



Computational metallurgy and changes of scale / Métallurgie numérique et changements d'échelle
Mesoscale simulations of the kinetics of solid–solid phase transformations: Selecting the relevant interfacial compositions for shape-preserved growth

Simulation à l'échelle mésoscopique de la cinétique des transformations de phases solide–solide : Le choix des compositions d'interface pour une croissance de forme constante

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ABSTRACT

A brief overview of the current state-of-the-art in choosing the interfacial compositions (or boundary conditions), for mesoscale, diffusion-controlled phase transformations, as practiced by the numerical metallurgy community, is presented. The physical processes that are currently thought to influence these values and the assumptions underlying the most common choices for the interfacial compositions are outlined. The need for a properly coupled, multiscale approach, that uses mesoscale simulation techniques to describe diffusion in the bulk phases, and atomistic simulation tools to describe the processes occurring within the interface (that influence the boundary conditions for the diffusion problem), is highlighted.

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RÉSUMÉ

On présente dans cet article une rapide revue de l'état de l'art sur la question du choix des conditions à l'interface (ou conditions aux limites) pour des transformations de phases contrôlées par la diffusion, modélisées à l'échelle mésoscopique. On décline les procédés physiques qui sont actuellement admis comme contrôlant ces compositions d'interface, et les hypothèses sous jacentes aux différents choix communément sélectionnés. On insiste sur la nécessité de coupler correctement, dans une approche multiéchelle, impliquant en particulier l'échelle mésoscopique pour la description des champs de diffusion, et l'échelle atomistique pour décrire les procédés spécifiques de l'interface.

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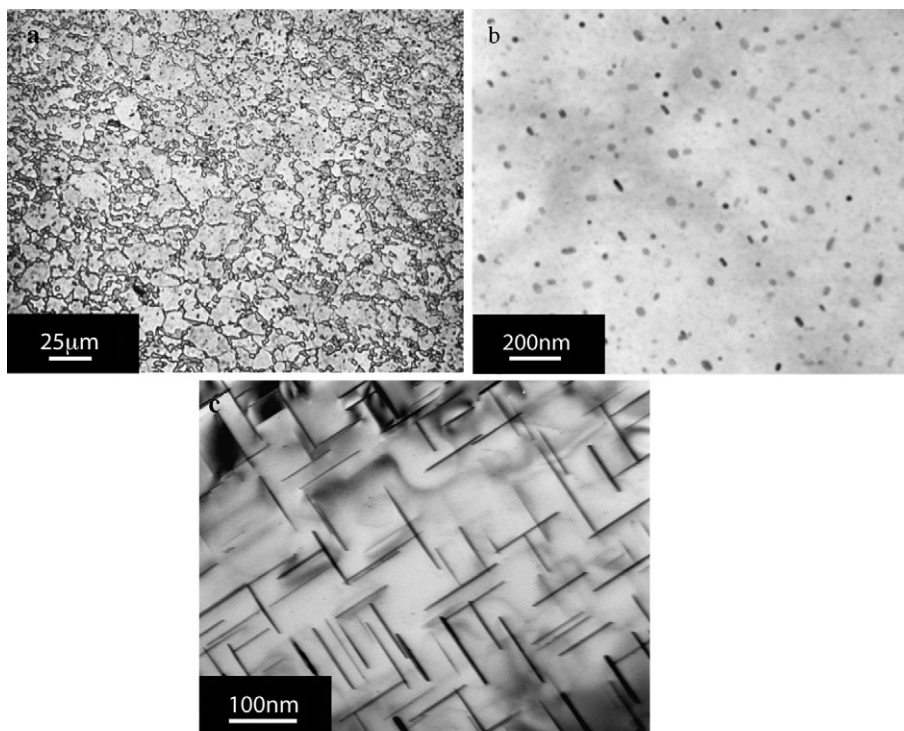


Fig. 1. (a) Optical micrograph of a dual phase (DP) steel showing the large ferrite (α) grains which have grown from the parent austenite (γ) phase. The smaller, darker etching phase is all that remains of the original parent phase. (b) Transmission electron micrograph (TEM) showing the precipitation of ~ 5 nm Cu-rich, relatively equiaxed precipitates in the ferrite matrix of an Fe–Cu alloy. (c) TEM micrograph showing the precipitation of plate-shaped Al_2Cu in an Al–Cu alloy.

