Mo at 775°C

Figure IV.10 shows the obtained ferrite fractions as function of time for the 0.2Mo containing system at the three temperatures 730°C, 750°C and 775°C, respectively. Under the chosen conditions, the predicted ferrite fractions using the PE and LE model are similar as shown in figure IV.10. As for the previous cases, a parabolic growth is observed at the beginning of the transformation and the ferrite fraction tends toward a plateau. For the three examined temperatures, the ferrite fractions at the plateaus are lower than the LE/PE predicted values (table 8).

#### IV.3.4 Fe-C-Mn-Cr system

The measured ferrite fraction as a function of time for the quaternary Fe-0.26C-1Mn-1Cr system at 730°C is shown in figure IV.11. At the beginning of the transformation, the growth is parabolic and tends towards a constant fraction (31%). The experimental kinetics lie between the LE and PE predicted ones.



Figure IV.11: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of PE (dashed blue line), LE (dashed green line) and solute drag (dashed red line) models for the Fe-0.26C-1Mn-1Cr at 730°C

### IV.4 Discussion

#### IV.4.1 Fe-C-Mn system

The solute drag model was applied to predict the measured ferrite growth kinetics in the Fe-C-Mn system as a function of composition and temperature. The predicted kinetics are plotted along with the measured ones as well as the LE and PE calculations in figures IV.5 and IV.6. In all cases except the 0.7Mn alloy at 775°C, excellent agreement was obtained between the model and the experiments. The model successfully predicted the measured kinetics in cases where both LE and PE failed to do so. It is to be noted that the two conditions (0.7wt.% and 1wt.% at 775°C) are located on and above the zero partition line where growth mode can be controlled by manganese diffusion in austenite (LEP mode). As it was mentioned, the model considers that growth is always controlled by carbon diffusion only and the deviation from PE conditions is due to a dissipation of the available transformation energy due to manganese diffusion in the interface. Thus, the model is not applicable when the partitioning of the substitutional element is not negligible.

The Fe-Mn interaction parameters used in the solute drag model to obtain the best fit of the experimental results are summarized in table 9. Results show a small decrease of the Fe-Mn interaction parameter with increasing temperature ( $\Delta L_{Fe,Mn:Va}$  : -0.5  $kJ.mol^{-1}$ when increasing temperature from 730°C to 775°C). However, the Fe-Mn interaction parameter seems to be independent of composition (or at least this dependency is weak).

Zurob et al. [11] investigated the ferrite growth kinetics using decarburization experiments in Fe-C-Mn systems and reported a binding energy of -2.5  $kJ.mol^{-1}$  to model the observed kinetics. The binding energy was calculated under PE conditions (i.e. at high interface velocity). Using the same calculation conditions, the obtained biding energy in the present

T(°C)	Fe-C-Mn	$\begin{array}{c} L_{Fe,Mn:Va} \\ (kJ.mol^{-1}) \end{array}$	Fe-C-Mn	$\begin{array}{c} L_{Fe,Mn:Va} \\ (kJ.mol^{-1}) \end{array}$	Fe-C-Mn	$\begin{array}{c} L_{Fe,Mn:Va} \\ (kJ.mol^{-1}) \end{array}$
730	0.3Mn	-1.4	0.7Mn	-1.5	1Mn	-1.5
750	0.3Mn	-1.6	0.7Mn	-1.8	1Mn	-1.8
775	0.3Mn	-1.9	0.7Mn	-2	1Mn	-2

Table 9: The Fe-Mn interaction parameter  $L_{Fe,Mn:Va}$  used in the solute drag modeling for the different Fe-C-Mn systems.

study is +1.5  $kJ.mol^{-1}$  for all the studied manganese compositions and at the three temperatures. In both Zurob's modeling and the present one, only the Fe-Mn interaction parameter was used as a fitting parameter. The difference between the two obtained binding energies (+1.5  $kJ.mol^{-1}$  and -2.5  $kJ.mol^{-1}$ ) can be attributed to the difference in the thermodynamic properties of the interface as used by Zurob et al. [11] and in the present study. The carbon-iron interaction parameter used by Zurob [11] is -34  $kJ.mol^{-1}$ (as in autenite) versus a value of -50  $kJ.mol^{-1}$  in the present study. Moreover, in the present version of the model, the Wagner interaction between manganese and carbon ( $\epsilon_{MnC}$ ) was modified to capture a similar value as in austenite. In Zurob's model [11], this parameter was not re-ajusted meaning that its value can be different from the one in austenite since this parameter depends on the value of the  $L_{Fe,Mn:Va}$  interaction as shown by Eq.IV.2.9.

In the following section, the effect of these two changes (Fe-C ( $L_{Fe,C:Va}$ ) and X-C ( $\epsilon_{XC}$  interaction parameters) on the solute segregation behavior is detailed. To this end, three cases representing the different modifications are studied. In the first case, no changes are made on the Fe-C nor the X-C interaction parameters. This approach is similar to the one used by Zurob et al. [11]. In the second frame, the Fe-C interaction parameter at the interface is modified to -50  $kJ.mol^{-1}$  but the X-C interaction parameter is not re-adjusted to a similar value as that in austenite. Finally, the last case represents the current configuration of the model, where the Fe-C interaction parameter is modified to -50  $kJ.mol^{-1}$  and the X-C interaction parameter is re-adjusted to the austenite value.

Figure IV.12 shows an example of the fitted growth kinetics in a Fe-C-1Mn at 730°C using the three approaches. Table 10 summarizes the calculated binding energies that yielded the best fit of the experimental data for the Fe-C-Mn using the three approaches. When using the same approach as in Zurob's study (i.e no modification of the Fe-C nor the X-C interaction parameters), a binding energy of -1.5  $kJ.mol^{-1}$  was used to model the experimental results in the Fe-C-03Mn and Fe-C-07Mn systems and +0.5  $kJ.mol^{-1}$  to model the obtained results for the FeC1Mn system as shown in table 10. By modifying only the Fe-C interaction parameter at the interface from -34  $kJ.mol^{-1}$  to -50  $kJ.mol^{-1}$ , the used binding energies where -1.5  $kJ.mol^{-1}$ , +0.5  $kJ.mol^{-1}$  and +1.5  $kJ.mol^{-1}$  for the FeC03Mn, FeC07Mn and FeC1Mn at the three temperatures, respectively (table 10). As

stated before, changing these two parameters induces a change of the X-C interaction parameter as explained by Eq.IV.2.9. By setting an Mn-C interaction parameter (( $\epsilon_{MnC}$ ) at the interface similar to that in austenite, the new calculated binding energies were +1.5  $kJ.mol^{-1}$  for the whole range of composition and at the three temperatures.



Figure IV.12: Comparison between the measured ferrite growth kinetics in the FeC1Mn at 730°C (solid black line) and the predictions of solute drag model using the three different approaches in the description of the interaction parameters at the interface (green, blue and red dashed lines), as well as velocity evolution as a function of time during ferrite growth predicted by the solute drag model.

Table 10: The binding energies  $(kJ.mol^{-1})$  used to obtain the best fit of the experimental growth kinetics using the three different approaches for the Fe-C-Mn system.

			1	
		Fe-C $(L_{Fe,C:Va})$ :	Fe-C:	Fe-C:
E-0.96CM-		$-34 \ kJ.mol^{-1}$	$-50 \ kJ.mol^{-1}$	$-50 \ kJ.mol^{-1}$
re0.2001/111	1(0)	Mn-C $(\epsilon_{MnC})$ :	$\operatorname{Mn-C}(\epsilon_{MnC})$ :	Mn-C $(\epsilon_{MnC})$ :
		not re-ajusted	not re-ajusted	as in austenite
0.3Mn	730	-1.5	-1.5	+1.5
0.3Mn	750	-1.5	-1.5	+1.5
0.3Mn	775	-1.5	-1.5	+1.5
0.7Mn	730	-1.5	+0.5	+1.5
0.7Mn	750	-1.5	+0.5	+1.5
0.7Mn	775	-1.5	/	/
1Mn	730	+0.5	+1.5	+1.5
1Mn	750	+0.5	+1.5	+1.5
1Mn	775	+0.5	+1.5	+1.5

Figure IV.13 shows the evolution of the total dissipated energy and the dissipation due

to manganese transfer at each atomic plane calculated using Eq.IV.2.4, as a function of velocity for the FeC1Mn at 730°C using the 3 different approaches used to model the experimental growth kinetics. The total dissipated energies are comparable for the three cases, with a maximum of 45  $J.mol^{-1}$  attained at medium velocities  $(1e^{-7} \text{ to } 1e^{-9} \text{ m/s})$ . At high velocities, the dissipated energy is mostly due to the diffusion of manganese from ferrite to the first interfacial atomic plane (flux J1). It can be noticed that the maximum dissipated energy due to this flux (SD1) is different for the three approaches. When changing the Fe-C interaction parameter from -34  $kJ.mol^{-1}$  (Fig.IV.13-a) to -50  $kJ.mol^{-1}$  (Fig.IV.13-b), the maximum dissipated energy (SD1) decreases from 30  $J.mol^{-1}$  to 28  $J.mol^{-1}$ . When setting the Mn-C interaction parameter to be similar to that of austenite (Fig.IV.13-c), the maximum dissipated energy (SD1) increases to 34  $J.mol^{-1}$ .



Figure IV.13: The dissipated free energy due to Mn diffusion across the interface as function of the interface velocity for the Fe0.26C1Mn at 730°C calculated using the three approaches to describe the interaction parameters at the interface. a) Fe-C : -34  $kJ.mol^{-1}$ , Mn-C : not re-adjusted. b) Fe-C : -50  $kJ.mol^{-1}$ , Mn-C : not re-adjusted. c) Fe-C : -50  $kJ.mol^{-1}$ 

With decreasing velocity, the dissipated energy (SD2) due to the flux of manganese from the first atomic plane to the second one starts to increase. The maximum dissipated energy SD2 follows the same trend as SD1. At low velocities, the total dissipated energy is mostly due to the flux of Mn atoms from the second interfacial atomic plane to the austenite interface side. The maximum dissipated energy due to this flux (J3) is independent of the used approach and is approximately 33  $J.mol^{-1}$ .



Figure IV.14: Evolution of Mn content at the different atomic planes of the interface as well as the carbon content at the austenite interface side as function of interface velocity for the Fe0.26C1Mn at 730°C calculated using the three approaches to describe the interaction parameters at the interface. a) Fe-C :  $-34 \ kJ.mol^{-1}$ , Mn-C : not re-adjusted. b) Fe-C :  $-50 \ kJ.mol^{-1}$ , Mn-C : as in austenite.

The effect of the approach used to describe the interaction parameters at the interface is more noticeable when comparing the solute segregation at the different interfacial atomic layers. The evolution of manganese contents at the different atomic planes as well as the carbon content at the austenite interface side are plotted as function of velocity in figure IV.14. The carbon content at the austenite interface side decreases with decreasing interface velocity and its evolution is comparable for the three approaches. When no modifications are made on the Fe-C and Mn-C interaction parameters (Fig.IV.14-a), the segregation of Mn at the interface (Mn int1 and Mn int2) reaches a maximum of 340% compared to the bulk composition ( $K_{max}$ = 3.4) at low interface velocities (< 1 $e^{-9}$ ). The Mn content at the austenite interface reaches a maximum of 310% at low velocities. When changing the Fe-C interaction parameter to -50  $kJ.mol^{-1}$  (Fig.IV.14-b), the maximum of Mn segregation at the two atomic planes decreases to 270%. This can be explained by the higher content of carbon present at the interface when using a Fe-C interaction of -50  $kJ.mol^{-1}$ . As a result, less manganese is needed to obtain the same ferrite growth kinetics (the same carbon evolution at the austenite interface side). Moreover, setting the Fe-C interaction parameter to -50  $kJ.mol^{-1}$  induces a change in the Mn-C interaction parameter (Eq.IV.2.9) and results in a less attractive value between Mn and C at the interface compared to austenite.

When re-adjusting the Mn-C interaction parameter at the interface to a similar value as in austenite (Fig.IV.14-c), the maximum of Mn segregation at the interface increases to 290% compared to the bulk composition ( $K_{max}$ = 2.9). As stated before, the Mn-C Wagner interaction parameter is dependent on the Fe-Mn and Fe-C interaction parameters ( $L_{Fe,Mn:Va}$  and  $L_{Fe,C:Va}$ , respectively) at the interface. By taking into account this effect, the new interaction between Mn-C is more attractive compared to the case where only the Fe-C interaction parameter was changed. As a result, the required Mn content at the interface in order to obtain the same ferrite growth kinetics is lower than the former case (only Fe-C interaction parameter is changed).

As stated before, comparing the binding energies to express the segregation behavior of the element to the interface can be misleading. For a better understanding of the segregation behavior of solute elements at the interface, one should compare the segregation profiles. In Zurob's study [94], the manganese enrichment factor  $(K_{max})$  calculated at 775°C for a Fe0.57C0.94Mn (%wt.) steel composition is 3.1. At the same temperature, the manganese enrichment factor obtained by the present modeling for the FeC1Mn is 2.17. Van Landeghem et al. [30] used atom probe tomography to study solute segregation at the austenite/ferrite interface in Fe-C-X alloys. The authors reported an enrichment factor of 2.47 for a Fe2.61C0.94Mn (%at.) alloy transformed at 775°C. One has to note that the interface width assumed in Van Landeghem et al.'s [30] study is 3 nm compared to 1 nm in the present model. As a result, the enrichment factor as calculated by Van Landeghem et al. can be higher if a 1 nm interface width is considered. Danoix et al. [29] measured the segregation of manganese at the austenite ferrite interface of a Fe0.12C-2Mn (wt.%) alloy at 680°C obtained by precipitation experiment. In their study, Danoix et al. used an interface width of 1 nm as considered in the present study. The authors reported an enrichment factor of manganese of 3.7 at 680°C. Using the expression of the enrichment factor as function of the effective binding energy and temperature (Eq. IV.2.8) and assuming that the effective binding energy is independent on temperature, the  $K_{max}$ estimated at  $775^{\circ}$ C is 3.2. The obtained enrichment factor in the present study (2.17) is slightly lower but comparable to the measured ones (2.47 and 3.2). To have a better comparison, the enrichment factor must be calculated at the same temperature as well as at comparable carbon and solute contents. Moreover, the supposed interface width can affect the calculated enrichment factors [29].

Danoix et al. [29] estimated an effective binding energy of manganese of -6  $kJ.mol^{-1}$  using the formula in Eq.IV.2.8. Using the same approach, the effective binding energy calculated for the FeC1Mn at 730°C in the present study is -5  $kJ.mol^{-1}$  with  $\Delta E$  as -4.4  $kJ.mol^{-1}$  calculated using TCFE9 database of ThermoCalc. This value is comparable with the reported segregation energies of manganese on austenite grain boundaries (-8  $(+/-3) kJ.mol^{-1}$  [80]) or at ferrite grain boundaries [146] (-5.5  $kJ.mol^{-1}$ ). However, the reported values represent the intrinsic segregation energies (intrinsic binding energies) of manganese. As it was mentioned, the effective binding energy as calculated using Eq.IV.2.8 does not take into account the effect of other segregated elements at the interface such as carbon in the present case.

The effect of carbon on the intrinsic binding energy can be estimated using Guttmann's approach [80,146] of grain boundary segregation in interacting multi-component systems. The intrinsic segregation of an X element ( $\Delta G_X^0$ ) in a Fe-C-X system where X is a substitutional element and C is an interstitial element (carbon) is estimated using Eq IV.4.1.

$$\Delta G_X^0 = \Delta G_X + 2\beta_{FeX}(Y_X^{boun} - Y_X^B) - \beta_{XC}(Y_C^{boun} - Y_C^B)$$
(IV.4.1)

where  $Y_X^{boun} = \frac{x_X^{boun}}{1 - x_X^{boun}}$ ,  $Y_X^B = \frac{x_X^B}{1 - x_X^B}$ , *B* is the bulk phase, *boun* is the boundary phase and  $\Delta G_X$  is the effective binding energy (similar to E<sub>0</sub> in Eq.IV.2.8) estimated at equilibrium between the bulk (B) and the boundary (boun) ( $\mu_X^{boun} = \mu_X^B$ ) as follows :

$$\frac{Y_X^{boun}}{1 - Y_X^{boun}} = \frac{Y_X^B}{1 - Y_X^B} \exp(-\frac{\Delta G_X - \Delta E}{RT})$$
(IV.4.2)

 $\beta_{FeX}$  and  $\beta_{XC}$  are the interaction parameters of Fe and X and X and C assumed to be similar in the bulk phase and at the interface and their values are resumed in table 11. The  $\beta_{FeX}$  interaction parameter was estimated using the L interaction parameters of the two-sublattice model as [147]:

$$\beta_{FeX} = {}^{0} L_{Fe,X:Va} + {}^{1} L_{Fe,X:Va} (1 - 4Y_X)$$
(IV.4.3)

 $\beta_{XC}$  represent the interaction between substitutional elements and carbon and its value can be calcualted using [147]:

$$\beta_{XC} = {}^{o} G_{Fe} + {}^{o} G_{XC} - {}^{o} G_{FeC} - {}^{o} G_X$$
(IV.4.4)

 ${}^{o}G_{Fe}$  and  ${}^{o}G_{X}$  are the standard free energy of pure Fe and pure X, respectively.  ${}^{o}G_{XC}$  and  ${}^{o}G_{FeC}$  are the Gibbs free energies of hypothetical compounds where all of the interstitial sites are filled with carbon and all the substitutional sites are filled with X elements and iron, respectively. The values of  $\beta_{XC}$  were extracted from [147].

However, to apply this approach in the present case, a hypothesis must be made on the nature of the bulk phase. In the following procedure, the bulk phase is considered as austenite. Moreover, in Guttmann's approach, the boundary phase is considered to have

Х	$\beta_{FeX} J.mol^{-1} [147]$	$\beta_{XC} \ J.mol^{-1} \ [147]$
Mn	$-7762 + 3.865 * T - (1 - 4 * Y_X) * 259$	-48500
Ni	-12054.355+3.27413*T	46000
Mo	+28347-17.691*T	-89080
Cr	$+10833-7.477*T +1410*(1 - 4*Y_X)$	-251160 + 118*T

Table 11: Numerical values of  $\beta_{FeX}$  and  $\beta_{XC}$  coefficients in Fe-C-X used in austenite and the boundary phase.

the same thermodynamic properties as the bulk with the difference that the standard chemical potentials of Fe and X are shifted by  $\sigma_1 A$  and  $\sigma_2 A$ , respectively, where  $\sigma_1$  and  $\sigma_2$  are the grain boundary energies of pure Fe and X elements and A is the molar area of atoms at the interface. Using this approach, the intrinsic segregation energy of the X element can simply be estimated as  $(\Delta G_X^0 = \sigma_1 A - \sigma_2 A)$ .

Here again, the present model uses a different approach, where the segregation of the elements are expressed by modifying Fe-X interaction parameter  $(L_{Fe,X:Va;0})$  of the interface and the  $\sigma_1 A$  and  $\sigma_2 A$  are set to  $+3500 \ J.mol^{-1}$  for iron and all substitutional elements. However, Guttmann's approach can be used as an analogy on the present case, meaning that the results of the present model (the segregation contents) are used to calculate the segregation energy using Eq.IV.4.2 and then the intrinsic segregation energy of the X element is estimated using Eq. IV.4.1 assuming a thermodynamic approach of the interface similar to Guttmann's. Using this approach, the calculated intrinsic segregation energy of manganese is  $-2.2 \ kJ.mol^{-1}$ . This value is higher than the estimated intrinsic segregation energy of manganese as reported in literature ((-8 (+/- 3) kJ.mol^{-1} and -5.5 kJ.mol^{-1}) [80, 146].

The solute drag modeling shows that segregation of manganese at the  $\alpha/\gamma$  interface is increased due to the presence of carbon (effective binding energy of -5  $kJ.mol^{-1}$ ) and that its intrinsic segregation (-2.2  $kJ.mol^{-1}$ ) is weak to such interfaces. Van Landeghem et al. [114] used APT to measure manganese segregation at the austenite ferrite interface in Fe-C-Mn and Fe-N-Mn alloys. Manganese has an attractive interaction with both carbon and nitrogen in austenite and ferrite. It was reported that nitrogen, in contrast of carbon segregates little at grain boundaries. Van landeghem et al. [114] reported a significant segregation of manganese at the austenite ferrite interface in the Fe-C-Mn and a weak or nonexistent segregation in the FeNMn system. These observations suggest that the presence of carbon at the austenite ferrite interface is the main factor responsible for manganese segregation at the austenite and ferrite. This is in perfect agreement with the calculations made in the present study.

#### IV.4.2 Fe-C-Ni system

The solute drag model was also applied to the Fe-C-Ni system at the three temperatures 730°C, 750°C and 775°C. As in the Fe-C-Mn system, the interaction parameter between iron and carbon  $(L_{Fe,C:Va;0})$  at the interface was set to -50  $kJ.mol^{-1}$  and the interaction parameter between nickel and carbon at the interface was modified using Eq.IV.2.9 to capture the same value as in austenite. The interaction parameter between nickel and iron at the interface was used as the only fitting parameter. Using this set of parameters, good agreement between the experimental results and the predicted kinetics were obtained at 730°C and 750°C as shown in Fig.IV.8. For the 775°C, the predicted growth kinetics is faster than the measured one. The Fe-Ni interaction parameter that gave the best fit of the experimental data is -11.7  $kJ.mol^{-1}$  at 730°C, -11.8  $kJ.mol^{-1}$  at 750°C and -11.9  $kJ.mol^{-1}$  at 775°C corresponding to a binding energy of -6.5  $kJ.mol^{-1}$  for the three temperatures. The binding energy was calculated under para-equilibrium conditions. Qiu et al. [94] used a binding energy (calculated under the same conditions) of +1.5  $kJ.mol^{-1}$  for predicting ferrite growth kinetics in Fe-C-Ni systems. Oi et al. [93] on the other hand reported a nickel binding energy calculated under the same conditions of -4  $kJ.mol^{-1}$ .



Figure IV.15: a) Dissipated free energy due to Ni diffusion across the interface as function of the interface velocity for the Fe0.22C1Ni at 730°C. b) Evolution of Mn content at the different atomic planes of the interface as well as the carbon content at the austenite interface side as function of interface velocity.

An example of the dissipated energy as function of velocity for the Fe-C-Ni at 730°C is shown in figure IV.15-a. The evolution of nickel segregation at different atomic planes as well as the interfacial carbon content as function of interface velocity are illustrated in figure IV.15-b. It can be noticed that the transformation energy is mostly dissipated by diffusion of nickel from ferrite to the first atomic plane and from the first atomic plane to the second one. The maximal dissipated energy (63  $J.mol^{-1}$ ) is reached at  $1e^{-8} m.s^{-1}$ . The maximal segregation of nickel at the interface (atomic planes 1 and 2) is 360% ( $K_{max} = 3.6$ ) compared to the bulk composition and 1.6 times higher than the nickel segregation at the austenite interface side which represent the LENP spike. When increasing the temperature to 750°C, the maximal dissipated energy increases to 65  $J.mol^{-1}$  and the enrichment factor of nickel ( $K_{max}$ ) at the interface to 3.7. At 775°C the maximum dissipated energy is 80  $J.mol^{-1}$  and the nickel segregation is 380% compared to the bulk composition ( $K_{max} = 3.8$ ). Although, a higher maximal dissipated energy is attained at 775°C, the predicted kinetics is faster than the HEXRD measurements. It is interesting to notice that this condition (1% at 775°C) is located on the zero partition line. The very low measured ferrite fraction indicates that the transformation is controlled by nickel diffusion in austenite i.e. under LEP conditions. Again, the present model is not applicable under such conditions.

The predicted segregation values of nickel at the interface are surprising since the reported APT measurements on the Fe-C-Ni system show no segregation or very low segregation of nickel at the interface [30]. However, one internal study of Zurob's group reported a small segregation peak of Ni at the ferrite/austenite interface in a decarburized sample. The measured segregation is about 100%, which is still lower than the predicted value using solute drag model in the present study. It is to be noted that all the reported APT measurements on Fe-C-Ni systems were conducted on decarburized experiments. Moreover, Qiu et al. [94] studied ferrite growth kinetics in a Fe-0.74C-1.46Ni (wt. %) alloy and reported a  $K_{max}$  of 2.4 at 755°C corresponding to an effective binding energy of  $-4 k J.mol^{-1}$  calculated using Eq.IV.2.8. It has to be noted that the authors used a binding energy of  $+2.5 k J.mol^{-1}$  (as calculated under para-equilibrium conditions). This again shows that calculating the binding energy under these conditions is not representative of the segregation tendency of an element.

The calculated effective binding energy using Eq.IV.2.8 of the Fe-C-1Ni at 730°C is -7.5  $kJ.mol^{-1}$  with a  $\Delta E$  of -3.4  $kJ.mol^{-1}$  calculated using the TCFE9 database of Thermo-Calc. The difference between the present value and the one estimated by Qiu et al. (-4  $kJ.mol^{-1}$ ) is partially due to the carbon segregation at the interface, which is enhanced in the present study due to the modification of the interaction parameter between carbon and iron at the interface. The estimated value in the present study (-7.5  $kJ.mol^{-1}$ ) is also lower than the reported intrinsic energies in the literature, -3 (+/- 3)  $kJ.mol^{-1}$  in a ferrite grain boundary [146] and (> -7  $kJ.mol^{-1}$ ) in an austenitic grain boundary [80]. Again, the reported values are the intrinsic segregation energies of nickel at grain boundaries. However, given the repulsive interaction between carbon and nickel at the interface (as taken in the present model), the intrinsic binding energy of nickel would be even lower than -7.5  $kJ.mol^{-1}$  if the effect of carbon is taken into account. Using Guttmann's approach, the intrinsic segregation energy of nickel for the Fe-C-1Ni alloy at 730°C is -9.5  $kJ.mol^{-1}$ .

In an attempt to reduce the needed solute drag energy to model the experimental ferrite growth kinetics in the Fe-C-Ni system, the interface friction was incorporated into solute drag calculations. The energy dissipation due to interface friction can be written as:

$$\Delta G_m^{fric} = \frac{v}{M} \tag{IV.4.5}$$

$$M = M_0 exp(-\frac{Q}{RT}) \tag{IV.4.6}$$

where  $M_0$  is the intrinsic interface mobility an Q is the activation energy. In the present study, the  $M_0$  and Q were taken as  $Q = 140 \ kJ.mol^{-1}$  [63] and  $M_0 = 0.5 \ m.mol.(Js)^{-1}$ , respectively. The  $M_0$  value was calibrated by fitting growth kinetics obtained for a Fe-C binary composition and the obtained value represents an intermediate value between the reported intrinsic interface mobilities in literature [51, 148]. The new Fe-Ni interaction parameter ( $L_{Fe,Ni:Va;0}$ ) that gave the best fit of the experimental data was the same as the one without mobility -11.7  $kJ.mol^{-1}$  corresponding to a binding energy calculated under para-equilibrium conditions of -6.5  $kJ.mol^{-1}$ .



Figure IV.16: Comparison between the measured ferrite growth kinetics (solid black line) and the predictions of solute drag without interface friction (dashed red line) solute drag with interface friction effect (dashed blue line) for the Fe-0.22C-1 Ni at 730°C

The calculated ferrite growth kinetics is compared with the experimental result and with the solute drag modeling without taking into account the interface mobility in figure IV.16. The same modeled ferrite growth kinetics is obtained when taking into account the interface friction and in case where this energy is not considered. This is due to the fact that the interface friction contributes to the dissipated energy at very high interface velocities (>  $1e^{-6} \text{ m.s}^{-1}$ ). These interface velocities are encountered in precipitation experiments only at very early stages of the transformation (first milliseconds). Atom probe tomography (APT) was used to investigate nickel segregation at the austenite/ferrite interface for the treated sample at 730°C for 15 min. The microstructural observations showed formation of pearlite during quenching. As a result, it was not possible to investigate a martensite ferrite interface but rather an interface between proeutectoid ferrite and pearlite (Fig.IV.17). The composition profiles, shown in IV.18 displays clear segregation of nickel at the interface. This result is, of course, not an evidence of nickel segregation at the austenite ferrite interface. However, it points out the necessity of a proper investigation of nickel segregation to the transformation interface.



Figure IV.17: a)ATP specimen showing the ferrite pearlite interface. b) 3D atom maps for C, Fe, and Ni in the interface vicinity between ferrite and a carbine for the Fe-0.22C-1 Ni.



Figure IV.18: Nickel distribution across the studied ferrite carbide interface.

#### IV.4.3 Comparison between Fe-C-Mn and Fe-C-Ni systems

Figure IV.19 compares the interface velocity as well as the evolution of substitutional elements at the interface vicinity and at the austenite interface side during the austenite-to-ferrite phase transformation in the Fe-0.26C-1Mn (Fig. IV.19-a) and Fe-0.22C-1Ni (Fig. IV.19-b) systems at 730°C. For both systems, the cessation of transformation seems to be mainly due to the segregation of Mn and Ni to the interface. The buildup of the Mn/Ni at the austenite side of interface contributes as well, but to a lower extent. The same behavior was reported by Zurob et al [11] showing that solute drag has a considerable effect on ferrite growth kinetics in the Fe-C-Mn and the Fe-C-Ni systems and that the good agreement generally observed between the experimental kinetics in these alloys and the LENP predictions can also be explained by a combined contribution of a partial Mn/Ni "spike" and the dissipated energy due to Mn/Ni diffusion across the interface.



Figure IV.19: Evolution of interface velocity as well as substitutional element concentration at the interface and on the austenite side of the interface as function of time during ferrite growth in : a) Fe-0.26C-1Mn at 730°C and b) Fe-0.22C-1Ni at 730°C.

