Cluster dynamics in AIZr and AISc alloys

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Keywords: precipitation kinetics, cluster dynamics, AlZr, AlSc

Abstract

The homogeneous precipitation kinetics of the ordered phases Al₃Zr and Al₃Sc in Al solid solutions has been simulated at the mesoscopic scale by the cluster dynamics method. The polyatomic clusters, embedded in the solid solution, have an L1₂ structure and exchange solute atoms via absorption and emission reactions controlled by interfacial and long range diffusion. The time evolution of the cluster distribution is determined numerically, solving a set of master differential equations coupled through monomer exchanges. Results are presented for different temperatures and solute supersaturations and are discussed in terms of the classical schemes of precipitation and of recent atomistic Monte-Carlo simulations.

1. Introduction

Precipitation kinetics is usually modelled assuming that three successive stages can be distinguished and separately solved: the initial nucleation step, to which succeed for supercritical precipitates growth and coarsening. Although this classification offers the advantage of simplicity and easy numerical handling, all steps obviously operate simultaneously in real systems and this simplification can possibly be an oversimplification under extreme conditions such as nonisothermal heat treatments. In order to obtain a better insight into this problem we have developed, similarly to previous works [1-3], a cluster dynamics method where the life of the whole cluster or precipitate assembly is permanently and globally monitored at the mesoscopic scale.

2. Cluster Dynamics Method

The physical basis of the cluster dynamics method is the same as for the classical theory [4]. In a binary system the isolated solute atoms gather to form clusters. These clusters react through the exchange of monomers which are the only mobile species: the cluster grow (shrink) by absorption (emission) of solute atoms. The time evolution of the cluster size distribution then follows a set of master differential equations:

$$\left(\frac{\partial C_n}{\partial t}\right)_{n\geq 2} = \alpha_{n+1}C_{n+1} + \beta_{n-1}C_{n-1} - (\beta_n + \alpha_n)C_n$$

$$\frac{\partial C_1}{\partial t} = \sum_{2}^{\infty} \alpha_n C_n - \sum_{2}^{\infty} \beta_n C_n - 2\beta_1 C_1 + \alpha_2 C_2$$
(1)

 C_n is the concentration of the clusters of size *n*, the number of solute atoms within the cluster. β_n is the probability that a cluster of size *n* catches a monomer and transforms into a (n+1) cluster (absorption rate), α_n is its probability to emit a monomer to transform into a (n-1) cluster (emission rate). Given the kinetic coefficients α_n and β_n and initial t=0 conditions, the cluster size distribution $C_n(t)$ is obtained by numerical integration of the set of master equations (1). From $C_n(t)$ one can deduce any quantity of interest: the amount of solute within the clusters and in solid solution, the number density of clusters, the nucleation current, the cluster average size, etc...

We study here the binary alloys AlZr(Sc): the clusters have the ordered structure $L1_2$ with the stoichiometry Al₃Zr(Sc). The transformation kinetics are controlled by the motion of the atomic species Zr(Sc) which substitute in the fcc solid solution with Al on the Zr(Sc) $L1_2$ sublattice. *n* is taken as the number of solute atoms within the cluster and the total number of atoms is (4*n*).

The solute absorption rate β_n is controlled either by the last jump frequency for a monomer to impinge on the cluster (sticking), or by long range diffusion in the matrix when a solute depleted zone exists around large enough clusters. We use for β_n the expression proposed by Waite [5] in a general treatment of the kinetics of diffusion-limited reactions, in which the above two mechanisms operate in series. If one assumes that the $n \ge 2$ clusters are immobile, and that reaction occurs only via monomer diffusion, the following expression for β_n is obtained for spherical clusters of radius R_n :

$$\beta_n = S_n D\left(\frac{C_1}{\Omega}\right) \frac{1}{R_n + \frac{1}{\omega}}$$
(2)

D is the solute diffusion coefficient in Al. x_1 is the monomer concentration in the matrix; Ω is the Al atomic volume. ϖ , which is related to the last atomic jump, has the expression:

$$\varpi = \frac{a v \exp\left(\frac{-\Delta E}{kT}\right)}{D} \approx \frac{\exp\left(\frac{-\Delta E}{kT}\right)}{a \exp\left(-\frac{Q}{kT}\right)}$$
(3)

a is the jump distance (interface thickness)), ν is the jump frequency which brings in contact cluster and monomer. Q is the activation energy of the bulk solute diffusion coefficient and ΔE is the energy required for the condensation to occur.

