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Finite element simulation of interfacial segregation in dilute alloys

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Abstract The finite element software Comsol is used to simulate surface or grain boundary segregation in dilute alloys. The model computes simultaneously the evolution of interfacial concentration and diffusion in the bulk. The solute exchange between bulk and interface is governed by Darken's equation. The model is able to reproduce thermodynamic and kinetic aspects of the phenomenon, in particular the saturation segregation level and the short-time segregation kinetics expressed by the McLean approximation. It is also able to reproduce experimental trends in the case of surface segregation of sulphur in a Ni superalloy. In the case of the grain boundary segregation of impurities (P or S) in engineering alloys, the present approach provides a practical tool, as it can be coupled to other finite element simulations (heat transfer and/or mechanics). Thus, it becomes possible to predict the risk of synergetic segregation and thermomechanical damage during service or processing (forging, welding,...).

Introduction

Interfacial segregation consists of accumulation, on a particular interface (free surface, grain or interphase boundary...), of a solute element, usually present in very small concentrations in the material, either deliberately added in extremely small quantities to metallic alloys (boron, zirconium, rare-earth elements...), or occurring as contamination by impurities that cannot be completely removed (sulphur, phosphorus...) [1].

The technological consequences of interfacial segregation are of great importance, as surface and grain boundary chemistry govern many industrial phenomena, such as the intermediate and high temperature strength and ductility of engineering alloys, as well as their oxidation resistance (intergranular corrosion, oxide scale adhesion), the growth and adhesion of thin films in the electronic industry and of blade coatings in aeroengines, catalytic activity in the chemical industry or in fuel cells, etc.

The interfacial segregation phenomenon has been widely investigated in the past decades, both from the thermodynamic and kinetic points of view [2–13]. For instance, the general theory predicts that the equilibrium segregation level decreases when temperature increases. However, because the kinetics of segregation is mainly diffusion-controlled, actual segregation is usually very slow—if not impossible—at low temperatures. This competition between equilibrium and kinetic aspects can explain, for instance, the classical loss of ductility of nickel base alloys in the temperature range 600–1,000 °C, due to sulphur grain boundary segregation. It is therefore useful to try and model interfacial segregation kinetics.

In the first part of this paper, the classical theories of interfacial segregation are briefly presented, as well as existing approaches to describe the phenomenon with a mathematical form (analytical or numerical). To our present knowledge, no finite element approach exists to model interfacial segregation. The aim of the paper is to demonstrate that a user-friendly commercially available finite element code, Comsol [14], formerly known as Femlab,

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can be used to implement in a simple manner the basic differential equations of the interfacial segregation phenomenon. The developed model will then be tested and validated by comparison to experiments and to basic physical principles. The second novelty of our work is to solve simultaneously the segregation, heat transfer and mechanical equations, for any component submitted to complex thermal and/or thermo-mechanical treatments. This is useful, for instance, to predict the cracking tendency of alloys during service or industrial processes like heat treatment, forging, rolling, welding, etc.

The classical theory of interfacial segregation

Thermodynamics of segregation

In this section we describe the classical thermodynamic laws for the interfacial segregation of a solute in a metallic alloy. The aim is to calculate the equilibrium concentration of a solute in a grain boundary as a function of temperature and bulk concentration of the solute. Because we are interested in segregation of deleterious elements in metallic alloys that are common substitutional solutes (e.g., S, P, Sn, Te...) and present at very low concentration, it will be implicitly supposed in the following that these two hypotheses are fulfilled. For more details about the thermodynamics of segregation the comprehensive review of Lecjeck and Hoffman can be consulted [2].

Interfacial segregation of a solute I in a matrix M can be represented as a reversible chemical reaction by Eq. (1):

$$M^{\phi} + I \leftrightarrow M + I^{\phi}, \tag{1}$$

where the superscript Φ indicates that the term refers to the interface. The thermodynamic equilibrium is given by:

$$\frac{X^{\phi}_{\mathrm{eq}}}{X^{\phi}_{\max} - X^{\phi}_{\mathrm{eq}}} = \frac{X^{\mathrm{v}}}{1 - X^{\mathrm{v}}} \exp\left(-\frac{\Delta G_I}{RT}\right) \tag{2}$$

where:

- $\Delta G_I = \Delta H_I^{\mathrm{o}} - T\Delta S_I^{\mathrm{o}} - 2\alpha_{IM}(X^{\phi}_{\mathrm{eq}} - X^{\mathrm{v}})$ is the free energy for segregation,
- X^{ϕ}_{eq} is the equilibrium atomic fraction of solute in the interface,
- $X^{\phi}_{\max}$ is the maximum fraction of sites in the interface that can be occupied by the solute atoms, it is equal to 1 if the segregation is perfectly substitutional and lower if for geometrical reasons all sites cannot be occupied by the solute,
- X^{v} is the bulk atomic fraction of free solute, “free” meaning that for example solutes trapped in precipitates, or yet segregated are not taken into account,
- ΔH_I^{o} and ΔS_I^{o} are, respectively, the enthalpy and entropy for segregation of I in the interface,
- α_{IM} is the interaction energy between solute and matrix in the interface, with this formulation a positive value denotes an attractive interaction,
- R is the gas constant and T is the temperature.

By substituting $X^{\phi}_{\mathrm{eq}}/X^{\phi}_{\max}$ by θ_{eq}, the equilibrium coverage ratio of the interface, and assuming that $1 - X^{\mathrm{v}} \approx 1$ in the case of low solute concentration, Eq. (2) simplifies to:

$$\frac{\theta_{\mathrm{eq}}}{1 - \theta_{\mathrm{eq}}} = X^{\mathrm{v}} \exp\left(-\frac{\Delta G_I}{RT}\right) \tag{3}$$

Although the interaction energy between matrix and solute atoms, α_{IM}, can be relatively high at grain boundaries compared to surfaces, we will neglect it in the following discussion to avoid numerical complications. Actually, if the interaction term is not equal to 0, it implies a circular reference in Eq. (3), i.e., θ_{eq} depends on ΔG_I, which itself depends on θ_{eq} through X^{ϕ}_{eq}.