Fig. 1. (a) Microscopie optique d'un acier « dual-phase » montrant les gros grains de ferrite (α) qui ont cru dans l'austénite (γ). Le fin contraste sombre est tout ce qui reste de la phase mère. (b) Microscopie électronique en transmission montrant la précipitation, à une échelle de 5 nm, d'une phase riche en Cuivre sous forme de précipités relativement équiaux dans une matrice de ferrite dans un alliage Fer Cuivre. (c) Microscopie électronique en transmission montrant la précipitation de plaquettes Al_2Cu dans un alliage aluminium–cuivre.

1. Introduction

The microstructures of most structural engineering alloys are the product of one or more solid–solid phase transformations. It is the interaction of dislocations and other defects with this microstructure that largely determines the mechanical properties. As a consequence, an understanding of, and ultimately a control over the phase transformations is the primary means to manipulate the properties of engineering alloys. These properties, it should be emphasized, may evolve during service as a result of the continued evolution of the microstructure, e.g. during use in a nuclear power plant or in a passenger aircraft.

Three examples of engineering alloy microstructures are shown in Fig. 1. Fig. 1a is an optical micrograph from a dual phase (DP) steel. The microstructure is characterized by a distribution of relatively equiaxed grains separated by boundaries across which there is crystallographic discontinuity. A small fraction of finer grains is also visible. The mechanical properties are largely controlled by the size distribution and mechanical properties of these grains. These grains form via a nucleation and growth process from a parent solid phase that is almost fully consumed by the reaction. Fig. 1b is a transmission electron micrograph from an Fe–Cu alloy. This microstructure is formed by the nucleation and growth of nanometer size spherical Cu particles (precipitates) from a parent Fe-rich solid phase. In this case the parent phase (matrix) is not fully consumed by the transformation. The mechanical properties depend on the strength of the Cu particles, their sizes and spacing, in this case ~ 5 nm and ~ 100 nm, respectively. A similar case is shown in Fig. 1c, taken from an Al–Cu alloy. In this case the precipitates (an intermetallic phase, Al_2Cu) exhibit a plate-shaped morphology with a well-defined crystallographic relationship to the Al matrix. The shape of the particles has a strong effect on the resulting mechanical properties, e.g. [1,2].

In each of the three cases illustrated in Fig. 1, the microstructure formation results from the nucleation and growth of one solid phase from another. In this contribution emphasis is placed on quantitatively describing the growth stage. In most cases, the growth of the new phase is accompanied by a change in chemistry that is mediated by diffusion in the solid state. Since diffusion occurs by individual atomic jumps in crystalline metals, it appears natural to appeal to atomistic simulation approaches to describe the growth process and how this depends on processing variables such as time, temperature and alloy chemistry. Clouet and Soisson [3] have discussed some of these atomistic approaches in their contribution to this volume. Since the atomistic approaches consider individual atomic movements, there are intrinsic computational limitations to

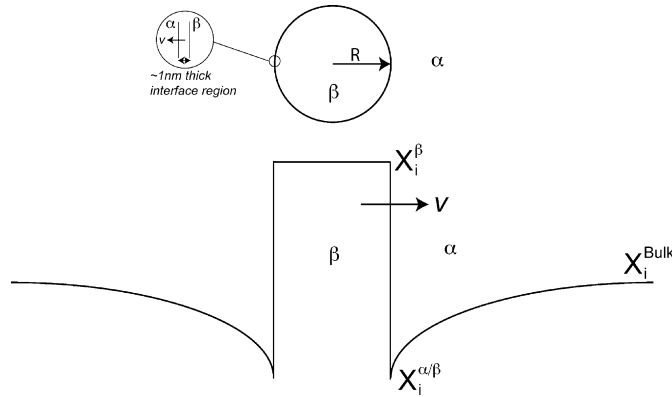


Fig. 2. Schematic illustration of the solute concentration profile around a solute-rich spherical β particle growing from a solute poor α phase.

Fig. 2. Schéma illustrant les profils de concentration autour d'un précipité sphérique de phase β riche en soluté croissant dans une matrice α pauvre en soluté.

the number of atoms and the number of atomic jumps that can realistically be considered. This translates to a limitation in both the time and length scales that can be considered. Whilst these approaches provide crucial contributions to the understanding of the processes governing the nucleation and growth of one solid phase from another at the very earliest stages of a transformation they are unable to currently describe the transformation kinetics over the time scales corresponding to typical thermal treatment times (e.g. ~ 12 h for a precipitation hardenable Al alloy) or to describe length scales large enough to be considered representative of a typical structural engineering alloy for the purposes of mechanical property determination (e.g. 1 mm^3).

