

Phase Field Modeling of Precipitation Kinetics in Al-Sc Alloys

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The coarsening kinetics of γ' precipitates in binary Al-Sc alloys is studied by using the three-dimensional phase-field simulations. Our focus is on the influence of volume fractions of precipitates on the coarsening kinetics. The simulation results demonstrate that for the small volume fraction of ordered γ' particles the coarsening rate is approximately constant and rapidly increases from 18% of $L1_2$ particles. Our simulation results are in good agreement with experimental observations.

Keywords: Al-Sc alloys, phase field modeling, $L1_2$ ordering, coarsening.

1. Introduction

Al-Sc alloys were studied for their excellent mechanical properties at room temperature. The addition of small quantities of scandium to pure aluminium can lead to a number of benefits, including grain refinement, an increase in strength and enhanced resistance to recrystallization [1]. These effects can be attributed to the presence of $L1_2$ ordered Al_3Sc precipitates. The low diffusivity and the low solubility of scandium lead to the high resistance of the Al_3Sc particles for coarsening. However, coarsening of these particles cannot be avoided in the over-aging condition. Consequently, the knowledge of kinetics path in the Al-Sc alloys is indispensable for their designing and industrial application.

The small misfit between the matrix and Al_3Sc precipitates means that homogeneous nucleation of spherical particles is often observed [2]. In Al-Sc alloys with low concentration of Sc the equilibrium volume fraction of ordered $L1_2$ precipitates is small and the interparticle spacing is quite large with respect to the particle size. Therefore, the interaction between the particles is small and coarsening is controlled by atomic diffusion and the minimization of interfacial energy. This makes coarsening in these alloys an ideal opportunity to test Lifshitz-Slyozov-Wagner (LSW) coarsening theory. In several works the coarsening kinetics in Al-Sc systems was compared with theoretical predictions [3,4]. The influence of volume fraction of ordered precipitates on the rate of coarsening have been investigated by Ardell and Novotny [4]. It was shown that the particle size distributions were in excellent agreement with those of the LSW theory at early aging times. At longer aging times the distribution became broader. It was also observed the remarkable stability of Al_3Sc precipitates to coarsening and deviation from diffusion-controlled coarsening behaviour.

The aim of this work is the study of coarsening kinetics in Al-Sc alloys with different volume fraction of precipitates using three-dimensional (3-D) phase-field simulations. Eight aluminium-scandium alloys with different volume fractions of ordered phase were investigated. The simulation results are compared with experimental data.

2. Model

An arbitrary multi-phase microstructure can be described by a few mesoscopic field parameters. To describe the $L1_2$ ordered structure we need to employ three long range order (lro) parameters, $\eta_1(\mathbf{r},t)$, $\eta_2(\mathbf{r},t)$, and $\eta_3(\mathbf{r},t)$. To describe the concentration profile, we should add in the model another field parameter, $c(\mathbf{r},t)$, where \mathbf{r} represent spatial coordinate and t is time. The spatio-temporal evolution of the lro parameters can be obtained by solving the time-dependent Ginzburg-Landau equation and

the temporal evolution of the concentration field can be described by non-linear Cahn-Hilliard diffusion equation, i.e.

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = \nabla M(\mathbf{r}, t) \nabla \left(\frac{\partial F}{\partial c(\mathbf{r}, t)} \right) + \xi \quad (1)$$

$$\frac{\partial \eta_i(\mathbf{r}, t)}{\partial t} = -L \frac{\partial F}{\partial \eta_i(\mathbf{r}, t)} + \zeta_i \quad i=1,2,3 \quad (2)$$

Where L et M are respectively structural relaxation and diffusion mobilities, F is the total free energy of the system, ξ and ζ are the Langevin's noise terms describing the compositional and structural thermal fluctuations, respectively. The total free energy of system is consisted of two terms: the elastic energy E_{el} and chemical free energy F_{ch} .