In Fig. 1, the equilibrium coverage ratio of grain boundaries is plotted versus temperature for three different bulk atomic fractions of the solute in the bulk, and for a chosen value of $\Delta G_I = -80$ kJ/mol. The coverage ratio decreases with temperature and increases with solute bulk atomic fraction.

Diffusion and segregation kinetics

Interfacial segregation kinetics is controlled by bulk diffusion. We consider a metal–solute binary system in which solute can segregate to a given type of interface (surface or grain boundary). Let us imagine the situation where there is

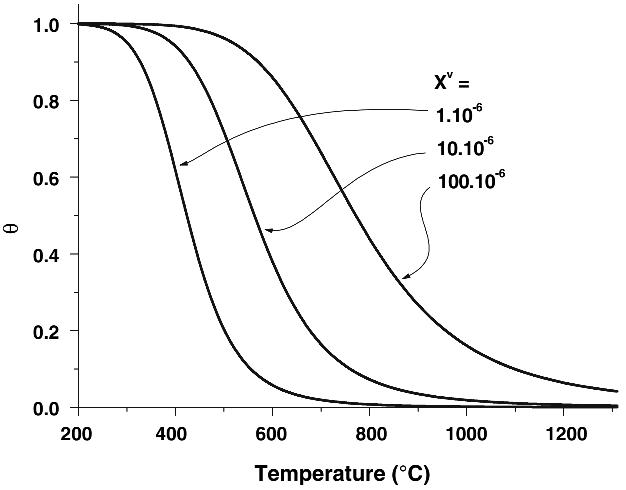

Fig. 1 Equilibrium segregation level, or coverage ratio, as a function of temperature for a given segregation free energy and three different bulk solute atomic fractions

no solute segregation at $t = 0$, which means that the solute atomic fraction is the same in the bulk and in the interface. When annealing the material at a temperature T where diffusion is possible, the solute will diffuse from the bulk to the interface until the equilibrium is reached between bulk and interface solute atomic fractions, according to Eq. (2) or (3). The solute concentration profile in the bulk during the annealing is illustrated in Fig. 2.

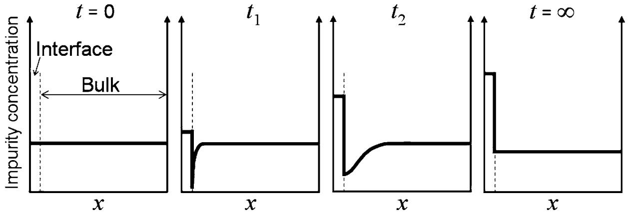

Fig. 2 Typical evolution of solute concentration profiles during interfacial segregation

The McLean analytical model

What is usually called "segregation kinetics" is the evolution of the interfacial solute concentration with time. In 1957, McLean [3] proposed an analytical model based on the resolution of a diffusion equation (Fick's second law). In order to get an analytical solution, he had to assume that the interfacial solute concentration is always proportional to the bulk concentration immediately below the interface (which is in fact not true). He obtained the well-known expression:

$$X^{\phi}(t) = X_0^{\phi} + (X_{\text{eq}}^{\phi} - X_0^{\phi}) \times \left(1 - \exp\left(\frac{f^2 Dt}{\delta^2 \beta^2}\right) erfc\left(\frac{f\sqrt{Dt}}{\delta\beta}\right)\right) \tag{4}$$

where:

- $X^{\phi}(t)$ is the interfacial solute atomic fraction at time t,
- X_0^{ϕ} is the interfacial solute atomic fraction at $t = 0$,
- f is equal to 1 for surface segregation (solute diffuses from one side of the interface only) and 2 for grain boundary segregation (solute diffuses from both sides of the interface),
- D is the solute diffusion coefficient in the bulk,
- δ is the interface thickness,
- β is called the enrichment factor. In the McLean approach, β is considered not to depend on time, and is defined as:

$$\beta = \frac{X_{\text{eq}}^{\phi}}{X^{\text{v}}} \tag{5}$$

X^{v} is considered to be the same before and after interfacial segregation, which is the case for the semi-infinite medium considered here. X^{v} is therefore taken equal to the initial bulk atomic fraction of solute, X_0^{v}.

Assuming that $X_0^{\phi} \approx 0$, Eq. (4) becomes for short times:

$$X^{\phi}(t) = \frac{2fX_0^{\text{v}}}{\delta}\sqrt{\frac{Dt}{\pi}} \tag{6}$$

Interfacial segregation and desegregation

Two examples of atomic fraction versus time plots for segregation obtained from Eq. (4) are given in Fig. 3. The first example illustrates a surface segregation process ($X_0^{\phi} < X_{\text{eq}}^{\phi}$ at $t = 0$) and the second one a surface desegregation process ($X_0^{\phi} > X_{\text{eq}}^{\phi}$ at $t = 0$).

It can be observed on Fig. 3 that, while the interfacial solute atomic fraction X^{ϕ} is lower than the equilibrium atomic fraction X_{eq}^{ϕ} (case ①), the solute diffuses from the bulk to the interface until X^{ϕ} reaches X_{eq}^{ϕ} (segregation process). On the other hand, if $X^{\phi} > X_{\text{eq}}^{\phi}$ (case ②), solute atoms go from the interface into the bulk and diffuse away from the interface (desegregation process) until X^{ϕ} reaches X_{eq}^{ϕ}.