The cessation of the transformation translates into a rapid decrease of interface velocity. In the FeC1Mn alloy, the rapid drop of interface velocity occurs at a higher velocity compared to the Fe-C-1Ni alloy  $(1e^{-8} m.s^{-1} \text{ and } 1e^{-9} m.s^{-1} \text{ respectively})$ . It is due to a rapid decrease of the carbon content on the austenite side of the interface. In the case of the Fe-C-1Mn system, this results in an inversion of the carbon profile near the austenite interface and stops the interface movement completely.

#### IV.4.4 Fe-C-Mo and Fe-C-Cr systems

The recorded ferrite growth kinetics in the Fe-C-Mo system showed slower kinetics than those predicted by both PE and LE. Moreover, at the chosen composition and temperatures, both LE and PE predicted similar kinetics meaning that the observed experimental deviation from both models is essentially due to the dissipated energy caused by molybdenum diffusion across the interface. This is attributed to the fact that under these conditions, the chemical potentials of molybdenum in austenite and ferrite are almost the same. The predicted kinetics using the solute drag model are in good agreement with the experimental at all three temperatures. The best fit of the experimental results was obtained using a Fe-Mo interaction parameter of -7.1  $kJ.mol^{-1}$ , -7.5  $kJ.mol^{-1}$  and -7.9  $kJ.mol^{-1}$  corresponding to a binding energy of -15  $kJ.mol^{-1}$  for the three temperatures as calculated under equilibrium conditions. Zurob et al. [11] reported the same binding energy calculated under the same conditions to model ferrite growth kinetics in a Fe-0.51Mo-0.54C (%wt.) alloy at 806°C and 825°C.

Hutchinson et al. [85] measured the ferrite growth kinetics in a Fe-0.54C-0.51Mo (%wt) steel at 775°C using decarburization experiments. The authors reported a deviation from the LENP/PE model predictions and attributed this difference to an additional energy dissipation due to solute drag effect. The estimated dissipated energy needed to shift the LENP/PE kinetics to the measured ones was 43  $J.mol^{-1}$ . The authors reported that the magnitude of this energy decreases with increasing temperature. In the present study, the same trend was observed concerning the maximal dissipated energy as function of temperature, 84  $J.mol^{-1}$ , 70  $J.mol^{-1}$  and 56  $J.mol^{-1}$  at 730°C, 750°C and 775°C, respectively.

Figure IV.20-a shows an example of the dissipated energies due to molybdenum diffusion across the interface as function of velocity for the 730°C temperature. The corresponding evolution of molybdenum segregation at the interface as well as carbon interfacial content as a function of interface velocity is plotted in figure IV.20-b. It can be noticed that the total dissipated energy is principally due to the molybdenum diffusion across the interface and that the molybdenum 'spike' has a small effect on the dissipated energy. The maximal dissipated energy decreases with increasing temperature as well as the molybdenum segregation at the interface. The maximum molybdenum segregation at the interface is 2000%, 1800% and 1450% ( $K_{max}$ : 20, 18 and 14.5) compared to the bulk composition at the temperatures 730°C, 750°C and 775°C, respectively. The reported APT measurements conducted by Van Landeghem et al. [30] on the Fe2.48C0.29Mo (at.%) system at 806°C showed a  $K_{max}$  of 8.48 corresponding (Eq.IV.2.8) to a  $K_{max}$  of 9 at 775°C. The experimental value is thus lower than the value predicted by the present modeling (14.5). One possible cause of this difference can emerge from the assumed interface thickness in the APT measurements (3 nm) and in the SD model (1 nm). Using the reported effective binding energy by Van Landeghem et al. [30] for the same alloy considering a 1 nm interface width, the adjusted  $K_{max}$  from APT results is 12.5 compared to 14.5 in the present study.

The calculated effective binding energy using equation IV.2.8 for the Fe-C-02Mo at 730°C is -25  $kJ.mol^{-1}$ . Enomoto et al. [80] reported a intrinsic binding energy of molybdenum



Figure IV.20: a) and c) Dissipated free energy due to element X (a. Mo and c. Cr) diffusion across the interface as function of the interface velocity for Fe-0.26C-0.2Mo at 730°C and Fe0-.26C-1Cr at 750°C, respectively. The evolution of Mo (b) and Cr (d) content at the different atomic planes of the interface as well as the carbon content at the austenite interface side as a function of interface velocity.

at austenitic grain boundaries of  $(-15 + /-3 kJ.mol^{-1})$ . On the other hand, Guttmann et al. [146] estimated a very low binding energy of molybdenum at ferrite grain boundaries  $(0.1 kJ.mol^{-1})$  and claimed that the observed molybdenum segregation is only due to carbon presence at the interface. However, Murayama et al. [149] showed that molybdenum can segregate at  $\alpha$ -Fe grain boundaries and estimated an intrinsic segregation energy of  $-28 kJ.mol^{-1}$  at 800°C. Liu et al. [150] used a solute drag approach to model ferrite growth kinetics in a Fe-C-Mo alloy and reported a binding energy of  $-17 kJ.mol^{-1}$ . It has to be noted that the authors neglected the carbon segregation at the interface in their calculations. If one considers the effect of high interaction between carbon and molybdenum at the interface (considered as in austenite in the present model), the intrinsic segregation energy of molybdenum must be higher than the calculated one using Eq.IV.2.8. Using Guttmann's approach, the intrinsic segregation energy of molybdenum for the FeC0.2Mo alloy at 730°C is estimated to  $-14.5 kJ.mol^{-1}$  which is good agreement with the reported value in austenitic grain boundaries  $(-15 + /-3 kJ.mol^{-1})$  [80]. The experimental results obtained for the Fe0.26C1Cr system at  $750^{\circ}$ C and  $775^{\circ}$ C were finally compared with the predictions of the different models. Both PE and LE predicted kinetics are slower than the experimental observations indicating an extra dissipation of energy due to solute drag. The Fe-Cr interaction parameter was modified to fit the experimental kinetics. The best fit was obtained using an Fe-Cr interaction parameter of  $+2.2 \ kJ.mol^{-1}$  at 750°C and  $+1.9 \ kJ.mol^{-1}$  at 775°C, corresponding to a binding energy calculated under para-equilibrium conditions of  $+1.5 \ kJ.mol^{-1}$  and  $-1.5 \ kJ.mol^{-1}$ , respectively. Panahi et al. [151] used the solute drag model to predict ferrite growth kinetics in a Fe-2Cr-0.58C (%wt.) alloy at different temperatures (775°C to 850°C) and reported a binding energy of  $-1.5 \ kJ.mol^{-1}$  as calculated at para-equilibrium conditions. The dissipated energies as a function of velocity are shown in figure IV.20-c for the 750°C case. As for the Fe-C-Mo system, the dissipation due to solute diffusion across the interface contributes the most to the total dissipated energy. In contrast to the previous observation in the Fe-C-Mo system, a similar dissipated energy is observed at higher temperatures. At 750°C, the maximal dissipated energy is 68  $J.mol^{-1}$ , as is the case at 775°C. Béché et al. [84] estimated the dissipated energy necessary to bring the PE model in agreement with the observed kinetics in a Fe0.58C2Cr (wt.%) steel. At 775°C, the authors reported a dissipated energy of 50  $J.mol^{-1}$ . The maximum chromium segregation was 430% ( $K_{max}$ : 4.3) for both temperatures 750°C and 775°C, respectively. The  $K_{max}$  value reported by Van Landeghem et al. [30] using APT measurements is 2.7 for a Fe2.64C2.10Cr (%at.) at  $806^{\circ}$ C corresponding to 2.9 for 775°C. This value is lower than the predicted one using the present model, namely 4.3. However, if one considers the effect of the interface thickness, the new experimental  $K_{max}$  estimated in Van Landeghem's [30] study is 5.3.

The corresponding effective binding energy calculated using Eq.IV.2.8 for the Fe-C-1Cr alloy at 750°C is -12  $kJ.mol^{-1}$ . The intrinsic binding energy of chromium as estimated using the Guttmann's approach is -1.9  $kJ.mol^{-1}$ . Enomoto et al. [80] reported an intrinsic segregation energy of chromium at an austenitic grain boundary of -10  $kJ.mol^{-1}$ . Aaronson et al. [99] reported an effective binding energy of chromium at austenite ferrite interfaces of -8  $kJ.mol^{-1}$  at 660°C. It is to be noted that the intrinsic segregation energy of chromium at a ferritic grain boundary is estimated at 0  $kJ.mol^{-1}$  [146]. The present result is higher than the reported values in austenite grain boundaries and comparable to the reported ones in ferrite grain boundaries.

#### IV.4.5 Fe-C-Mn-Cr system

The quaternary version of the solute drag model was used to predict the ferrite growth kinetics in the FeC1Mn1Cr system at 730°C. To this end, the same Fe-Mn and Fe-Cr interaction parameters used to successfully predict growth kinetics in the FeC1Mn (at 730°C) and Fe-C-1Cr (at 750°C) were used to model the expected kinetics in the quaternary Fe-C-Mn-Cr system. It is to be noted that ferrite growth kinetics could not be
measured in the Fe-C-Cr system at 730°C due to pearlite formation. As for the ternary systems, the Fe-C interaction parameter  $(L_{Fe,C:Va;0})$  at the interface was adjusted to -50  $kJ.mol^{-1}$ , and the Mn-C and Cr-C Wagner interactions ( $\epsilon_{MnC}$  and  $\epsilon_{CrC}$ , respectively) were modified to capture the same Wagner interaction parameters as in austenite for both Mn and Cr using Eq.IV.2.9. As mentioned before, the modification of the Fe-Mn and Fe-Cr ( $L_{Fe,Mn:Va;0}$  and  $L_{Fe,Cr:Va;0}$ ) parameters induces a modification of the Mn-Cr Wagner interaction parameter ( $\epsilon_{MnCr}$ ) (Eq.IV.2.10). In the present study, this parameter was adjusted to capture the same Mn-Cr interaction as austenite. Good agreement was obtained between the model predictions and the experimental results as shown in figure IV.11. This is an interesting result since the parameters used to successfully predict the growth kinetics were directly extracted from the ternary systems and no further calibration was needed.



Figure IV.21: a) The dissipated free energy due Mn and Cr elements diffusion across the interface as function of the interface velocity for Fe-0.26-C-1Mn-1Cr at 730°C. b) The evolution of Mn and Cr contents at the different atomic planes of the interface as well as the carbon content at the austenite interface side as function of interface velocity.

The dissipated energies due to manganese and chromium diffusion across the interface as function of the interface velocity are shown in figure IV.21-a. The maximal total dissipated energy (86  $J.mol^{-1}$ ) is attained at medium velocities ( $5e^{-8} m.s^{-1}$ ). The maximal dissipated energy of Mn and Cr are 38  $J.mol^{-1}$  and 50  $J.mol^{-1}$ , respectively. When comparing with the obtained dissipated energies for the ternary systems (Fe0.26C1Mn and Fe0.26C1Cr) at the same temperature using the same binding energies, the maximal dissipated energies for Mn and Cr were 44  $J.mol^{-1}$  and 96  $J.mol^{-1}$ , respectively.

Figure IV.21-b shows the evolution of Mn and Cr contents at the different interface atomic planes as well as the evolution of C at the austenite side of the interface as function of velocity. Both Mn and Cr show the same segregation behavior as in the ternary systems. The Mn and Cr contents start to deviate from PE conditions and segregate at the different atomic layers with decreasing velocity. A higher maximum segregation of Cr is reached at low velocities compared to Mn (Cr :  $K_{max} = 3.18$ , Mn :  $K_{max} = 2.64$ ).

The obtained manganese enrichment factor in the Fe-C-Mn-Cr is similar to the calculated one in the ternary Fe-C-Mn system (2.9). On the other hand, the chromium enrichment factor obtained for the quaternary Fe-C-Mn-Cr system is lower than the calculated one in the ternary Fe-C-Cr system at the same temperature, 730°C ( $K_{max}$ : 5). It has to be noted that the interaction between chromium and manganese is slightly attractive  $(\epsilon_{CrMn}: -0.13)$  and thus cannot be the orgin of the observed segregation behavior. The calculated effective binding energies for manganese and chromium are,  $-3.8 k J.mol^{-1}$  and - $9.2 kJ.mol^{-1}$  respectively. The intrinsic segregation energies for manganese and chromium are calculated using Eq.IV.4.2 to de-correlate the carbon cosegregation effect. One should note that the effect of the interaction between chromium and manganese is neglected here. This can be accepted as a simplification since the interaction between these two elements is weak  $(\epsilon_{CrMn})$  compared to the interactions between carbon and manganese or carbon and chromium. Calculations show an intrinsic binding energy of  $-1.4 \ kJ.mol^{-1}$  for manganese and  $-2 kJ.mol^{-1}$  for chromium. These values are comparable to the obtained ones for the ternary systems,  $-2.2 \ kJ.mol^{-1}$  for manganese at 730°C and  $-1.2 \ kJ.mol^{-1}$  for chromium at 750°C.

To highlight the effect of taking in consideration the different interaction parameters (Fe-C, Mn-C, Cr-C and Mn-Cr), the solute drag model was applied to the FeC1Mn1Cr system where :

a) the Fe-C ( $L_{Fe,C:Va;0}$ ) interaction parameter is modified, the Mn-C and Cr-C ( $\epsilon_{MnC}$ ) and  $\epsilon_{CrC}$ , respectively) are adjusted to their values in autenite, the Mn-Cr ( $\epsilon_{MnCr}$ ) interaction parameter is not adjusted to its value in austenite.

b) the Fe-C interaction parameter is not modified, the Mn-C, Cr-C and Mn-Cr interaction parameters are not adjusted.

c) only the Fe-C interaction parameter was modified

In all cases, the same Fe-Mn and Fe-Cr interaction parameters used to obtain the best fit in ternary systems Fe-C-Mn and Fe-C-Cr were used in to model the quaternary FeCMnCr. The calculated kinetics and the observed one are plotted in figure IV.22. In the first case (a) where the Fe-C, Mn-C and Cr-C parameters are modified and the Mn-Cr is not adjusted, the obtained kinetics are in good agreement with the experimental result. The dissipated energy and the segregated values are similar to the former case where the Mn-Cr interaction parameter was adjusted to a similar value in austenite. This can be explained by the small difference in the Mn-Cr interaction parameter between austenite and the interface caused by the modification of the Fe-Mn and Fe-Cr parameters. The Wagner interaction parameter (Eq.IV.2.10) calculated in austenite and at the interface after changing the Fe-Mn and the Fe-Cr parameters are -0.83 and -1.3, respectively.

In a second stage, no modifications were made on the Fe-C, Mn-C, Cr-C and Mn-Cr interaction parameters. The model predicts a faster growth kinetic and a lower final



Figure IV.22: Comparison between the measured ferrite growth kinetics (solid black line) of the FeC1Mn1Cr at 730°C, and the predictions of the solute drag (dashed lines) model obtained using different approaches in the description of the interaction parametters.

fraction compared to measurements. As already mentioned, the used Fe-Mn and Fe-Cr interaction parameters gave good results for the ternary systems. The same result was obtained when only the Fe-C interaction parameter was modified (-50  $kJ.mol^{-1}$ ) and no adjustments were conducted on the Mn-C, Cr-C and Mn-Cr interaction parameters.

These results highlight the importance of considering the whole thermodynamic description of the different interaction parameters when modeling ferrite growth kinetics in multicomponent systems. The complex interaction between substitutional elements as well as carbon must be considered in the description of the interface.

## IV.5 Conclusion

The effect of alloying elements and temperature on ferrite growth kinetics during austenite to ferrite phase transformation was studied using HEXRD experiments in different ternary Fe-C-X systems (where X : Mn, Ni, Mo and Cr) as well as in a quaternary FeCCrMn system. The comparison between the experimental results and the classical PE and LE models showed that these models cannot be used to describe ferrite growth kinetics at all conditions. Moreover, the Fe-C-Mo and Fe-C-Cr systems showed ferrite growth kinetics slower than both LE and PE predections, indicating an additional dissipated energy that can be interpreted as solute drag effect. These experimental results were compared to the predictions of a modified version of the solute drag model initially developed by Zurob [11]. In the present version of the model, the interaction between carbon and iron at the interface was modified to capture the reported significant carbon segregation at the austenite ferrite interface. Moreover, it was shown that the interaction parameters at the interface are related and cannot be changed individually. The comparison between the measured kinetics and the solute drag model predictions showed good agreement for almost all studied systems. The estimated intrinsic segregation energies showed that manganese segregates weakly to the interface and that its segregation is enhanced by the presence of carbon at the interface. Nickel on the other hand segregates highly to the interface contrary to the reported behavior of this element at grain boundaries and interfaces. The tendency of molybdenum and chromium to segregate at the interface is also enhanced by the presence of carbon at the interface. The solute drag model was also applied to a quaternary Fe-C-Mn-Cr system and was compared to the experimental results obtained using HEXRD experiments. Results supported the importance of considering the whole set of thermodynamical properties in solute drag modeling. Even if the effect of temperature on ferrite growth kinetics was shown in the present study, the effect of solute composition remains not clear. To this end, the use of diffusion couples, which will be presented in the next chapter, will provide some needed insight into the effects of solute content on the austenite to ferrite phase transformation.

## Chapter V

# Ferrite growth kinetics in compositionally graded Fe-C-X ternary alloys

The following chapter presents an overview of the obtained results for the ternary Fe-C-X systems during the second HEXRD campaign at DESY in Hamburg, Germany. This campaign lasted 4 days from 30/11/2019 to 03/12/2019. The treated samples during were prepared using the second attempt of diffusion couples fabrication as detailed in chapter III. The obtained ferrite growth kinetics are also compared with the prediction of the different models.

## V.1 Fe-C-Ni system

A diffusion couple between Fe-C and Fe-C-1Ni was used to study the effect of nickel content on ferrite growth kinetics at three different temperatures  $730^{\circ}$ C,  $750^{\circ}$ C and  $775^{\circ}$ C. To this end, the diffusion couple was austenitized at 910°C, quenched to the intercritical temperature ( $730^{\circ}$ C,  $750^{\circ}$ C or  $775^{\circ}$ C) and held at this temperature for 15 min. The nickel content measured using EPMA varies from 0 % to 1 % over a distance of 6 mm. A constant carbon content of 0.22 % was measured across the diffusion couple. An example of the obtained ferrite fraction evolution as a function of time across the diffusion couple treated at  $730^{\circ}$ C is shown in figure V.1-a. The observed oscillations in ferrite fraction couple for the data, the obtained ferrite fractions are sorted as function of composition. In a first step, the fraction evolution as a function of time at each motor position is extracted by combining figure V.1-a and figure V.1-b. Next, each motor position is linked to its corresponding carbon and nickel contents using EPMA measurements (figure V.1-c). In figure V.1-d, each curve corresponds to the evolution of ferrite fraction as function of time at each motor position of time time.

of a single nickel composition. Considering the beam size of 80  $\mu$ m used during these HEXRD experiments, the variation of nickel composition within the beam is maximum 0.018 %. This result illustrates the effect of nickel content on the ferrite growth kinetics. Ferrite growth rates, as well as the ferrite fraction reached at the plateau, decrease with increasing nickel content. This dependency of ferrite growth rate on nickel composition was obtained using one single experiment illustrating the efficiency of high-throughput methods to provide rich databases that can be used to understand phase transformation kinetics in steels.



Figure V.1: Ferrite volume fraction evolution as function of time during the isothermal holding of the Fe-C/Fe-C-Ni diffusion couple at 730°C. The oscillations represent the sample translation over the composition gradient. b) Motor position as function of time during the isothermal holding. c) Nickel and carbon contents across the diffusion couple plotted as a function of the motor position. d) Ferrite fraction evolution as function of time and nickel content during the isothermal holding.

Figure V.2-a and V.2-b show the ferrite fraction evolution as a function of time and nickel contents for the same diffusion couple FeC/Fe-C-Ni at the two temperatures 750°C and 775°C. The effect of nickel on ferrite growth kinetics is more pronounced at higher temperature. This effect is illustrated in figure V.3 which compares the ferrite fraction

reached at the end of the isothermal holding for the three temperatures as a function of nickel composition. The final fraction decreases with increasing nickel content and increasing temperature.



Figure V.2: Evolution of ferrite fraction measured using HEXRD as a function of time and nickel composition along the Fe-C-Ni diffusion couple during the isothermal holding at : a) 750°C and b) 775°C.



Figure V.3: Ferrite fractions from HEXRD experiments along the gradient of the Fe-C-Ni diffusion couple at the end of the isothermal holding (15 min) at 730°C (black dots), 750°C (blue dots) and 775°C (red dots).

The recorded final ferrite fractions using HEXRD will be now compared with the ones obtained using LE (LENP/LEP) and PE calculations carried out using DICTRA software, TCFE9 and Mob2 database. Calculations were performed using an initial spherical microstructure parent grain. The grain size was measured by metallography techniques along the composition gradient of the graded sample. A constant grain size was measured along the Fe-C-Ni diffusion couples, namely  $50\mu$ m for both samples treated at  $730^{\circ}$ C and 750°C and 70 $\mu$ m for the sample treated at 775°C. In some cases, the same graded sample was reused to investigate ferrite growth kinetics at multiple temperatures, which explains the different grain sizes. The temperature gradient was evaluated *in situ* on the diffusion couple. To this end, the control thermocouple was welded at the ternary Fe-C-1Ni composition end, providing a direct measurement at this point. The temperature at the binary Fe-C composition was estimated by matching the fraction calculated with the Thermocalc software package with the TCFE9 database to that observed experimentally after 900 s. This temperature can be used as a measurement since the transformation is known to proceed until equilibrium values in the binary system. As a result, a gradient of about 1.6°C/mm was found between the two extremities of the composition gradient. It is to be noted that modeling was conducted using the local measurements of carbon and substitutional elements contents, grain size and the estimated temperature.



Figure V.4: Isothermal sections of the Fe-C-Ni phase diagram at : a) 730°C, b) 750°C and c)775°C, showing the different growth modes (LEP-LENP and PE) for the composition range of the Fe-C-Ni diffusion couple (gray circles).

Figures V.4-a, b and c illustrate the isothermal sections of the Fe-C-Ni phase diagram

at 730°C, 750°C and 775°C respectively, calculated using the TCFE9 database of ThermoCalc, showing the different growth modes for the composition range of the diffusion couple. At the three temperatures, the whole composition gradient is located below the zero partition line where both LENP or PE are theoretically possible transformation modes. At 775°C, the 1%Ni side of the gradient is at the limit of the zero partition line. First, the ferrite fractions reached at the end of the isothermal holding are compared with the predicted values using the different models as function of nickel composition as illustrated in figure V.5-a, b and c at 730°C, 750°C and 775°C, respectively. For the three temperatures, PE fails to predict the final fraction evolution as function of nickel content. The gap between the measurements and the predicted final fraction increases with nickel content and temperature. A better but not perfect agreement is obtained between the fractions calculated using LE and the measured ones. At 730°C and 750°C, the LE model successfully predicts the measured final fractions up to 0.6 % Ni. At 775°C, the divergence between the model predictions and measurements starts at 0.4 % Ni.



Figure V.5: Comparison between the ferrite fractions measured after 900 s (open circles) and the predictions of PE (triangles), LE (filled circles) and solute drag (crosses) models as a function of nickel content at : a) 730°C, b) 750°C and c) 775°C

To illustrate the degree of agreement between the LE and PE models and the measurements, the incomplete (IC) transformation degree is calculated using the formula  $\frac{f(PE/LENP)-f(EX)}{f(PE/LENP)}$ , where f(PE/LENP) is the obtained ferrite fraction using PE or LENP conditions and f(EX) is the measured ferrite fraction at the plateau, as introduced by Chen et al. [91]. Figure V.6 compares the evolution of the degree of incomplete transformation as function of nickel content at the three temperatures. It can clearly be noticed that even though the LE model predicts fairly well the final fractions at 730°C and 750°C, ferrite growth cannot be described using this model at 775°C.

As shown in Fig.V.3 the measured ferrite fraction at the nickel rich side of the graded sample at 775°C is 5% or less indicating a slow ferrite growth mode (LEP conditions). As indicated in the phase diagram in figure V.4, the transition between the LENP and LEP is predicted to occur at nickel contents higher than 1%. However, if one considers the temperature gradient over the diffusion couple, the zero partition line would pass through a lower nickel content (0.85%Ni at 780°C). The measured ferrite fractions on the diffusion couple suggests that this transition is more likely between 0.9% and 1% of nickel.



Figure V.6: The LE (circles) and PE (triangles) degree of incomplete transformation as function of nickel content at 730°C (black) b) 750°C (blue) and 775°C (red).

Second, the measured full kinetics using HEXRD are compared to the predicted ones using the LE and PE models. Figure V.7 presents a map of ferrite fraction as function of time and nickel content, which gives an overall picture of the ferrite growth kinetics, as obtained by HEXRD at 730°C and by calculation using the PE and LE models. It is clear from these heat maps that both PE and LE fail to predict the experimental kinetics dependency on nickel content. The divergence between the measured kinetics and the calculated ones is more noticeable at high nickel contents.

For a more quantitative comparison, ferrite growth kinetics can be compared to the predictions of the different models for a given nickel composition and temperature as shown in figure V.8 for two chosen nickel compositions (0.5Ni and 1Ni) at the three temperatures,  $730^{\circ}$ C,  $750^{\circ}$ C and  $775^{\circ}$ C. For all conditions, the PE predicted kinetics are faster than the measured ones. The LE predicted kinetics are faster than the measured ones at  $730^{\circ}$ C and  $775^{\circ}$ C for both compositions. At  $750^{\circ}$ C, the predicted kinetics using the LE model is in good agreement with the measurements at low nickel compositions (0.5%) but faster than the measured kinetics at high nickel contents (1%).



Figure V.7: Heat maps representing the evolution of ferrite fraction as function of time and nickel composition at 730°C, as measured using high-energy X-ray diffraction measurements (Exp.) and the modeled ones using solute drag (SD) calculations, paraequilibrium (PE) and local equilibrium negligible partitioning (LENP) models.

In summary, performing HEXRD experiments on Fe-C-Ni diffusion couples allowed measuring ferrite growth kinetics for a series of nickel contents (between 0 an 1%) at three different temperatures. The large obtained data set was compared with the predictions of the PE and LE models and showed that ferrite growth kinetics deviates from the PE and LE predictions especially at high temperatures (775°C). These results can be added to the observations made by Qiu et al. [96] where measured ferrite growth kinetics in decarburized Fe-C-Ni alloys showed faster kinetics than the LE predictions. This can be added as new evidence that the generally reported agreement between measured kinetics and the LE predicted ones in the Fe-C-Ni system cannot be generalized over the whole



Figure V.8: Ferrite growth kinetics measured using HEXRD experiments of the Fe-C-Ni diffusion couple during the isothermal holding for the two compositions : Fe-0.22C-0.5Ni (%wt.) at : a) 730°C, b) 750°C and c) 775°C. and Fe-0.22C-1Ni (%wt.) at : d) 730°C, e) 750°C and f) 775°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

range of composition and temperature.

#### Solute drag modeling:

The solute drag model was used to predict ferrite growth kinetics as a function of nickel content and temperature. The thermodynamic description of the interface is detailed in chapter IV, i.e. the carbon-iron interaction parameter was adjusted to -50  $kJ.mol^{-1}$  and the Ni-C interaction parameter at the interface was calculated using Eq.IV.2.9 and re-adjusted to the austenite value. Only the Fe-Ni interaction parameter ( $L_{Fe,Ni:Va}$  at the interface was used as a fitting parameter).

As shown in figure V.5, good agreement was obtained between the experimental measured final ferrite fractions and the predictions of solute drag modeling at the two temperatures 730°C and 750°C. It is to be noted that the same Fe-Ni interaction parameter was used to model the whole nickel composition for both temperatures, this value being slightly

adjusted between the two temperatures  $(-11.7 \ kJ.mol^{-1} \ and -11.8 \ kJ.mol^{-1} \ at 730^{\circ}C$  and 750°C, respectively). The calculated binding energy under para-equilibrium conditions, i.e. high interface velocity was  $-6.5 \ kJ.mol^{-1}$  for the whole gradient of nickel composition and at the two temperatures 730°C and 750°C. This binding energy is calculated as the difference between chemical potential of nickel at the interface and the average of chemical potentials of nickel in austenite and ferrite. At 775°C, good agreement was obtained between experiments and the predictions of solute drag model up to 0.7%.wt nickel content using the same binding energy  $-6.5 \ kJ.mol^{-1}$ , corresponding to a Fe-Ni interaction parameter of  $-11.9 \ kJ.mol^{-1}$ . At higher nickel contents, the calculated ferrite fractions are higher than the measured ones. By modifying the Fe-Ni interaction parameter to  $-15 \ kJ.mol^{-1}$  (binding energy of  $-9.5 \ kJ.mol^{-1}$ ), the predicted final ferrite fractions are in better agreement with the experiments at higher nickel contents as shown in figure V.9. However, with this high value the model underestimates the final fractions at the nickel lean side of the diffusion couple (Fig.V.9).



Figure V.9: Comparison between the measured ferrite fractions reached after 900 s of the isothermal holding (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of nickel content at 775°C using two Fe-Ni interaction parameters.

Solute-drag-based calculations were also able to describe the measured ferrite growth kinetics better than both PE and LE for all nickel contents at the two temperatures, 730°C and 750°C, as illustrated in the heat map (figure V.7) for the diffusion couple treated at 730°C, as well as in figure V.8, showing the evolution of ferrite fraction during the isothermal holding for different compositions and temperatures. It is important to note that this agreement was obtained using a single set of interface-related parameters (Fe-X, Fe-C and XC) at each temperature. For the 775°C temperature, it can be also considered that the solute drag model predicts with good accuracy the measured ferrite growth

kinetics using a same Fe-Ni interaction parameter as for the two other temperatures (E<sub>0</sub> = -6.5  $kJ.mol^{-1}$ ) as shown in fig.V.8.