As a result, a means of linking the observations at the atomistic scale to methods capable of simulating the kinetics of phase transformations at larger length and time scales is required. This need will be discussed further at the end of this contribution. The most common approaches in numerical metallurgy make use of Fick's continuum equations for diffusion to describe the mass transfer that accompanies the formation of one solid phase from another. Such approaches are capable of describing quantitatively the larger time and length scales required and are referred to as 'Mesoscale' simulation approaches in the microstructural simulation community.

In a few special cases, Fick's law for diffusion has been solved approximately for the moving phase boundary problem [4]. Clearly the shape of the new phase (the diffusion geometry) must be known in advance. An example is the growth of approximately spherical precipitates shown in Fig. 1b. If they remain spherical during growth, and are assumed to be non-interacting (i.e. the concentration of solute in the matrix far from the interface is unchanging), then their growth rate can be approximated by [5]:

$$\frac{dR}{dt} = \frac{D_i}{R} \frac{X_i^{\text{Bulk}} - X_i^{\alpha/\beta}}{X_i^{\beta} - X_i^{\alpha/\beta}} \quad (1)$$

dR/dt is the time rate of change of the radius of a particle of β phase of radius R , D_i is the diffusion coefficient of the rate-limiting diffusing species, X_i^{Bulk} is the bulk composition of solute element i , X_i^{β} is the concentration of solute element i in the growing β phase at the migrating interface, and $X_i^{\alpha/\beta}$ is the concentration of solute element i in the matrix α phase at the interface with the growing phase (Fig. 2).

Such an equation was used by Deschamps and Perez [6] in the preceding article to describe the growth kinetics of precipitates such as those shown in Fig. 1b. Similar equations can be written if the product phase grows with a planar boundary [5], or if the phase has a rod or plate shape [7–13] (e.g. Fig. 1c). Such cases are considered to be examples of 'shape-preserved growth'. If the shape of a growing phase evolves significantly during growth, as it does in many cases, then alternative approaches must be used that properly couple the description of the kinetics mediated by diffusion, and the change in phase shape, which influences the diffusion geometry. Finel et al. [14] discuss a particularly convenient approach for dealing with topological changes in the following contribution to this volume.

For diffusion mediated, shape-preserved growth, the kinetic problem basically reduces to choosing appropriate values for the boundary conditions of the diffusion problem, i.e. X_i^{β} and $X_i^{\alpha/\beta}$ in Eq. (1). These values correspond to the solute concentration at the interface between the growing and shrinking phases and are shown schematically for a phase forming with a larger solute content than the bulk alloy in Fig. 2.

This contribution attempts to provide a brief overview of the current state-of-the-art in choosing these interfacial compositions (or boundary conditions), as practiced by the numerical metallurgy community, the physical processes that are currently thought to influence these values and the assumptions underlying the most common choices.

2. 'Local equilibrium' interfacial conditions

The most common choice of interfacial conditions at the migrating phase boundary is to select the compositions that the phases would have under equilibrium conditions (i.e. stationary, planar interfaces). This is known as the local equilibrium assumption, and was used by Deschamps and Perez [6] in the preceding contribution. In many cases this assumption works well, so long as it takes into account the effect of the curvature of the interface (the capillarity effect [15,16]). However, there are many cases where the local equilibrium assumption does not work well and additional effects must be considered. Experimentally measured phase growth kinetics that are both faster (e.g. [17]) and slower (e.g. [18–20]) than those predicted by the local equilibrium assumption have been observed.

For the phase boundary shown schematically in Fig. 2 to migrate there are at least three physical processes that should occur:

1. There must be diffusion in the bulk phases. In the case shown in Fig. 2, there must be diffusion of solute towards the interface. This process is well described by Fick's law for diffusion and is the basis for the derivation of growth rate equations such as Eq. (1).
2. The atoms must rearrange from the crystal structure of the parent phase to that of the product phase as they traverse the boundary separating the two phases. Examination using high-resolution electron microscopy shows that the structural width of the boundary separating the product and parent phases is typically ~ 1 nm or less.
3. A net flux of solute from one side of the phase boundary to the other must occur so the required change in composition is realized. In the case shown schematically in Fig. 2, the thin slab of material in the parent phase at the interface with composition $X_i^{\alpha/\beta}$ must transform to material of composition X_i^β as it crosses the ~ 1 nm wide boundary.