If $\Delta E << Q$, or $R_n \varpi >> 1$, (3) reduces to the long range diffusion expression:

$$\beta_n = 4\pi R_n D\left(\frac{C_1}{\Omega}\right) \tag{4}$$

If $\Delta E >> Q$, or $R_n \varpi <<1$, (3) reduces to the interfacial term:

$$\beta_n = \frac{S_n}{a} D\left(\frac{C_1}{\Omega}\right) p \exp\left(-\frac{\Delta E - Q}{kT}\right)$$
(5)

The emission rate α_n is evaluated, as in the classical nucleation theory, using the principle of detailed balance applied to a constrained equilibrium of the cluster distribution, namely:

$$\frac{\alpha_{n+1}}{\beta_n} = \frac{C_n}{\overline{C_{n+1}}} \tag{6}$$

 $\overline{C_n}$ is the *n* cluster concentration under these equilibrium conditions and is given by the Maxwell-Boltzmann distribution:

$$\overline{C}_n = \exp\left(-\frac{\Delta G_n}{kT}\right) \tag{7}$$

where ΔG_n is the free enthalpy of formation of the *n* cluster.

Combining the previous equations gives the set of kinetic coefficients for spherical $AI_3Zr(Sc)$ clusters:

$$\beta_{n} = S_{n} D\left(\frac{C_{1}}{\Omega}\right) \frac{1}{R_{n} + a \exp\left(\frac{\Delta G_{n+1} - \Delta G_{n}}{2kT}\right)}$$

$$\alpha_{n+1} = S_{n} D\left(\frac{C_{1}}{\Omega}\right) \frac{\exp\left(\frac{\Delta G_{n+1} - \Delta G_{n}}{kT}\right)}{R_{n} + a \exp\left(\frac{\Delta G_{n+1} - \Delta G_{n}}{2kT}\right)}$$
(8)

In the following the capillary approximation has been used to evaluate ΔG_n :

$$\Delta G_n = 4n\Omega \Delta G_V + An^{2/3}\gamma \tag{9}$$

 ΔG_V is the usual thermodynamical driving force and γ is the cluster-matrix interface specific energy. It has been evaluated using the Bragg-Williams approximation for the free energy of the solid solution and ab-initio calculations for the enthalpy of formation of the ordered phases [6-8].

The numerical solution of the set of master equations 1 is detailed in reference [9]. It operates by an iterative procedure. The cluster size distribution is truncated at a maximum size reaching presently $n=10^6$.

3. Simulation Results and Discussion

Simulation results for isothermal ageing treatments following a perfect quench are presented for AlZr and AlSc alloys. Different nominal solute compositions and ageing temperatures have been tested. Only diffusional kinetic coefficients 4 have been considered.

The values of the parameters used as input data are listed in Table 1: interaction parameter of the AI solid solution $\lambda = 12\omega_1 + 6\omega_2$ defined in terms of first and second neighbour pair interactions ω_i , the formation enthalpy $\Delta H(A_3B)$ and solubility limit $x(i)^{eq}$ of the A₃B phases, diffusion coefficients D_i , interface specific energy $\gamma(A_3B)$ and the Ω_{AI} AI atomic volume.

Table 1: Physical Arameters Values

AlZr	AISc
$\begin{array}{c} \lambda_{\text{AIZr}} = -1.3975 \text{ eV} \\ \Delta H(\text{AI}_3 Zr) = -0.530 + 73.2 \times 10^{-6} \text{T eV} \\ x^{\text{eq}}(\text{Zr}) = \exp((-0.620 + 155 \times 10^{-6} \text{T}) \text{ eV/kT}) \\ \gamma(\text{AI}_3 Zr) = 100 \text{ mJ.m}^{-2} \\ D_{\text{Zr}} = 7.28 \times 10^{-2} \exp(-2.51 \text{ eV/kT}) \text{ m}^2.\text{s}^{-1} \end{array}$	$\begin{array}{l} \lambda_{AISc}\mbox{=}-1.1327\ eV\ at\ 450\ ^{\circ}C\\ \Delta H(AI_3Sc)\mbox{=}-0.701\mbox{+}23x10\ ^{-6}T\ eV\\ x^{eq}(Sc)\mbox{=}exp((-0.701\mbox{+}23x10\ ^{-6}T)\ eV/kT)\\ \gamma(AI_3Sc)\mbox{=}113\ mJ.m\ ^{-2}\\ D_{Sc}\mbox{=}5.31x10\ ^{-4}exp(-1.79\ eV/kT)\ m\ ^{2}.s\ ^{-1} \end{array}$
$\Omega_{AI} = 1.66 \times 10^{-29} \text{ m}^3$	

Characteristics of the Al₃Zr(Sc) precipitation kinetics at 450°C are summoned in Figure 1 and 2. Figure 1 shows the time evolution of the cluster size distribution for an Al-1at%Zr alloy at 450°C. Figures 2a) to 2c) show quantities deduced from Figure 1: a) the solute concentration within the precipitates, b) the number density of the precipitates and c) the mean cluster radius for Al-1at%Zr and Al-1at%Sc.