In the following section, a comparison is made between the obtained results using the solute drag model for the three temperatures 730°C, 750°C and 775°C. For the 775°C case, the comparison is made using a Fe-Ni interaction parameter of -11.9  $kJ.mol^{-1}$  (binding energy of -6.5  $kJ.mol^{-1}$ ).

An example of the calculated dissipated energies due to nickel diffusion across the interface as a function of the interface velocity for the Fe-C-1Ni at the three temperatures is plotted in figure V.10-a. The dissipated energy increases with decreasing interface velocity and goes through a maximum at medium velocities  $(1e^{-7} \text{ m.s}^{-1} \text{ to } 1e^{-8} \text{ m.s}^{-1})$ , then decreases with the interface velocity. The dissipated energy increases with increasing temperature as shown in figure V.10-a. The maximum dissipated energy as a function of nickel content and temperature is presented in figure V.10-b showing an increase of the maximum dissipated energy with increasing nickel content.



Figure V.10: a) Dissipated free energy due to nickel diffusion across the interface as function of the interface velocity for the Fe0.22C1Ni at the three temperatures, 730°C, 750°C and 775°C. b) Maximum dissipated energy as a function of nickel content for the three temperatures

As explained in the introduction, the dissipated energy results from the interaction between the diffusing substitutional element (nickel in this case) with the moving interface. This effect is illustrated in figure V.11-a showing the evolution of nickel content at the interface (only the second atomic plane -Fig.I.21- is shown here) as a function of the interface velocity for the Fe-C-1Ni alloy at the three temperatures 730°C,750°C, 775°C. At high interface velocities (PE conditions), the interface inherits a nickel content similar to that of the bulk (ferrite). As the interface velocity decreases, nickel content at the interface increases due to solute drag effect. The maximum segregation is reached at slow interface velocities ( $< 1e^{-10}$  m.s<sup>-1</sup>) and this value increases with temperature.

For a better illustration of the segregation behavior of nickel as a function of its bulk

composition and temperature, the enrichment factor is calculated using Eq.IV.2.8 at low interface velocities (approaching equilibrium conditions) and plotted in figure V.11-b as a function of nickel content and for the three temperatures. The enrichment factor increases slightly with increasing nickel content and temperature. However, the change in the enrichment factor is small over the whole studied range of composition (0 to 1%) and for the three temperatures and its value is around 3.5 ( $\pm$  0.2). Moreover, the enrichment factors calculated across the composition gradient do not correspond strictly to a constant temperature. As mentioned, a temperature gradient of ~1.5°C.mm<sup>-1</sup> was measured from the HEXRD experiments going from high temperatures at the nickel lean side of the graded sample to lower temperatures at the nickel rich side. To check the effect of temperature, the nickel enrichment factor was calculated as a function of nickel content at a constant temperature (730°C) and results are shown in figure V.12. It can be seen that the temperature gradient has nearly no effect on the enrichment factor.



Figure V.11: a) Evolution of Ni content at the different atomic planes of the interface as well as the carbon content at the austenite interface side as a function of interface velocity for the Fe0.22C1Ni at 730°C, 750°C and 775°C. b) Enrichment factors  $K_{max}$ and the corresponding effective binding energy (E<sub>0</sub> calculated using IV.2.8 evolution as a function of nickel content for the three temperatures, 730°C, 750°C and 775°C.

Using the expression in Eq.IV.2.8 the effective binding energy was estimated from the enrichment factor as a function of nickel content and temperature. The results plotted in figure V.11 show an increase of the effective binding energy with increasing nickel content and temperature. Again this dependency of the effective binding energy on composition and temperature is weak, -7.2 ( $\pm$  0.6)  $kJ.mol^{-1}$ , -7.6 ( $\pm$  0.6)  $kJ.mol^{-1}$  and -8.2 ( $\pm$ 0.7)  $kJ.mol^{-1}$  at 730°C, 750°C and 775°C, respectively. Note that the initial calculated binding energies (under para-equilibrium conditions) were constant for the whole composition range, -6.5  $kJ.mol^{-1}$  at 730°C and 750°C. The calculated effective binding energies using the solute drag model are lower than the reported ones in the literature (-3 ( $\pm$  3)  $kJ.mol^{-1}$ ) at ferrite grain boundaries [146] and at the lower limit of the reported one



Figure V.12: Comparison between the evolution of the enrichment factor  $K_{max}$  and the corresponding effective binding energy (E<sub>0</sub>) as a function of nickel content calculated at 730°C with the ones calculated at the temperatures of the 730°C experimental run, accounting for the thermal gradient.

 $(> -7 \ kJ.mol^{-1})$  at austenite grain boundaries) [80]. Moreover, the reported APT measurements on decarburized Fe-C-Ni alloys show no segregation or very low segregation of nickel at the austenite ferrite interface, contrarily to the high nickel segregation predicted by the present model ( $K_{max}$  3.5) [30]. As mentioned in chapter IV, the effective binding energy calculated form the enrichment factor using Eq.IV.2.8 does not take into account the effect of other segregated elements such as carbon in the present case. However, given the repulsive interaction between carbon and nickel at the interface, taking into account this effect would decrease the segregation energy of nickel even further.

To illustrate this effect, the intrinsic energy of segregation of nickel is estimated using Guttmann's approach as explained in chapter IV. The new calculated intrinsic segregation energies of nickel are plotted in figure V.13 as function of the bulk nickel content for the two temperatures, 730°C and 750°C. The intrinsic segregation energy of nickel slightly decreases with increasing nickel content and with decreasing temperature. The intrinsic segregation energy should be independent from the composition but can be affected by temperature. The observed change of the intrinsic segregation energy with nickel composition can be attributed to the temperature gradient along the diffusion couple. However, this small change could also be attributed to the simplifications made in Guttmann's approach as used in the present study. A mean value of -11 ( $\pm$  0.4)  $kJ.mol^{-1}$ , -10.8 ( $\pm$  0.4)  $kJ.mol^{-1}$  and -10.6 ( $\pm$  0.4)  $kJ.mol^{-1}$  can be considered as the intrinsic segregation energy for nickel at 730°C, 750°C and 775°C, respectively.

As shown in figure V.5, good agreement was obtained between the measured final ferrite fractions and the predicted ones using solute drag modeling at 775°C up to 0.7%wt of nickel. By modifying the Fe-Ni parameter to -15  $kJ.mol^{-1}$  (binding energy of -9.5  $kJ.mol^{-1}$ ), the predicted final ferrite fractions were in better a agreement with the ex-



Figure V.13: The intrinsic segregation energy as a function of nickel content calculated using Eq.IV.4.1 for the two temperatures 730°C and 750°C.

periments at high nickel contents. However, the solute drag model underestimated the measured ferrite fractions at low nickel contents. As it was already mentioned, the solute drag model as described in the present study does not apply on conditions where ferrite growth is controlled by nickel diffusion in austenite. As shown in figure V.4-c, the zero partition line passes through the 1%Ni concentration. As mentioned, if further one considers the temperature gradient over the diffusion couple, the zero partition line would pass through a lower nickel content (0.85%Ni at 780°C). This can be also noticed by the low ferrite fraction formed at nickel contents higher than 0.8 %, which indicates a phase transformation with slow solute diffusion in austenite (LEP transformation mode). Moreover, the calculated dissipation energies using a binding energy of -9.5  $kJ.mol^{-1}$  were much higher than the calculated ones at 730°C and 750°C as shown in figure V.14.



Figure V.14: The maximum dissipated energy as a function of nickel content calulated at 775°C using a binding energy of -9.5  $kJ.mol^{-1}$ .

One other possible explanation can also be related to the effect of the nucleation process,

which is not taken into account in our solute drag model. In the present model, the ferrite is supposed to form on the austenite grain boundaries and grow into the bulk by diffusion process. At high temperatures, the driving force for nucleation decreases, which can promote edge and corner nucleation sites compared to the grain boundary sites. Thus, the growth behavior of ferrite would be different from that considered in the present study. If for example, ferrite nucleates at grain edges instead of grain boundaries, ferrite can grow as elongated pyramids, with a lengthening rate much higher than the thickening rate [152]. For the above listed reasons, the comparison between the measured kinetics at high temperatures and the solute drag calculations should be treated with caution.

## V.2 Fe-C-Mn system

A diffusion couple containing a gradient of manganese was used to study the effect of manganese content on ferrite growth kinetics at two different temperatures, 730°C and 750°C. The manganese content varies from 0 to 0.9 % over a distance of 3 mm. A constant carbon content was measured across the diffusion couple, namely 0.22% wt. The estimated temperature gradient over the manganese composition gradient was 10°C ( $3.3^{\circ}C/mm$ ), which is much higher than the measured temperature gradient for the other samples (~1.5°C/mm). This is probably due to difference in the sample's geometry used for the other diffusion couples (cylindrical) and the one used for the Fe-C-Mn diffusion couples (parallelepiped, with a smaller section). A constant grain size was measured along the Fe-C-Mn diffusion couples, namely, 50 $\mu$ m at 730°C and 70 $\mu$ m at 750°C.



Figure V.15: Evolution of ferrite fraction measured using HEXRD as a function of time and manganese composition along the Fe-C-Mn diffusion couple during the isothermal holding at 730°C.

The graded samples were austenitized at 910°C, quenched to 730°C or 750°C and held at this temperature for 15 min. An example of the measured ferrite fractions evolution at 730°C is shown in figure V.15. Each curve corresponds to the evolution of ferrite fraction as function of time for a single manganese composition. The maximum variation of manganese composition within the beam of 80  $\mu$ m is of 0.024 %. At both temperatures, ferrite growth rates and the ferrite fraction reached at the plateau decrease with increasing manganese content. The isothermal sections of the Fe-C-Mn phase diagrams at 730°C and 750°C are shown in figures V.16-a and V.16-b, respectively. At both temperatures, the studied composition range is located below the zero partition line where both LENP and PE are possible growth modes.



Figure V.16: Isothermal sections of the Fe-C-Mn phase diagram showing the gradient of manganese composition of the diffusion couple (grey circles) at : a) 730°C and b) 750°C.



Figure V.17: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LE (filled dots) and solute drag (crosses) models as function of manganese content at : a) 730°C and b) 750°C.

Figure V.17 compares the measured final ferrite fractions reached at the plateau (at the end of the isothermal holding i.e. after 15 min) with the predicted values using the different models as function of manganese composition at 730°C and 750°C, respectively. For both temperatures, the PE model fails to predict the measured ferrite fraction when

manganese content increases. The discrepancy between the predicted PE fraction and the measured one increases with increasing manganese content and with temperature. On the other hand, the LE model describes well the final ferrite fraction formed at  $750^{\circ}$ C for the whole composition range and up to 0.6% for the 730°C case. At higher manganese contents, the LE predicted ferrite fraction is lower than the measured value (5% lower at 0.9wt% of Mn).



Figure V.18: Experimental ferrite growth kinetics measured using HEXRD experiments for different compositions of the Fe-C-Mn diffusion couple during the isothermal holding for the three compositions : Fe-0.22C-03Mn (%wt.) at : a) 730°C and b) 750°C. Fe-0.22C-0.6Mn (%wt.) at : c) 730°C and d) 750°C. Fe-0.22C-0.8Mn (%wt.) at : e) 730°C and f) 750°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

The measured ferrite growth kinetics using HEXRD experiments will now be compared with the predictions of the PE and LE models for a series of compositions (figure V.18 a to f). The PE predicted kinetics are faster than the measured ones for all the studied conditions. Figure V.17 shows that the LE mode successfully describes the measured growth kinetics at 750°C. A small deviation is noticed for high manganese contents at 730°C. The comparison between the measured growth kinetics and the calculated ones using PE and LE models indicates that the interfacial conditions during austenite to ferrite phase transformation in the Fe-C-Mn system could be described using the LENP model, at least under the studied conditions ( 0 to 0.9 %Mn at  $730^{\circ}$ C and  $750^{\circ}$ C).

#### Solute drag modeling:

The solute drag model was used to predict ferrite growth kinetics as a function of manganese content and temperature. Only the Fe-Mn interaction parameter was used as a fitting parameter. As shown in figures V.17 and V.18, the measured final fractions as well as the growth kinetics in the FeC/Fe-C-Mn diffusion couple were in good agreement with the predicted ones using the LE model at 750°C for the whole range of manganese composition and up to 0.6%wt at 730°C. The solute drag calculations show also a good agreement between the predicted ferrite growth kinetics and the measured ones using HEXRD as shown in figure V.18. It is to be mentioned that the LE predicted kinetics were in a better agreement with measurements than the solute drag calculations at high manganese contents at 750°C. The solute drag model also succeeded to predict the ferrite fractions reached at the end of the isothermal holding for the whole range of manganese composition and at both temperatures (Fig. V.17). The Fe-Mn interaction parameter used for solute drag modeling was -1.4  $kJ.mol^{-1}$  at 730°C and -1.7  $kJ.mol^{-1}$  at 750°C corresponding to a binding energy calculated at the para-equilibrium conditions of +1.5  $kJ.mol^{-1}$  for both temperatures.

The calculated maximum dissipated energy increases with increasing manganese content and with increasing temperature as shown in figure V.19. The effect of temperature is more noticeable at high manganese contents.



Figure V.19: Maximum dissipated energy due to manganese diffusion across the interface as a function of the bulk manganese content at two temperatures, 730°C (black dots) and 750°C (blue dots).

Figure V.20 shows the evolution of the enrichment factor as a function of the bulk man-

ganese content at 730°C and 750°C. The enrichment factor decreases slightly with increasing manganese content and increasing temperature. The enrichment factor for the 0.9%Mn composition decreases from 2.8 to 2.5 when increasing temperature from 730°C to 750°C. The effective binding energy calculated from the enrichment factor using IV.2.8 as a function of bulk manganese content and temperature is also illustrated in figure V.20. Results show an increase of the effective binding energy with increasing manganese content and increasing temperature. The average effective binding energies are -4.6 ( $\pm$ 0.4)  $kJ.mol^{-1}$  and -4.2 ( $\pm$  0.5)  $kJ.mol^{-1}$  at 730°C and 750°C, respectively. The intrinsic segregation energies calculated using Guttmann's approach is -1.95 ( $\pm$  0.1)  $kJ.mol^{-1}$  at both temperatures. These values are higher than the reported values for the intrinsic segregation energies of manganese at austenitic grain boundaries (-8 ( $\pm$  3)  $kJ.mol^{-1}$ ) [80] or at ferrite grain boundaries (-5.5  $kJ.mol^{-1}$ ) [146].



Figure V.20: Evolution of the enrichment factor  $K_{max}$  (a) and the corresponding effective binding energy (E<sub>0</sub>) (b) calculated using IV.2.8 as a function of manganese content for the two temperatures, 730°C and 750°C.

The solute drag modeling shows that segregation of manganese at the  $\alpha/\gamma$  interface is mostly due to the presence of carbon and its intrinsic segregation is weak to such interfaces. Van Landeghem et al. [114] used APT to measure manganese segregation at the austenite ferrite interface in Fe-C-Mn and FeNMn alloys. Manganese has an attractive interaction with both carbon and nitrogen in austenite and ferrite. Moreover, it was reported that nitrogen does not segregate at grain boundaries, as opposed to carbon. Van landeghem et al. [114] reported a significant segregation of manganese at the austenite ferrite interface in the Fe-C-Mn system and a weak or nonexistent segregation in the FeNMn system. These observations suggest that the presence of carbon at the austenite-ferrite interface is the main reason for manganese segregation. This is in perfect agreement with the calculations made in the present study.

## V.3 Fe-C-Si system

To study the effect of silicon content on ferrite growth kinetics, a diffusion couple created between Fe-C and Fe-C-Si was austenitized at 980°C, quenched at 730°C, 750°C and 775°C and held at these temperatures during 15min. The diffusion couple contains a gradient of silicon varying from 0% to 1.2% wt over a distance of 12 mm. An important gradient of carbon was measured across the diffusion couple, 0.24 % at the silicon lean side to 0.18% at the rich side of silicon. This carbon content gradient is due to the effect of silicon on the chemical potential of carbon. The measured gradient of carbon was taken into account for modeling. Moreover, a temperature gradient of 6°C was estimated across the silicon composition gradient and was also taken into account in modeling. This gradient  $(0.5°C.mm^{-1})$  is also different from the other measured gradients due to the different shape of the diffusion couple (a smaller sample was used in this case). The evolution of ferrite fraction as a function of time and silicon composition is plotted in figure V.21 for the three temperatures 730°C, 750°C and 775°C.



Figure V.21: Evolution of ferrite fraction measured using HEXRD as a function of time and silicon composition along the Fe-C-Si diffusion couple during the isothermal holding at : a) 730°C b) 750°C and c) 775°C.

A gradient of grain size was measured along the graded sample varying from  $20\mu$ m on the silicon lean side of the diffusion couple to  $30\mu$ m on the silicon rich side. Again, all these parameters (carbon content, temperature and grain size) were used as input variables for modeling. Results show that ferrite growth kinetics as well as the reached final fraction at

the plateau increase with increasing silicon content. It has to be mentioned here that this variation of the final fraction is influenced by the important carbon gradient as measured using EPMA as well as the temperature gradient.



Figure V.22: Isothermal sections of the Fe-C-Si phase diagram showing the gradient of composition of the diffusion couple FeC/Fe-C-Si (grey circles) at : a) 730°C, b) 750°C and c 780°C. The equilibrium tie-lines of the two phase field are shown in green.

The isothermal sections of the Fe-C-Si phase diagram are illustrated in figure V.22 showing the studied gradient of silicon composition at the three temperatures. For all the studied composition and temperature conditions, both PE and LENP are possible growth modes. The comparison between the predicted final fractions using PE and LE models and the obtained results using HEXRD experiments is shown in figure V.23. For the three temperatures, the final ferrite fraction is overestimated by both PE and LE models and the gap between measurements and model predictions becomes larger with increasing silicon content and increasing temperature.



Figure V.23: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of silicon content at : a) 730°C, b) 750°C and c) 775°C

Figure V.24 compares the measured ferrite growth kinetics and the modeled ones using PE and LE models, for two silicon compositions (0.5Si and 1Si (wt.%)) at the three temperatures 730°C, 750°C and 775°C. The ferrite growth kinetics as well as the final fractions predicted using both LE and PE models are quite similar. For all the shown composition and temperature conditions, the measured kinetics are slower than both PE and LE calculations, indicating different interfacial conditions from both classical models during ferrite growth in the Fe-C-Si system. Moreover, the results contradicts the assumption of a transition between PE and LE conditions during the transformation since the measured kinetics is slower than both PE and LE predicted ones.



Figure V.24: Experimental ferrite growth kinetics measured using HEXRD experiments in the Fe-C-Si diffusion couple during the isothermal holding for the two compositions : Fe-0.21C-0.5Si (%wt.) at : a) 730°C, b) 750°C and c) 775°C. and Fe-0.19C-1Si (%wt.) at : d) 730°C, e) 750°C and f) 775°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

#### Solute drag modeling:

The solute drag model was used to predict ferrite growth kinetics in the Fe-C-Si system as a function of silicon composition and temperature. As shown in figure V.23, the obtained final fractions are in good agreement with the experimental results at the three temperatures and for the whole studied composition range. Moreover, the ferrite growth kinetics calculated using the solute drag model were in good agreement with the measurements as shown in figure V.24. Table 12 summarizes the Fe-Si interaction parameters at the interface that gave the best fit of the experimental results as well as the calculated binding energies ( $E_b$ ) of silicon under para-equilibrium conditions. At each temperature, the same fitting parameter was used for the whole range of silicon composition (0-1.2 %). The Fe-Si interaction parameters and the corresponding binding energies increase with increasing temperature. Qiu et al. [96] reported a binding energy of -9  $kJ.mol^{-1}$  calculated under the same conditions (para-equilibium conditions) to model ferrite growth kinetics in Fe-C-Si systems at different temperatures. The difference between the two models comes from the different description of the thermodynamic properties of the interface as explained in chapter IV.

Table 12: The Fe-Si interaction parameter  $L_{Fe,Si:Va}$  and the corresponding binding energies (calculated under para-equilibrium conditions) used in the solute drag modeling at the three different temperatures.

T(°C)	$L_{Fe,Si:Va} \\ (kJ.mol^{-1})$	$E_b \ (kJ.mol^{-1})$
730	-105.5	-20
750	-100	-15
775	-96	-12



Figure V.25: Maximum dissipated energy due to solute drag effect as a function of silicon content at the three temperatures, 730°C (black dots), 750°C (blue dots) and 775°C (red dots).

Figure V.25 shows the maximum total dissipated energy due to silicon diffusion across the interface as a function of the bulk silicon composition for the three temperatures. The total dissipated energy is the sum of the dissipated energies due to silicon diffusion across the interface at each atomic plane. The calculations show that with increasing silicon content, the dissipated energy increases to reach a plateau at high silicon contents. The maximum dissipated energy decreases with increasing temperature. This effect of silicon composition on the maximum dissipated energy is due to the effect of carbon on the chemical potential of silicon. The segregation of carbon at the interface increases the chemical potential of silicon at the interface and results in a lower driving force for silicon diffusion and thus a lower dissipated energy.

In contrast to the Fe-C-Ni system, in the Fe-C-Si system there is a clear temperature dependence of the Fe-X interaction parameter. This parameter increases with increasing temperature. In order to have a better understanding of the segregation behavior of silicon, figure V.26-a shows the enrichment factor calculated using Eq.IV.2.8 at low interface velocities as a function of silicon content and temperature. Figure V.26-b shows the corresponding calculated effective binding energies using IV.2.8 as a function of silicon composition and temperature. The enrichment factor decreases with increasing silicon content and with increasing temperature. The enrichment factor for the 1.2%. Si content varies from 2 at 730°C to 1.6 at 750°C and 1.5 at 775°C. The corresponding effective binding energies are -4.4  $kJ.mol^{-1}$ , -2.9  $kJ.mol^{-1}$  and -2.1  $kJ.mol^{-1}$  at 730°C, 750°C and 775°C, respectively. Qiu et al. [94] reported a  $K_{max}$  value of 2.4 and 2 for two different Fe0.74CSi alloys (0.45wt and 0.85 %.Si) at 775°C corresponding to an effective binding energy of -6.1  $kJ.mol^{-1}$  and -4.8  $kJ.mol^{-1}$ , respectively. For similar silicon contents and at the same temperature, the present study predicts an effective binding energy of -4.4  $kJ.mol^{-1}$  and -2.9  $kJ.mol^{-1}$ , respectively. The difference between the two values is due on the one hand, to the different carbon content between the Fe-C-Si systems studied in Qiu's work [96] and the present work, and on the other hand, to the difference in the iron carbon interaction parameter as used in the present study and in the initial version of Zurob's model [11] as used in Qiu's work [96]. The higher segregation of carbon predicted in the present model inhibits silicon segregation at the interface resulting in lower enrichment factors.

As shown in figure V.26-b, the effective binding energies calculated at equilibrium conditions change with composition and temperature. The effective binding energy increases with increasing silicon content and increasing temperature. This behavior is probably enhanced with the effect of the carbon gradient across the graded sample as well as the temperature gradient (5°C).

In an attempt to de-correlate the effect of carbon, the intrinsic Gibbs segregation energies were estimated using Guttmann's approach as explained in chapter IV. The  $\beta_{FeSi}$  and  $\beta_{SiC}$ used in calculations are listed in table 13. The average values of the intrinsic segregation energies of silicon are, -25 (±1)  $kJ.mol^{-1}$  at 730°C, -20(± 1)  $kJ.mol^{-1}$  at 750°C and -15 (± 1)  $kJ.mol^{-1}$  at 775°C. The calculated intrinsic segregation energies of silicon are in good agreement with the reported intrinsic segregation energies in austenite grain boundaries, -23 (± 6  $kJ.mol^{-1}$ ) but lower than the reported ones for ferrite grain boundaries (-7  $kJ.mol^{-1}$ ).

Table 13: The interactions parameters  $\beta_{FeSi}$  and  $\beta_{SiC}$  used to calculated the intrinsic segregation energies of silicon.



Figure V.26: a) Enrichment factor  $K_{max}$  and b)the corresponding effective binding energy (E<sub>0</sub>) calculated using IV.2.8 evolution as a function of silicon content for the two temperatures, 730°C, 750°C and 775°C.

### V.4 Fe-C-Mo system

A diffusion couple between Fe-C and Fe-C-Mo was used to study the effect of molybdenum on ferrite growth kinetics. The molybdenum gradient varies from 0 to 0.2% over a distance of 1.5 mm with a constant carbon content of 0.25% The low molybdenum content (0.2%) was chosen to avoid the formation of carbides. The temperature gradient was estimated to 3°C across the molybdenum composition gradient. The austenite parent grain size was measured to be  $40\mu$ m for the diffusion couples treated at 730°C and 750°C and 65 $\mu$ m for the diffusion treated at 780°C. The diffusion couple was austenitized at 910°C for 30 s, quenched to the intercritical temperatures 730°C, 750°C and 780°C and held at these temperatures for 15 min. Figure V.27 illustrates ferrite fraction evolution as function of molybdenum content during the isothermal holding for the three temperatures 730°C, 750°C and 775°C, respectively.

The isothermal sections of the Fe-C-Mo phase diagrams are shown in figure V.28 illustrating the studied composition gradient. For the three temperatures, both LENP and PE are possible growth modes. Moreover, under the considered conditions (composition and temperatures) the equilibrium tie-lines are almost horizontal (as shown in green lines in figure V.28) and thus coincide with the para-equilibrium tie-lines. As a consequence, the predicted kinetics using LE (LENP) or PE should be similar.

Figure V.29 compares the final fractions reached at the end of the isothermal holding with



Figure V.27: Evolution of ferrite fraction measured using HEXRD as a function of time and molybdenum composition along the Fe-C-Mo diffusion couple during the isothermal holding at : a) 730°C b) 750°C and c) 780°C.

the predicted values using LE and PE models as a function of molybdenum composition and temperature. It is interesting to note that the experimentally measured final fractions are approximately constant across the molybdenum composition gradient. This can also be impacted by the small temperature gradient along the samples ( $\sim$ 3°C). For the three studied temperatures, the predicted LE/PE final fraction is slightly higher than the measured one and the difference increases with increasing molybdenum content and with decreasing temperature. The measured kinetics are compared with the LE/PE predicted ones for two molybdenum compositions (0.08% and 0.2% wt.) at the three temperatures, 730°C, 750°C and 780°C in figures V.30-a to V.30-f.

It can be seen that the predicted LE/PE kinetics is faster than the measured one in all shown conditions. This difference increases with increasing molybdenum composition and temperature. The fact that LE and PE models predict faster kinetics than the measured ones is a strong indication of an additional dissipated energy related to the diffusion of molybdenum across the interface. The additional dissipated energy increases with increasing molybdenum content and with increasing temperature. The present results are consistent with the traditionally reported ferrite growth retardation in [85].



Figure V.28: Isothermal sections of the Fe-C-Mo phase diagram showing the gradient of composition of the diffusion couple (grey circles) at : a) 730°C, b) 750°C and c 780°C. The equilibrium tie-lines of the two phase field shown in green are almost horizontal making the predicted kinetics using LENP and PE identical.



Figure V.29: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of silicon content at 730°C (black), 750°C (blue) and 780°C (red)



Figure V.30: Experimental ferrite growth kinetics measured using HEXRD experiments in the Fe-C-Mo diffusion couple during the isothermal holding for the two compositions : Fe-0.25C-0.08Mo (%wt.) at : a) 730°C, b) 750°C and c) 780°C. and Fe-0.25C-0.2Mo (%wt.) at : d) 730°C, e) 750°C and f) 780°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

#### Solute drag modeling:

The measured ferrite growth kinetics in the Fe-C-Mo system were compared to the predictions of solute drag modeling as a function of molybdenum composition at the three temperatures  $730^{\circ}$ C,  $750^{\circ}$ C and  $780^{\circ}$ C. As shown in figures V.29, good agreement was obtained between the measured final fractions and the calculated ones. Moreover, the solute drag model describes well the measured kinetics for the whole molybdenum gradient (0 to 0.2%) and for the three temperatures (Fig.V.30).

The Fe-Mo interaction parameters that gave the best fit of the experimental data were, -7.2  $kJ.mol^{-1}$ , -7.5  $kJ.mol^{-1}$  and -8  $kJ.mol^{-1}$  at 730°C, 750°C and 780°C, respectively. A same Fe-Mo interaction parameter was used for the whole range of composition at each temperature. Using these parameters, the corresponding binding energy calculated under para-equilibrium conditions was -15  $kJ.mol^{-1}$  for the three temperatures and for all molybdenum compositions.

The maximum dissipated energies due to molybdenum diffusion across the interface increase with increasing Mo content and with decreasing temperature as shown in figure V.31. The effect of temperature is more noticeable at high molybdenum content. As it was mentioned in chapter IV, the dissipated energy in the Fe-C-Mo system is mainly due to the interaction between molybdenum and the interface at the two first atomic planes, in contrast with other observation in the other systems (for austenite stabilizers (Ni, Mn) elements), where the segregation at the austenite interface side contributes to increase the total dissipated energy.



Figure V.31: Maximum dissipated energy due to solute drag effect as a function of molybdenum content at the three temperatures, 730°C (black dots), 750°C (blue dots) and 780°C (red dots).

Figure V.32-a shows the enrichment factors calculated at very low interface velocity (ap-

proaching the equilibrium conditions) as a function of the molybdenum bulk composition for the three temperatures. The enrichment factor increases slightly with molybdenum content. The effect of composition is more pronounced at lower temperatures. On the other hand, the enrichment factor clearly decreases with increasing temperature. One can note that the relative segregation (enrichment factor) of molybdenum at the interface is approximately six times higher than that of silicon at the same bulk composition and the same temperature. This is due to the difference in the interaction of silicon and molybdenum with carbon at the interface. Molybdenum segregation is enhanced by the presence of carbon at the interface due to its attractive interaction with carbon. On the other hand, the segregation of silicon is limited by the presence of carbon, due to their repulsive interaction.