Interfacial segregation and temperature

From the kinetic point of view, an increase of temperature will increase the solute diffusion coefficient and will make the solute interfacial segregation faster, as predicted by Eq. (4). On the other hand, from the thermodynamics point of view, Eq. (2) or (3) predicts that the interfacial solute atomic fraction at equilibrium X_{eq}^{ϕ} will be lowered if temperature is increased. This situation is illustrated on Fig. 4

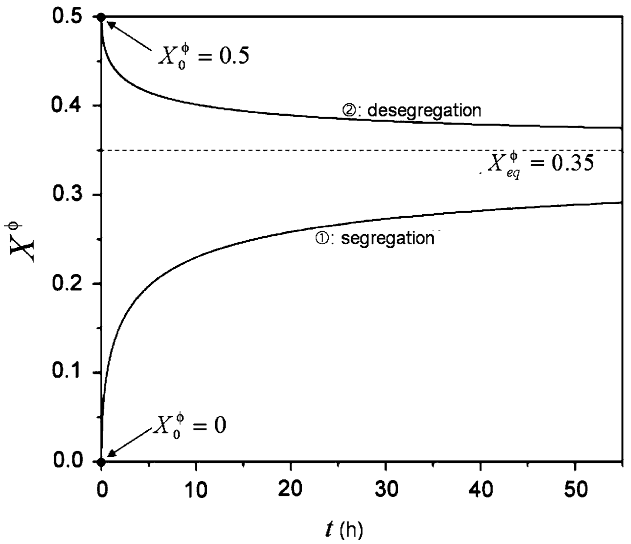

Fig. 3 Examples of segregation and desegregation kinetics plotted using Eq. (4) with $X_{\text{eq}}^{\phi} = 0.35$, $f = 1$ (surface segregation), $D = 1.2 \times 10^{-11}$ cm^2 s^{-1}, $\delta = 2.5$ Å, β=17,500 and X^{v}=20 at ppm

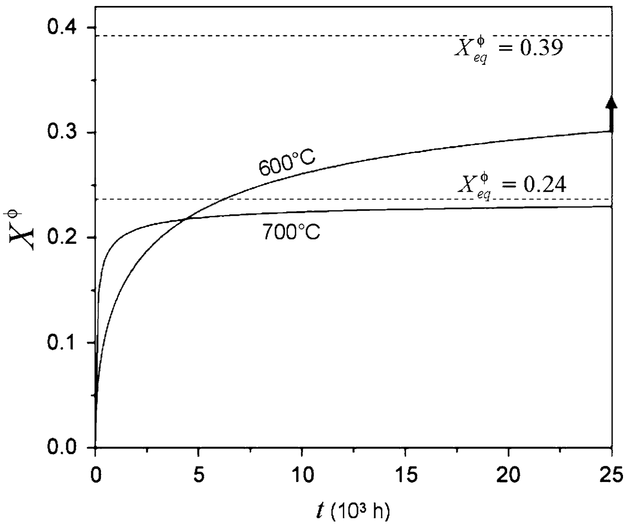

Fig. 4 Kinetics of grain boundary segregation in nickel at 600 and 700 °C, plotted using Eq. (4) with $X^{\phi}_{\mathrm{eq}} = 0.39$ at 600 °C, $X^{\phi}_{\mathrm{eq}} = 0.24$ at 700 °C, $f = 2$ (grain boundary segregation), $D = 2.16 \times 10^{-13}$ cm^2 s^{-1} at 600 °C, $D = 3.66 \times 10^{-12}$ cm^2 s^{-1} at 700 °C, $\delta = 5$ Å, $\beta = 78{,}000$ at 600 °C, $\beta = 48{,}000$ at 700 °C, X^{v}=5 at ppm

concerning grain boundary segregation at 600 and 700 °C in a model system: for short times, the slope of the segregation kinetics is higher at 700 °C than at 600 °C but the equilibrium interfacial solute atomic fraction is lower at 700 °C ($X^{\phi}_{\mathrm{eq}} = 0.24$) than at 600 °C ($X^{\phi}_{\mathrm{eq}} = 0.39$). X^{ϕ}_{eq} was calculated at 600 and 700 °C using Eq. (3) with ΔG_I = 98 kJ mol^{-1} and $X^{\phi}_{\max} = 0.5$.

The limitations of the McLean analytical model

The McLean analytical model of Eq. (4) gives a realistic description of interfacial segregation kinetics only in very simple situations:

- temperature does not depend on time (in other words X^{ϕ}_{eq} and D do not depend on time)
- D does not depend on position in the bulk,
- the bulk concentration is homogeneous at $t = 0$,
- segregation has negligible effect on the bulk concentration,
- only one species segregates,
- there is no interaction between atoms in the interface,
- ...

In many cases, the situation is more complicated and it is no longer possible to describe interfacial segregation kinetics by an analytical equation such as Eq. (4). That is why some numerical models for interfacial segregation have been proposed [4–7]. One of the most reliable is the one proposed by Du Plessis and van Wyk [7]. It is based on the Darken "chemical diffusion" approach [8] of the interfacial segregation problem, that makes it possible to reproduce "uphill" diffusion, i.e., solute diffusing from a low concentration region (the bulk) to a high concentration region (the interface). In this "Darken—du Plessis" model, the atom fluxes are expressed as a function of chemical potential gradients and not as a function of concentration gradients. The Darken—du Plessis model was very successfully tested in various complicated situations: surface segregation during linear programmed heating [9], surface segregation with a strong surface interaction parameter [10], surface segregation in a multicomponent system [11], surface segregation during ion sputtering [12], surface segregation with inhomogeneous bulk concentrations [13]...

However, its implementation is not straightforward for the end user, e.g., in industry, as it requires fine programming skills and it is not readily available or implementable in commercially available software. Additionally, interfacial segregation is mainly of interest in applications where it may cause a severe embrittlement of the material, e.g., in the case of sulphur in nickel alloys or phosphorus in steels, which means that the user is almost always simultaneously interested in the thermal and mechanical stress states. Therefore, the present paper aims at implementing, in a rather simple way, segregation thermokinetics in a user-friendly commercial software, Comsol, which can also compute thermomechanical stresses.

Finite element modelling of interfacial segregation

The finite element software

The chosen tool for the treatment of interfacial segregation phenomena is the finite element software Comsol [14] (formerly known as Femlab). Its main advantage is its simplicity to deal with multiphysics problems when equations are formulated as partial differential equations (PDE), with the possibility to solve simultaneously several problems involving strong coupling (heat transfer, structural mechanics, diffusion, electromagnetics...). The various problems solved in a single model can even be of different dimensionality (volume, surface, line, and point).