The shape of these curves is quite general and is indeed characteristic of a nucleationgrowth process: the size distribution shows clearly that a subcritical cluster quasiequilibrium distribution following an exponential decay as in equation (7) is very quickly established after the quench. After a certain incubation time some clusters become supercritical and grow, shifting the size distribution to the right. A two-step growth process is observed, the final stage corresponding to coarsening or a Lifschitz-Slyozov-Wagner stage occurring at zero supersaturation, with a $t^{1/3}$ kinetics. At the same time a trough is formed in the distribution and small clusters are stabilized in the residual solid solution.

The driving forces for precipitation in the AISc and AIZr are of course different, but at 450°C, the differences observed in precipitation are controlled predominantly by the differences in Zr and Sc diffusitivity. The much more rapid Sc diffusion (at 450°C Sc diffuses 1000 times faster than Zr) explains the large shift of all kinetics towards earlier times. The influence of temperature is shown for AI-1at%Zr in Figure 3, where the kinetics have been calculated for three different temperatures. As expected, a T increase induces a decrease in the driving force and an increase in atomic mobility. The results show that at 550°C, the system has still not reached the nose of the TTT curve. At 550°C, it is also easier to distinguish the three conventional precipitation stages (nucleation, growth, coarsening) whereas at 450°C, the system enters quickly into the coarsening regime.

The cluster dynamics treatment is a mesoscopic approach; it combines atomic processes like diffusion and cluster fluxes, with macroscopic quantities like precipitate-matrix interface energy and driving forces. A critical point is the minimum cluster size for which the capillary approximation is a good description of the small cluster's free energy. It is therefore interesting to compare the cluster dynamics description of nucleation stage with another simulation tool: kinetic Monte Carlo simulations of an Ising model. This tool is, a priori, more suitable to deal with subnanometric clusters because the only input data are the interatomic pair-potentials: AI-Sc, AI-Zr, Zr-Sc, AI-V, Sc-V, Zr-V (V=vacancy). Such an approach has been made by Clouet et al [8] in the same alloys. A comparison of the respective results is given in Figure 4 for the precipitate number density during the nucleation period in AIZr and AISc systems aged at 450°C. In the figures the time scale for the cluster dynamics simulations has been shifted by a factor 2 with respect to the Monte Carlo simulations. Large ageing times, here 4000 s., can not be reached within reasonable CPU times by Monte Carlo simulations due to the structure of the algorithm itself. Cluster

dynamics method does not have any problem of this nature: the time integration step is made variable and can be adapted to the reaction rate.

Within these limitations it can be concluded that the comparison between the simulations is indeed quite satisfactory. This agreement makes reliable cluster dynamics simulations possible for much lower supersaturated systems, inaccessible by kinetic Monte Carlo methods.



Figure 1: Cluster size distribution for Al-1at%Zr for different times at 450° C



(a)

Figure 2: Precipitation kinetics in Al-1at%Zr and Al-1at% Sc at 450°C: a) solute content in the precipitates, b) precipitate number density, in atomic fraction, c) mean radius size.





Figure 3: influence of temperature on the precipitation kinetics of Al-1at%Zr: a) precipitate average radius size, b) precipitate number density in atomic fraction.



Figure 4: comparison between the nucleation kinetics aged at 450°C simulated by cluster dynamics (CD) and kinetic Monte Carlo (MC) [8] methods for different supersaturations: a) cluster number density for AlZr, b) cluster number density for AlSc.

4. Conclusion

A kinetic model for precipitation based on cluster dynamics has been presented and applied to AISc and AIZr alloys for the precipitation of L1₂ phases. Stages of nucleation, growth and coarsening are treated in a single frame work and results are presented for isothermal ageings. The comparison with atomistic Monte Carlo simulations shows a good agreement for the most delicate nucleation stage.

The application of cluster dynamic method to anisothermal quench and ageing conditions, and the extension to ternary alloys is under investigation.

Acknowledgements

This work was supported by CNRS and Pechiney and Arcelor companies, in the framework of the "CPR precipitation" contract. They are greatly acknowledged for the grant of L. Lae and their interest in the fundamental aspects of the program.

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