Figure V.32: The enrichment factor  $K_{max}$  (a) and the corresponding effective binding energy (E<sub>0</sub>) (b) calculated using IV.2.8 evolutions as a function of molybdenum content for the two temperatures, 730°C, 750°C and 780°C. The intrinsic segregation energy of molybdenum is also shown in (b).

Moreover, the binding energies as calculated under para-equilibrium conditions are the same at 750°C for molybdenum and silicon (-15  $kJ.mol^{-1}$ ). This is a good example to illustrate that the binding energy as calculated at the para-equilibrium conditions is not an indicator of the segregation behavior of the solute elements at the interface. The calculated effective binding energies using IV.2.8 at low interface velocities (approaching the equilibrium conditions) are plotted in figure V.32-b as a function of molybdenum content and temperature. The effective binding energy increases with increasing temperature but it is almost constant over the molybdenum gradient of composition. Results show an average effective binding energy of -23.5 ( $\pm$  0.7)  $kJ.mol^{-1}$ , -22.5 ( $\pm$  0.3)  $kJ.mol^{-1}$  and -20.5 ( $\pm$ 0.2)  $kJ.mol^{-1}$  at 730°C, 750°C and 780°C respectively. The intrinsic segregation energy of molybdenum was estimated using Guttmann's approach and the results are plotted in figure V.32-b. Nearly the same intrinsic segregation energy was obtained for the three temperatures. This value is around -14.5 ( $\pm$  0.5)  $kJ.mol^{-1}$  and it is in good agree-

ment with the reported intrinsic segregation energy of molybdenum in austenitic grain boundaries (-15 ( $\pm$  3) kJ.mol<sup>-1</sup>). On the other hand, Guttmann et al. [146] estimated a very low binding energy of molybdenum at ferrite grain boundaries  $(0.1 \ kJ.mol^{-1})$  and claimed that the observed molybdenum segregation is only due to carbon presence at the interface. However, Murayama et al. [149] showed that molybdenum can clearly segregate at  $\alpha$ -Fe grain boundaries and estimated an intrinsic segregation energy of -28 kJ.mol<sup>-1</sup> at 800°C. Liu et al. [150] used a solute drag approach to model ferrite growth kinetics in a Fe-C-Mo alloy and reported a segregation energy of  $-17 \ kJ.mol^{-1}$ . It has to be noted that the authors neglected the carbon segregation at the interface in their calculations. Based on our calculations, we can conclude that molybdenum segregates at the austenite ferrite interfaces due on one hand to its intrinsic binding energy as well as its high interaction with carbon. The present results are in agreement with the reported behavior of molybdenum at  $\alpha/\gamma$  interfaces. As stated by Aaronson et al. [99] molybdenum has a tendency to segregate at  $\alpha/\gamma$  interfaces and its segregation is enhanced by the high concentration of carbon at these interfaces. This was called solute drag like effect. Hutchinson et al. [85] classified molybdenum as an element with high interaction with both carbon and  $\alpha/\gamma$  interface.

## V.5 Fe-C-Cr system

A diffusion couple created between Fe-C and Fe-C-Cr was used to study the effect of chromium content on ferrite growth at three different temperatures, 730°C, 750°C and 775°C. The chromium gradient varies form 0% (resp. 0.2% carbon) to 1%w. (resp. 0.22% carbon) over a distance of 6.5 mm. The estimated temperature gradient is ~ 10°C over the 6.5 mm. A constant grain size of 55  $\mu$ m was measured across the diffusion couple. The obtained ferrite growth kinetics as a function of time and chromium content during the isothermal holding at 750°C is shown in figure V.33. The obtained results at 730°C and 775°C are not presented here due, on the one hand, to the formation of pearlite in the first case (730°C) and on the other hand, to the noisy data obtained at 775°C.

Figure V.34 shows the evolution of the ferrite fraction reached at the end of the isothermal holding as a function of chromium composition, measured using HEXRD as well as the predicted ones using LE and PE models. As shown by the isothermal section of the Fe-C-Cr phase diagram at 750°C presented in figure V.35, both LENP and PE are possible growth modes for the studied gradient of chromium. The predicted LE final fractions are in good agreement with the measured ones. A small deviation is observed between the measurements and the LE predictions at chromium contents higher than 0.6%

Ferrite fraction evolution as function of time during the isothermal holding is shown in figure V.36 for four different compositions. The measured kinetics is slower than both the predicted kinetics using PE and LE models and the difference increases with increasing


Figure V.33: Evolution of ferrite fraction measured using HEXRD as a function of time and chromium composition along the Fe-C-Cr diffusion couple during the isothermal hold-ing at 750°C.



Figure V.34: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of chromium content at 750°C.

chromium content. Although the predicted final fractions are in good agreement with the LE predictions, the growth kinetics are overestimated by the model. This discrepancy between the predicted PE/LE and the measured kinetics indicates again the presence of a possible additional energy dissipation due to solute drag effect.



Figure V.35: Isothermal sections of the Fe-C-Cr phase diagram showing the gradient of composition of the diffusion couple (grey circles) at 730°C. The equilibrium tie-lines of the two phase field are shown in green.



Figure V.36: Experimental ferrite growth kinetics measured using HEXRD experiments in the Fe-C-Cr diffusion couple during the isothermal holding for the four compositions : a) Fe-0.20C-0.2Cr (%wt.) at 758°C, b) Fe-0.21C-0.4Cr (%wt.) at 756°C, c) Fe-0.21C-0.6Cr (%wt.) at 754°C and d) Fe-0.20C-0.8Cr (%wt.) at 752°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

#### Solute drag modeling:

The solute drag model was used to predict ferrite growth kinetics in the Fe-C-Cr system as a function of chromium content at 750°C. The best fit was obtained using a Fe-Cr interaction parameter + 5.3  $kJ.mol^{-1}$  corresponding to a binding energy calculated at para-equilibrium conditions of + 1.5  $kJ.mol^{-1}$ . Good agreement was found between the measured ferrite fractions at the end of the isothermal holding and the predicted ones using solute drag model as shown in figure V.34. Moreover, a better description of the measured ferrite growth kinetics was obtained using solute drag modeling compared to LE and PE models as illustrated in Fig.V.36.



Figure V.37: a) Maximum dissipated energy due to chromium diffusion across the interface as a function of the bulk chromium content at 750°C. b) Evolution of the enrichment factor  $K_{max}$  and the corresponding effective binding energy (E<sub>0</sub>) calculated using Eq.IV.2.8 as a function of chromium content at 750°C. The intrinsic segregation energy of chromium is also shown.

The solute drag calculations show an increase of the maximum dissipated energy due to chromium diffusion across the interface with increasing bulk chromium content as illustrated in figure V.37-a. The enrichment factor of chromium calculated using Eq.IV.2.8 increases from 3.7 at low chromium content (0.01%Cr) to 4.3 at 0.9%Cr (Fig.V.37-b). It is to be noted that this variation is also impacted by the carbon and temperature gradients as estimate across the chromium composition gradient. The effective binding energies calculated at low interface velocities using Eq.IV.2.8 are plotted in figure V.37-b. Results show a decrease of the effective binding energy with increasing chromium content. As for the enrichment factor, this change in the effective binding energy is impacted by the temperature gradient. The average effective binding energy is estimated to -11.2 ( $\pm$  0.5)  $kJ.mol^{-1}$ . To de-correlate the carbon effect on the segregation energy of chromium, the intrinsic segregation energy was estimated using Guttmann's approach as explained in chapter IV. Calculations predicted an average intrinsic segregation energy of -1.4 ( $\pm$  0.1)  $kJ.mol^{-1}$  for chromium on the temperature range (750°C - 760°C) as shown in figure V.37-b. Enomoto et al. [80] reported an intrinsic segregation energy of chromium at an austenitic grain boundary of  $-10 \ kJ.mol^{-1}$ . Aaronson et al. [99] reported an effective binding energy of chromium at austenite ferrite interfaces of  $-8 \ kJ.mol^{-1}$  at 660°C. It is to be noted that the intrinsic segregation energy of chromium at a ferritic grain boundary is estimated to  $0 \ kJ.mol^{-1}$  [146]. The present result is higher than the reported values in austenite grain boundaries but comparable with the reported ones for ferrite grain boundaries.

# V.6 Decoupled effect of substitutional element content on ferrite growth kinetics

It was shown that the solute drag model succeeded in predicting with a good accuracy the evolution of ferrite fraction as a function of solute content and temperature in the studied Fe-C-X systems (X : Ni, Mn, Si, Mo and Cr). However, the characterization of transformation kinetics in the graded samples involved not only the variation sought in substitutional elements, but also some unwanted variation in temperature, carbon content and grain size. In order to investigate the effect of the substitutional element content (alone) on ferrite growth kinetics, solute drag calculations were conducted using a single temperature, carbon content and grain size for all the above listed Fe-C-X systems. For each system, only the temperatures where solute drag modeling gave good results were studied. The same Fe-X interaction parameters that gave best fit of the experimental data were used here. The carbon content used in modeling was 0.22%wt and the grain size was  $40\mu$ m. In the following section, these results are presented briefly for the different systems and at the end, a comparison is made between the different systems at a same temperature, carbon and grain size.

Figure V.38 shows the obtained results for the Fe-C-Ni system at 730°C and 750°C in terms of the evolution of ferrite fraction as a function of time and nickel content (Fig.V.38-a and b) and the reached final fractions (Fig.V.38-c). Results show a decrease of the ferrite fraction reached at the end of the isothermal holding with increasing nickel content and with increasing temperature. Similarly, ferrite growth kinetics decreases with increasing nickel content and decreasing temperature.

The effect of manganese content, an austenite stabilizer element such as nickel, on ferrite growth kinetics is shown in figure V.39 at two temperatures 730°C and 750°C. As for the Fe-C-Ni system, ferrite growth kinetics as well as the final ferrite fraction decrease with increasing manganese content and with increasing temperature.

For the Fe-C-Si system, the effect silicon content on ferrite growth kinetics is shown in figures V.40-a, b and c for the three temperatures 730°C, 750°C and 775°C. The final ferrite fraction reached at the end of the isothermal holding is plotted as a function of silicon content for the three temperatures in figure V.40-d. Results show a small effect



Figure V.38: Heat maps representing the evolution of the calculated ferrite fraction as function of time and nickel composition at : a) 730°C and b) 750°C. c) Evolution of the final ferrite fraction as a function of nickel content at a the two temperatures, 730°C (black crosses) and 750°C (blue crosses).

of silicon content on the final ferrite fraction at 730°C but a clear dependency of ferrite growth kinetics on the silicon content. On the other hand, ferrite growth kinetics seems to be unaffected by the silicon content at 750°C and 775°C, contrary to the final fraction which increases with increasing silicon content at both temperatures. The effect of silicon on ferrite growth rate results from a competition between the ferrite stabilizing effect of silicon and the dissipated energy due to its interaction with the moving interface. At lower temperatures (730°C), the Fe-Si interaction parameter is higher as shown in section V.3, resulting in a higher dissipated energy due to silicon diffusion across the interface. The dissipated energy increases with increasing silicon content and results in a slower ferrite growth kinetics. As temperature increases, the dissipated energy due to silicon diffusion across the interface decreases due to a lower Fe-Si interaction parameter. As a result, the ferrite growth kinetics is less impacted and the final ferrite fraction increases due to the ferrite stabilizing effect of silicon. Moreover, it can be seen from figure that the the maximum dissipated energy is less affected by the silicon content at higher temperatures, which can explain the similar growth kinetics observed at 750°C and 775°C. These results



Figure V.39: Heat maps representing the evolution of the calculated ferrite fraction as function of time and manganese composition at : a) 730°C and b) 750°C. c) Evolution of the final ferrite fraction as a function of manganese content at a the two temperatures, 730°C (black crosses) and 750°C (blue crosses).

show that the measured ferrite growth kinetics using HEXRD experiments for the Fe-C-Si diffusion couple were mainly affected by the carbon gradient along the silicon composition gradient.

The calculated ferrite growth kinetics for the Fe-C-Mo system are shown in figure V.41 as a function of the molybdenum content at  $730^{\circ}$ C,  $750^{\circ}$ C and  $775^{\circ}$ C. Again the final ferrite fraction is weakly affected by molybdenum content. This is probably related to the studied molybdenum content range (0 - 0.2%).

Finally, the effect of chromium on ferrite growth kinetics was modeled at 750°C and results are shown in figure V.42. Increasing the chromium content decreases the ferrite growth rate as well as the final ferrite fraction reached at the end of the isothermal holding.



Figure V.40: Heat maps representing the evolution of the calculated ferrite fraction as function of time and silicon composition at : a) 730°C, b) 750°C and b) 775°C. d) Evolution of the final ferrite fraction as a function of silicon content at a the three temperatures, 730°C (black crosses), 750°C (blue crosses) and 775°C (red crosses).



Figure V.41: Heat maps representing the evolution of the calculated ferrite fraction as function of time and molybdenum composition at : a) 730°C, b) 750°C and b) 775°C. d) Evolution of the final ferrite fraction as a function of molybdenum content at a the three temperatures, 730°C (black crosses), 750°C (blue crosses) and 775°C (red crosses).



Figure V.42: a) Heat map representing the evolution of the calculated ferrite fraction as function of time and chromium composition at 750°C. b) Evolution of the final ferrite fraction as a function of chromium content at a 750°C.

## V.7 Conclusion

The effect of substitutional element contents on ferrite growth kinetics in ternary Fe-C-X systems (where X : Ni, Mn, Si, Mo, Cr) has been determined at different temperatures using the developed combinatorial methodology. The large dataset obtained in this study highlights the critical contribution of using HEXRD technique coupled with compositionally graded materials in accelerating the investigation of ferrite growth kinetics in ternary Fe-C-X systems. The obtained results were compared with the predictions of the PE and LE models as well as the modified version of the solute drag model as detailed in chapter IV. For all the studied Fe-C-X systems, the PE model failed to predict the measured ferrite growth kinetics. Moreover, it was shown that the LE model cannot be used to fully describe ferrite growth kinetics for the whole substitutional composition gradient in the Fe-C-Ni and Fe-C-Mn systems, where it is generally reported that the LE model can be considered as a natural state of ferrite precipitation [94]. It was also shown that even in cases where the LE model predicted well the final ferrite fractions, it failed to describe the evolution of the ferrite transformed kinetics.

	FeCNi			FeCSi		
$T(^{\circ}C)$	730	750	775	730	750	775
$\begin{array}{c} {\rm L}_{Fe,X:Va}\\ (kJ.mol^{-1}) \end{array}$	-11.7	-11.8	-11.9	-105.5	-100	-96
$E_0 (kJ.mol^{-1})$	-6.5	-6.5	-6.5	-20	-15	-12
	FeCMo			FeCMn		FeCCr
$T(^{\circ}C)$	730	750	780	730	750	750
$L_{Fe,X:Va}$						
$(kJ.mol^{-1})$	-7.2	-7.5	-8	-1.4	-1.7	+5.3

Table 14: Fe-X ( $L_{Fe,X:Va}$  interaction parameters and their corresponding binding energies used that gave the best fit of the measured ferrite growth kinetics.

The solute drag model was also used to predict ferrite growth kinetics as a function of the solute content and temperature. The only fitting parameter was the Fe-X interaction parameter at the interface. Results showed very good agreement between the measured ferrite growth kinetics and the calculated ones using the solute drag model. For all the studied systems, the used Fe-X interaction parameters were independent from the X composition but showed a dependency on temperature as summarized in table 14. The calculated enrichment factors and the effective binding energies were in good agreement with the reported ones in literature, except for the Fe-C-Ni system, where the calculated segregations are higher than the experimentally measured ones.

# Chapter VI

# Ferrite growth kinetics in compositionally graded Fe-C- $X_1X_2$ quaternary alloys

The following section presents an overview of the obtained results for the Fe-C- $X_1X_2$  quaternary systems during the HEXRD campaign at DESY, Hamburg in Germany as well as comparison with the prediction of the different models.

## VI.1 Fe-C-Ni-Mo system

A diffusion couple between Fe-C-1Ni and Fe-C-0.2Mo was used to study the dependency of ferrite growth kinetics on nickel and molybdenum contents. The diffusion couple contains opposite gradients of nickel and molybdenum ranging from 0%Ni (resp. 0.2% Mo) to 1%Ni (resp. 0% Mo) over a distance of 3 mm (Fig.VI.1-a). A gradient of carbon was measured along the diffusion couple (0.18% wt. at the nickel rich side and 0.2% wt. at the molybdenum rich side). This carbon gradient was taken into account in modeling. As for the ternary systems, the graded sample was austenized at 910°C for 30 s, quenched to the intercritical temperatures, 730°C, 750°C and 775°C, and held 15 min at these temperatures. A temperature gradient of 5°C was estimated over the composition gradient based on the estimated temperature gradients in the ternary systems (1.6°C.mm<sup>-1</sup>). The measured grain size was ~45  $\mu$ m along the three diffusion couples.

The evolution of ferrite fraction as function of time, nickel and molybdenum contents is shown in figure VI.1-b, c and d for the three temperatures,  $730^{\circ}$ C,  $750^{\circ}$ C and  $775^{\circ}$ C. Each curve corresponds to ferrite growth kinetics of a given nickel and molybdenum contents at a given temperature. Considering a beam size of  $80\mu$ m, each curve corresponds to a nickel and molybdenum maximum variation of 0.026% and 0.005%, respectively. Ferrite growth kinetics decreases with increasing nickel content (resp. decreasing molybdenum content) and with increasing temperature.



Figure VI.1: a) Nickel, molybdenum and carbon contents across the diffusion couple as measured using EPMA. b) to d) Evolution of ferrite fraction measured using HEXRD as a function of time and nickel and molybdenum composition along the Fe-C-Ni-Mo diffusion couple during the isothermal holding at : b) 730°C, c) 750°C and d) 775°C.

Figures VI.2 compares the measured final ferrite fractions at the end of the isothermal holding with the predicted ones using LE and PE models as function of nickel and molybdenum contents for the three temperatures, 730°C, 750°C and 775°C, respectively. The formed ferrite fraction decreases with increasing nickel content (i.e. decreasing molybdenum content) and with increasing temperature. The effect of nickel and molybdenum composition is more noticeable at higher temperatures. At 775°C, the formed ferrite fraction at the end of the isothermal holding varies from 55 % on the molybdenum rich side to 9 % on the nickel rich side. For the three temperatures, the PE model fails in predicting the measured values. The gap between measurements and PE predictions increases with increasing nickel content (i.e. decreasing molybdenum content) and increasing temperature. At 730°C, the predicted ferrite fractions using the LE model are higher than the measured ones for the whole range of nickel/molybdenum composition. A nearly constant difference is noticed between the measurements and the predicted LE fractions (+ 3 to 5 %). It is to be noted that the measured ferrite growth kinetics for the ternary Fe-C-Ni



Figure VI.2: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of nickel content at : a) 730°C, b) 750°C and c) 775°C

system at 730°C showed good agreement with the LE model predictions up to 0.6% of nickel with a same relative difference between the measured fraction and the LE predicted one at 1% of nickel (5%). On the other hand, the measured ferrite growth kinetics in the ternary Fe-C-Mo system were systematically lower than the calculated ones using the LE model.

At 750°C, good agreement is obtained between the LE calculations and the measurements at the nickel rich side. With increasing molybdenum content (decreasing nickel content), a divergence between the LE predictions from measurements is noticed. At 775°C, the LE model fails in predicting the measured ferrite fraction reached at the end of the isothermal holding, for the whole range of nickel and molybdenum compositions. The divergence between the LE calculations and measurements increases with increasing nickel content. Now, the measured ferrite growth kinetics are compared with the predictions of both the LE and PE models. Figure VI.3 shows a full comparison of the experimental phase transformation kinetics maps in (time, composition) space with the PE and LE models predictions at the 730°C temperature. It can clearly be noticed that the predicted kinetics using both LE and PE models are faster than the measured values at this temperature



for the whole range of nickel and molybdenum composition.

Figure VI.3: Heat maps representing the evolution of ferrite fraction as function of time, nickel and molybdenum composition at 730°C, as measured using high-energy X-ray diffraction measurements (Exp.) and the modeled ones using solute drag (SD) calculations, paraequilibrium (PE) and local equilibrium negligible partitioning (LENP) models.

In figure VI.4, the ferrite growth kinetics of two selected nickel and molybdenum compositions (0.4%Ni-0.12%Mo and 0.7%Ni-0.06%Mo) are compared with the predictions of the different models at the three temperatures, 730°C, 750°C and 775°C. The PE predicted growth kinetics are faster than the measured ones for all the shown conditions (i.e. nickel and molybdenum compositions and temperatures). The divergence between measurements and the PE predicted growth kinetics increases with increasing temperature and with increasing nickel content. The LE model predicts kinetics slower than the PE model but still faster than the measured ones. Even in cases where the LE model succeeded in predicting the final fractions, the predicted kinetics does not fit with the experiments as it is shown in figures VI.4-b and VI.4-e.



Figure VI.4: Experimental ferrite growth kinetics measured using HEXRD experiments in the Fe-C-Ni-Mo diffusion couple during the isothermal holding for the two compositions : Fe-0.19C-0.4Ni-0.12Mo (%wt.) at : a) 732°C, b) 752°C and c) 777°C. and Fe-0.19C-07Ni-0.06Mo (%wt.) at : d) 733°C, e) 753°C and f) 778°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

#### Solute drag modeling :

The quaternary version of the solute drag model was used to predict ferrite growth kinetics as a function of nickel and molybdenum contents at the three temperatures,  $730^{\circ}$ C,  $750^{\circ}$ C and  $775^{\circ}$ C. As for the ternary systems, the Fe-C interaction at the interface was adjusted to  $-50 \ kJ.mol^{-1}$  and the Ni-C, Mo-C interaction parameters were modified to capture the same Wagner interaction parameters as in austenite using Eq.IV.2.9. The only fitting parameters are thus the Fe-Ni and Fe-Mo interactions parameters. Two approaches can be used to calibrate these parameters, the first one is to use the same parameters as for the ternary systems studied in chapter V (eg. Fe-C-Ni and Fe-C-Mo systems for the quaternary Fe-C-Ni-Mo alloy) at similar temperatures. One other way is to calibrate these parameters using the ternary compositions of the present quaternary system since the extremes of the composition gradient can be considered as ternary compositions. For the Fe-C-Ni-Mo system, this corresponds for example to the Fe-0.18C-1Ni at 735°C and Fe-0.2C-0.2Mo at  $730^{\circ}$ C.

In the present study, the Fe-Ni and Fe-Mo, (or Fe-X1 and Fe-X2 for other systems) interaction parameters were first gathered from the results of the solute drag modeling of the ternary systems. These parameters were then tested on the ternary compositions of the quaternary diffusion couple before being used on the whole composition gradient, with the condition that the interaction parameters succeed in predicting ferrite growth kinetics for the ternary compositions. Otherwise, a further calibration of the Fe-Ni and Fe-Mo interaction parameters using the two extremes of the composition gradient was realized. Then, the same Fe-Ni and Fe-Mo interaction parameters were kept for the whole range of composition.

As mentioned in chapter V, the modifications of the Fe-Ni and Fe-Mo  $(L_{Fe,Ni:Va;0})$  and  $L_{Fe,Mo:Va;0}$  interaction parameters induce a modification of the Wagner Ni-Mo interaction parameter as shown by Eq.IV.2.10. In the present study, this parameter was adjusted to capture the same Ni-Mo (or X<sub>1</sub>-X<sub>2</sub>) Wagner interaction as in austenite.

Table 15 summarizes the Fe-Ni, Fe-Mo interaction parameters and the corresponding binding energies as calculated under para-equilibrium conditions that gave the best fit of the experimental results. The calculated final ferrite fractions as well as the ferrite growth kinetics using solute drag modeling are shown in figures VI.2 and VI.4. Very good agreement was obtained between measurements and solute drag modeling at the three temperatures, 730°C, 750°C and 775°C in terms of the final ferrite fraction as well as the evolution of ferrite fraction as a function of time.

Table 15: Fe-Ni  $(L_{Fe,Ni:Va})$  and Fe-Mo  $(L_{Fe,Mo:Va})$  interaction parameters and the corresponding binding energies (calculated under para-equilibrium conditions) used in the solute drag modeling at the three different temperatures.

T(°C)	$L_{Fe,Ni:Va}$ $(kJ.mol^{-1})$	$E_b(Ni) \ (kJ.mol^{-1})$	$\begin{array}{c} L_{Fe,Mo:Va} \\ (kJ.mol^{-1}) \end{array}$	$E_b(Mo) \ (kJ.mol^{-1})$
730	-11.7	-6.5	-7	-15
750	-9.7	-4.5	-7.4	-15
775	-11.9	-6.5	-7.8	-15

The Fe-Ni and Fe-Mo interactions that gave the best fit at 730°C were  $-11.7 \ kJ.mol^{-1}$  and  $-7 \ kJ.mol^{-1}$ , respectively, these are the same parameters as those used for the ternary systems Fe-C-Ni and Fe-C-Mo in chapter V. The corresponding binding energies for nickel and molybdenum calculated at para-equilibrium conditions are  $-6.5 \ kJ.mol^{-1}$  and  $-15 \ kJ.mol^{-1}$ , respectively. At 750°C, the best fit was obtained using a Fe-Ni interaction parameter of  $-9.7 \ kJ.mol^{-1}$  and a Fe-Mo interaction parameter of  $-7.4 \ kJ.mol^{-1}$  corresponding to a binding energy of  $-4.5 \ kJ.mol^{-1}$  for nickel and  $-15 \ kJ.mol^{-1}$  for molybdenum. The Fe-Mo interaction parameter is the same as the one used to model ferrite growth kinetics in the ternary Fe-C-Mo system at 750°C. However, a different Fe-Ni interaction

parameter from the one used for the Fe-C-Ni ternary system at 750°C was used here. It is to be noted that this cannot be a consequence of being in a quaternary system since the Fe-Ni interaction parameter was calibrated on the experimental result obtained at the nickel rich side of the graded sample, which is a ternary system. To check the sensitivity of the Fe-Ni interaction parameter, the solute drag calculations were also conducted using the same Fe-Ni interaction parameter as used for the ternary Fe-C-Ni system at 750°C, namely -11.7  $kJ.mol^{-1}$  and the results are shown in figure VI.5. It can be noticed that using the same Fe-Ni interaction parameter as for the ternary system, good agreement is obtained between the measured and the modeled final ferrite fraction up to 0.5% nickel content. At the nickel rich side, the relative difference between the measured fraction and the predicted one using solute drag model is 5%.



Figure VI.5: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) models as well as solute drag (cross) model using two different binding energies as function of nickel content at 750°C.

At 775°C, the best fit of the measured kinetics was obtained using the same Fe-Ni and Fe-Mo interaction parameters as used for the ternary systems, namely -11.9  $kJ.mol^{-1}$  and -8  $kJ.mol^{-1}$  respectively. The corresponding binding energies as calculated at para-equilibrium conditions are -6.5  $kJ.mol^{-1}$  and -15  $kJ.mol^{-1}$  for nickel and molybdenum, respectively. It was shown in chapter V that the solute drag model failed in predicting the ferrite growth kinetics in the ternary Fe-C-Ni system at high nickel contents (>0.7%) at 775°C using a Fe-Ni interaction parameter of -11.9  $kJ.mol^{-1}$ .

An example of the dissipated energy due to nickel and molybdenum diffusion across the interface as a function of the interface velocity is shown in figure VI.6 for the FeC0.5Ni0.1Mo composition at 732°C. This is a classical solute drag curve where the dissipated energy increases with decreasing the interface velocity to reach a maximum at medium velocities ( $\sim 3e^{-8} \text{ m.s}^{-1}$ ) and then decreases again with decreasing the interface velocity. On the



Figure VI.6: Dissipated free energy due to nickel and molybdenum diffusion across the interface as a function of the interface velocity for the Fe0.19C0.5Ni0.1Mo at 732°C.

same figure are plotted the dissipated energies due to nickel diffusion and the one due to molybdenum diffusion across the interface. The dissipated energy due to molybdenum diffusion starts at higher interface velocities compared to the dissipated energy due to nickel diffusion. This is due to the higher diffusion coefficient of molybdenum from ferrite to the first atomic plane of the interface  $(D_{Mo}^{\alpha}: \sim 8e^{-17} \text{ m}^2.\text{s}^{-1})$  compared to the one for nickel  $(D_{Ni}^{\alpha}: \sim 3e^{-17} \text{ m}^2.\text{s}^{-1})$ . The dissipated energy due to nickel diffusion contributes more at lower velocities (v < 1e^{-9} \text{ m.s}^{-1}).

The total maximum dissipated energy due to nickel and molybdenum diffusion across the interface is shown in figure VI.7-a as a function of the nickel and molybdenum bulk composition at 730°C. In the same figure is plotted the maximum dissipated energy due to nickel diffusion and the one due to molybdenum diffusion across the moving interface. Both the individual dissipated energies increase with increasing the substitutional solute content. The total dissipated energy (which is the sum of the two individual dissipated energies) is higher at the molybdenum rich side (83  $J.mol^{-1}$ ) than the one at the nickel rich side (67  $J.mol^{-1}$ ). The total maximum dissipated energy decreases with increasing nickel content (decreasing molybdenum content) to reach a minimum at a nickel content of 0.8% Ni (0.02% Mo) and increases again with increasing nickel content. The same dissipated energies due to nickel and molybdenum diffusion across the interface were calculated for the ternary Fe-C-Mo and Fe-C-Ni systems at the same temperature as a function of the diffusing element.