Coupling of diffusion with interfacial segregation equations

In the present case, interfacial segregation kinetics is treated by coupling two equations. In the material bulk, represented by a 1D domain, the solute diffusion is treated by solving the classical Fick's laws, which are already implemented in a specialised module of the Comsol software. Inputs are the initial solute atomic fraction, X_0^{v}, or concentration in the bulk, C_0^{v}, expressed in mol/m^3, and the solute diffusion coefficient, D. At each time step of the problem resolution, X^{v} and C^{v} are related via the atomic concentration in the bulk. D can be entered either as a numerical value or as an expression of temperature (for instance when the segregation model is coupled to a heat transfer model), as:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{7}$$

where Q is the activation energy for diffusion, D_0 is the pre-exponential factor, T is the temperature and R is the gas constant. The boundary condition, expressed at the location of the segregation interface, is the solute flux, J, between the bulk and the interface, which corresponds to the model proposed by Darken [8]:

$$J = -\frac{D \cdot C^{v}(\phi)}{RT}\frac{\Delta\mu}{\Delta x} \tag{8}$$

$C^{v}(\phi)$ is the concentration of the solute in the bulk at the vicinity of the interface. $\Delta\mu/\Delta x$ is the chemical potential gradient between the interface and the adjoining bulk [7]: $\Delta\mu$ is defined as $(\mu_I^{\phi} - \mu_M^{\phi}) - (\mu_I^{v}(\phi) - \mu_M^{v}(\phi))$, with μ_I^{ϕ} and μ_M^{ϕ} being, respectively, the chemical potentials of the solute and matrix metal in the interface, and $\mu_I^{v}(\phi)$ and $\mu_M^{v}(\phi)$ being, respectively, the chemical potentials of the solute and matrix metal in the bulk at the vicinity of the interface. This flux is physically an exchange of solute between the two adjacent atomic planes, hence Δx is to be taken equal to the interatomic plane spacing, δ, characteristic of the considered material. This gives:

$$J = -\frac{D \cdot C^{v}(\phi)}{\delta}\frac{\Delta\mu}{RT} \tag{9}$$

$\Delta\mu$ is given by:

$$\Delta\mu = \Delta G_I + RT \ln\frac{\theta(1 - X^{v}(\phi))}{X^{v}(\phi)(1-\theta)} \tag{10}$$

$X^{v}(\phi)$ is the mole fraction of the solute in the bulk at the vicinity of the interface, and θ is the coverage ratio.

Combining Eqs. (9) and (10) yields the expression of the flux to be calculated by the finite element software:

$$J = -\frac{D \cdot C^{v}(\phi)}{\delta}\left(\frac{\Delta G_I}{RT} + \ln\frac{\theta(1 - X^{v}(\phi))}{X^{v}(\phi)(1-\theta)}\right) \tag{11}$$

It should be noted at this point that the solute flux will tend towards zero when the equilibrium coverage ratio, expressed by Eq. (3), is approached.

On the other hand, the evolution of the interfacial concentration of solute, C^{ϕ}, is computed in a separate domain (a single point) of the model, localised on the interface. It is calculated through another differential equation, using the so-called "weak" mode of the software:

$$\frac{dC^{\phi}}{dt} = -f \cdot J \tag{12}$$

with f is a coefficient equal to 1 for a surface and to 2 for a grain boundary (to account for the diffusion fluxes coming from both adjacent crystals). C^{ϕ} is related to the coverage ratio θ via the density of accessible segregation sites on the interface, $C_{\max}^{\phi}$, expressed in mol/m^2, by:

$$\theta = \frac{X^{\phi}}{X_{\max}^{\phi}} = \frac{C^{\phi}}{C_{\max}^{\phi}} \tag{13}$$

It is important to note that both the boundary condition of the bulk diffusion model and the solution of the interfacial model depend on each other's solution, which cannot be solved by conventional approaches as this generates a "circular reference"; conversely the "weak" mode of Comsol is dedicated to such tasks. The software allows to create progressive mesh (Lagrange quadratic elements), with small elements near the interface (of the order of the interatomic distance), where huge concentration gradients are expected. Typically, several tens or hundreds of elements and/or degrees of freedom are sufficient to obtain smooth solutions within computing times of the order of a few seconds on 3 GHz clock computers. The time-dependent direct inversion solver "UMFPACK" is used.

A number of different simulations is performed, in order to check that the physics of the phenomenon are well described (isothermal segregation, continuous heating or continuous cooling segregation, comparison between surface and grain boundary segregation kinetics) and to reproduce the results of actual experiments (successive isothermal treatments in a Ni-base superalloy).

Results and discussion

Isothermal surface segregation

The first validation concerns the simple isothermal segregation of sulphur in nickel, with no initial segregation, and the following data: $X_0^{v} = 20 \times 10^{-6} = 20$ ppm (corresponding to $C_0^{v} = 3.045$ mol/m^3), $\Delta G_I = -80$ kJ/mol, $D_0 = 10^{-4}$ m^2/s, $Q = 130$ kJ/mol, and $T = 800$ K. The maximum surface concentration, $C_{\max}^{\phi}$, is taken equal to 1.34×10^{-5} mol/m^2, considering segregation on a (100) atomic plane. Indeed, in nickel alloys, it is admitted that the maximum density of segregation sites does not exceed half of the atomic density of the considered plane ($X_{\max}^{\phi} = 0.5$)

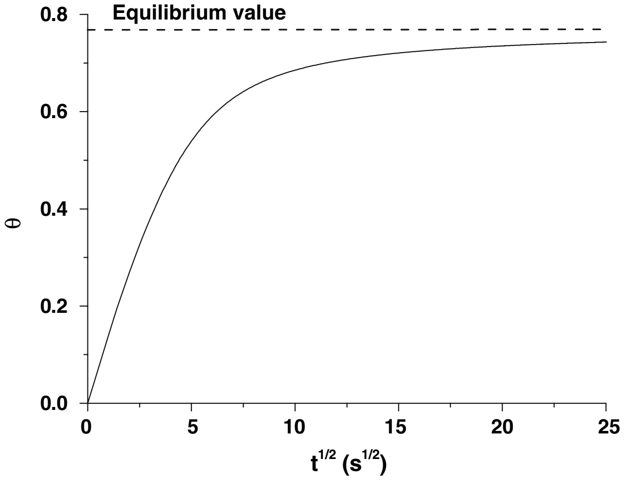

Fig. 5 Simulated evolution of θ as a function of the square root of time in the case of an isothermal segregation at 800 K

