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Atomistic Modeling of Kinetics in Intermetallics

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Abstract. Phenomenological treatments have been widely used for modeling diffusion-controlled phenomena. There are however cases where such treatments are difficult to handle, either because they require unknown parameters (like transfert coefficients across an interface) or because of the complexity of the dynamics (e.g. displacement cascades in a concentrated alloy under irradiation). An alternative modeling procedure is provided by atomistic simulations. After a brief review of the latter, we will illustrate their application through two problems: the segregation induced by irradiation at sinks in concentrated alloys and the roughening of interfaces in an alloy under plastic deformation or under irradiation.

1. INTRODUCTION

Diffusion-controlled phenomena often play an important role on the long term stability of an alloy. The assessment of the life time of nuclear reactor vessels is a typical example: the shift to higher temperatures of the ductile-to-brittle transition temperature of these ferritic steels may be due, at least partially, to the precipitation of minor elements like copper (for a recent discussion see [1]), although other mechanisms such as irradiation-induced segregation at boundaries can also be important.

In such situations, phenomenological models are often difficult to parametrize and to use. From an atomistic point of view, a diffusion-controlled evolution of the microstructure in a closed system is solely governed by the thermally activated motion of point defects: the knowledge of the nature of the mobile point defects and their jump frequencies is all the information required for predicting the ageing of a microstructure. Even in the simplest situations where only vacancies need be considered, getting this information is a challenge since the vacancy jump frequencies depend strongly on the local environment of the vacancy, e.g. on the local chemistry (composition, chemical order) and the local structure (close to dislocation, a surface...). Furthermore non-local effects coming for instance from stress fields will also enter into play. When systems are driven far from equilibrium by an external forcing (e.g. alloys under irradiation or plastic deformation) the situation can become even more difficult because additional point defects must be considered (such as interstitials) or because new dynamics are introduced by the external forcing (replacements and displacements events under irradiation, glide of dislocations under plastic deformation).

Despite these difficulties, the use of a simplified atomic modeling is already of a great help in many situations of interest in materials science. After a brief description of this simple kinetic atomistic model and its statistical treatments in section 2, we will give two examples of its application: the mixing of immiscible elements forced by plastic deformation (which is relevant for ball milling experiments) in section 3; and the segregation induced by irradiation in concentrated alloys under irradiation in section 4.

2. SIMPLE KINETIC ATOMIC MODEL

We briefly recall here the simplified atomic kinetic model that has been used extensively [1-9] and reviewed in refs. [10,11]. The first simplification is to restrict the applications to cases where stress effects can be neglected and where all transformations take place on a single crystallographic structure (i.e.

restricting to coherent interfaces). It is then adequate to describe the system by the occupancy of lattice sites on a rigid lattice. Vacancies simply correspond to vacant sites, while for interstitials specific assumptions must be made concerning their stable configurations (they usually form dumbbells in metallic alloys) and their migration mechanisms.

The jump frequency of a defect to a neighboring site is computed in the framework of rate theory: this frequency is the product of an attempt frequency and a thermally activated exponential in which enters the activation barrier for that particular jump. This activation barrier is estimated using a broken bond model: it is the energy required to remove the jumping species from its environment minus the energy recovered when the jumping species is at the saddle point position. Different expressions are possible for this last contribution, the saddle point energy; in the simplest case, it is taken as a constant. Such activation barriers contain information both on the thermodynamics and the kinetics of the alloy. The timescale of the evolution is set through the pre-exponential term. For a binary alloy, one is left with a small set of parameters (typically from 5 to 8) which can be fitted using physical properties of the elements and the alloy (such as cohesive energies, enthalpy of mixing, vacancy migration energies...); see ref. [1] or [7] for application to specific systems.

Various simulation techniques can be used for building a time evolution of the system. The more detailed ones rely on a kinetic Monte-Carlo algorithm: this retains all the information at the microscopic level. A residence time algorithm makes it possible to follow the evolution of the system as a function of physical time instead of Monte-Carlo steps. Furthermore this algorithm is easily extended to non-equilibrium situations where one may want to introduce a second dynamics at a controlled rate (number of events per real second) (e.g. ballistic jumps for systems under irradiation or shift of atomic planes for systems under plastic deformation). See refs. [1], [9] or [10] for more information about this algorithm. The example discussed in section 3 has been obtained using this algorithm.

When one is mainly interested in following the evolution of average quantities like chemical order parameters, it is possible to perform mean-field averages of the microscopic variables and to construct mean-field kinetic descriptions. The simplest and, indeed, a very common one is based on a Bragg-Williams approximation (the "point approximation") leading to equations often called rate equations. Better descriptions are obtained by taking into account more correlation functions. A generic framework for deriving these different levels of approximation is provided by the Path Probability Method (PPM) introduced by Kikuchi [12] (see [13] for comprehensive discussion of its variational aspect and for the link between various mean-field approximations). Such mean-field approximations are particularly helpful to introduce the non-conservative character of point defects, with explicit description of sources and sinks (such as free surfaces). The example discussed in section 4 will emphasise this point.

We now turn to two illustrations of the above methods.