The same trend of the total dissipated energy evolution as a function of the bulk content is noticed at 750°C (fig.VI.7-b) with a maximum at the molybdenum rich side of 70  $J.mol^{-1}$ (Vs 83  $J.mol^{-1}$  at 730°C) and a minimum at 0.9%Ni of 26  $J.mol^{-1}$  (Vs a minimum of



Figure VI.7: Maximum dissipated energy due to nickel and molybdenum diffusion across the interface as a function of bulk composition at, a)730°C, b) 750°C and c)775°C.

65  $J.mol^{-1}$  at 0.8%Ni at 730°C). The dissipated energy on the nickel rich side is also smaller at 750°C than at 730°C (42  $J.mol^{-1}$  and 67  $J.mol^{-1}$ , respectively). At 775°C, the total maximum dissipated energy at the molybdenum rich side is 56  $J.mol^{-1}$  versus 85  $J.mol^{-1}$  at the nickel rich side as shown in figure VI.7-c. The same evolution of the total dissipated energy as for previous temperatures can be noticed here with a slight decrease when increasing nickel content (up to 0.2%) before increasing again.

One can notice that the dissipated energy of molybdenum clearly increases with decreasing temperature. On the other hand, the change in the dissipated energy due to nickel diffusion is not monotonous with temperature. Moreover, the maximum dissipated energies due to molybdenum diffusion are similar to those obtained when modeling ferrite growth kinetics in the ternary Fe-C-Mo system. For nickel, a different dissipated energy was needed to model ferrite growth kinetics at 750°C. This result is surprising since nearly the same conditions (temperature, carbon and nickel contents) were met for both systems (Fe-C-Ni and FeCNiMo). Moreover, for the other temperatures, 730°C and 775°C, the dissipated energies on the ternary Fe-C-Ni system and the quaternary Fe-C-Ni-Mo were similar. One possible cause of this result can be related to the experimental conditions, as for example a wrong reading of temperature. One can imagine that this would also affect the molybdenum rich side. However, as it was seen in chapter V, the effect of temperature on the ferrite fraction is more visible in the containing nickel system than in the Fe-C-Mo systems.

The enrichment factors of nickel and molybdenum were calculated using Eq.IV.2.8 and the results are shown in figure VI.8-a as a function of the nickel and molybdenum bulk contents at the three temperatures, 730°C, 750°C and 775°C. The nickel enrichment factor is almost the same across the composition range  $(3.5 (\pm 0.1))$  for both 730°C and 775°C, while it is only 2.8 ( $\pm$  0.1) at 750°C. On the other hand, the enrichment factor of molybdenum shows a dependency on the nickel/molybdenum bulk content and temperature. The  $K_{max}$  of molybdenum decreases from 23.1 at 0.2% Mo (0.01%Ni) to 17.8 at 0.01% Mo (Resp. 1%Ni) at 730°C. When increasing temperature to 750°C, the molybdenum enrichment factor at the molybdenum rich side decreases to 18.5 and decreases further with increasing nickel content to reach 14.4 at the nickel rich side. At 775°C, the molybdenum  $K_{max}$  decreases form 14.5 to 11.3 when increasing nickel content (i.e. decreasing molybdenum content). To summarize, the enrichment factor of nickel seems to be weakly affected by temperature, its bulk composition or the presence of other segregated elements (molybdenum and carbon in the present case). On the other hand, the enrichment factor of molybdenum clearly changes with changing temperature and bulk composition (nickel/molybdenum/carbon contents).



Figure VI.8: a) Enrichment factors  $K_{max}$  and b) Effective binding energy (E<sub>0</sub>) of nickel (dots) and molybdenum (triangles) evolution as a function of the bulk composition for the three temperatures, 730°C (black), 750°C (blue) and 775°C (red).

The corresponding effective binding energies as calculated using Eq.IV.2.8 are shown in figure VI.8-b as a function of the nickel and molybdenum bulk contents for the three temperatures. Results show a small change of the effective binding energy of nickel as a function of composition, -6.8 ( $\pm$  0.2)  $kJ.mol^{-1}$  at 730°C, -5.1 ( $\pm$ 0.3)  $kJ.mol^{-1}$  at 750°C and -7.9 ( $\pm$  0.5)  $kJ.mol^{-1}$  at 775°C. On the other hand, the effective binding energy of molybdenum changes with changing the bulk composition as well as temperature.

At 730°C, the effective binding energy of molybdenum increases from -23.5  $kJ.mol^{-1}$  at 0.2%Mo (0.01%Ni) to -21.5  $kJ.mol^{-1}$  at 0.01%Mo (1%Ni). At 750°C, the effective binding energy of molybdenum increases to -22.2  $kJ.mol^{-1}$  at the molybdenum rich side and increases with increasing molybdenum content to reach -20.4  $kJ.mol^{-1}$  at the nickel rich side. The same trend is observed at 775°C, where the E<sub>0</sub> of molybdenum increases from -20.5  $kJ.mol^{-1}$  to -18.4  $kJ.mol^{-1}$  when increasing molybdenum content. It is to be noted that nearly the same relative change in the effective binding energy is notice for nickel and molybdenum as a function of composition (~ 10%).

As for the enrichment factor, the effective binding energy of nickel seems to be weakly affected by the bulk composition and temperature. The obtained values are comparable to those calculated for the ternary Fe-C-Ni system as shown in table 16. However, the change with temperature is not monotonous as it was for the ternary Fe-C-Ni system. This is due to the 750°C case, where a different Fe-Ni parameter was used to model the measured kinetics in the ternary Fe-C-Ni system and the quaternary Fe-C-Ni-Mo alloy. For molybdenum, the effective binding energy is dependent on both the bulk composition and temperature. When comparing with the obtained average effective binding energies for the ternary Fe-C-Mo system, one finds similar values as shown in table 16.

Table 16: Comparison between the enrichment factors $(K_{max})$ and the effective binding
energies $(E_0)$ of nickel and molybdenum caluclated for the ternary Fe-C-X (X : Ni, Mo)
systems and the ones calculated for the quaternary Fe-C-Ni-Mo system at the three
temperatures.

	Ternary Fe-C-X (X :Ni , Mo)			Quaternary FeCNiMo		
T (°C)	730	750	775	730	750	775
K <sub>max</sub> Ni	3.5	3.5	3.5	3.5	2.8	3.5
	$(\pm 0.2)$	$(\pm 0.2)$	$(\pm 0.2)$	$(\pm 0.1)$	$(\pm 0.1)$	$(\pm 0.1)$
E <sub>0</sub> Ni	-7.2	-7.6	-8.2	-6.8	-5.1	-7.9
$kJ.mol^{-1}$	$(\pm 0.6)$	$(\pm 0.6)$	$(\pm 0.6)$	$(\pm 0.2)$	$(\pm 0.3)$	$(\pm 0.5)$
K <sub>max</sub> Mo	22.1	17.8	13.4	20.5	16.5	12.9
	$(\pm 1.2)$	$(\pm 0.7)$	$(\pm 0.4)$	$(\pm 2.6)$	$(\pm 2)$	$(\pm 1.6)$
E <sub>0</sub> Mo	-23.5	-22.5	-20.5	-22.5	-21.3	-19.5
$kJ.mol^{-1}$	$(\pm 0.7)$	$(\pm 0.3)$	$(\pm 0.2)$	$(\pm 1)$	$(\pm 0.9)$	$(\pm 1)$

It has to be mentioned that this change of the effective binding energy can be enhanced by the carbon gradient as measured across the diffusion couple. For example, the high carbon content at the rich molybdenum side enhances the molybdenum segregation at the interface due to their attractive interaction. It would be interesting to de-correlate this effect by calculating the intrinsic segregation energy using Guttmann's approach as described in chapter IV. Moreover, the attractive interaction between nickel and molybdenum ( $\epsilon_{NiMo} = -6.3$  at 730°C, calculated using the TCFE9 database of ThermoCalc) can also affect the segregation behavior of both elements at the interface. To take into account this last interaction effect, the intrinsic segregation of the substitutional element X1 can be written as follows:

$$\Delta G_{X1}^{0} = \Delta G_{X1} + 2\beta_{FeX1} (Y_{X1}^{boun} - Y_{X1}^{B}) - \beta_{X1C} (Y_{C}^{boun} - Y_{C}^{B}) - \beta_{X1X2} (Y_{X2}^{boun} - Y_{X2}^{B}) \quad (\text{VI.1.1})$$

where  $\beta_{X1X2}$  is the interaction parameter between the two substitutional elements (nickel and molybdenum in the present case) and is expressed using the  $L_{Fe,X,Y:Va}$  interaction parameter in the sublattice model. The results of calculations are summarized in table 17 for both nickel and molybdenum at the three temperatures. The calculated intrinsic segregation energy of nickel at 730°C and 775°C is similar to the calculated one in the ternary Fe-C-Ni system. This is an expected result since the intrinsic segregation energy is independent from composition and from other elements present in the system. This was not the case for the 750°C temperature, where a different intrinsic segregation energy was found for nickel in the ternary and quaternary system as shown in table 17. Note that, in all cases, the calculated intrinsic segregation energy for nickel is lower than the reported values in literature as it was mentioned in chapter V.

Table 17: Comparison between the intrinsic segregation energy ( $\Delta G^0$ ) of nickel and molybdenum calculated for the ternary Fe-C-X (X : Ni, Mo) systems and the ones calculated for the quaternary Fe-C-Ni-Mo system at the three temperatures.

	Ternary Fe-C-X (X :Ni , Mo)			Quaternary FeCNiMo		
$T (^{\circ}C)$	730	750	775	730	750	775
$\Delta G^0$ Ni	-11	-10.8	-10.8	-10	-8	-10
$kJ.mol^{-1}$	$(\pm 0.4)$	$(\pm 0.4)$	$(\pm 0.4)$	$(\pm 0.1)$	$(\pm 0.1)$	$(\pm 0.1)$
$\Delta C^0 M_0$	-14.5	-14.5	-14.5	-14.9	-15	-14.8
ΔG MO	$(\pm 0.5)$	$(\pm 0.5)$	$(\pm 0.5)$	$(\pm 0.5)$	$(\pm 0.5)$	$(\pm 0.3)$

Finally, it is interesting to note that the solute drag model was able to predict with a very good accuracy the measured ferrite fraction evolutions in the quaternary Fe-C-Ni-Mo system at three different temperatures and for the whole range of composition, using the same parameters (or a closer parameter as for the 750°C temperature) as used for the ternary systems. Moreover, the calculated intrinsic segregation energies show comparable values with the obtained ones for the ternary systems, which must be the case since this value is independent from composition and from the co-segregated elements (unlike the effective binding energy).

### VI.2 Fe-C-Ni-Cr system

The effect of nickel and chromium composition on ferrite growth kinetics was studied using a diffusion couple between two ternary Fe-C-1Ni and Fe-C-1Cr alloys. The diffusion couple contains opposite gradients of nickel and chromium over a distance of 5.5 mm with a constant carbon content of 0.2% wt as shwon in figure VI.9-a. An important grain size difference was noticed along the graded sample,  $90\mu$ m on the chromium rich side and  $40\mu$ m on the nickel rich side as shwon in figure VI.9-b. A temperature gradient of  $1.6^{\circ}$ C.mm<sup>-1</sup> was assumed over the composition gradient. Ferrite growth kinetics was studied at three different temperatures, 730°C, 750°C and 775°C. However, the obtained results at 730°C showed the presence of pearlite at the chromium rich side and thus this set of data will not be detailed here.



Figure VI.9: Nickel, chromium and carbon contents across the Fe-C-Ni-Cr diffusion couple as measured using EPMA. b) Grain size distribution across the composition gradient.



Figure VI.10: Evolution of ferrite fraction measured using HEXRD as a function of time, nickel and chromium composition along the Fe-C-Ni-Cr diffusion couple during the isothermal holding at : a) 750°C and b) 775°C.

The evolution of ferrite fraction as a function of time, nickel and chromium contents is shown in figure VI.10 for the two temperatures, 750°C and 775°C. It can be seen that ferrite growth kinetics as well as the final ferrite fraction decrease with increasing chromium content (i.e. decreasing nickel content) and with increasing temperature. The important grain size difference noticed along the graded sample (90 $\mu$ m on the chromium rich side and 40 $\mu$ m on the nickel rich side), can also play a role in the observed growth kinetics.

The formed ferrite fraction at the end of the isothermal holding as a function of nickel and chromium contents is shown in figure VI.11 for the two studied temperatures. On the same figure are plotted the predicted ferrite fractions under the same conditions using PE and LE models.

The PE model overestimates the measured fractions at all the studied conditions. The gap between measurements and the predictions of the PE model increases with increasing nickel content and with increasing temperature. At 750°C, the LE model predicted ferrite fractions are much closer to the measurements especially at the chromium rich side  $\left(\frac{f(Exp)-f(LE)}{f(Exp)}\right) = 3\%$  at the 1%Cr side). The discrepancy between LE predictions and measurements increases with increasing nickel content to reach a relative difference of 8% at 1% of nickel. At 775°C, the predicted LE final fractions are in good agreement with the measurements at the chromium rich side and start diverging from the measured fractions with increasing nickel content.



Figure VI.11: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of nickel and chromium contents at : a) 750°C and b) 775°C.

Figure VI.12 compares the measured ferrite fraction evolution as a function of time with the predictions of the PE and LE models for three nickel and chromium compositions, namely 0.2Ni0.8Cr, 0.5Ni0.5Cr and 0.8Ni0.2Cr, and at two different temperatures, 750°C, 775°C. Under all the studied conditions, the PE predicted growth kinetics are faster than the measurements at both temperatures. The LE predicted ferrite growth kinetics are also faster than the measured ones even in cases where the LE model predicted well the final fractions as shown in figure VI.12-d.



Figure VI.12: Experimental ferrite growth kinetics measured using HEXRD experiments for different compositions of the Fe-C-Ni-Cr diffusion couple during the isothermal holding for the three compositions : Fe-0.2C-0.2Ni-0.8Cr (%wt.) at : a) 752°C and d) 777°C, Fe-0.2C-0.5Ni-0.5Cr (%wt.) at : b) 755°C and e) 780°C and Fe-0.2C-0.8Ni-0.2Cr (%wt.) at : c) 758°C and f) 783°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

#### Solute drag modeling :

The solute drag model was used to predict ferrite growth kinetics in the Fe-C-Ni-Cr system as a function of nickel and chromium contents at the two temperatures, 750°C and 775°C. The same procedure as for the Fe-C-Ni-Mo system was used here, .i.e. the Fe-Ni and the Fe-Cr interaction parameters were taken from the ternary Fe-C-Ni and Fe-C-Cr systems in a first stage and tested on the ternary composition of the extremes of the diffusion couple gradient. The Fe-C interaction parameter was set to -50  $kJ.mol^{-1}$  and the Ni-C, Cr-C and Ni-Cr interaction parameters were adjusted to a similar value as in austenite using Eq.IV.2.9 and Eq.IV.2.10. Using this configuration, good agreement was obtained between measurements and solute drag modeling in terms of not only the final fractions reached at the end of the isothermal holding, as shown in figure VI.11, and also in terms of growth kinetics as shown in figure VI.12.

The best fit of the experimental data at 750°C was obtained using the same Fe-Ni and Fe-Cr interaction parameters as used for the ternary systems in chapter **V**, namely -11.8  $kJ.mol^{-1}$  and +5.3  $kJ.mol^{-1}$ , respectively. The corresponding binding energies as calculated at para-equilibrium conditions were -6.5  $kJ.mol^{-1}$  and +1.5  $kJ.mol^{-1}$ , respectively. At 775°C, the Fe-Ni and Fe-Cr interaction parameters used to fit the experimental data were -11.9  $kJ.mol^{-1}$  and +6.1  $kJ.mol^{-1}$ , respectively. The corresponding binding energies calculated at para-equilibrium conditions are -6.5  $kJ.mol^{-1}$  and +2.5  $kJ.mol^{-1}$  for nickel and chromium, respectively. The Fe-Cr interaction parameter was calibrated using the obtained growth kinetics from the ternary Fe-02C-1Cr composition of the present diffusion couple since no data is available on the ternary Fe-C-Cr system at the same temperature. The Fe-Ni interaction parameter was the same used in modeling ferrite growth kinetics in the ternary Fe-C-Ni-Mo system at 775°C.

The maximum total dissipated energies due to nickel and chromium diffusion across the interface are plotted as a function of the nickel and chromium bulk compositions for the 750°C temperature in figure VI.13-a. Both individual maximum dissipated energies increases with increasing their respective diffusing solute element. The resulting maximum dissipated energy decreases from 67  $J.mol^{-1}$  at the chromium rich side with increasing nickel content and decreasing chromium content to reach a minimum at 0.5%Ni (0.5%Cr), then increases again to reach 72  $J.mol^{-1}$  at the nickel rich side. At 775°C, the maximum dissipated energy at the chromium rich side is  $35 J.mol^{-1}$  and increases with increasing nickel content (i.e. decreasing chromium content) to reach a maximum of 89  $J.mol^{-1}$  at the nickel rich side (Fig. VI.13-b). It is interesting to note that the dissipated energy due to chromium diffusion across the interface decreases with decreasing temperature (67  $J.mol^{-1}$  at 750°C and 35  $J.mol^{-1}$  at 775°C for the 1%Cr). On the other hand, the dissipated energy due nickel diffusion increases with increasing temperature (72  $J.mol^{-1}$  at 760°C and 89  $J.mol^{-1}$  at 785°C for the 1%Ni).

The enrichment factors of both nickel and chromium as a function of the bulk composition are shown in figure VI.14. At 750°C, the enrichment factor of chromium is 4.3 at the chromium rich side (Resp.  $K_{max}$  (Ni) = 2.8) and decreases with increasing nickel content accompanied by an increase of the enrichment factor of nickel. At the nickel rich side, the enrichment factor of chromium is 2.5 (Resp.  $K_{max}$  (Ni) = 3.7). At 775°C, the enrichment factor of chromium decreases form 2.8 at the chromium rich side to 1.9 at the nickel rich side. At the same time, the enrichment factor of nickel increases from 3.1 to 3.7 when increasing nickel content (ie decreasing chromium content). The enrichment factor of nickel is comparable for both ranges of temperatures. Meanwhile, the enrichment factor of chromium decreases markedly with increasing temperature. The estimated



Figure VI.13: The maximum dissipated energy due to nickel and chromium diffusion across the interface as a function of the bulk composition at the two temperatures, a) 750°C and b) 775°C.



Figure VI.14: Enrichement factors  $K_{max}$  of nickel and chromium evolution as a function of the bulk composition for the two temperatures a) 750°C and b) 775°C.

effective binding energies of nickel and chromium using Eq.IV.2.8 are shown in figures VI.15-a and VI.15-b for the two temperatures, 750°C and 775°C. It can be noticed that the effective binding energy of nickel decreases with increasing nickel content and increasing temperature. The average effective binding energy of nickel can be estimated to -8 ( $\pm$  1.2)  $kJ.mol^{-1}$  at 750°C and -7.6 ( $\pm$  1.1)  $kJ.mol^{-1}$  at 775°C. The effective binding energy of chromium on the other hand decreases with increasing chromium content and with decreasing temperature. At 750°C, the effective binding energy of chromium decreases form -6.8  $kJ.mol^{-1}$  to -11.1 when increasing chromium content (and decreasing nickel content). At 775°C, the effective binding energy decreases from -4.2  $kJ.mol^{-1}$  to -7.8  $kJ.mol^{-1}$  when increasing chromium content. The dependency of the binding energy of chromium on temperature is opposite to that of nickel. The effective binding energy of nickel and chromium at 750°C are comparable with the obtained ones for the ternary sys-

tems at the same temperature, -7.6 (±0.6)  $kJ.mol^{-1}$  for nickel and -11.2 (±0.5)  $kJ.mol^{-1}$  for chromium.



Figure VI.15: Effective binding energy  $E_0$  of nickel and chromium evolution as a function of the bulk composition for the two temperatures a) 750°C and b) 775°C.

As it was mentioned earlier, the effective binding energy is impacted by the segregation of other elements at the interface. To de-correlate this effect, the intrinsic segregation energy of nickel and chromium is calculated using Guttmann's approach as explained in section VI.1. The interaction between nickel and chromium is weak ( $\epsilon_{NiCr} = 0.08$  at 750°C) and can thus be neglected in calculations. The obtained results show an intrinsic segregation of nickel and chromium of -9.8 ( $\pm$  0.2) kJ.mo and -1  $kJ.mol^{-1}$  ( $\pm$  1)  $kJ.mol^{-1}$ , respectively for both temperatures. These values are comparable with the ones obtained for nickel and chromium for the ternary Fe-C-Ni and Fe-C-Cr systems.

#### VI.3 Fe-C-Cr-Mo system

The dependency of ferrite growth kinetics dependency on chromium and molybdenum contents was studied using a diffusion couple created between Fe-C-1Cr and FeC0.2Mo. The graded sample contains opposite gradients of chromium and molybdenum varying over a 1.6 mm distance (Fig.VI.16-a). The carbon content as measured using EPMA showed a continuous gradient from 0.26% C at the chromium rich side (1% Cr and 0% Mo) to 0.25%C at the molybdenum rich side (0.2%Mo and 0%Cr). Ferrite growth kinetics were measured at three different temperatures, 730°C, 750°C and 775°C. The temperature gradient was estimated to about 3°C over the composition gradient. Again, only the results obtained at 730°C are not shown here for the same reason as all the chromium containing systems at this temperature, i.e. formation of pearlite. An important grain size difference was measured between the extremes of the composition gradient, going from  $40\mu m$  (at the molybdenum rich side) to  $60\mu m$  (at the chromium rich side) for the sample treated at 750°C and from  $60\mu m$  to  $75\mu m$  for the diffusion couple treated at 775°C (Fig.VI.16-b). The obtained ferrite fraction evolution as a function of time, chromium and molybdenum contents during the isothermal holding is shown in figure VI.17 for the two temperatures, 750°C and 775°C.



Figure VI.16: a) Chromium, molybdenum and carbon contents across the Fe-C-Cr-Mo diffusion couple as measured using EPMA. b) Grain size distribution across the composition gradient.

Figure VI.18 compares the evolution of the final ferrite fraction as a function of chromium and molybdenum content with PE and LE calculations for the two studied temperatures, 750°C and 775°C. As for the all investigated systems in the present study, the PE model overestimates the measured final ferrite fraction for all the studied conditions (chromium and molybdenum concentrations and temperature). The LE model also failed in predicting the measured final ferrite fractions at both temperatures. As for the PE model, the gap between the predicted LE values and measurements increases with increasing



Figure VI.17: Evolution of ferrite fraction measured using HEXRD as a function of time and chromium/molybdenum content along the Fe-C-Cr-Mo diffusion couple during the isothermal holding at : a) 750°C and b) 775°C.



Figure VI.18: Comparison between the measured final ferrite fractions (open circles) and the predictions of PE (triangles), LENP (filled dots) and solute drag (crosses) models as function of nickel and chromium contents at : a) 750°C and b) 775°C.

chromium content. It is interesting to note that, contrary to the present case, the LE model did manage to predict the final fractions in certain Fe-C-Cr systems of the present work. The recorded ferrite fractions were in good agreement with LE predictions for both the ternary Fe-C-Cr (section V.6) and the quaternary Fe-C-Ni-Cr graded samples, which both present a carbon composition of about 0.20 % Meanwhile, LE predictions failed for the Fe-C-Cr fixed composition alloy (section IV.5) and the present Fe-C-Cr-Mo graded sample, which feature a higher carbon content of 0.26 % These results suggest that a larger carbon content increases the deviation from LE for a given chromium composition. Figure VI.19 compared the measured ferrite growth kinetics for three selected chromium and molybdenum contents with the predictions of the LE and PE models at both temperatures, 750°C and 775°C. Results show that both models predict faster kinetics than the measured ones at both temperatures and of the whole studied range of composition, with



Figure VI.19: Experimental ferrite growth kinetics measured using HEXRD experiments for different compositions of the Fe-C-Cr-Mo diffusion couple during the isothermal holding for the three compositions : Fe-0.52C-0.2Cr-0.16Mo (%wt.) at : a) 755°C and d) 781°C, Fe-0.25C-0.5Cr-0.1Mo (%wt.) at : b) 754°C and e) 780°C and Fe-0.26C-0.8Cr-0.04Mo (%wt.) at : c) 753°C and f) 779°C. The calculated kinetics using PE, LE and SD models are shown for the different compositions.

the exception for the molybdenum rich side of the graded sample treated at 750°C, where the measured ferrite growth kinetics are well described using the PE/LE model as shown in figureVI.19-a. One can note that at this temperature, the ferrite fraction reached at the plateau decreases with time at the molybdenum rich side, which is an indication of a change in temperature. This behavior is probably due to an error in temperature reading by the thermocouple. The change in temperature is estimated to 2°C.

#### Solute drag modeling :

The solute drag model was used to predict ferrite growth kinetics in the quaternary Fe-C-Cr-Mo system dependency on chromium and molybdenum contents at the two temperatures, 750°C and 775°C. As shown in figures VI.18 and VI.19, good agreement was found between the measurements and the predictions of the model for both temperatures and for the whole range of composition. The Fe-Cr and Fe-Mo interaction parameters

that gave the best fit for the experimental data are summarized in table as well as the corresponding binding energies calculated under para-equilibrium conditions. At both temperatures, the same Fe-Mo interaction parameters as the ones used to model ferrite precipitation in the ternary Fe-C-Mo system were used to predict ferrite growth kinetics in the quaternary Fe-C-Cr-Mo system. The Fe-Cr interaction parameter used in modeling ferrite growth kinetics at 750°C was the same as for the ternary system. On the other hand, at 775°C, the Fe-Cr interaction parameter was further calibrated using the ternary composition of the quaternary diffusion couple. Note that the Fe-Cr interaction parameter used at 775°C is different from the one used to model ferrite growth kinetics for the Fe-C-Ni-Cr system at a similar temperature, namely  $+6.1 \ kJ.mol^{-1}$ . This significant difference in the Fe-Cr interaction parameter at 775°C is surprising and one possible explanation is the carbon content difference between the two systems. However, this should have resulted in a different Fe-Cr interaction parameter at 750°C also, which is not the case here. This can also be related to a wrong calibration of the Fe-C interaction parameter at the interface in the present study. As it was mentionned, this parameter was modified to express the observed carbon segregation at the interface. However, the numerical value of this parameter must be further calibrated using experimental results.

Table 18: Fe-Cr  $(L_{Fe,Cr:Va})$  and Fe-Mo  $(L_{Fe,Mo:Va})$  interaction parameters and the corresponding binding energies (calculated under para-equilibrium conditions) used in the solute drag modeling at the three different temperatures.

T(°C)	) $\begin{array}{ c c } L_{Fe,Cr:Va} \\ (kJ.mol^{-1}) \end{array}$	$E_b(Cr) \ (kJ.mol^{-1})$	$ \begin{array}{c} L_{Fe,Mo:Va} \\ (kJ.mol^{-1}) \end{array} $	$E_b(Mo) \ (kJ.mol^{-1})$
750	+5.2	+1.5	-7.6	-15
775	+1.9	-1.5	-8	-15

FigureVI.20 shows the evolution of the maximum dissipated energy as a function of chromium and molybdenum bulk contents at 750°C and 775°C. The maximum dissipated energy is the sum of the two individual dissipated energies due to chromium and molybdenum diffusion across the interface. At 750°C, the resulting dissipated energy is nearly constant for the whole range of chromium and molybdenum content (~ 68  $J.mol^{-1}$ ). At 775°C, the maximum dissipated energy at the molybdenum rich side is 54  $J.mol^{-1}$  and increases with increasing chromium content to reach 73  $J.mol^{-1}$  at the chromium rich side.

The enrichment factors of both chromium and molybdenum are plotted as a function of the bulk composition for both temperatures in figure VI.21-a. The enrichment factor of chromium seems to be unaffected by the bulk composition and increases slightly when increasing temperature (4.2 at 750°C and 4.5 at 775°C). On the other hand, the enrichment factor of molybdenum decreases when increasing temperature but varies little with the bulk composition (17.5 at 750°C and 13.5 at 775°C).



Figure VI.20: Maximum dissipated energy due to molybdenum and chromium diffusion across the interface as a function of the bulk composition at the two temperatures, a) 750°C and b) 775°C.

The effective binding energies of chromium and molybdenum are shown in figure VI.21b as a function of the bulk composition. A nearly constant effective binding energy is obtained for chromium at both temperatures,  $-10.8 (+/-0.1) kJ.mol^{-1}$  and  $-11.9 (+/-0.1) kJ.mol^{-1}$ 0.1)  $kJ.mol^{-1}$  at 750°C and 775°C, respectively. For molybdenum, the effective binding energy is also unaffected by the bulk composition and its value is  $-22 (+/- 0.1) kJ.mol^{-1}$ at 750°C and -20.5 (+/-0.1)  $kJ.mol^{-1}$  at 775°C. It has to be noted that the average effective binding energy of chromium was estimated to  $-11.2 (+/-0.5) kJ.mol^{-1}$  for the Fe-C-Cr ternary system, which is comparable to the value obtained in the present study at a same temperature. On the other hand, it was shown that the effective binding energy of chromium changes with the bulk composition for the Fe-C-Ni-Cr system (-6.8  $kJ.mol^{-1}$  to -11.1  $kJ.mol^{-1}$ , when increasing chromium content from 0% to 1%) at the same temperature. This can be related to the carbon content difference in both systems (Fe-C-Cr-Mo and FeCNiCr) but also to the temperature gradient as estimated for the two diffusion couples (3°C for the Fe-C-Cr-Mo system and 10°C for the Fe-C-Ni-Cr system). For molybdenum, the average effective binding energies calculated at both temperatures are comparable with obtained ones for the Fe-C-Mo ternary system as well as for the Fe-C-Ni-Mo quaternary system at similar temperatures.