Elastic strain energy arises due to the misfit between matrix and ordered $L1_2$ phase. The deformation ε_0 is considered to be dependent solely on the composition $\varepsilon_0 = \frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma}(c_{\gamma} - c_{\gamma'})}$. The

parameter ε_0 may be estimated from the $\gamma/L1_2$ lattice misfit, and $\frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma}} = 0.0105$ at 375°C [5]. If

Vegard's law is assumed, at this temperature $c_{\gamma} = 0.0001$ and $c_{\gamma'} = 0.25$, the estimation for ε_0 gives around 0.042. Khachaturyan's model [6] is used for the description of elastic energy with a homogeneous modulus approximation. It has been shown that the total elastic energy of an elastically homogeneous and elastically anisotropic system can be written as:

$$E_{relax} = -\frac{1}{2} \int_V B(\mathbf{n}) |c(k)|^2 \frac{d^3k}{(2\pi)^3} \quad (3)$$

where the integral is over the reciprocal Fourier space, $\mathbf{n}=\mathbf{k}/|\mathbf{k}|$ is a unit vector in the k direction and $c(k)$ is the Fourier transform of the composition field $c(\mathbf{r})$. The function $B(\mathbf{n})$ contains all information on the elastic properties of the systems and depends on the elastic constants c_{11} , c_{12} and c_{44} and deformation ε_0 .

Assuming an isotropic interfacial energy, the chemical energy F_{ch} in the diffuse-interface description can be written as:

$$F_{ch} = \int_V \left(f(c, \eta_j) + \frac{\alpha}{2} (\nabla c)^2 + \frac{\beta}{2} (\nabla \eta_j)^2 \right) dV \quad (4)$$

where the gradient terms represent the contribution from the interphase boundary energy, α and β are gradient energy coefficients and f is the local free energy density. In this work, isotropic interphase boundary energy is assumed. The chemical energy density can be approximated using a Landau free energy polynomial:

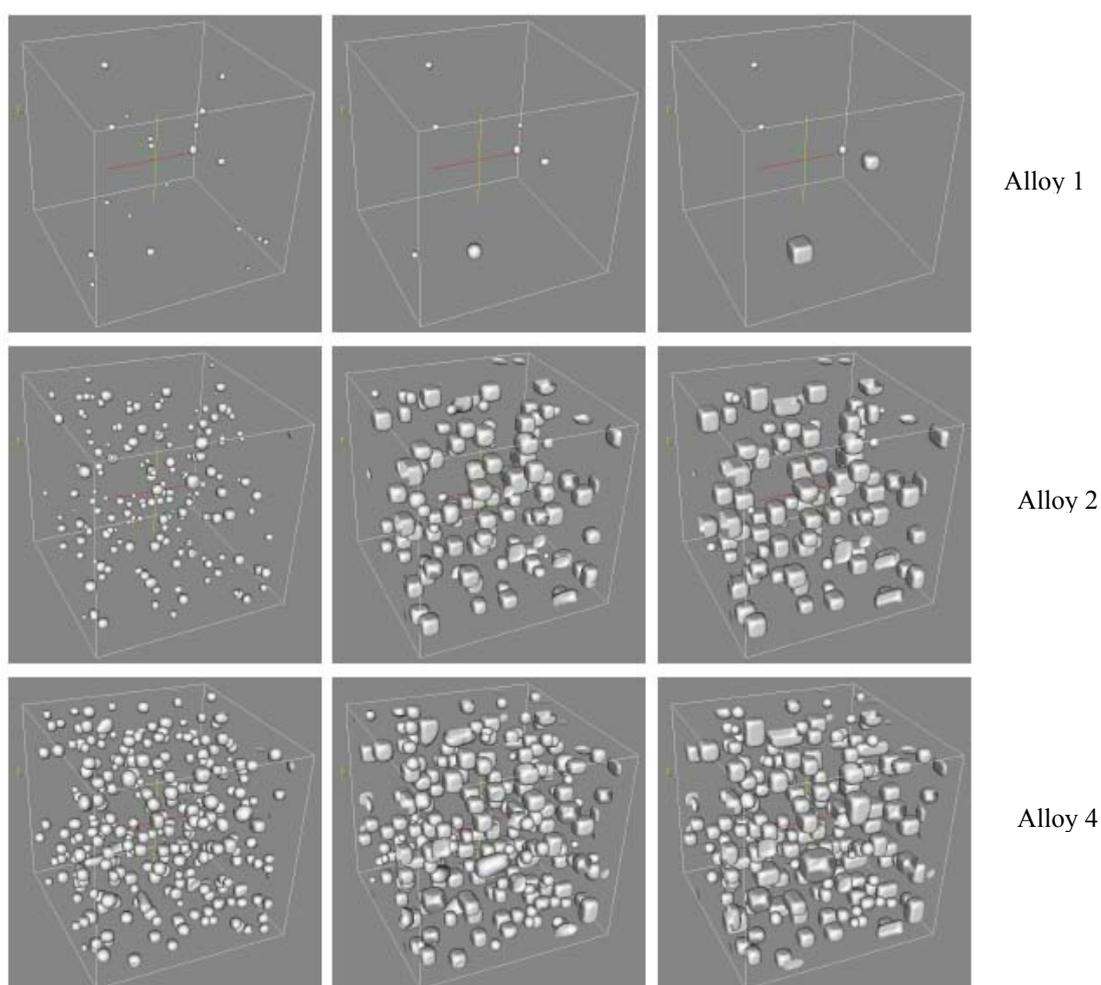
$$f(c, \eta_1, \eta_2, \eta_3) = \frac{A_1}{2} (c - c_1)^2 + \frac{A_2}{2} (c_2 - c) (\eta_1^2 + \eta_2^2 + \eta_3^2) + \frac{A_3}{6} \eta_1 \eta_2 \eta_3 + \frac{A_4}{24} (\eta_1^4 + \eta_2^4 + \eta_3^4) + \frac{A_5}{24} (\eta_1^2 \eta_2^2 + \eta_1^2 \eta_3^2 + \eta_2^2 \eta_3^2) \quad (5)$$