3. KINETIC ROUGHENING OF INTERFACES UNDER SHEAR

The work described here has been published in refs. [9,14]. It was motivated by experiments showing that ball milling can force immiscible elements to be mixed through their spinodals to solid solutions: such is the case (for instance) for Cu-Fe [15] or Cu-Co [16] alloys. Monte-Carlo simulations were performed for a binary alloy on a Face Centred Cubic lattice exhibiting a miscibility gap (with a critical temperature $T_c=1573$ K) where atoms can move by either of two mechanisms acting in parallel: by thermally activated exchange with a vacancy or by shift of atomic planes due to dislocation gliding in $\{111\}$ planes.

It is shown in fig. 1 that keeping the temperature constant ($T=400$ K here) and increasing the rate of shearing, γ_{sh} , leads to an evolution of steady-states from two-phase systems (fig. 1a) to nearly random solid solutions (fig. 1c). One remarkable feature is that interfaces become rough under shear and that this kinetic roughening may account for the refined morphologies observed by Scanning Electron Microscopy by many authors (see for instance [15,16]). The simulations also predict that at intermediate shearing rates (fig. 1b) it is possible to stabilize mesoscopic structures with refined microstructures. Experiments have been undertaken to check this prediction. Notice that these last microstructures do not have any counterpart in the equilibrium phase diagram of this alloy. These features illustrate the fact that phase stability cannot be studied in such a driven system from only equilibrium thermodynamics. In fact approaches based on stability analysis of dynamical systems have been developed and shown to be useful for these situations [10].

Figure 1: Typical (111) cut at steady-states for (a) $\gamma_{sh} = 1 \text{ s}^{-1}$, (b) $\gamma_{sh} = 10^3 \text{ s}^{-1}$ and (c) $\gamma_{sh} = 10^5 \text{ s}^{-1}$; temperature was kept constant at $T=400 \text{ K}$. The simulation cell contains $64 \times 64 \times 64$ atoms (from ref. [9]).

4. IRRADIATION-INDUCED SEGREGATION AT SURFACES

This example is part of the thesis work of Y. Grandjean and partially published in ref. [7]. In alloys under irradiation, permanent fluxes of point defects are sustained towards sinks such as free surfaces or interfaces. The coupling between point defect fluxes and chemical species fluxes may induce a modification of the composition field, as first demonstrated by Anthony [17] and by Okamoto and Wiedersich [18]. In austenitic stainless steels, this leads to a chromium depletion at the grain boundaries, and this depletion is suspected to favour stress corrosion cracking in core components of Pressurised Water Reactors.

Figure 2 : Amount of surface segregation, $s(t)$, (see refs. [7,19] for the definition) as a function of the irradiation time and for different irradiation temperatures. The open symbols correspond to calculations performed for a flux of 4×10^{-4} displacement per atom per second, the filled symbols correspond to the experiments from [19]: a/ for a $\text{Ni}_{90}\text{Cu}_{10}$ composition ; b/ for a $\text{Ni}_{40}\text{Cu}_{60}$ composition. Notice the inversion of segregation as a function of time as the sign of $s(t)$ changes (from ref. [7]).

Many models have been proposed to explain radiation-induced segregation; however, these models do not describe kinetics and thermodynamics in the system at the same level of approximation (see [7] for a discussion of these models). Following the model discussed in the first part, Grandjean et al. [7] have proposed a new model, based on rate equations for heterogeneous systems (here a one-dimensional system

made of up to two thousand atomic planes). Since it is essential to retain the non-conservative character of the point-defects, chemical species and point defects local concentrations are treated as variables, and the rates of production, recombination and elimination at sinks for each species are calculated. Furthermore, a new boundary condition has been derived which allows for the thermal production of vacancies. As a result, this model can describe equilibrium and non-equilibrium segregations on the very same footing. It has been applied to the Cu-Ni system, successfully predicting an inversion of segregation under irradiation: at equilibrium, surfaces are enriched in copper because of the lower surface tension of this element, while under irradiation surfaces are observed to be enriched in nickel [19]. As seen from fig. 2, with the same set of parameters for two compositions and three temperatures, a very good agreement is found with the experimental data, for the amount of segregation as well as for the kinetics. Only one adjustable parameter was used, the cohesive energy of copper. The experimental results are correctly reproduced by just allowing vacancies to contribute to segregation, contrary to what has been obtained from others models [19]. In the simulations, the nickel enrichment at the surface results from the lower exchange rate between nickel atoms and vacancies, as compared to the exchange rate between copper atoms and vacancies (inverse Kirkendall effect).

5. CONCLUSION

Kinetic models or simulations based on atomistic processes are most useful when evolutions of microstructure are too complex for descriptions by phenomenological theories. Detailed informations about atomic jump mechanisms can be incorporated in such models; this in turn offers the possibility to study equilibrium and far from equilibrium systems. Complex phenomena such as roughening of interfaces or surface segregation under irradiation can be studied in details and results compare well with available experimental data; in the case of ball milling, simulations are shown to provide a rationalization scheme for known experimental results and to suggest new experiments. Further developments of this modeling scheme should make possible it to include stress effects on diffusion, and thus on the microstructural evolution.

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