The intrinsic segregation energies were estimated using Guttmann's approach for both chromium and molybdenum at both temperature. The mutual interaction between chromium and molybdenum in austenite is attractive ( $\epsilon_{CrMo} = +3.5$  at 750°C). Results show an intrinsic segregation energy of -0.8 (+/- 0.8)  $kJ.mol^{-1}$  and -4.2 (+/- 0.7)  $kJ.mol^{-1}$  for chromium at 750°C and 775°C, respectively and -14.6 (+/- 0.1)  $kJ.mol^{-1}$  for molybdenum at both temperatures. The same values for the intrinsic segregation energies were estimated for molybdenum for the ternary Fe-C-Mo system at similar temperatures. For chromium, the intrinsic segregation energy caculated at 750°C is the similar to the one



Figure VI.21: Enrichment factors  $K_{max}$  of chromium and molybdenum evolution as a function of the bulk composition for the two temperatures a) 750°C and b) 775°C.

calculated for the tenary Fe-C-Cr system and the quaternary Fe-C-Ni-Cr system at a comparable temperature. On the other hand, the intrinsic segregation energy estimated at 775°C is different from the value calculated from the Fe-C-Ni-Cr results ( $-1 \ kJ.mol^{-1}$ ) at the same temperature. As it was stated before, the intrinsic segregation energy should not be affected by the alloy composition or the co-segregated elements, which is not the case here for the chromium intrinsic segregation energy at 775°C. This again points out an important question about the used interaction parameters in the solute drag modeling. The investigation of the carbon effect on the segregation behavior of substitutional elements is now required. The Fe-C-Cr system at 775°C seems to be an interesting case study, where carbon content seems to have an important impact on ferrite growth kinetics.

#### VI.4 Conclusion

This chapter was dedicated to the investigation of ferrite growth kinetics in quaternary Fe-C-X<sub>1</sub>-X<sub>2</sub> systems (X<sub>1</sub> and X<sub>2</sub> : Ni, Cr or Mo) at different temperatures. These results were recorded using graded samples as explained in chapter III. Ferrite growth kinetics in the different systems was compared with the predictions of the different models, namely PE, LE and SD models. As for the ternary systems shown in chapter V, the PE model overestimated the measured growth rates for all the studied systems and temperatures. It was also shown that the LE model cannot be used to describe ferrite growth kinetics over the whole composition range and under at all temperatures. The solute drag model was also used to predict ferrite growth kinetics in the studied systems. The fitting interaction parameters were in a first stage gathered from the ternary Fe-C-X systems at similar temperatures. Good results were obtained using the solute drag model for almost all the studied systems using the same ternary parameters, which means that no fitting parameters were used in these cases. The calculated enrichment factor and the intrinsic

segregation energies were in good agreement with the calculated ones for the ternary systems. However, some compelling points were noticed concerning the used parameters to predict ferrite growth kinetics in some systems. It was observed that different Fe-Cr interaction parameters were used to model ferrite growth kinetics in the chromium containing systems at 775°C and that this difference is probably related to a difference in the carbon content. These results suggest a further investigation of the carbon effect on chromium segregation at the interface in the Fe-C-Cr systems at this temperature. It was also pointed that a deeper investigation of the Fe-C interaction parameter used to express the carbon segregation at the interface must be conducted.

# Summary

The aim of this study was to develop a new high-throughput methodology to study the effect of solute content on ferrite growth kinetics in steels. The main idea of this methodology is to fabricate diffusion couples containing gradients of substitutional elements with a several mm length scale, and in a second stage, to gather ferrite growth kinetics using space- and time-resolved high-energy X-ray diffraction (HEXRD). This methodology is also applicable to any other phase transformation in any other metallic system. As it was shown in this manuscript, for a suitable use of the graded samples in studying phase transformations using HEXRD, several requirements must be fulfilled. First, the diffusion couples must contain extensive unidimensional composition gradients of substitutional elements with a smooth variation and a relatively constant carbon content. Moreover, the grain size must be small enough to meet the HEXRD requirements for accurate phase quantification. Finally, the HEXRD in situ experiments must be carried out in an appropriate environment to avoid oxidation as well as decarburization, and requires using sophisticated equipment that can perform continuous translation and rotation of the sample and allow good temperature and atmosphere control. The development of this combinatorial methodology was very challenging and required skills and knowledge in a variety of disciplines including, metallurgy, thermodynamics, chemistry, physics and instrumentation.

After several attempts, a complete methodology was proposed and detailed in chapter III. This methodology can be summarized as follows :

Diffusion couples are generated using hot compression between different binary Fe-C and ternary Fe-C-X alloys to create solid bonds between the different samples. The second step consists in high temperature diffusion to generate gradients of composition. In order to obtain millimeter-scale composition gradients, samples are decarburized to perform diffusion in the delta ferrite range where the diffusion coefficient of substitutional elements is two orders of magnitude higher than in austenite. At the end of this step, the required amount of carbon is reintroduced by re-carburizing treatment. In order to ensure a sufficiently small grain size suitable for quantitative HEXRD measurements, samples are subsequently subjected to a rapid cyclic heat treatment and to limited transverse rolling..
 For the HEXRD experiments, a specific furnace for *in situ* measurements is used with high-precision low-inertia temperature control, restrained temperature gradient along the
composition gradient, accurate control of the atmosphere during the experiment and fast sample rotation to improve the powder diffraction conditions. The low weight of the furnace allows using a translation stage with sufficiently high velocity to gather time and space resolved phase transformation kinetics.

The use of this methodology allowed obtaining a large data set of ferrite growth kinetics using very limited number of experiments. This data was then compared with the predictions of the different models describing ferrite growth kinetics in steels, such as the classical PE and LE models as well as solute drag models, which showed very satisfying results in previous studies. In the present study, a modified version of the three jumps solute drag model initially developed by Zurob et al. [11] was developed to describe ferrite growth kinetics as a function of the solute element content. The modifications made to the original version of the model concerned essentially the thermodynamic description of the interface. On the one hand, carbon segregation at the interface was enhanced to meet the reported experimental observations. This was performed by modifying the Fe-C interaction parameter of the Thermocalc database. On the other hand, the interaction between carbon and the substitutional elements, as well as the mutual interaction between the two substitutional elements were set to similar values as in austenite. This version of the three jumps model was first calibrated on a preliminary set of experiments carried out using samples with constant compositions at constant temperatures. The obtained results and the comparison with the different models was presented in chapter IV. In general, very good agreement was obtained between the predictions of the new model and the measured ferrite growth kinetics for different ternary FeCX systems (X : 1Mn, 1Ni, 0.2Mo and 1Cr) as well as for a quaternary FeC1Mn1Cr system. The major outcome of this chapter was that the thermodynamic description of the interface should be considered as a whole and that the interaction parameter  $L_{Fe,X2:Va}$  interaction parameters are related and cannot be treated individually. Moreover, the binding energy as presented in previous studies should not be used as an indication of the segregation behavior of the solute element at the interface. It was also shown that carbon co-segregation at the interface plays an important role on the interaction parameter of the X element with the moving interface (Fe-X). Results showed that Mn and Cr have a weak intrinsic segregation energy at the interface and that their segregation is enhanced by the presence of carbon. Molybdenum has simultaneously a strong interaction with carbon as well as a high intrinsic segregation energy. Finally, nickel was shown to segregate at the interface, contrarily to the reported experimental observations that show no segregation or very limited segregation at the austenite/ferrite interfaces. However, a preliminary APT result showed a clear segregation of nickel at a proeutectoid ferrite/pearlite interface. More experiments must be conducted using a martensite-ferrite interface to confirm this result.

The developed combinatorial methodology was used to study ferrite growth kinetics in 5 ternary Fe-C-X systems (X : Ni, Mn, Si, Mo and Cr) as well as 3 quaternary Fe-

 $C-X_1-X_2$  systems (X<sub>1</sub>, X<sub>2</sub> : Ni, Cr and Mo) as function of solute composition and at different temperatures. The obtained results are shown in chapter V and VI. Using this methodology, a large set of ferrite growth kinetics were obtained and sorted as a function of the composition elements as well as temperature. These results highlight the importance of using high-throughput methods to accelerate data gathering. Indeed, size of the dataset obtained using this methodology is in rupture with all those previously found in literature.

In a second stage, a full comparison with the measured ferrite growth kinetics and the predicted ones using PE, LE and SD models was discussed in the two chapters. In chapter V, the data obtained for the ternary Fe-C-X systems showed that the solute drag model was able to predict the measured ferrite evolution using only one fitting parameter, namely the Fe-X interaction parameter. Results also showed that this parameter is independent from solute composition. However, it can change with changing temperature, as it was the case for the Fe-C-Si and the Fe-C-Cr systems. For the Fe–CNi system, a good description of the measured kinetics was obtained at two temperatures, 730°C and 750°C using the same Fe-Ni interaction parameter. At 775°C, it was shown that the solute drag model fails to predict the growth kinetics at high nickel contents, indicating a possible limitation of this model in describing very ferrite growth kinetics occuring with a very low driving force. The comparison between the enrichment factors of the segregated elements at the interface were in good agreement with the experimentally measured ones, except for the Fe-C-Ni system.

In chapter VI, the obtained results for the quaternary Fe-C-X<sub>1</sub>-X<sub>2</sub> systems were presented and compared with the predictions of the different models mentioned above. For these systems, the Fe-X1 and Fe-X2 interaction parameters should be the same as those used for the ternary Fe-C-X<sub>1</sub> and Fe-C-X<sub>2</sub> systems since these parameters were found to be independent from solute contents. This was the case for nearly all the studied systems, FeCNiMo (at 730°C and 775°C), Fe-C-Ni-Cr (750°C) and Fe-C-CrM-o (at 750°C). However, fitting the experimental results in some other systems, namely Fe-C-Ni-Mo at 750°C, FeCNiCr and Fe-C-Cr-Mo at 775°C required using different interaction parameters from those used for the ternary systems. For the Fe-C-Ni-Mo system, the Fe-Ni interaction parameter was different from that used in the ternary Fe-C-Ni system at the same temperature. This was the only case where a different Fe-Ni interaction parameter was used for solute drag modeling out of eight cases. This observation makes us believe that an anomaly in the experimental procedure can be the origin of this observed change in the Fe-Ni interaction parameter.

On the other hand, it was observed that the Fe-Cr interaction parameter used to fit the experimental data at 775°C was not always the same and seemed to be related to the carbon content of the system. It was noticed that the same Fe-Cr interaction parameter was used when the carbon content is similar. This result points an important question regarding the choice of the Fe-C interaction parameter at the interface. It is clear that

this parameter must be further calibrated using segregation measurements of carbon in different systems.

Some open questions arise concerning the thermodynamic description of the interface. The interaction between the solute elements and the interface is expressed using the  $L_{Fe,X:Va}$  interaction parameter (the fitting parameter). Even though good results were obtained using this method, one must consider using other fitting parameters, such as the  $L_{X:Va}$  parameter. The same idea can be applied for the Fe-C interaction parameter which is expressed using the  $L_{Fe,C:Va}$  interaction parameter, which may be replaced by the  $L_{C:Va}$  interaction parameter.

The obtained modeling results for the Fe-C-Ni system are surprising and suggest that nickel segregates at the austenite ferrite interface during ferrite growth. This result goes against all the reported nickel segregation measurements or calculations. However, it was shown that even if other solute drag models have predicted a small binding energy for this element, the obtained enrichment factors in these studies showed clear segregation of nickel at the interface. This indicates that the nickel segregation prediction of the solute drag model is not due to the used parameters of the present model. It is now clear that a more detailed investigation of this system must be carried out, starting with experimental measurements of nickel segregation using APT techniques in systems where a high segregation is predicted by the solute drag model.

This methodology can now be extended to study ferrite growth kinetics, or other phase transformations, in other Fe-C-X or even higher order systems. In the continuity of the present study, an investigation of ferrite growth kinetics at higher solute contents (> 1%)and at lower temperature where an important solute element segregation is expected at the interface can bring more insights into the dependency of ferrite growth kinetics on solute content. For quaternary systems, it can be interesting to study systems where an important interaction is expected between the two solute elements such as manganese and silicon. In the present work, we focused on studying ferrite growth kinetics but the same methodology can be extended to the bainitic transformation which, presents some interesting features such as the incomplete transformation character. Another useful application of the present methodology is to study the massive transformation in binary alloys where the interface mobility plays a major role in phase transformation. As it was already mentioned, this methodology is applicable to any phase transformation in any metallic systems. Besides phase transformations, this methodology can also be used to study other material properties, such as recrystallization kinetics and mechanical properties' dependency on solute composition. For mechanical properties, diffusion couples can be coupled with other characterization tools such as nanoindentation to study the effect of substitutional solute content, or microstrutures on mechanical properties.

The developed methodology allows accelerating data gathering and must be accompanied at the same time by fast predicting models. One interesting solution can be the use of machine learning approaches combined with the rich experimental libraries generated by the present methodology to create fast predictive models. The other option can be the integration of the artificial intelligence appraach in the existing physical models such as the solute drag model to accelerate the predictive capacity of the model, then new specialized databases can be created by exploring large parametric spaces.

## Appendix A Solute drag model implementation

In this section the numerical solute drag implementation is detailed. Solute drag modeling is separated into two blocks as shown in figure A.1.



Figure A.1: A simplified flowchart showing the solute drag code implementation. In the first block, the dissipated energy as a function of the interface velocity is calculated

for a given alloy at given temperature. The input parameters required for calculations are as summarized in table 19.

Table 19: The input parameters needed for solute drag calculations in case of a quaternary FeCX1X2 system.

$X_1$ element	the substitutional element (Ni, Cr, Mo, Mn)
$X_1$ %wt.	weight fraction of element $X_1$
$X_2$ element	the second substitutional element if quaternary system (Ni, Cr, Mo, Mn)
$X_2$ %wt.	weight fraction of element $X_2$
C %wt.	cabon weight content
Т	temperature of the isothermal holding (°C)
Fe-X <sub>1</sub>	the interation paramter $L_{Fe,X1:Va}$ ,
	or the binding energy of element $X_1$ calculated at PE conditions
Fe-X <sub>2</sub>	the interation paramter $L_{Fe,X2:Va}$ ,
	or the binding energy of element $X_2$ calculated at PE conditions
Fe-C	the interation paramter $L_{Fe,C:Va}$

The solute drag calculations are carried out using ThermoCalc databases to calculate the different thermodynamic properties. To this end, the numerical code written in python is coupled with the module TCPython which allows carrying thermoCalc calculations. As it was already mentioned, in the solute drag scheme, contrarily to the classical LE and PE models, the interface is considered as a thick phase with its proper thermodynamic properties. This phase is not defined in ThermoCalc and should be generated. To this end, a GES file is initially used containing the thermodynamic properties of the interface which are the same as in austenite with the difference that the  $L_{Fe:Va}$  and  $L_{X:Va}$  parameters are shifted by  $3.5 \ kJ.mol^{-1}$  to capture an interface energy of  $0.5 \ J.mol^{-1}$  as explained in the introduction. This file was initially created by Prof. Zurob. In the present study, an additional modification is made in this file, the Fe-C interaction parameter ( $L_{Fe,C:Va}$ ) initially at  $-34 \ kJ.mol^{-1}$  is modified to  $-50 \ kJ.mol^{-1}$ . This operation is done for all calculations independently on the input parameters.

The Fe-X (or Fe-X<sub>1</sub> and Fe-X<sub>2</sub>) interaction parameter is then set to the user defined value by modifying the  $L_{Fe,X:Va}$  parameter in ThermoCalc. The other possibility is to fix as an input parameter the binding energy of the X<sub>1</sub> element (and or X<sub>2</sub> element) and the corresponding Fe-X interaction parameters will be calculated using the python code as shown in appendix B.1.

The last interaction parameter to be set is the X-C interaction parameter at the interface. To this end, the  $\epsilon_{XC}$  interaction parameter in austenite and at the interface is evaluated using EqA.1 and the difference is accommodated by changing the  $L_{Fe,X:C,Va}$  interaction parameter.

$$\epsilon_{XC} = -\left\{ \left( {}^{0}L_{Fe,X:Va} + {}^{1}L_{Fe,X:Va} + {}^{2}L_{Fe,X:Va} \right) + \left( {}^{0}L_{Fe,C:Va} - {}^{1}L_{Fe,C:Va} + {}^{2}L_{Fe,C:Va} \right) - \left( {}^{0}L_{X,C:Va} - {}^{1}L_{X,C:Va} + {}^{2}L_{X,C:Va} \right) - \left( {}^{0}L_{Fe,X:C} + {}^{1}L_{Fe,X:C} + {}^{2}L_{Fe,X:C} + {}^{2}L_{Fe,X:C} \right) - \left( {}^{2}L_{Fe,X:C} + {}^{2}L_{Fe,X:C} + {}^{2}L_{Fe,X:C} + {}^{2}L_{Fe,X:C} + {}^{2}L_{Fe,X:C} \right) - L_{Fe,X:C,Va} \right\} / RT$$
(A.1)

In case of the quaternary Fe-C-X<sub>1</sub>-X<sub>2</sub> systems, the same procedure is done for the X<sub>1</sub>-X<sub>2</sub> interaction parameter, meaning that the  $\epsilon_{X1X2}$  term is calculated in both austenite and the interface (EqA.2) and the difference is this time accommodated by changing the  $L_{X1,X2:Va}$  interaction parameter.

$$\epsilon_{X1X2} = -\left\{ \left( {}^{0}L_{Fe,X1:Va} + 2\left( {}^{1}L_{Fe,X1:Va} \right) + 3\left( {}^{2}L_{Fe,X1:Va} \right) \right) + \left( {}^{0}L_{Fe,X2:Va} + 2\left( {}^{1}L_{Fe,X2:Va} \right) + 3\left( {}^{2}L_{Fe,X2:Va} \right) \right) - \left( {}^{0}L_{X1,X2:Va} \right) - \left( {}^{L}L_{Fe,X1:Xa} \right) \right\} / RT$$
(A.2)

Once the desired thermodynamic properties of the interface are defined, the solute drag calculations can be started.

As explained in the introduction, PE conditions are assumed to be the initial state of the interface conditions. Thus, the first step in the solute drag calculations is to determine the PE interfacial conditions for the given conditions. In other words, determining the carbon concentration at the austenite interface side in PE conditions. This can be done by resolving the following equation:

$$\Delta G_m^{chem} = \frac{(u_X^{\alpha} + u_X^{\gamma})}{2} (\mu_X^{\gamma,i} - \mu_X^{\alpha,i}) + \frac{(u_{Fe}^{\alpha} + u_{Fe}^{\gamma})}{2} (\mu_{Fe}^{\gamma,i} - \mu_{Fe}^{\alpha,i})$$
(A.3)

To do this, the U-fractions of iron and the element X are calculated in both phases (austenite and ferrite) by varying the carbon content at the austenite interface side, and assuming that the carbon potential is the same in both phases. To this end, we need to calculate for every carbon value, the different thermodynamic properties, such as the chemical potentials of all the elements as well as their concentrations. The python function that resolves this equation is given in appendix B.2.

Once the carbon content at the interface is defined, the second step is to calculate the solute drag energies due to the diffusion of element X across the interface as a function of the interface velocity. This calculations can be written using the set of equations:

$$dx_X^i \frac{\delta}{V_m dt} = J_X^i - J_X^{i+1} + \frac{v}{V_m} (x_X^{i+1} - x_X^i)$$
(A.4)

$$J_X^i = -\frac{D_X^i}{V_m RT} x_{Fe}^{i-1} x_X^{i-1} \frac{(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})}{\delta}$$
(A.5)

$$\Delta G_m^{diss,X} = \sum_{i=1}^{i=3} -\frac{V_m}{v} J_X^i [(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})]$$
(A.6)

$$\Delta G_m^{diss} = \sum^X \Delta G_m^{diss,X} \tag{A.7}$$

For a given velocity  $v_i$ , the corresponding X concentrations at each interface are calculated using Eq. to do this, the X concentration at the ferrite interface is assumed to be known at each interface velocity (PE condition). The X content at the first atomic plane of the interface is found by minimizing Eq.A.4. The corresponding dissipated energies are calculated using Eq.A.6 and A.7. The same procedure is used to determine X contents at the second atomic plane and at the austenite interface side. Note that at each velocity, we can calculate solute contents and carbon content at each atomic plane and the corresponding dissipated energies at each jump as well as the total dissipated energy. All these values are stored in a table as a function of the interface velocity. Here again, the python script is coupled with the TCPython module to calculate the different thermodynamic properties, such as chemical potentials for Eq.A.5 and solute and carbon contents for Eq.A.4. The python code that allows making these calculations is shown in appendix B.3.

The next step is to find again the carbon content at the austenite interface side that gives a zero driving force acting over the interface, taking into account this time the dissipated energy due to solute drag effect. This is also done by solving Eq.A.3 with the added solute drag energy calculated in step 2. The new equation is written as follows:

$$\Delta G_m^{chem} = \frac{(u_X^{\alpha} + u_X^{\gamma})}{2} (\mu_X^{\gamma,i} - \mu_X^{\alpha,i}) + \frac{(u_{Fe}^{\alpha} + u_{Fe}^{\gamma})}{2} (\mu_{Fe}^{\gamma,i} - \mu_{Fe}^{\alpha,i}) + \Delta G_m^{diss}$$
(A.8)

The carbon content at the interface will be used to solve the diffusion equation of carbon in austenite to calculate ferrite growth kinetics. In fact, one should solve this equation in terms of the chemical potentials and not carbon contents. One way to get around this problem, as mentioned by Qiu et al. [94], is to calculate a representative carbon content at the interface using the chemical potential of carbon and taking into account the solute spike at the austenite interface side. The python code that calculates this value is shown in appendix B.4.

These calculations are repeated for different interface velocities going from  $1e^{-5}$  m.s<sup>-1</sup> to  $1e^{-11}$  m.s<sup>-1</sup>. A total number of 800 velocities are calculated for each set of parameters. At the end of these calculations, we have a list containing the interface velocities as introduced by the user and the corresponding dissipated energies, at each atomic plane as well as the total dissipated energy, the corresponding solute contents at each atomic plane but the most important, is the corresponding carbon content at the austenite interface side. This value is used in the calculation of ferrite fraction evolution as a function of time. This is the only value needed to calculated ferrite precipitation kinetics. The total time to calculate a solute drag table using the present code is 20 min for a ternary Fe-C-X system and 2 h and 30 min for a quaternary Fe-C-X<sub>1</sub>-X<sub>2</sub> system. Note that the solute drag models that uses Fortran TQ modules to calculated the tharmodynamic properties using ThermoCalc are much faster (2 min for a ternary Fe-C-X calculations). We believe that this is due to the slow crossing between TCPython library and ThermoClac.

The second part is thus to calculate ferrite fraction evolution as a function of time by

solving the diffusion equation of carbon in austenite.

A spherical austenitic grain is considered as a starting scheme for modeling with a ferrite nuclei of 100 nm ( $p_0$ ) at the surface of the spherical grain (Fig.A.2). the carbon content in ferrite is assumed to be constant over the whole ferrite domain due to the high carbon diffusion coefficient in ferrite. The carbon profile in austenite at time = 0 is assumed to evolve from the carbon PE interface carbon condition to the bulk condition far in austenite as shown in figure A.3.



Figure A.2: Schematic depicting of an austenite grain with a ferrite nucleate at the grain boundary.



Figure A.3: Carbon profiles in ferrite and austenite as assumed in ferrite growth modeling. The mass balance equation relating the interface velocity to the net flux of atoms trans-

ferred across the interface is written as follows :

$$v = \frac{J_C^{\gamma}}{x_C^{i,\gamma} - x_C^{i,\alpha}} \tag{A.9}$$

Ferrite growth evolution as function of time is estimated using the following steps:

- 1. The initial interface velocity is calculated from the initial carbon profile in austenite,  $v = \frac{dC^{\gamma}}{dx}$ .
- 2. Using this velocity the new position of the interface (p) can be defined as,  $p = p_0 + vdt$ , and the new ferrite fraction (f) as,  $\frac{\frac{1}{2}gs^3 (\frac{1}{2}gs p)^3}{\frac{1}{2}gs^3}$ , where gs is the grain size.
- 3. The carbon content at the austenite interface side is assumed to evolve as a function of the interface velocity. The calculated velocity is thus used to estimate the carbon content at the interface from the table generated in the first solute drag calculations. A polynomial interpolation of the calculated velocities is used calculate the carbon content form the velocities table.
- 4. Now, the next step is to calculate the new carbon profile in austenite at time  $t + \Delta(t)$ . This is done by solving Eq.A.10.

$$\frac{\partial C}{\partial t} = \nabla . (D\Delta C) \tag{A.10}$$

In the present study, the Murray-Landis [153] method is used to numerically solve Eq.A.10 for diffusion in a sphere. The finite difference equation can be written as:

$$C_{i}^{t+\Delta t} = C_{i}^{t} + \Delta t \left( \frac{A-B}{\delta R^{2}} + v \frac{(n-1)(C_{i+1}^{t} - C_{i-1}^{t})}{2n\Delta x} \right)$$
(A.11)

where :

$$A = \frac{C_{i-1}^t - C_{i-1}^t}{\Delta x} 4D\pi \left( \left(\frac{gs}{2} - p\right) - \left( (i - 1.5)\Delta x \right) \right)^2$$
(A.12)

$$B = \frac{C_i^t - C_{i+1}^t}{\Delta x} 4D\pi \left( \left( \frac{gs}{2} - p \right) - \left( (i - 0.5)\Delta x \right) \right)^2$$
(A.13)

$$\delta R^3 = \frac{4\pi}{3} \left( \left(\frac{gs}{2} - p\right) - \left((i - 1.5)\Delta x\right) \right)^3 - \frac{4\pi}{3} \left( \left(\frac{gs}{2} - p\right) - \left((i - 0.5)\Delta x\right) \right)^3$$
(A.14)

5. Once the new carbon concentration profile in austenite is calculated, the new velocity is calculated using step 1. then the same procedure step 2 - 4 is repeated for every time step  $\Delta t$ . The interface position  $p_0$  is replaced by the interface position calculated at time t. The new grid size  $\Delta x$  is estimated using  $\Delta x = \frac{g_s}{n} - p = \frac{1}{n}$ . In the total number of gird points number.

The python code that allows calculating ferrite growth kinetics is shown in appendix 5. Some comments are made here concerning the numerical stability of the diffusion model.

1. It was noticed that the fraction evolution is very dependent on the velocity estimation from the carbon profile in austenite. Indeed, the velocity is estimated linearly using two points from the carbon profile as shown in fig. Thus, the position of the second point used to calculate velocity has a major impact on the ferrite fraction evolution. One way to check if the used procedure is correct is to apply the calculation using the PE conditions i.e. fixing the carbon content at the interface at the PE value and compare the results with the predicted PE kinetics using ThermoCalc.

Using this procedure, it was observed that the velocity estimation depends on temperature and the carbon content. This issue made that calculations could not be automated in the present study since for every couple (temperature, carbon content), the model should be calibrated on PE conditions before used in solute drag calculations. One possible solution is to use the python code to change the velocity determination method and to compare the results with the PE calculations to define the best starting procedure to calculate velocity from the carbon profile.

- 2. Since the carbon content at the interface changes as a function of time, this can affect the calculated velocity at the interface in cases where an important change of carbon content occurs at the interface, leading to an instability of the numerical calculations. This was fixed using two solutions in the present study:
  - the time step is reduced when an abrupt change of carbon content at the interface occurs (higher than a defined threshold limit).
  - the velocity is calculated using an onward point in the carbon profile (Fig.A.4) to minimize the velocity change between two time steps. This should be used with care to avoid affecting the ferrite fraction as mentioned in 1. To this end, the error in the calculated velocity using the new point and the original one should not exceed 0.1%.
- 3. In some cases, the carbon interface drops to values lower than the bulk composition, due a very high dissipated energy. In these cases, the interface velocity is negative, meaning that the interface should move in the opposite direction, leading to austenite growth. Since no experimental evidence that confirms this behavoir exists, in the present study, the interface velocity was set to the very low value (1e<sup>-11</sup> m.s<sup>-1</sup>).



Figure A.4: Schematic description of how velocity is calculated using an onward point of the carbon profile to avoid abrupt changes in the calculated interface velocity.

Finally, it is to be noted that the total time for a diffusion calculation can vary from 20 min to several hours, depending on the stability of the carbon porfile as explained above.