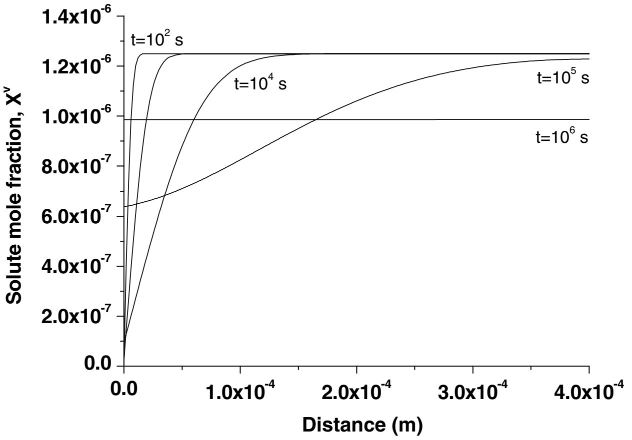

Fig. 6 Evolution with time of the solute atomic fraction profile in the bulk. The surface is on the left of the figure

[15]. The evolution of the coverage ratio, θ, is presented in Fig. 5 as a function of the square root of time. The two major features of isothermal segregation are verified: (i) the coverage ratio tends towards the equilibrium value given by Eq. (3), i.e., 0.77 in the present case, and (ii) for short times the coverage ratio is well described by McLean's approximation of Eq. (6), and is proportional to the square root of time. The slope of the graph for short times is then given by:

$$\frac{d\theta}{d\sqrt{t}} = \frac{2f}{\delta}\frac{X_0^{\mathrm{v}}}{X_{\max}^{\phi}}\sqrt{\frac{D}{\pi}} = 2f\frac{C_0^{\mathrm{v}}}{C_{\max}^{\phi}}\sqrt{\frac{D}{\pi}} = 2\frac{C_0^{\mathrm{v}}}{C_{\max}^{\phi}}\sqrt{\frac{D}{\pi}} \qquad (14)$$

In the present case, there is excellent agreement between the modelled and the above "theoretical" slope (0.146 $s^{-1/2}$).

Because segregation kinetics is normally limited by solute diffusion in the bulk, it is also interesting to observe the bulk solute concentration profiles during the segregation phenomenon. Figure 6 shows the evolution of solute atomic fraction profiles as segregation proceeds. At short times there is a huge driving force for segregation and the solute is strongly depleted near the surface. Then, progressively and when the coverage ratio tends towards its equilibrium value, the bulk atomic fraction profile tends towards a flat distribution, as expected by thermodynamics. This is again consistent with basic physical principles (see for instance Fig. 2).

Surface segregation and desegregation during continuous heating

In real problems, such as service behaviour or processing of alloys, isothermal situations are rather rare, and complex thermal histories are often encountered. Our modelling approach should thus be able to predict the segregation behaviour in such cases. To assess this, non-isothermal simulations are performed. The first case is surface segregation (and desegregation) during continuous heating at different rates. All parameters are the same as in "Isothermal surface segregation" section, except the temperature, which is increasing continuously, with different heating rates (0.15 K/s, 4 K/s and 100 K/s). The evolution of the coverage ratio as a function of temperature is presented in Fig. 7, for the three different heating rates. In all cases, the coverage ratio first remains very low, which is due to the extremely sluggish diffusion, although the thermodynamic equilibrium value is close to one. Then, as temperature increases, solute diffusion accelerates and θ increases. Finally, when diffusion becomes fast enough,

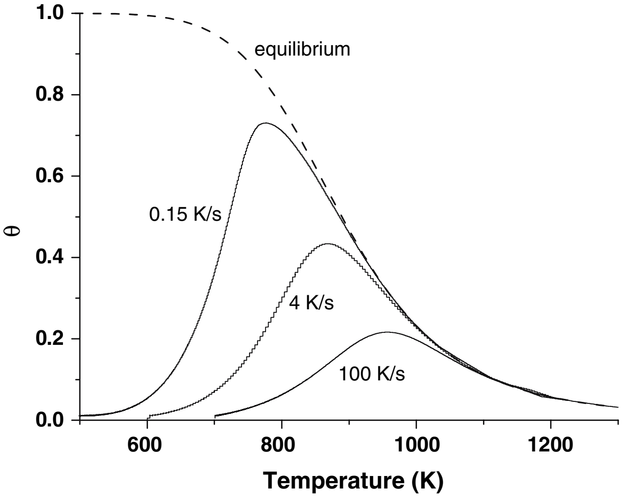

Fig. 7 Evolution of the coverage ratio as a function of temperature in the case of continuous heating with three different heating rates. The equilibrium curve is given for comparison purposes

there is almost a “real-time” adjustment of the coverage ratio to its equilibrium value, which therefore decreases as dictated by thermodynamics. The influence of the heating rate is in agreement with theoretical expectations: when the heating rate decreases, the process gets progressively closer to equilibrium conditions, even for low temperatures where diffusion is very slow.

Surface segregation during continuous cooling

Such important kinetic effects can also be encountered during cooling from high temperature. Simulations of surface segregation during continuous cooling have been performed with the same parameters as above, with cooling rates of −0.15 K/s, −4 K/s and −100 K/s. Results are presented in Fig. 8. In all cases, at the beginning of the process the temperature is high enough to activate fast diffusion, so that the coverage ratio follows the equilibrium curve. Then, as temperature decreases, solute diffusion slows down and the coverage ratio progressively deviates from equilibrium. Eventually, for low temperatures, diffusion virtually stops and the coverage ratio saturates to a fixed value, even if the thermodynamic equilibrium value is close to one. Once again, this dynamic phenomenon gets closer to equilibrium when the rate of temperature change decreases.