Each of these three physical processes requires a driving force to proceed. The driving forces originate from the chemical potential differences of the different elemental species in the material. The local equilibrium assumption assumes that the chemical potential gradient for all species across the interface is zero. This implies that the driving force for processes 2 and 3 listed above is zero and that the microscopic processes controlling both the crystal structure and chemistry changes across the interface occur infinitely easily. Of course this is not true, and if the energy required for either of these processes occurring during phase boundary motion requires a significant driving force, then a deviation in interfacial conditions from the local equilibrium values would be expected. The problem is how to choose more appropriate interfacial conditions.

3. Deviations from local equilibrium

3.1. Interface friction (finite boundary mobility)

During the migration of a phase boundary separating phases of different crystal structures, a rearrangement of the atomic arrangements must occur across the interface. The driving force for this rearrangement is provided by the difference in chemical potential of the atomic species across the interface and this is a function of the interfacial compositions.

It may be expected that this structural rearrangement is easiest when the two phases are crystallographically similar and when the interface is migrating very slowly (allowing more time for the rearrangement to take place). It may also be expected that the ease of atomic rearrangement will depend on the local atomic arrangement at the boundary and this may vary substantially with the crystallographic orientation of the boundary. The kinetic parameter used to characterize the ease with which the structural rearrangement across the interface occurs is the boundary mobility (M). It is usually assumed that driving force required for the structural rearrangement ($\Delta G^{Structural}$) is proportional to the boundary velocity (v) and the proportionality constant is the reciprocal of the mobility (Eq. (2)):

$$\Delta G^{Structural} = \frac{v}{M} \quad (2)$$

The boundary mobility has the unfriendly units of $\text{mmol}/(\text{J}\cdot\text{s})$ or $\text{m}^4/\text{J}\cdot\text{s}$ and can be thought of as a kind of interface friction. The local equilibrium assumption for interfacial compositions assumes that the boundary mobility is infinite.

Unfortunately, a general theory allowing calculation of the phase boundary mobility is not currently available. During the last ten years, computer simulations using molecular dynamics have investigated the mobility of grain boundaries [21] but only recently is a general picture emerging [22,23]. Phase boundaries are yet to be considered. The development of a quantitative theory for phase boundary mobility, as a function of local crystallographic orientation, chemistry, crystal structures and driving force is a major challenge for numerical metallurgy in the coming decade.

The driving force for the structural rearrangement in Eq. (2) is a function of the interfacial compositions: $\Delta G^{Structural} = f(X_i^\beta, X_i^{\alpha/\beta})$. Eqs. (1) and (2) are two expressions for the phase boundary velocity as a function of a number of kinetic parameters and the interfacial compositions. The key aspect is the interfacial compositions must be chosen so that evaluation of the boundary velocity according to Eqs. (1) and (2) is the same. The result of incorporating a finite interface mobility is that the kinetics will be slower than those predicted according to the local equilibrium assumption.

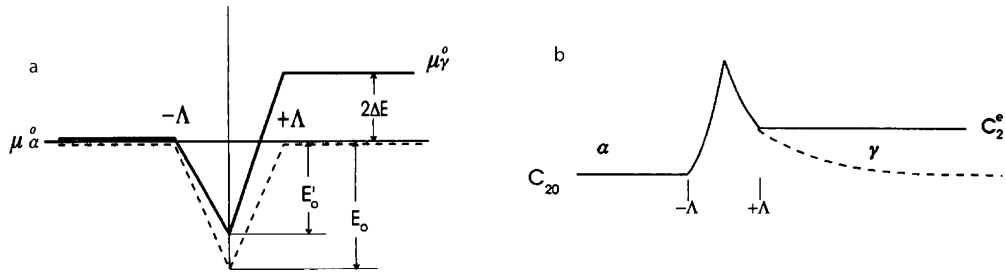


Fig. 3. (a) The interaction profile of solute 2 with the phase boundary of thickness 2Δ , shown as a full line, in this case for a solute that partitions in equilibrium to the α phase. The effective depth of the potential well is E_o^l . (b) The equilibrium substitutional solute (2) profile through the interface is shown as a solid line. The solute is attracted to the interface and preferentially segregates to the γ phase in equilibrium. The broken line represents a possible solute field in front of a slowly moving boundary, such that the solute is not partitioned by the transformation [28].