## Appendix B

## The solute drag model written in python

Listing B.1: The core python code for the solute drag model

```
1 import math
2 import numpy as np
3 from operator import itemgetter
4 from XC_Rep_xy import *
5 from DF_eval_xy import *
6 from SD_eval_xy import *
7 import pickle
8 import os
9 from wagner_estimation_xy import *
10
11 #Defining input variables
12 parameters = {
          'system' : 'Quat',
13
          'element_1' : 'Ni',
14
          'element_2' : 'Mo',
15
          'C_wt': 0.26e-2,
16
          'X_wt': 1e-2,
17
          'Y_wt' : 1e-2,
18
          'Tk': 273.15+730,
19
          'Eb_1' : 1500,
20
          'Eb_2' : 1500,
21
          'int_C' : True,
22
          'L_FeCVa_0' : -50000,
23
          'int_XC' : True,
24
          'int_YC' : True,
25
          'int_XY' : True,
26
           'Dint = Daus' : False,
27
          }
28
29 Tk = parameters['Tk']
```

```
30 E_mid = []
31 E_mid.extend([parameters['Eb_1'], parameters['Eb_2']])
32 WC = parameters['C_wt']
33 WX = []
34 WX.extend([parameters['X_wt'], parameters['Y_wt']])
35
36 XElem = []
37 XElem.extend([parameters['element_1'], parameters['element_2']])
38
39 \, s_W X = []
40 s_WX.append("%02d"%(WX[0]*1000))
41 s_WX.append("%02d"%(WX[1]*1000))
42
_{43} if (WX[0] == 0.01):
      s_WX[0] = "%1d"%(WX[0]*100)
44
45 if (WX[1] == 0.01):
      s_WX[1] = "%1d"%(WX[1]*100)
46
47
48 #Creating folders for data sorting
49
50 name = 'Fe-'+str("%03d"%(WC*10000))+'C-'+s_WX[0]+XElem[0]+'-'+s_WX[1]+
     XElem [1] + '-'
51
52 name = name +str(int(Tk-273.15))+'C_Eb1_'+str(abs(int(E_mid[0])))+str('
      _pos'if(np.sign(E_mid[0])==1)else'_neg')+'_Eb2_'+str(abs(int(E_mid
      [1])))+str('_pos'if(np.sign(E_mid[1])==1)else'_neg')
53
54 if (parameters['int_C']) : name = name +'_intC'
55 if (parameters['int_XC']) :
      name = name + '_intXC'
56
57
58 if (parameters['int_YC']) :
      name = name +'_intYC'
59
60
61 if (parameters['int_XY']) :
      name = name + '_intXY'
62
63
64 if (parameters['Dint = Daus']) : name = name +'_Din_as_Daus'
65
66 name dir1 = 'mod iso'
67 name_dir2 = str(name_dir1)+'/FeC'+s_WX[0]+XElem[0]+s_WX[1]+XElem[1]+'/'
68 name_dir = str(name_dir2)+str(name)
69
70 print(name_dir)
71
72 if not os.path.exists(name_dir1):
73 os.mkdir(name_dir1)
```

```
74
75 if not os.path.exists(name_dir2):
      os.mkdir(name_dir2)
76
77
78 if not os.path.exists(name_dir):
      os.mkdir(name_dir)
79
80
81 file_name = str(name)+'_parameters.txt'
%2 with open(str(name_dir)+'/'+file_name,'wb') as output:
       pickle.dump(parameters, output)
83
84
85
  parameters = pickle.load(open(str(name_dir)+'/'+file_name, 'rb'))
86
87 #Wriring parameters...
ss f_par = open(str(name_dir)+"/par_"+str(name)+".txt" , "w")
89 f_par.write("system \t Fe-C-"+str(parameters['element_1']) +"-"+str(
      parameters['element_2']) +"\n")
90 f_par.write("Carbon content in wt% \t "+str(parameters['C_wt']*100.0)+"\
      n")
91 f_par.write(str(parameters['element_1'])+" content in wt% \t "+str(
      parameters ['X_wt'] *100.0) + "\n")
92 f_par.write(str(parameters['element_1'])+" content in wt% \t "+str(
      parameters['Y_wt'] *100.0)+"\n")
93
94 f_par.write("Temperature K \t "+str(parameters['Tk'])+"\n")
95 f_par.write("Grain size (m) \t "+str(parameters['G_size'])+"\n")
96 f_par.write(str(parameters['element_1'])+" Eb to midpoint\t "+str(
      parameters['Eb 1'])+"\n")
97 f_par.write(str(parameters['element_2'])+" Eb to midpoint\t "+str(
      parameters['Eb_2'])+"\n")
98
99
100
101 Daus = parameters['Dint = Daus']
102 print("Solute drag calculations for : Fe-C-"+str(parameters['element_1'
      ]) +"-"+str(parameters['element_2']) +" system")
103
104 print("carbon content (wt%) : ", parameters['C_wt']*100.0)
105 print(str(parameters['element_1']) + " content (wt%): ", parameters['
      X wt']*100.0)
106 print(str(parameters['element_2']) + " content (wt%): ", parameters['
      Y_wt']*100.0)
107
108
109 R=8.314
110
```

```
112 A_X = []
113 element = ['element_1', 'element_2']
114
115 print(element)
116
117 for i in element :
       if (str(parameters[i]) == 'Ni') :
118
           A_X.append(58.6934)
119
       elif (str(parameters[i]) == 'Mo' ) :
120
           A_X.append(95.95)
       elif (str(parameters[i]) == 'Mn') :
122
           A_X.append(54.93)
123
       elif (str(parameters[i]) == 'Cr') :
124
           A_X.append(51.996)
125
126
       elif (str(parameters[i]) == 'Si') :
           A_X.append(28.08)
127
128
       else : (print("error in element"))
129
130
_{131} A_Fe = 55.84
132 A_C = 12.0
133
134
135 D_X=[]
136 D_X.append([0.0, parameters['DX_1'], parameters['DX_2'], parameters['DX_3'
      ], parameters ['DX_4']])
137
138
139 D_X.append([0.0, parameters['DY_1'], parameters['DY_2'], parameters['DY_3'
      ], parameters ['DY_4']])
140
141 XCBulk = (WC/A_C)/((WC/A_C)+(WX[0]/A_X[0])+(WX[1]/A_X[1])+((1.0-WC-WX
      [0]-WX[0])/A_Fe))
142
143 XXBulk = []
144
145 XXBulk.append((WX[0]/A_X[0])/((WC/A_C)+(WX[0]/A_X[0])+(WX[1]/A_X[1])
      +((1.0-WC-WX[0]-WX[1])/A_Fe)))
146 XXBulk.append((WX[1]/A_X[1])/((WC/A_C)+(WX[0]/A_X[0])+(WX[1]/A_X[1])
      +((1.0-WC-WX[0]-WX[1])/A_Fe)))
147
148 UXBulk = []
149
150 UXBulk = np.array(XXBulk)/(1-XCBulk)
152 XXIntAus = XXBulk
153 XXIntFer = XXBulk
```

```
154
155 XCA = []
L_{par} = [+11823.355, +11212.222]
157 ges_par = ["G(boun,fe,"+str(XElem[0])+":va;0)","G(boun,fe,"+str(XElem
      [1])+":va;0)"]
158 #%%
159 with TCPython() as start:
       print("-----Searching diffusion coeffcients
160
      ----")
       calc_diffusion= (start.
161
      select_thermodynamic_and_kinetic_databases_with_elements("TCFE9", "
      mob2", ["Fe", "C", XElem[0], XElem[1]]).
       without_default_phases().select_phase("FCC_A1").select_phase("BCC_A2
162
      ").get_system())
       coef=(calc_diffusion.with_single_equilibrium_calculation().
163
      set_condition("t", Tk).set_condition("n", 1.0).set_condition("p", 1e5
      ).set_condition(("w(C)"),0.2e-2).
             set_condition(("w("+XElem[0]+")"),WX[0]).set_condition(("w("+
      XElem[1]+")"),WX[1]))
165
       D_X[0][1] = coef.calculate().get_value_of(ThermodynamicQuantity.
      chemical_diffusion_coefficient('bcc', XElem[0], XElem[0], 'fe'))
       D_X[1][1] = coef.calculate().get_value_of(ThermodynamicQuantity.
167
      chemical_diffusion_coefficient('bcc', XElem[1], XElem[1], 'fe'))
       D_X[0][3]= coef.calculate().get_value_of(ThermodynamicQuantity.
168
      chemical_diffusion_coefficient('fcc', XElem[0], XElem[0], 'fe'))
       D_X[1][3]= coef.calculate().get_value_of(ThermodynamicQuantity.
169
      chemical_diffusion_coefficient('fcc',XElem[1],XElem[1],'fe'))
       D_X[0][2] = math.sqrt(D_X[0][3]*D_X[0][1])
170
       D_X[1][2] = math.sqrt(D_X[1][3]*D_X[1][1])
172
173
       if (Daus) :
174
           D_X[2] = D_X[3]
175
176
       D_X[0][4] = D_X[0][3]
177
       D_X[1][4] = D_X[1][3]
178
179
180
181 #writing parameters
       f_par.write(XElem[0]+ " Diffusion coef. in Ferrite D1 \t "+str(D_X
182
      [0] [1] + " \setminus n ")
       f_par.write(XElem[0]+" Diffusion coef. in interface D2 \t "+str(D_X
183
      [0][2]) + " \setminus n ")
      f_par.write(XElem[0]+" Diffusion coef. in Austenite D3 \t "+str(D_X
184
      [0][3]) + " \setminus n ")
       f_par.write(XElem[1]+" Diffusion coef. in Ferrite D1 \t "+str(D_X
185
```

```
[1][1]) + " \setminus n ")
       f_par.write(XElem[1]+" Diffusion coef. in interface D2 \t "+str(D_X
186
       [1][2]) + " \setminus n ")
       f_par.write(XElem[1]+" Diffusion coef. in Austenite D3 \t "+str(D_X
187
       [1][3]) + " \setminus n ")
       f_par.close()
188
       cond_x = 1e5
189
       cond_y = 1e5
190
  #Defining the Fe-X1 and Fe-X2 parameters for a given binding energy
192
193
194
       calc_equi = (start.select_user_database_and_elements("HATEM_verN.TDB
      ", ["Fe", "C", XElem[0], XElem[1]]).get_system().
                          run_ges_command("readfecmn.GES5"))
195
196
       L_par[0] = calc_equi.get_ges_parameter(ges_par[0])
197
       L_par[1] = calc_equi.get_ges_parameter(ges_par[1])
198
       L_FeCVa_0 = calc_equi.get_ges_parameter('L(boun,Fe:C,va;0)')
199
       L_FeXCVa = calc_equi.get_ges_parameter("L(boun,fe,"+str(XElem[0])+":
200
      c, va; 0)")
       L_FeYCVa = calc_equi.get_ges_parameter("L(boun,fe,"+str(XElem[1])+":
201
      c, va;0)")
       L_XYVa = calc_equi.get_ges_parameter("L(boun,"+str(XElem[0])+','+str
202
      (XElem[1])+":va;0)")
       L_FeXYVa = calc_equi.get_ges_parameter("L(boun,fe,"+str(XElem[0])+',
203
      '+str(XElem[1])+":va;0)")
204
       if (parameters['int_C']) : L_FeCVa_0 = parameters['L_FeCVa_0']
205
206
       L_first_par = []
207
       L_second_par = []
208
       Laa = []
209
       for n,i in enumerate(L_par[0][1:]) :
210
           if i.isdigit():
211
                L_aa.append(i)
212
           elif (i == '.'):
213
                L_aa.append(i)
214
           else : break
215
       a = "".join(L_aa)
216
       L_first_par.append(float(a))
217
218
       L_second_par.append(L_par[0][n+1:])
219
220
       L_aa = []
221
       for n,i in enumerate(L_par[1][1:]) :
222
           if i.isdigit():
223
                L_aa.append(i)
224
```

```
elif (i == '.'):
225
               L_aa.append(i)
226
           else : break
227
       a = "".join(L_aa)
228
       L_first_par.append(float(a))
229
       L_second_par.append(L_par[1][n+1:])
230
       while (cond_x > 2.0 and cond_y >2.0) :
231
232
           calc_equi = (start.select_user_database_and_elements("HATEM_verN
233
      .TDB", ["Fe", "C", XElem[0], XElem[1]]).get_system().
                         run_ges_command("readfecmn.GES5").set_ges_parameter
234
      (ges_par[0], str(L_first_par[0])+str(L_second_par[0])).
                         set_ges_parameter(ges_par[1], str(L_first_par[1])+
235
      str(L_second_par[1])).
                         set_ges_parameter("L(boun,fe,"+str(XElem[0])+":c,va
236
      ;0)", str(L_FeXCVa) ).
                         set_ges_parameter("L(boun,fe,"+str(XElem[1])+":c,va
237
      ;0)", str(L_FeYCVa)).
                         set_ges_parameter("L(boun,fe,"+str(XElem[0])+','+
238
      str(XElem[1])+":va;0)", str(L_FeXYVa)).
                         set_ges_parameter("L(boun,Fe:C,va;0)", str(
239
      L_FeCVa_0)))
240
           calc=(calc_equi.with_single_equilibrium_calculation().
241
           set_condition("t", Tk).set_condition("n", 1.0).set_condition("p"
242
      , 1e5))
           L_FeX = calc_equi.get_ges_parameter("L(boun,fe,"+str(XElem[0])+"
243
      :va;0)")
           L_FeY = calc_equi.get_ges_parameter("L(boun,fe,"+str(XElem[1])+"
244
      :va;0)")
245
246 #Evaluation of the wagner interaction terms in both austenite and at the
       interface
           wag_fcc_X, wag_fcc_Y, wag_X, wag_Y, L_FeXCVa, L_FeYCVa,
247
      wag_fcc_XY, wag_XY, L_XYVa,L_FeXYVa = wagner(calc_equi, Tk, XElem,
      XCBulk, XXBulk)
248
249 #Evaluating the difference between the two wagner interaction parameters
       in the two phases and accomadate the difference
           diff_wag_X = (wag_X - wag_fcc_X)*R*Tk
250
           diff_wag_Y = (wag_Y - wag_fcc_Y)*R*Tk
251
           diff_wag_XY = (wag_XY - wag_fcc_XY)*R*Tk
252
           T= Tk
253
           if (parameters['int_XC']) : L_FeXCVa = eval(L_FeXCVa) -
254
      diff_wag_X
           if (parameters['int_YC']) : L_FeYCVa = eval(L_FeYCVa) -
255
      diff_wag_Y
```

```
if (parameters['int_XY']) : L_FeXYVa = eval(L_FeXYVa) -
256
      diff_wag_XY
257
258
259 #Setting the L parmaeters
           calc_equi = (start.select_user_database_and_elements("HATEM_verN
260
      .TDB", ["Fe", "C", XElem[0], XElem[1]]).get_system().
                         run_ges_command("readfecmn.GES5").set_ges_parameter
261
      (ges_par[0], str(L_first_par[0])+str(L_second_par[0])).
                         set_ges_parameter(ges_par[1], str(L_first_par[1])+
262
      str(L_second_par[1])).
263
                         set_ges_parameter("L(boun,fe,"+str(XElem[0])+":c,va
      ;0)", str(L_FeXCVa) ).
                         set_ges_parameter("L(boun,fe,"+str(XElem[1])+":c,va
264
      ;0)", str(L_FeYCVa)).
                         set_ges_parameter("L(boun,fe,"+str(XElem[0])+','+
265
      str(XElem[1])+":va;0)", str(L_FeXYVa)).
                         set_ges_parameter("L(boun,Fe:C,va;0)", str(
266
      L_FeCVa_0)))
267
268 #Evaluation of the wagner interaction terms in both austenite and at the
       interface
           wag_fcc_X, wag_fcc_Y, new_wag_X, new_wag_Y, L_FeXCVa, L_FeYCVa,
269
      new_wag_fcc_XY, new_wag_XY, L_XYVa,L_FeXYVa = wagner(calc_equi, Tk,
      XElem, XCBulk, XXBulk)
270
           result = (calc.set_phase_to_suspended("*").set_phase_to_entered(
271
      "fcc",1.0).set condition(("x(c)"),XCBulk).
                     set_condition("x("+XElem[0]+")",XXBulk[0]).
      set_condition("x("+XElem[1]+")",XXBulk[1]).
                     calculate())
273
           fccpot_x = result.get_value_of("mu("+XElem[0]+")")
274
           fccpot_y = result.get_value_of("mu("+XElem[1]+")")
275
276
           result = (calc.set_phase_to_suspended("*").set_phase_to_entered(
277
      "bcc",1.0).set_condition(("x(c)"),XCBulk).
                      set_condition("x("+XElem[0]+")",XXBulk[0]).
278
      set_condition("x("+XElem[1]+")",XXBulk[1]).
                     calculate())
279
           bccpot x = result.get value of ("mu("+XElem[0]+")")
280
           bccpot_y = result.get_value_of("mu("+XElem[1]+")")
281
282
           result = (calc.set_phase_to_suspended("*").set_phase_to_entered(
283
      "boun",1.0).set_condition(("x(c)"),XCBulk).
                      set_condition("x("+XElem[0]+")",XXBulk[0]).
284
      set_condition("x("+XElem[1]+")",XXBulk[1]).
                     calculate())
285
```

```
boupot_x = result.get_value_of("mu("+XElem[0]+")")
286
           boupot_y = result.get_value_of("mu("+XElem[1]+")")
287
           cond_x = abs(boupot_x - (((bccpot_x+fccpot_x)/2.0)+E_mid[0]))
288
           cond_y = abs(boupot_y - (((bccpot_y+fccpot_y)/2.0)+E_mid[1]))
289
290
291
           if (abs(boupot_x - (((bccpot_x+fccpot_x)/2.0)+E_mid[0]))) > 2.0
292
      :
               L_first_par[0] = L_first_par[0] - (boupot_x - (((bccpot_x+
293
      fccpot_x)/2.0)+E_mid[0]))
294
           if (abs(boupot_y - (((bccpot_y+fccpot_y)/2.0)+E_mid[1]))) > 2.0
295
      :
               L_first_par[1] = L_first_par[1] - (boupot_y - (((bccpot_y+
296
      fccpot_y)/2.0)+E_mid[1]))
297
298 # writing parameters
       f_par = open(str(name_dir)+"/par_"+str(name)+".txt" , "a+")
299
       f_par.write("L_Fe"+XElem[0]+"Va_0 parameter : \t "+str(L_FeX1)+"\n")
300
       f_par.write("L_Fe"+XElem[1]+"Va_0 parameter : \t "+str(L_FeX2)+"\n")
301
       f_par.write("L_FeCVa_0 parameter : \t "+str(L_FeCVa_0)+"\n")
302
       f_par.write("L_Fe"+XElem[0]+"CVa parameter : \t "+str(L_FeXCVa)+"\n"
303
      )
       f_par.write("L_Fe"+XElem[1]+"CVa parameter : \t "+str(L_FeYCVa)+"\n"
304
      )
       f_par.write("L_"+XElem[0]+"-"+XElem[1]+"Va parameter : \t "+str(
305
      L_XYVa) + " \setminus n ")
       f_par.write("L_Fe"+XElem[0]+"-"+XElem[1]+"Va parameter : \t "+str(
306
      L FeXYVa)+"\n")
       f_par.close()
307
308
       XFeBulk = 1 - XCBulk - XXBulk[0] - XXBulk [1]
309
       XC_inf = XCBulk*0.05
310
       XC_sup = XCBulk*20
311
312
       XCIntAus, CPotIntAus, XXIntAus, XXIntFer, XPotFer, FePotFer, XCFer =
313
       DF_eval(Tk, XCBulk , XXIntAus, XXIntFer, XElem, 1, calc, 0.0, XC_inf
      , XC_sup)
314
       calc.remove condition("x(c)")
315
       calc.remove_condition("x("+XElem[0]+")")
316
       calc.remove_condition("x("+XElem[1]+")")
317
318
       calc.set_condition("mu(c)", CPotIntAus)
319
       XX_inf = XXIntAus[0]*0.05
320
       XX_sup = XXIntAus[0]*20
321
       RAus = []
322
```

```
RAus.append(XXIntAus[0]/(1.0-sum(XXIntAus)-XCIntAus))
323
       RAus.append(XXIntAus[1]/(1.0-sum(XXIntAus)-XCIntAus))
324
325
       XCIntAus, XXIntAus = XC_Rep(Tk, XXIntAus, UXBulk, XElem, RAus, calc,
326
       XX_inf, XX_sup)
327
328
329 #defining variable for solute drag calculations
       dist = 2.5e - 10
                             #interplanes distance
330
       dt= 1e-5
331
       vmax, vmin = 3e-5, 1e-11
                                      #velocities max and min
332
       vstep = 1000
333
                                      #number of calculated velocities
       CPot = CPotIntAus
334
335
336
       calc.remove_condition("mu(c)")
       calc.remove_condition("x("+XElem[0]+")")
337
       calc.remove_condition("x("+XElem[1]+")")
338
       calc.remove_condition("x(c)")
339
340
       upper = math.log(vmax)
341
       lower = math.log(vmin)
342
       step = (upper - lower)/vstep
343
       v = [0.0] * vstep
344
       XXIntSeg = [[[0.0]*vstep for i in range(3)] for j in range(len(
345
      XXIntAus))]
       SD_Glob = [[[0.0]*vstep for i in range(3)] for j in range(len(
346
      XXIntAus))]
       SDtot = []
347
       SDtot x = []
348
       SDtot_y = []
349
       XCA = []
350
       XCR = []
351
       XXA = []
352
       XXF = []
353
       XCF =[]
354
355
       XCIntSeg = [[0.0]*vstep for i in range(3)]
356
       XX_sup = [[XXIntAus[i] * 20]*5 for i in range(len(XXIntAus))]
357
       XX_inf = [[XXIntAus[i] * 0.005]*5 for i in range(len(XXIntAus))]
358
359
       for k in range (0,vstep):
360
           v[k]=math.exp(upper-(k)*step)
361
           i=0
362
           j=0
363
           XXFer = XXIntFer
364
           XFeFer = 1.0- sum(XXIntFer)- XCFer
365
366 #Initializing
```

```
calc.remove_condition("mu(c)")
367
           calc.remove_condition("x("+XElem[0]+")")
368
           calc.remove_condition("x("+XElem[1]+")")
369
           calc.remove_condition("x(c)")
370
371
372 #Calculating Solute drag energies, X1, X2 and C contents as a function
      of velocity at each atomic plane
           SD_x, SD_y, SD, SD_glob, XXIntSeg_temp, XX_sup, XX_inf, XCInt =
373
      SD_eval(Tk, v[k], vstep, XPotFer, FePotFer, XXFer, XFeFer, dist, dt,
      XElem, CPotIntAus, D_X, calc, XX_sup, XX_inf)
374
375
           SDtot_x.append(SD_x)
           SDtot_y.append(SD_y)
376
           SDtot.append(SD)
377
           for i in range (len(XXIntSeg_temp[0])):
378
379
                SD_Glob[0][i][k] = SD_glob[0][i]
380
                SD_Glob[1][i][k] = SD_glob[1][i]
381
                XXIntSeg[0][i][k] = XXIntSeg_temp[0][i]
382
                XXIntSeg[1][i][k] = XXIntSeg_temp[1][i]
383
                XCIntSeg[i][k] = XCInt[i]
384
385
  #Initializing
386
           calc.remove_condition("mu(c)")
387
           calc.remove_condition("x("+XElem[0]+")")
388
           calc.remove_condition("x("+XElem[1]+")")
389
           calc.remove_condition("x(c)")
390
           xi = [0.0, 0.0]
391
           xi[0] = XXIntSeg[0][len(XXIntSeg)][k]
392
           xi[1] = XXIntSeg[1][len(XXIntSeg)][k]
393
394
395 #Evaluation of XC that gives a zero driving force
           XCIntAus, CPotIntAus, XXIntAus, XXIntFer, XPotFer, FePotFer,
396
      XCFer = DF_eval(Tk, XCBulk , xi, XXIntFer, XElem, 2, calc, SD, XC_inf
      , XC_sup)
397
           XC_inf = XCIntAus*0.05
398
           XC_sup = XCIntAus*5
399
           XCA.append(XCIntAus)
400
           XCF.append(XCFer)
401
  #Initializing
402
           calc.remove_condition("x("+XElem[0]+")")
403
           calc.remove_condition("x("+XElem[1]+")")
404
           calc.remove_condition("x(c)")
405
           calc.set_condition("mu(c)", CPotIntAus)
406
407
408 #XX upper and lower limits used for minimizing XC_rep function
```

```
XX_inf_1 = XXIntAus[0]*0.01
409
          XX_sup_1 = XXIntAus[0]*20
410
411
          RAus = []
412
          RAus.append(XXIntAus[0]/(1.0-sum(XXIntAus)-XCIntAus))
413
          RAus.append(XXIntAus[1]/(1.0-sum(XXIntAus)-XCIntAus))
414
415
          XCIntAus, XXIntAus = XC_Rep(Tk, XXIntAus, UXBulk, XElem, RAus,
416
     calc, XX_inf_1, XX_sup_1)
417
          XCR.append(XCIntAus)
418
          XXA.append(XXIntAus)
419
420
          calc.remove_condition("mu(c)")
421
          calc.remove_condition("x("+XElem[0]+")")
422
          calc.remove_condition("x("+XElem[1]+")")
423
          calc.remove_condition("x(c)")
424
  #writing results in files
425
      f = open(str(name_dir)+"/V_"+str(name)+".txt" , "w")
426
      f.write("#velocity\t SDtot\t SDtot_X\t SDtot_Y\t XXIntSeg1\t
427
     XXIntSeg2\t XXIntSeg3\t XYIntSeg1\t XYIntSeg2\t XYIntSeg3\n")
      for i,j,k,l,m,n,o,p,q,r in zip(v,SDtot, SDtot_x, SDtot_y,XXIntSeg
428
     [0] [0],XXIntSeg[0][1],XXIntSeg[0][2],XXIntSeg[1][0],XXIntSeg[1][1],
     XXIntSeg[1][2]):
          429
     ,k,l,m,n,o,p,q,r))
      f.close()
430
431
      h = open(str(name_dir)+"/SD_"+str(name)+".txt" , "w")
432
      h.write("#velocity\t SDtot\t SDtot_X\t SDtot_Y\t SDX_1\t SDX_2\t
433
     SDX_3\t SDY_1\t SDY_2\t SDY_3\t SDXY_1\t SDXY_2\t SDXY_3\n")
      for i,j,k,l,m,n,o,p,q,r,s,t,u in zip(v,SDtot, SDtot_x, SDtot_y,
434
     SD_Glob[0][0],SD_Glob[0][1], SD_Glob[0][2], SD_Glob[1][0], SD_Glob
     [1][1], SD_Glob[1][2], SD_Glob[0][0]+SD_Glob[1][0], SD_Glob[0][0]+
     SD_Glob[1][0], SD_Glob[0][0]+SD_Glob[1][0]):
          435
     %r\t %r\n"%(i,j,k,l,m,n,o,p,q,r,s,t,u))
436
      h.close()
437
438
439
      g = open(str(name_dir)+"/XC_"+str(name)+".txt", "w")
440
      g.write("vel\t xca\t xcr\t xxa\t xya\t xxif\t xc_int1\t xc_int2\t
441
     xc_int3\langle n'' \rangle
      for i,j,z,k,w,s,t,q,r in zip(v,XCA,XCR,XXA, XXA, XCF, XCIntSeg[0],
442
     XCIntSeg[1], XCIntSeg[2]):
          443
```

[0],w[1],s,t,q,r))

445 g.close()

444

Listing B.2: Python code for the driving force evaluation

```
1 import math
2 from tc_python import *
3 from scipy.optimize import minimize_scalar, bracket, minimize
4 import numpy as np
6 R=8.314
7
8 #tc_function to calculate the thermodynamic properties of the system
9 def tc(XElem, XX, XC, result):
10
      XPot = []
11
12
      for i in range(len(XElem)):
13
          XPot.append(result.get_value_of("mu("+XElem[i]+")"))
14
      FePot=result.get_value_of("mu(Fe)")
16
      CPot=result.get_value_of("mu(C)")
17
      XC=result.get_value_of("x(C)")
18
19
20
      UX=np.array(XX)/(1.0-XC)
21
      XFe = 1.0 - np.sum(XX)
22
      UFe = (XFe / (1.0 - XC))
23
24
      return XPot, FePot, UX, UFe, CPot, XC
25
26
27 #calc_DF funtion to calculate the dirving force
28 def calc_DF(XC, XXIntAus, XXIntFer, calc, XElem, SD, par, condPE, RAus,
     Rsum):
29
30
      if (condPE == 1):
31
          XXsum = (1.0-XC)/(1.0+(1.0/Rsum))
32
          XFe = 1.0 - XXsum - XC
33
          XXIntAus=np.array(RAus) * XFe
34
35
36 # we fix austnite as the only phase to calculate the thermodynamic
     properties of X and C in austenite
      phase = "fcc"
37
      XX=XXIntAus
38
      result=(calc.set_phase_to_suspended("*").set_phase_to_entered(phase
39
      ,1.0).set_condition(("x(c)"),XC).
```

```
set_condition("x("+XElem[0]+")",XX[0]).set_condition("x("+
40
     XElem[1]+")",XX[1]).
               calculate())
41
42
      XPotAus, FePotAus, UXAus, UFeAus, CPot, XCAus = tc(XElem, XX, XC,
43
     result)
44
45
      calc.remove_condition("x(c)")
46
47
48 # same procedure with ferrite
      phase="bcc"
49
50
      XX = XXIntFer
51
      result2=(calc.set_phase_to_suspended("*").set_phase_to_entered(phase
     ,1.0).
               set_condition("x("+XElem[0]+")",XX[0]).set_condition("x("+
53
     XElem [1] + " ) ", XX [1] ).set_condition(("mu(c)"), CPot).
               calculate())
54
55
      XPotFer, FePotFer, UXFer, UFeFer, CPot, XCFer = tc(XElem, XX, XC,
56
     result2)
57
58 #evalution of the driving force
59
      DF= 0.5*((UXAus[0]+UXFer[0])*(XPotAus[0]-XPotFer[0])+(UXAus[1]+UXFer
60
     [1])*(XPotAus[1]-XPotFer[1])+(UFeFer+UFeAus)*(FePotAus-FePotFer)) -
     SD
61
      calc.remove_condition("mu(c)")
62
63
      if (par): return DF**2
64
      else : return DF , CPot, XPotFer, FePotFer, XPotAus, FePotAus, XCFer
65
66
67
68 def DF_eval(Tk, XCBulk, XXIntAus ,XXIntFer, XElem, condPE, calc, SD,
     XC_inf, XC_sup):
69
      Rsum = np.sum(XXIntAus)/(1-np.sum(XXIntAus)-XCBulk)
70
      RAus = np.array(XXIntAus)/(1-np.array(XXIntAus)-XCBulk)
71
      RFer = np.array(XXIntFer)/(1-np.array(XXIntFer)-XCBulk)
72
73
      if (condPE == 1):
                                #to calculate PE conditions
74
          XXsum = (1.0)/(1.0+(1.0/Rsum))
75
          XFe = 1.0 - XXsum
76
          XXIntFer=np.array(RFer) * XFe
77
78
```

```
par = True
79
80
      f = lambda x: calc_DF(x, XXIntAus, XXIntFer, calc, XElem, SD, par,
81
      condPE, RAus, Rsum)
82
83 # we use python functions to mimize driving force equation
      res = minimize_scalar(f, bounds=(XC_inf, XC_sup), method='bounded',
84
      options={'xatol': 1e-30})
85
86
      par = False
87
88
      XC = res.x
89
      DF, CPot, XPotFer, FePotFer, XPotAus, FePotAus, XCFer = calc_DF(XC,
90
      XXIntAus, XXIntFer, calc, XElem, SD, par, condPE, RAus, Rsum)
91
92 #Initializing all parameters
      calc.remove_condition("mu(c)")
93
       calc.remove_condition("x(c)")
94
       calc.remove_condition("x("+XElem[0]+")")
95
       calc.remove_condition("x("+XElem[1]+")")
96
       calc.set_phase_to_suspended("*").set_phase_to_entered('fcc',1.0).
97
      set_phase_to_entered('bcc',1.0)
98
99
      return XC, CPot, XXIntAus, XXIntFer, XPotFer, FePotFer, XCFer
100
```