Experimental assessment in the case of sulphur surface segregation in a Ni-base superalloy

The final assessment test consists in the simulation of segregation in a real alloy, and in its comparison with experimental measurements. The latter come from published results, made by in situ Auger Electron Spectroscopy during high temperature surface segregation of sulphur in a highly alloyed nickel-based single crystal superalloy [13]. Experimental details can be found in the above reference, although some features need to be repeated. Sulphur segregation was determined on a (001) plane surface, in an alloy with an initial atomic fraction $X_0^{\mathrm{v}} = 1.6$ ppm. Three successive isothermal heat treatments were performed under ultra-high vacuum, for three different durations and temperatures (25.6 h at 700 °C, then 100.8 h at 750 °C and finally 53.5 h at 800 °C) with intermediate removal of the segregated layer by ion etching. It is important to note that no annealing was made between the three isothermal segregation treatments, so that, when starting the second and third treatments, the bulk sulphur concentration profiles were those resulting from the previous treatments, and not flat. This peculiarity has been taken into account in our modelling approach: the bulk initial conditions of the simulations at 750 and 800 °C were the bulk final conditions of the simulations at 700 and 750 °C, respectively, in both cases the surface concentration was reset to zero. All parameters were set according to these experimental characteristics. The three remaining parameters, ΔG_I, D_0 and Q, were adjusted by curve fitting. The best fit is obtained with $\Delta G_I = -137{,}600$ J/mol, $D_0 = 3.31$ m^2/s and $Q = 274{,}000$ J/mol. The modelled and measured evolutions of the coverage ratio, for the three successive heat treatments, are presented in Fig. 9 as functions of time. An excellent agreement is obtained, with values of the diffusion coefficient similar to those reported in reference [13] (although some differences are obtained between the adjusted values of D_0 and Q, the values of D are very close in the investigated temperature range).

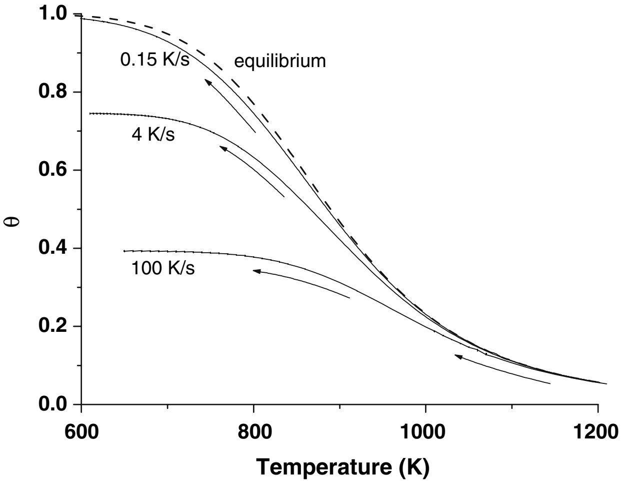

Fig. 8 Evolution of the coverage ratio as a function of temperature in the case of continuous cooling with three different cooling rates. The equilibrium curve is given for comparison purposes

Applications

An important practical consequence of solute segregation is the modification of interfacial cohesion by segregants in real alloys, such as grain boundary embrittlement by sulphur in nickel-base alloys or by phosphorus in steels, or the beneficial effect of grain boundary strengthening by carbon or boron. The first consequence is that it would be useful, in most cases, to simulate grain boundary segregation instead of surface segregation. However, the latter can be useful to determine, experimentally, thermodynamic and kinetic aspects of segregation, as in the previous section. The second important issue would be to couple segregation simulation to the modelling of actual service conditions or manufacturing processes (like rolling, forging, welding, heat treatment...). These two aspects are dealt with in the next sections.

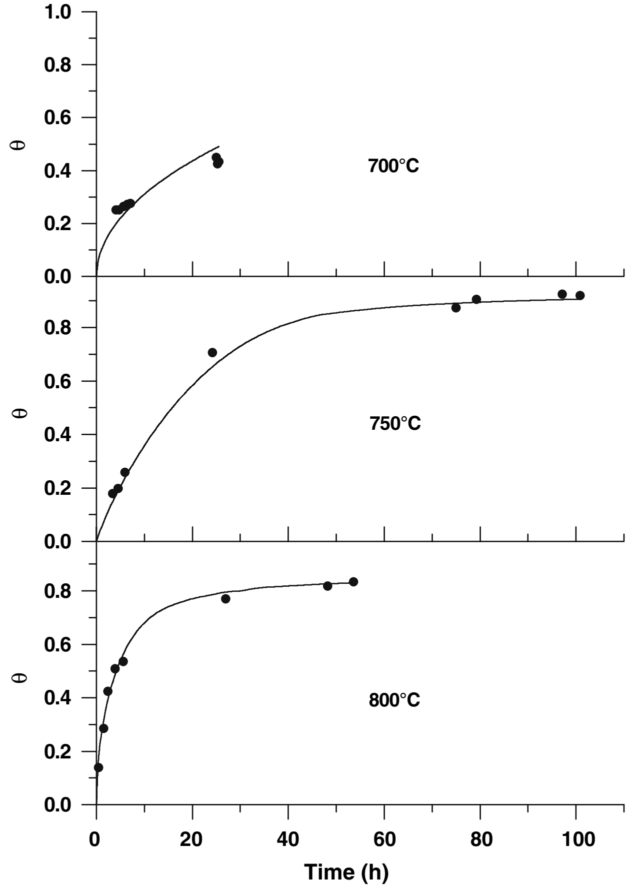

Fig. 9 Comparison between measured (*symbols*) and predicted (*solid lines*) evolution of the surface coverage ratio of sulphur as a function of time on a nickel-base superalloy (three successive isothermal treatments at different temperatures, with intermediate surface etchings)