Fig. 3. (a) Interaction du soluté avec l'interface de largeur 2Δ , montré en ligne continue, dans le cas d'une partition en équilibre avec la phase α . La profondeur effective du puit de potentiel est E_o^l . (b) La ligne continue donne le profil d'équilibre du soluté en substitution (2) au travers de l'interface. Ce soluté est préférentiellement attiré par l'interface et ségrège à l'équilibre dans la phase γ . La ligne pointillée donne un profil de soluté devant un interface migrant lentement, sans partition du soluté au cours de la transformation [28].

3.2. Dissipation of energy due to the mass transport across the interface ('Solute Drag')

As a boundary separating phases of different chemistries migrates, a net flux of solute from one side of the phase boundary to the other must occur so that the required change in composition is realized. In the case shown schematically in Fig. 2, the thin slab of material in the parent phase at the interface with composition $X_i^{\alpha/\beta}$ must transform to material of composition X_i^β as it crosses the ~ 1 nm wide boundary. This mass transfer requires a driving force and this is provided by the chemical potential difference of the transferring species across the interface. Under circumstances where the transferring species interacts strongly with the migrating interface (e.g. a tendency to segregate to the interface exists) a large driving force may be required. This may, in principal, result in large deviations in interfacial conditions from those predicted by local equilibrium and growth kinetics much slower than those expected.

The first attempt to theoretically describe this effect arose not from a consideration of migrating phase boundaries but rather from observations of grain boundary behavior. It was experimentally observed that the kinetics of grain boundary motion in ultra pure metals could be reduced by many orders of magnitude by minute additions of impurities [24]. Such effects are now known to be relatively general and became known as the 'impurity drag effect' and subsequently the 'solute drag effect'. The first theoretical treatment was due to Lucke and Detert [24] but since this time, two treatments have come to dominate the literature, namely, Cahn's 'force' approach [25] and Hillert and co-worker's 'dissipation' approach [26,27]. Cahn considered only the interaction of impurities with a migrating grain boundary whereas Hillert applied his formulation to both migrating grain and phase boundaries (although only phase boundaries where the concentration of solute, but not chemical potential, was equal on both sides of the boundary). Purdy and Brechet later applied Cahn's approach to phase boundaries [28].

The 'force' and 'dissipation' approaches both consider the migrating boundary as a continuum, across which the solute diffusivity and interaction energy vary continuously. An example wedge-shaped interaction profile for solute that preferentially segregates to an α/γ phase boundary is shown in Fig. 3a. The equilibrium solute profile across such a boundary is shown in Fig. 3b.

The solute profile across a moving boundary can be calculated by solving Fick's law of diffusion across the migrating boundary assuming descriptions of the interaction energy (e.g. Fig. 3a), the solute diffusivity across the boundary and the solute thermodynamics (none of which are known with certainty). Example calculations from the work of Purdy and Brechet [28] are shown in Fig. 4.

Cahn [25] and Purdy and Brechet [28] argue that an impurity atom in the interface will be attracted to the center of the boundary with a force dE/dx (Fig. 3a). The solute atom exerts an equal and opposite force on the boundary and the net force can be found by summing the forces from each of the atoms over the entire boundary. Clearly, for a stationary boundary with a symmetric equilibrium solute concentration profile, the number of atoms pulling the boundary to the left and the number pulling it to the right are nearly equal and the net force sums approximately to zero. For the asymmetric profiles shown in Fig. 4, the magnitude of the force pulling the boundary to the left is greater than that pulling it to the right and a significant net drag force can result.

Hillert's interpretation of the retarding effect of the solute is different from Cahn. Hillert argues that the retarding effect of the solute corresponds to work done by the boundary [26,27]. He identifies this work as a dissipation of Gibbs free energy (ΔG^{diss}) due to the irreversible nature of diffusion. This can be summed across the interface and in the region ahead of the interface ($x > 1$ in Fig. 4). In other words, the retarding effect of the solute arises wherever there is a deviation of the concentration from the equilibrium value. Hillert has discussed the differences between his and Cahn's approaches and the conditions under which they are expected to give the same result [29].