Listing B.3: Python code for solute drag energies calculations

1

```
2 from tc_python import *
3 import matplotlib.pyplot as plt
4 from scipy.optimize import minimize_scalar, bracket, minimize
5 import numpy as np
6
7 R = 8.314
9 #dx_c function to evaluate the flux, driving force dG and the new dx
10 def dx_c(XX, XXInt, XPot, XFeInt, FePot, v, J, i, calc, par, dt, dist,
     Tk, R, D_X, XElem, XCInt):
11
      X1 = XX[0]
12
      X2 = XX[1]
13
14
      result=(calc.set_condition("x("+XElem[0]+")",X1).set_condition("x("+
     XElem[1]+")",X2).
                   calculate())
16
17
```

```
FePot[i]=result.get_value_of("MU(Fe)")
18
      XPot[0][i]=result.get_value_of("MU("+XElem[0]+")")
19
      XPot[1][i]=result.get_value_of("MU("+XElem[1]+")")
20
      XFeInt[i]=result.get_value_of("X(Fe)")
21
      X1 = result.get_value_of("X("+XElem[0]+")")
22
      XCInt[i] = result.get_value_of("X(C)")
23
24
25 #calculating the driving forces Eq.
      dGx=(XPot[0][i]-XPot[0][i-1])-(FePot[i]-FePot[i-1])
26
      dGy=(XPot[1][i]-XPot[1][i-1])-(FePot[i]-FePot[i-1])
27
28
29
  #calculating flux J
                         Eq.
      J[0][i] = -(D_X[0][i]/(R*Tk))*(XXInt[0][i-1]*XFeInt[i-1])*(dGx)/dist
30
      J[1][i] = -(D_X[1][i]/(R*Tk))*(XXInt[1][i-1]*XFeInt[i-1])*(dGy)/dist
31
32
33 #evaluation of dx function for each element Eq.
      dx = (J[0][i-1]-J[0][i]+v*(X1-XXInt[0][i-1]))*(dt/dist)
34
      dy = (J[1][i-1]-J[1][i]+v*(X2-XXInt[1][i-1]))*(dt/dist)
35
36
37 #Initializing
      calc.remove_condition("MU("+XElem[0]+")")
38
      calc.remove_condition("x("+XElem[0]+")")
39
      calc.remove_condition("x("+XElem[1]+")")
40
41
42
43
      if (par) : return dx**2 + dy**2
44
      else : return X1, X2, J[0][i], J[1][i], XFeInt[i], FePot[i], XPot[0][i
45
     ], XPot[1][i], dGx,dGy, XCInt[i]
46 #SD_eval function to evaluate solute drag energy at each atomic plane.
47 def SD_eval(Tk, v, vstep, XPotFer, FePotFer, XXFer, XFeFer, dist,
                                                                         dt.
     XElem, CPot, D_X, calc, XX_sup, XX_inf):
  #defining variables .....
48
      J =[[0.0]*5 for i in range(len(XElem))]
49
      SD =[[0.0]*5 for i in range(len(XElem))]
50
      SDtot_x = 0.0
51
      SDtot_y =0.0
52
      SDtot = 0.0
53
54
55
      XPot = [[0.0]*5 for i in range(len(XElem))]
56
      FePot = [0.0] * 5
57
      for i in range (len(XElem)):
58
          XPot[i][0] = XPotFer[i]
59
60
      FePot[0] = FePotFer
61
62
```

```
XXInt=[[XXFer[i]]*5 for i in range(len(XElem))]
63
      XFeInt= [XFeFer] * 5
64
      XCInt = [0.0] * 5
65
      XXIntSeg = [[] for i in range(len(XElem))]
66
       SD_glob = [[] for i in range(len(XElem))]
67
68
69
70 #set ferrite to active phase to calculate the thermodynamic properties
      of X1 and X2 at the ferrite interface side
71
      calc.set_phase_to_suspended("*").set_phase_to_entered("bcc",1.0).
72
      set_condition(("MU(C)"),CPot)
      result=(calc.set_condition("x("+XElem[0]+")",XXFer[0]).set_condition
73
      ("x("+XElem[1]+")",XXFer[1]).
                   calculate())
74
75
76
77
      FePot[0]=result.get_value_of("MU(Fe)")
78
79
       for f in range (len(XElem)):
80
           XPot[f][0] = result.get_value_of("MU("+XElem[f]+")")
81
82
      XFeInt[0]=result.get_value_of("X(Fe)")
83
84
   #set boundary to active phase to calculate the thermodynamic properties
85
       of X1 and X2 at the boundary
86
       calc.set_phase_to_suspended("*").set_phase_to_entered("Boundary"
87
      ,1.0).set_condition(("MU(C)"),CPot)
88
      phase = 'bou'
89
90
91
      for i in range (1,4): # i is the atomic plane number
92
               if (i>=3) :
93
                   phase = 'fcc'
94
                   calc.set_phase_to_suspended("*").set_phase_to_entered("
95
      fcc",1.0).set_condition(("MU(C)"),CPot)
96
               par = True
97
               f = lambda x: dx_c(x, np.array(XXInt), XPot, XFeInt,FePot,
98
      v, J, i, calc, par, dt, dist, Tk, R, D_X, XElem, XCInt)
99
               bounds = ([XX_inf[0][i], XX_sup[0][i]], [XX_inf[1][i], XX_sup
100
      [1][i]])
               XX_initial = [XXInt[0][i], XXInt[1][i]]
```

```
res = minimize(f, XX_initial, method='L-BFGS-B', bounds=bounds
      , tol =1e-35, options={'xtol': 1e-35, 'ftol': 1e-35, 'disp': False})
               par = False
104
105
               XXInt[0][i],XXInt[1][i], J[0][i], J[1][i], XFeInt[i],FePot[i
106
      ], XPot[0][i], XPot[1][i], dGx,dGy, XCInt[i] = dx_c(res.x, np.array(
      XXInt), XPot, XFeInt, FePot, v, J, i, calc, par, dt, dist, Tk, R,
      D_X, XElem, XCInt)
108
109
  #calculate the solute drag energies
               SD[0][i] = -J[0][i]*dGx/v
               SD[1][i] = -J[1][i] * dGy/v
111
               SDtot_x += SD[0][i]
112
113
               SDtot_y +=
                           SD[1][i]
114
               SDtot +=SD[0][i] + SD[1][i]
116
117
               SD_glob[0].append(SD[0][i])
118
               SD_glob[1].append(SD[1][i])
119
  #the X content at each atomic plane
120
               XXIntSeg[0].append(XXInt[0][i])
121
               XXIntSeg[1].append(XXInt[1][i])
123
124 #changing the upper and lower limit of the boundary range to use in the
      function minimization
               XX_sup[0][i] = XXInt[0][i]*1.1
125
               XX_inf[0][i] = XXInt[0][i]*0.9
               XX_sup[1][i] = XXInt[1][i]*1.1
127
               XX_inf[1][i] = XXInt[1][i]*0.9
128
129
  #Initializing parameters
130
       calc.set_phase_to_suspended("*").set_phase_to_entered('fcc',1.0).
131
      set_phase_to_entered('bcc',1.0)
      return SDtot_x, SDtot_y, SDtot, SD_glob, XXIntSeg, XX_sup, XX_inf,
133
      XCInt
```

Listing B.4: Python code to calculate the XC representative

```
1 from tc_python import *
2 from scipy.optimize import minimize_scalar
3 import numpy as np
4
5 R=8.314
6
```

```
_7 #calc_UX to evaluate X1 and X2 that gives the same UX fraction as the UX
      fraction in bulk
8 def calc_UX(XX, XElem, RAus, calc, par, UXBulk):
9
      XY = XX * RAus [1] / RAus [0]
10
11
      result=(calc.set_condition("x("+XElem[0]+")",XX).set_condition("x("+
12
     XElem[1]+")",XY).set_phase_to_suspended("*").set_phase_to_entered("
     fcc",1.0).
                    calculate())
13
      XCRep=result.get_value_of("x(c)") #XC representative
14
      UX = XX/(1-XCRep)
16
                  return (UX-UXBulk[0])**2
      if (par):
17
      else : return UX, XCRep
18
19
20 def XC_Rep(Tk, XXIntAus, UXBulk, XElem, RAus, calc, XX_inf, XX_sup):
21
      par = True
22
      f = lambda x: calc_UX(x, XElem, RAus, calc, par, UXBulk)
23
24
      res = minimize_scalar(f, bounds=(XX_inf, XX_sup), method='bounded')
25
      par = False
26
27
      XX = res.x
28
      UX, XCRep = calc_UX(XX, XElem, RAus, calc, par, UXBulk)
29
      XXIntAus=[XX, XX*RAus[1]/RAus[0]]
30
31
      calc.set_phase_to_suspended("*").set_phase_to_entered('fcc',1.0).
32
     set_phase_to_entered('bcc',1.0)
    return XCRep, XXIntAus
33
```

Listing B.5: Python code for diffusion calculation

```
2
3 import math, csv
4 import numpy as np
5 import matplotlib.pyplot as plt
6 from erf import *
7 from scipy import interpolate
8 import pickle
9
10
11 #vel_landis to sove the diffusion equation using the Muray Landis
approach
12 def vel_landis(XC, v, p, Gsize, j, dt, calpha, cif):
13 global dtf, pf, dx, st, eff, time, stfactor
```

1

```
14
15 #setting the carbon content at the interface
      cinter = XC[0]
16
      cif = cinter
17
      c1[0] = cinter
18
19
  #calculating carbon content at each position
20
      exp = ((1.0/Tk) - 2.221e - 4)
21
      for i in range (1,n-1):
22
           y = XC[i]/(1.0-XC[i])
23
           if (i < eff+10) :
24
               Dc =4.53e-7 * (1.0 + y * (1.0-y) * (8339.9/Tk) ) * math.exp
25
      (-\exp*(17767.0-y*26436.0))
26
27
          if (i = int(st/2)) : Dc_v = Dc
28
           a = ((XC[i-1]-XC[i])/(dx)) * Dc *(4*3.14 )* ((Gsize/2.0 - p) - (
29
     i-1.5)*dx)**2
           b = ((XC[i]-XC[i+1])/(dx)) * Dc *(4*3.14 )* (((Gsize/2.0- p) - (
30
      i-0.5)*dx)**2)
31
           c1[i] =XC[i] + dt *((a - b) /((4*(3.14/3.)*((Gsize/2.0 - p) - (i
      -1.5)*dx)**3)- (4*(3.14/3.)*((Gsize/2.0 - p) - (i-0.5)*dx)**3) )+
                                                                              v
       *(n-i)*(XC[i+1]-XC[i-1])/((n)*2.0*dx) )
32
      c1[n-1] = c1[n-2]
33
34
      for i in range(eff-6,len(c1)-1):
35
36
           limit = 1.00001 # this value must be calibrated on PE conditions
37
           if ((c1[i]/c1[i+1])<limit) :</pre>
38
39
               eff = i - 20
40
               if (eff < 10) : eff =10
41
               if (time > 200 and eff < 50) : eff = 50
42
               break
43
44
      st = int((eff+stfactor)/5) #this value must be calibrated on PE
45
      conditions
      if(st <= 2) :st =3
46
47
      XC = c1
48
      er = p
49
      p += dt * v
50
      er = (p-er)/er
51
      dx = (Gsize/2.0-p)/(n)
53
      v = -1.*(Dc_v/(XC[0]-calpha))*(XC[st]-XC[2])/((st-2)*dx)
54
```

```
56 #calculatin velocity using a onward st position to avoid velocity
     instabilities
      v2 = -1.*(Dc_v/(XC[0]-calpha))*(XC[st+1]-XC[2])/((st+1-2)*dx)
57
      if (time > 20 and j/1000 == 0 and v > 5e-10 and (abs(v2-v)/v) < 2e-3
58
     and st <50) : stfactor +=1
59
      if (v > vtab[0]): v = vtab[0]
60
      if (v < vtab[-1]): v = vtab[-1]
61
62
      time += dt
63
64
65 #pf and dtf are the lists containing the interface positions and time
     steps
     if (j%5000 == 0 ) :
66
67
          pf = np.append(pf,p)
68
          dtf.append(time)
69
70
      j+=1
71
72
      return v, p, XC, j, time, er, cif
73
74
75 #-----load parameters -----
76
77 name = 'Fe-022C-10Ni-750C_Eb6500_neg_intC_intXC'
78 Para_equi = True #to perform para-equilibrium calculations
79
80 name_dir1 = 'mod_iso/'
81 name_dir2 = str(name_dir1)+'/FeC10Ni/'
82 name_dir = str(name_dir2)+str(name)
83
84 file_name = str(name_dir)+'/'+str(name)+'_parameters.txt'
86 parameters = pickle.load(open(file_name, 'rb'))
87
88 x = parameters['G_size']
                               #grain size
89
90 x = 50e-6 #if a different grain size is used
91
92 n = int(6* x *1.0e+6) #grid size
93
94 Tk = parameters['Tk']
95
96 j = 0
97 \text{ IntPos} = 1.0e-7
                                     #Initial interface position
98 pf = [1.0e-7]
                                   #list of interface position
```

55

```
99
100 dtf = [0.0]
                                          #list of dt
101 vtab = []
                                              # velocities
103 XCA, XCF, XXA, XYA = ([] for i in range(4))
                                                     #carbon and X contents at
       the austenite interface (A) and ferrite interface (F)
104
106 SD_tot, SD1, SD2, SD3 =([] for i in range(4)) #solute drag energies
      lists
107
108 XX1, XX2, XX3, XY1, XY2, XY3 =([] for i in range(6)) #X and Y contents
      at the interface atomic planes lists
109
110 #Reading the solute drag generated tables
111 xcf_num = 4
if (parameters['system'] == 'Quat') : xcf_num = 5
113
  with open(str(name_dir)+"/XC_"+str(name)+".txt", "r") as input :
114
       reader = csv.reader(input, delimiter = '\t')
115
       for s,i in enumerate(reader):
           if s>0 :
117
                aa = i[0]
118
               vtab.append(float(aa))
119
               XCA.append(float(i[2]))
120
               XXA.append(float(i[3]))
                if (parameters['system'] == 'Quat' ) : XYA.append(float(i
122
      [4]))
               XCF.append(float(i[xcf_num]))
123
124
125
126
  with open(str(name_dir)+"/V_"+str(name)+".txt", "r") as input :
127
       reader = csv.reader(input, delimiter = '\t')
128
       for s,i in enumerate(reader):
129
           if s>0 :
130
               aa = i[1]
131
               SD_tot.append(float(aa))
132
               SD1.append(float(i[2]))
133
               SD2.append(float(i[3]))
134
                if (parameters['system'] == 'Ter') :
135
                    SD3.append(float(i[4]))
136
                    XX1.append(float(i[5]))
137
                    XX2.append(float(i[6]))
138
                    XX3.append(float(i[7]))
139
                elif (parameters['system'] == 'Quat') :
140
                    SD3.append(float(i[4]))
141
```

```
XX1.append(float(i[4]))
                   XX2.append(float(i[5]))
143
                   XX3.append(float(i[6]))
144
                   XY1.append(float(i[7]))
145
                   XY2.append(float(i[8]))
146
                   XY3.append(float(i[9]))
147
148
149 SDtot_X = []
150 SDtot_Y = []
151
  if (parameters['system'] == 'Quat') :
152
      SDtot_X = SD1
153
      SDtot_Y = SD2
154
155
156 vmax = vtab[0]
157 vmin = vtab[-1]
158 upper = math.log(vmax)
159 lower = math.log(vmin)
160 vstep = len(vtab)
161 step = (upper - lower)/vstep
162
163 WX = []
164 A_X = []
                           # Atomic numbers
165 WC = parameters['C_wt']
166 #-----if ternary -----
167 if (parameters['system'] == 'Ter') :
      WX.extend([parameters['X_wt']])
168
169
170 #-----if quaternary ------
  if (parameters['system'] == 'Quat') :
171
      WX.extend([parameters['X_wt'], parameters['Y_wt']])
172
173
  for jj in range(0,2):
174
      if (jj == 0): element = 'element_1'
175
176
       elif ((jj == 1) and str(parameters['system']) == 'Quat') :
177
           element = 'element_2'
178
          print('vrai')
179
      else : break
180
      if (str(parameters[element]) == 'Ni') :
181
           A_X.append(58.6934)
182
      elif (str(parameters[element]) == 'Mo' ) :
183
           A_X.append(95.95)
184
       elif (str(parameters[element]) == 'Mn') :
185
           A_X.append(54.93)
186
      elif (str(parameters[element]) == 'Cr') :
187
           A_X.append(51.996)
188
```
```
elif (str(parameters[element]) == 'Si') :
189
           A_X.append(28.08)
190
191
192
       else : (print("error in element"))
193
194
195 print("Growth kinetics for Fe-"+str((WC*100))+"C-"+str((WX[0]*100))+str(
      parameters["element_1"]))
196
197
198 \text{ A}_{\text{Fe}} = 55.84
199 A_C = 12.0
200
201 #calculating atomic fractions
202 #-----if ternary -----
203 if (parameters['system'] == 'Ter') :
      XCBulk = (WC/A_C)/((WC/A_C)+(WX[0]/A_X[0])+((1.0-WC-WX[0])/A_Fe))
204
205
206 #-----if quaternary------
207 if (parameters['system'] == 'Quat') :
      XCBulk = (WC/A_C)/((WC/A_C)+(WX[0]/A_X[0])+(WX[1]/A_X[1])+((1.0-WC-
208
      WX[0]-WX[0])/A_Fe))
209
210
211 XC = [XCBulk] *(n)
                            #Initial Carbon pofile in austenite
212 \text{ XC}[0] = \text{XCA}[0]
213 cinter = XC[0]
                           #interface concentration
_{214} calpha = XCF[0]
                           #ferrite concentration
                      #interface concentration
215 cif = cinter
216
218 # calculating the intitial velocity from the initial carbon profile in
     austenite
y = XC[0]/(1.0-XC[0])
220 Dc =4.53e-7 * (1.0 + y * (1.0-y) * (8339.9/Tk) ) * math.exp(-((1.0/Tk)
      -2.221e-4 * (17767.0-y * 26436.0))
221
dx = (x/2.0 - IntPos)/(n)
                               #grid step
223 dt = dx *dx / (5. * Dc)
                               #time step
224
225 berf = erf(dx, XC[-1], XC[0], 100*dt, n)
226 print(berf[:20])
227 \text{ XC}[1:20] = \text{berf}[1:20]
228 for i in range(2,len(XC)):
      if (abs(XC[i]/XC[i+1])<1.001) :</pre>
229
           eff = i
230
          st = max(2, int(i/5.0))
231
```

```
break
232
233
234 vnew = 1.*(math.sqrt(Dc/(3.14*dt))/(cinter-calpha))*(XC[0]-XC[-1])
      #Initial Velocity
235
236 if (vnew > vtab[0]): vnew = vtab[0]
237 elif (vnew < vtab[-1]): vnew = vtab[-1]</pre>
238 c1 = XC
_{239} time = dt
241
242 \text{ er} = 1.0
_{243} factor = 1.0
_{244} stfactor = 0
245 vold=[]
_{246} XCO_temp = XC[0]
247
249 file_int = open(str(name_dir)+"/Int_cond_"+str(name)+"_interp.txt", 'w')
250 if (Para_equi) :
      file_int = open(str(name_dir)+"/Int_cond_"+str(name)+"_interp_pe.txt
251
     ", 'w')
252 if (parameters['system'] == 'Ter') :
      file_int.write("time\t velocity\t sd_tot\t sd1\t sd2\t sd3\t
253
     XCIntAust\t XCIntFer\t XXIntAus\t XX1 \t XX2 \XX3\n")
254
255 if (parameters['system'] == 'Quat') :
      file_int.write("time\t velocity\t sd_tot\t sdx_tot\t sdy_tot\t
256
     XCIntAust\t XCIntFer\t XXIntAus\t XYIntAus\t XX1 \t XX2 \XX3\t XY1 \t
      XY2 XY3 n")
257
258 while(time < 900) :
259
      vold.append(vnew)
260
      if (j>2 and j%10000 == 0) : del vold[0:-499]
261
262
264 # here this condition is to avoid carbon porfile inversion at the
     interface vicinity
      if (time > 10 and j%1000 == 0 and abs((XC[0]-XC0 temp)/XC0 temp) >
265
     0.0000007 and dt > 5e-6 and vnew > 2e-9) :
          factor = factor * 0.9
266
267 #However if the calcultions are stable the time step is increases again
      if (time > 50 and dt < 5e-4 and j%2000 == 0 and abs((XC[0]-XC0_temp
268
     )/XCO_temp) < 0.0000004 )
                              :
          factor = factor *1.1
269
```

```
271
       dt = factor * dx *dx / (5. * Dc) #time step
272
       if (time < 5 and dt < 1e-4): dt = factor * 1e-4 * time
273
       if(dt > 5e-4) : dt = 5e-4
274
275
      XCO_temp = XC[0]
276
       if (time> 30) :
277
           vnew = np.mean(vold[-500:-1]) #here we avreage velocity over the
278
       last 500 velocity for calculation stability
279
    280 #
      this part is to find the proper carbon content from the calculated
281 #
      interface velocity
      k = math.floor(((upper - math.log(vnew))/step)+1)
282
      if (k \ge vstep - 5) : k = vstep - 5
283
       if (k < 4) : k = 3
284
       f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],XCA[k-3:k+3])
285
       XC[0] = float(f(vnew))
286
287
       f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],XCF[k-3:k+3])
288
       calpha = float(f(vnew))
289
290
       f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],XXA[k-3:k+3])
291
       xaus = float(f(vnew))
292
293 #
294
      if (Para_equi) : XC[0] = XCA[0] #for PE calculations
295
296 #calculating the other parameters that correspond to the calculated
      interface velocity
       if (j>2 and j%5000 == 0 and parameters['system'] == 'Ter') :
297
298
           f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],SD_tot[k
299
      -3:k+3])
           sd = float(f(vnew))
300
301
           f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],SD1[k-3:k
302
      +31)
           sd1 = float((vnew))
303
304
           f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],SD2[k-3:k
305
      +3])
           sd2 = float(f(vnew))
306
307
           f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],SD3[k-3:k
308
      +3])
           sd3 = float(f(vnew))
309
310
```

```
f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],XX1[k-3:k
311
      +3])
          xx1 = float(f(vnew))
312
313
          f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],XX2[k-3:k
314
      +3])
          xx2 = float(f(vnew))
315
316
          f = interpolate.BarycentricInterpolator(vtab[k-3:k+3],XX3[k-3:k
317
      +3])
          xx3 = float(f(vnew))
318
319
          320
      t %r\t %r\n"%(time, vnew, sd, sd1, sd2, sd3, XC[0], calpha, xaus, xx1
      , xx2, xx3))
321
      vnew, IntPos, XC, j, time, er, cif = vel_landis(XC, vnew, IntPos, x,
322
      j, dt, calpha, cif)
323
324
325 file_int.close()
326
327 #data writing....
328 g = open(str(name_dir)+"/Kin_"+str(name)+"_gs"+str(int(x*1.0e+6/2))+"
      _interpolation.txt", 'w')
329 if (Para_equi) :
      g = open(str(name_dir)+"/Kin_"+str(name)+"_gs"+str(int(x*1.0e+6/2))+
330
      "_interpolation_pe.txt", 'w')
331
332 for i in range (len(pf)):
      frac = (math.pow(x/2.0,3) - math.pow((x/2.0 - float(pf[i])),3))/math
333
      .pow(x/2.0,3)
      g.write("%r\t %r\t %r\n"%(dtf[i],pf[i],frac))
334
335
336 g.close()
```

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# Titre: Développement d'alliages métalliques à gradient de composition pour l'exploration combinatoire des microstructures

### **Résumé:**

La transformation de l'austénite en ferrite dans les aciers présente un intérêt considérable pour le contrôle des propriétés finales des aciers, en particulier des aciers à haute résistance (AHSS) tels que l'acier dual phase (DP). Malgré les efforts considérables déployés pour comprendre les mécanismes qui contrôlent la cinétique de formation de la ferrite, le rôle des éléments substitutionnels pendant la croissance de la ferrite et leur interaction avec l'interface de migration  $\alpha/\gamma$  restent peu clair. Plusieurs modèles ont été développés pour décrire la cinétique de croissance de la ferrite dans les systèmes ternaires et les systèmes d'ordre supérieur. Les modèles 'solute drag' ont été utilisés avec succès pour prédire la cinétique de transformation pour plusieurs solutés et à de nombreuses compositions et températures dans les systèmes ternaires. Cependant, l'extension de ce modèle aux systèmes d'ordre supérieur a mis en évidence un comportement complexe de l'interaction entre les différents éléments interstitiels et substitutionnels à l'interface. La validation des modèles développés nécessite une étude expérimentale de l'effet de la composition et de la température sur la cinétique de croissance. L'objectif de cette contribution est de présenter une méthodologie combinatoire à haut débit complète pour accélérer l'étude l'effet de la concentration des solutés sur la transformation austénite-ferrite. Il convient toutefois de noter que cette nouvelle méthodologie pourrait être utilisée pour étudier toute autre transformation de phase dans tout autre alliage métallique. L'essence de la méthodologie est de fabriquer des matériaux avec des gradients de composition macroscopiques, et d'effectuer des expériences in situ de diffraction des rayons X à haute énergie, résolues dans le temps et dans l'espace, pour enregistrer la cinétique de transformation de phases austénite-ferrite en de nombreux points de l'espace de composition. Des couples de diffusion contenant des gradients de soluté à l'échelle millimétrique et une teneur en carbone presque constante ont été générés en utilisant la présente méthodologie et utilisés pour étudier la cinétique de croissance de la ferrite à des températures intercritiques en utilisant des expériences in situ de diffraction des rayons X à haute énergie. Pendant 4 jours d'expériences, plus de 1500 cinétiques ont été mesurées pour différentes compositions et à différentes températures. Cet ensemble de données d'une taille sans précédent a été utilisé pour valider une version modifiée du modèle 'three-jump solute drag' pour les systèmes ternaires et quaternaires. Les calculs du modèle correspondent parfaitement à la cinétique de transformation expérimentale à toutes les températures étudiées et sur presque toutes les plages de composition étudiées de Si, Cr, Mn, Ni et Mo, contrairement aux résultats des modèles de paraéquilibre (PE) et de partitionnement négligeable à l'équilibre local (LENP). En outre, il a été démontré que l'étalonnage des paramètres thermodynamiques dans les systèmes ternaires reste valable dans les systèmes quaternaires, ouvrant la voie à la modélisation de la transformation dans les systèmes d'ordre supérieur.

Mots clés: Cinétique de croissance de la ferrite, méthodologie combinatoire, Technique du haut-débit, solute drag.

### Title: Development of compositional-gradient metallic alloys for combinatorial investigation of microstructures

#### Abstract:

The transformation of austenite into ferrite in steels is of considerable interest in controlling the final properties of steels, in particular Advanced High-Strength Steels (AHSS) such as Dual Phase (DP) steel. Despite tremendous efforts in understanding the mechanisms controlling ferrite formation, the role of substitutional elements during ferrite growth and their interaction with the migrating  $\alpha/\gamma$  interface remain unclear. Several models have been developed to describe ferrite growth kinetics in ternary and higher systems. The solute drag based models have been successfully used to predict kinetics for multiple substitutional solutes, compositions and temperatures in ternary systems. However, the extension of this model to higher order systems highlighted a complex behavior of the interaction between the different interstitial and substitutional elements at the interface. Validation of the developed models requires an experimental study of the effect of both composition and temperature on growth kinetics. The aim of this contribution is to present a complete combinatorial high-throughput methodology to accelerate the investigation of the dependency of ferrite growth kinetics on substitutional composition in alloy steels. It is noteworthy, however, that this new methodology could be used to study any other phase transformation in any other metallic alloy. The essence of the methodology is to fabricate materials with macroscopic composition gradients, and to perform timeand space-resolved in situ high-energy X-ray diffraction experiments to gather the austenite-to-ferrite phase transformation kinetics in many points of the compositional space. Diffusion couples containing millimeter-scale solute gradients and an almost constant carbon content were generated using the present methodology and used to study ferrite growth kinetics at inter-critical temperatures using *in-situ* high-energy X-ray diffraction experiments. During 4 days of experiments, more than 1500 kinetics were gathered for different compositions and at different temperatures. This dataset of unprecedented size was used validate a modified version of the three-jump solute drag model for both ternary and quaternary systems. The model calculations matched experimental transformation kinetics at all investigated temperatures and over almost all the investigated composition ranges of Si, Cr, Mn, Ni, and Mo, contrary to results from para-equilibrium (PE) and local equilibrium negligible partitioning (LENP) models. Additionally, it was demonstrated that the calibration of thermodynamic parameters in ternary systems held true in quaternary systems, paving the way towards modeling of the transformation in higher-order systems. **Keywords:** Ferrite growth kinetics, high-throughput methodology, combinatorial approach, solute drag.