Grain boundary segregation

To simulate grain boundary segregation, the coefficient f of Eq. (12) is taken equal to 2, as:

$$\frac{\mathrm{d}C^{\phi}}{\mathrm{d}t} = -2 \cdot J \tag{15}$$

This allows, by solving diffusion in a single domain, to take into account solute fluxes reaching the interface from both adjacent grains. A comparison of surface and grain boundary segregation kinetics is presented in Fig. 10, for the Ni-base alloy of "Experimental assessment in the case of sulphur surface segregation in a Ni-base superalloy" section and in the case of an isothermal treatment at 700 °C. For comparison purposes, the segregation free energy has been taken equal for surface and grain boundary segregations. The coverage ratio is plotted as a function of the square root of time, to check the validity of short-time kinetics. The main expected features are verified: (i) in both cases the coverage ratio saturates at the equilibrium value predicted by thermodynamics; and (ii) the initial slope is doubled in the case of grain boundary segregation, which is given by:

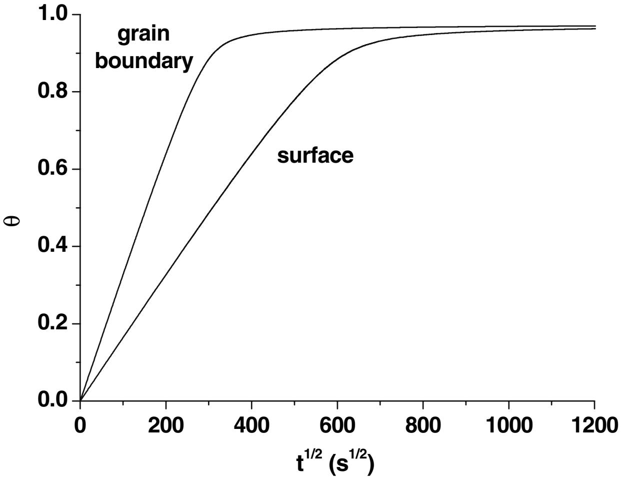

Fig. 10 Comparison between simulated surface and grain boundary sulphur segregation kinetics at 700 °C in a commercial nickel base alloy

$$\frac{\mathrm{d}\theta}{\mathrm{d}\sqrt{t}} = 2f\frac{C_0^{\mathrm{v}}}{C_{\max}^{\phi}}\sqrt{\frac{D}{\pi}} = 4\frac{C_0^{\mathrm{v}}}{C_{\max}^{\phi}}\sqrt{\frac{D}{\pi}} \tag{16}$$

This is once more consistent with theoretical expectations.

Effect of grain refinement on grain boundary segregation

The effect of grain size on grain boundary segregation is discussed in this section. Actually, a way to decrease grain boundary segregation in polycrystalline materials is to refine the microstructure by reducing the grain size. The characteristics of sulphur grain boundary segregation of "Surface segregation and desegregation during continuous heating" are considered, with a surface atomic density of 3.1×10^{-5} mol/m^2. An isothermal heat treatment is simulated at 800 °C. Evolution of interfacial segregation with time is followed for four different grain sizes (1 mm, 100, 10 and 1 μm). Results are presented in Fig. 11: the smaller the grain size, the lower the grain boundary coverage ratio. This is due to a stronger depletion of the solute in the bulk as the grain size is decreased. Indeed, when the grain size decreases, there is a more important grain boundary surface to be covered by the solute, resulting in lower solute coverage. This finally yields to a stronger solute depletion

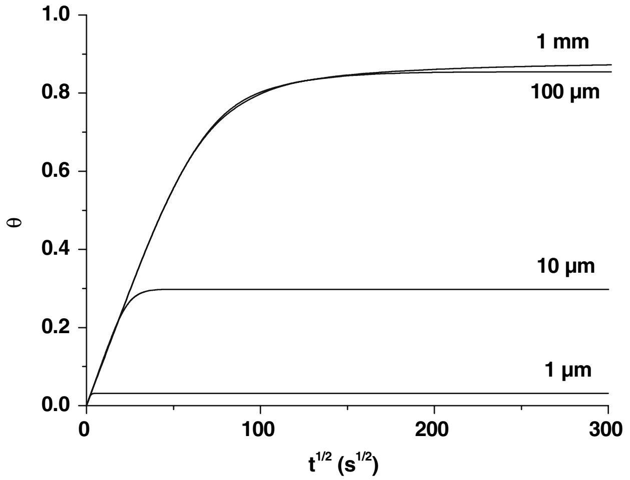

Fig. 11 Comparison between simulated grain boundary sulphur segregation kinetics at 800 °C, in a commercial nickel base alloy, for four different domain (grain) sizes

in the bulk, therefore to a lower value of X^v, and to a shift in the equilibrium value of θ_{eq}, as given by Eq. (3).

Multiphysics coupling: application to industrial cases

In the case of exposure to actual service conditions, or in the case of industrial processing of alloys like hot working, welding or heat treatment, complex thermal histories can be encountered, which has a great influence on both the segregation and desegregation cycles, hence on material properties: high temperature loss of ductility, weld cracking in the heat affected zone, degradation of creep resistance, etc. Such thermal conditions can already be simulated by most standard finite element codes, such as Comsol, and it would be useful to calculate both the evolution of temperature and of the resulting segregation level in any point of a given component.