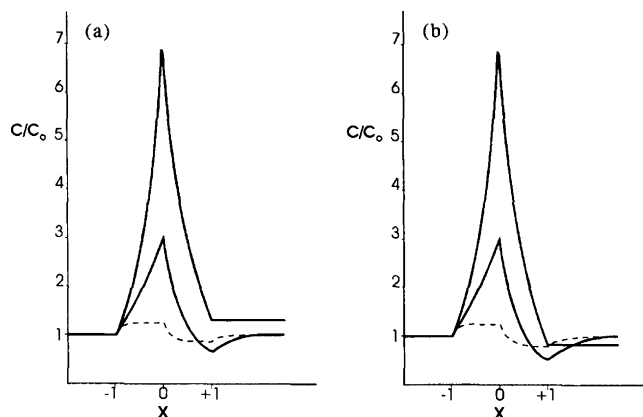


Fig. 4. A series of solute profiles through the moving interface; the profiles become flatter with increasing boundary velocity. The three dimensionless velocities portrayed here are $v = 0.0001$ (close to equilibrium), $v = 1.8$ (maximum drag) and $v = 10$ (the broken lines, a high velocity). Part (a) corresponds to a γ -stabilizing alloying element and (b) corresponds to an α -stabilizing element [28].

Fig. 4. Une série de profils de soluté au travers d'une interface en migration (a) pour un élément stabilisant la phase γ , (b) pour un élément stabilisant la phase α . Les vitesses normalisées correspondent à une situation proche de l'équilibre ($v = 0.0001$), à trainage de soluté maximal ($v = 1.8$), et à très forte vitesse ($v = 10$).

The key point is that part of the driving force is used up if a 'solute drag' effect on the migrating phase boundary exists and this must come from a chemical potential difference of the solute across the interface (i.e. it depends on the interfacial conditions). Since the solute drag effect depends on interface velocity, then this is a third process (in addition to diffusion in the bulk phases and a finite interface mobility), for which the choice of interfacial conditions must lead to a consistent interface velocity. Odqvist et al. have attempted to capture each of these three effects to identify a consistent interface velocity for the growth of ferrite from austenite in Fe–C–Ni steels [30]. Hillert has discussed the effects of solute drag and finite interface mobility on the interfacial compositions in detail and the interested reader is referred to the original publications for details [31–35].

3.3. Large differences in solute diffusivities (e.g. steels): 'ParaEquilibrium' interfacial conditions

The most heavily used of the engineering alloys are steels and the phase transformations that occur during the development of steel microstructures have attracted attention since the advent of metallurgy as a field. Steels contain both carbon, which is located interstitially in the Fe lattice, and other solutes such as Mn, Si, Cr, W, Ni, etc. that substitute with Fe on the same crystal lattice. The result is that steels contain multiple solutes that diffuse with different mechanisms: the substitutional solutes diffuse through a vacancy exchange mechanism on the Fe lattice and carbon (and sometimes nitrogen) diffuses by interstitial migration. A distinguishing feature is that the diffusivities of carbon and the substitutional solutes may differ by a factor of 10^6 . At relatively low temperatures ($< \sim 600^\circ\text{C}$), where many important solid–solid phase transformations occur in steels, the substitutional solutes may only make a couple of atomic jumps during the time frame of a given phase transformation. The implications of such low solute mobility on the ability for local equilibrium conditions to be maintained at a migrating phase interface were realized early by Hultgren [36]. After all, how can local equilibrium for both C and a substitutional solute be maintained at a migrating interface if the substitutional solute atoms cannot move!

Hultgren proposed the concept of 'ParaEquilibrium' as a type of constrained equilibrium. Hillert later considered in detail the thermodynamic characteristics of ParaEquilibrium [26,37]. It assumes that the compositions of the substitutional atoms across the migrating boundary are identical (i.e. no diffusion of the substitutional elements occurs in the bulk phases) and that the interfacial carbon compositions are selected so that the chemical potential difference across the interface for both carbon and for the *average* of the substitutional elements is zero (Eq. (3)). The basic idea is that since the substitutional solute cannot move, their individual chemical potentials have no meaning and they behave as if they are a single 'average' element.

$$\begin{aligned} \mu_C^\beta &= \mu_C^\alpha \\ \sum_i X_i^\beta \cdot \mu_i^\beta &= \sum_i X_i^\alpha \cdot \mu_i^\alpha \end{aligned} \quad (3)$$

μ_C^j is the chemical potential of carbon in phase j at the moving boundary, μ_i^j is the chemical potential of substitutional element i in phase j at the moving interface and X_i^j is the mole fraction of element i in phase j at the moving interface.