An example is given below, in the case of grain boundary sulphur segregation during heat treatment of a nickel-base alloy ingot (0.3 m in diameter). The annealing heat treatment consists of 12 h at 1,250 °C, followed by air cooling at room temperature. Both heating and cooling are achieved through an effective surface heat transfer coefficient of 50 $\mathrm{Wm^{-2}\,K^{-1}}$. Alloy properties are the following: specific heat 450 $\mathrm{J\,kg^{-1}\,K^{-1}}$, thermal conductivity 12 $\mathrm{W\,m^{-1}\,K^{-1}}$, density 8,200 $\mathrm{kg/m^3}$, Young's modulus 220 GPa, Poisson's ratio 0.2, thermal expansion coefficient $13 \times 10^{-6}\ \mathrm{K^{-1}}$. Both heat transfer and mechanical simulations (in elastic plane strain conditions) were performed. The temperature history of any given point can be used, *via* a so-called "extruded variable" (in our case temperature), as an input for the segregation model. As this example is given for illustrative purposes only, the characteristics of sulphur grain boundary segregation of "Experimental assessment in the case of sulphur surface segregation in a Ni-base superalloy" section are considered; they will be assumed to be representative of common Ni-base alloys. It should be noted that the temperature history, extracted *in a single point* of the whole component, is applied to a separate micrometric domain, supposed to account for a representative microstructural element (e.g., a grain or dendrite in the case of superalloys), where sulphur diffusion and interfacial segregation are solved. The software solves simultaneously the two multiphysics problems (heat transfer and mechanics on the one hand; sulphur diffusion and grain boundary segregation on the other hand), in two different domains (the macrometric component on the one hand; and a microstructural element, representing what happens at the chosen point of the component, on the other hand).

Some illustrative results are presented on Fig. 12, showing the calculated evolutions with time of temperature, first principal stress (which is likely to cause cracking), and coverage ratio in a point chosen 4 cm below the ingot surface. During heating, due to localised surface heating, thermomechanical stresses develop in the material,

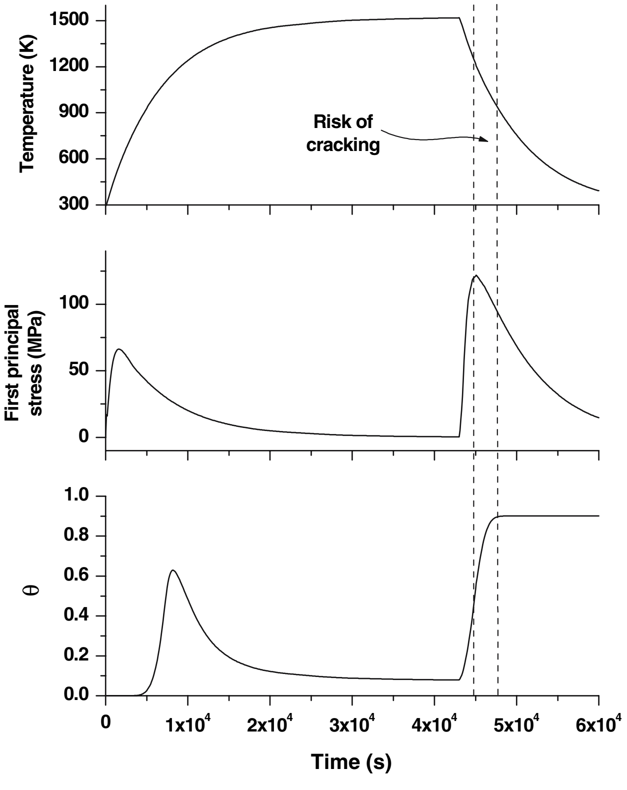

Fig. 12 Predicted simultaneous evolution of temperature, first principal stress and sulphur coverage ratio, at a point situated near the outer surface, during the annealing heat treatment of a nickel base alloy ingot

but reach a maximum value before the coverage ratio is sufficiently high to cause any noticeable embrittlement. Then, as temperature increases further, thermal homogeneity is obtained throughout the ingot, associated with zero stress and with a strong desegregation. Finally, during cooling, both important stresses and coverage ratios are reached simultaneously (with still relatively high temperatures), which could represent a severe risk of cracking.

Conclusions and perspectives

A new computational approach, based on the use of a user-friendly finite element code, has been developed to simulate interfacial segregation kinetics in dilute alloys. It has been verified, by comparison to experiment and to basic physical principles in simple cases, that the model is able to simulate in an accurate manner both the thermodynamic and kinetic aspects of the phenomenon. It can be used either in the case of surface or grain boundary segregation, for complex thermal histories, even for curved initial concentration profiles.

From a practical point of view, equations can be easily implemented in the Comsol software, even for non-specialists of finite elements. Additionally, it has been shown on a simple example that the model can be coupled to classical heat transfer and mechanical simulations, which are already available in the software, to predict the cracking tendency of metallic alloys during service or during industrial processes like forging, welding or heat treatment.

However, at present, only areas exhibiting simultaneously high temperatures, high stresses and high levels of segregation can be identified. It would be useful to predict actual cracking from the knowledge of the dependence of grain boundary cohesion (strength) on temperature and segregation level. This is a real challenge from a fundamental point of view, and neither a satisfactory model nor experimental evidences exist.

Also, it would be interesting to include in the finite element model the variation of the segregation free energy with temperature, i.e., to take into account both the enthalpy and entropy contributions, as defined in “Thermodynamics of segregation” section. Once again, the main difficulty is that data would be required to fit additional parameters to the experiment.

Another perspective would be to take into account the interaction energy between solute and matrix in the interface, α_{IM}, which represents a double challenge: (i) to determine its value, which requires again to fit an additional parameter to data, and (ii) to solve the problem numerically. Indeed, introducing an interaction term in the expression of the free energy has a major mathematical consequence: the system can become bi-modal in a given range of temperatures, which involves on the one hand that two equilibrium solutions can exist at the same time, and on the other hand that extremely steep (“instantaneous”) variations in the segregation level may occur. Both features are usually not easily dealt with by finite element methods.

Finally, problems involving simultaneously two or more segregating species (for instance S and P in nickel alloys) should be addressed, since rather similar equations can be used. In this case two additional equations would need to be solved for each additional segregant, one for diffusion of the species in the bulk, and one for its interfacial segregation. Depending on cases, a coupling between the individual problems would be necessary, either under the form of a site competition (taking into account the fact that the total coverage ratio is equal to the sum of the individual values), or under the form of an interaction between species (in which case, for instance, a species may start to segregate only if another one is already present in sufficient concentration in the interface). If the former case would not pose, a priori, any particular numerical problem, the latter case would probably raise numerical problems of the same nature as those coming from an interaction term in single-segregant cases. These issues will be addressed in future work.

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