ParaEquilibrium should not be considered as a source of deviation from local equilibrium interfacial conditions in the same sense as that arising from a finite interface mobility or solute drag effects. It is rather an alternative 'constrained' type of equilibrium [26,37]. The effect of finite interface mobility or solute drag effects can be incorporated into treatments

of phase growth that use a ParaEquilibrium formulation. ParaEquilibrium interfacial compositions are commonly employed in simulations of the kinetics of phase transformations in steels, particularly at low temperatures, where the assumption about immobility of the substitutional alloying elements is expected to be reasonable. Some authors have even developed models to describe transitions between ParaEquilibrium and local equilibrium interfacial compositions during phase growth in steels and this is a current active area of research [30,38]. The general trend is that ParaEquilibrium is observed at low temperatures and short times which is consistent with the relative ‘immobility’ of substitutional elements under these conditions.

A recent experimental observation of Zurob et al. [17] is worth highlighting. These authors measured very accurately the growth kinetics of the ferrite phase from the austenite phase in Fe–C–Mn steels using a decarburization approach. They illustrate that at temperatures in the range of 755–775 °C, the growth kinetics predicted assuming local equilibrium interfacial conditions show almost perfect agreement with the experimental measurements. However, at higher temperatures (815–841 °C), the measurements agree with predictions assuming ParaEquilibrium interfacial conditions. The observations of Zurob et al. are exactly the opposite of those expected theoretically. Zurob et al. [39] propose a simple model to explain their observations based on a preferred interaction between the solute and the migrating phase boundary. This work illustrates that the story is by no means closed with respect to the choice of the relevant interfacial compositions at migrating phase interfaces and much work is required to develop a consistent approach that captures all of the effects observed experimentally and is faithful to the atomic structure of the migrating boundary.

4. The need for a multiscale approach

As can be seen from the micrographs shown in Fig. 1, the microstructures of typical engineering alloys range in length scales up to at least $\sim 100 \mu\text{m}$, and often much more. For the purposes of understanding the mechanical properties of these materials, faithful phase transformation simulations at this length scale or greater are often required. Furthermore, the time scales required for the formation of typical microstructures may range from several minutes to many hours. Unfortunately, such length and time scales are beyond the current capabilities of atomistic simulation approaches and this is the reason for the use of the ‘mesoscale’ techniques that use continuum descriptions of the diffusion process. The basic problem, at least for ‘shape-preserved growth’ is then choosing the relevant interfacial compositions. We have attempted to illustrate in this contribution that the interfacial compositions required for the mesoscale simulations depend critically on the atomistic processes occurring within the interface (which may be only a few atomic spacings wide) as it migrates. The problem is intrinsically multiscale. So far, these processes have largely been described using continuum descriptions (e.g. solute drag) but the input parameters such as solute diffusivity across the interface, spatial variation of the interaction energy with the boundary, boundary mobility, etc. are not known with sufficient certainty for a critical comparison with experiment to be performed.

It may appear more natural to use atomistic simulation techniques to describe the processes occurring within the interface, and mesoscale simulation techniques to describe the bulk diffusion process. This multiscale approach certainly has its difficulties, but these authors feel that this is probably the most fruitful avenue to pursue to minimize the assumptions made in the continuum approaches for the interfacial processes and to provide some indication of the input parameters for the interfacial processes that are currently not known, all whilst hopefully remaining faithful to the atomic structure of the boundary and how this may depend on boundary velocity, chemistry and driving force.

5. Conclusions

The physical processes accompanying the migration of a phase boundary separating solid phases of differing chemistry are summarized from the perspective of the numerical metallurgy community. The assumptions underlying the most common choice for the interfacial compositions at the migrating boundary, ‘local equilibrium conditions’, are outlined and the effects of finite boundary mobility and a preferred interaction between the diffusing solute and the boundary on the interfacial conditions are outlined. An attempt has been made to emphasize that the interfacial compositions must be chosen so that the interface velocities predicted by the individual microscopic mechanisms controlling a) the diffusion of solute in the bulk phase, b) the structural rearrangement across the interface and c) the change in chemistry across the interface, give the same interface velocity.

The concept of ‘ParaEquilibrium’ introduced by Hultgren in 1947, in response to the limited mobility of substitutional solute additions in steels at low temperatures, is summarized as a further possible source of deviation from local equilibrium interfacial conditions.

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