where c_1 et c_2 are constants with values close to the equilibrium compositions of the matrix and precipitates, respectively and A_i s are constants for the given temperature. The coefficients and constants were chosen such that the free energy curve provides a qualitative description of the thermodynamics of the Al-Sc system at 375°C and in our simulations correspond to the next set of parameters: $A_1=512.41$, $A_2=256.10$, $A_3=-96.00$, $A_4=A_5=128.00$, $c_1=0.0001$ and $c_2=0.25$; Simulations were performed by numerically solving the four nonlinear Eq.1 and Eq.2, one for each field variable, using the semi-implicit Fourier-Spectral method [7]. In 3D computer simulations, 128^3 discrete grid

points are used and periodic boundary conditions are applied. A uniform time step Δt^* equal to 0.01 and a mesh size of $\Delta x = \Delta y = \Delta z = 1.0$ were chosen. The initial state was a homogeneous solution with small composition fluctuations around the average composition. Spherical nuclei with an average radius greater than the nucleation radius were randomly introduced in the computation domain. Since our focus is mainly to simulate the coarsening kinetics and not the whole sequence of transformation, the artificially-chosen initial configuration does not affect our results. Approximately one thousand particles were formed during the nucleation stage. The precipitate microstructure and coarsening kinetics were then extracted from the simulation results, which were averaged over five simulation runs with different initial locations of nuclei.

3. Results

To determine the influence of the volume fractions of Al_3Sc precipitates on the coarsening rate and on microstructure, eight aluminium-scandium alloys containing 3.2 at%, 3.83 at%, 4.18%, 4.49 at%, 5.13 at%, 6.48%, 8.38% and 11.68 at% Sc which correspond to the following volume fractions of the L1_2 phase, 12.8%, 15.4%, 16.7%, 18.03%, 20.6%, 27.1%, 33.5% and 46.3% were studied. We will refer to these as Alloy 1, 2, 3, 4, 5, 6, 7 and 8, respectively. The computer simulations were performed at $T = 350^\circ\text{C}$. The temporal microstructural evolution for five alloys (1, 2, 4, 5 and 7) during coarsening for three simulation times $t^* = 10000$, $t^* = 50000$ and $t^* = 100000$ is presented in Fig.1. The coherent ordered Al_3Sc precipitates are shown in white. Comparing different simulation times, it can be noted that number of precipitates decreases. It means that the main process in system is coarsening mode. The precipitates are single-domain particles, which form four antiphase domains.



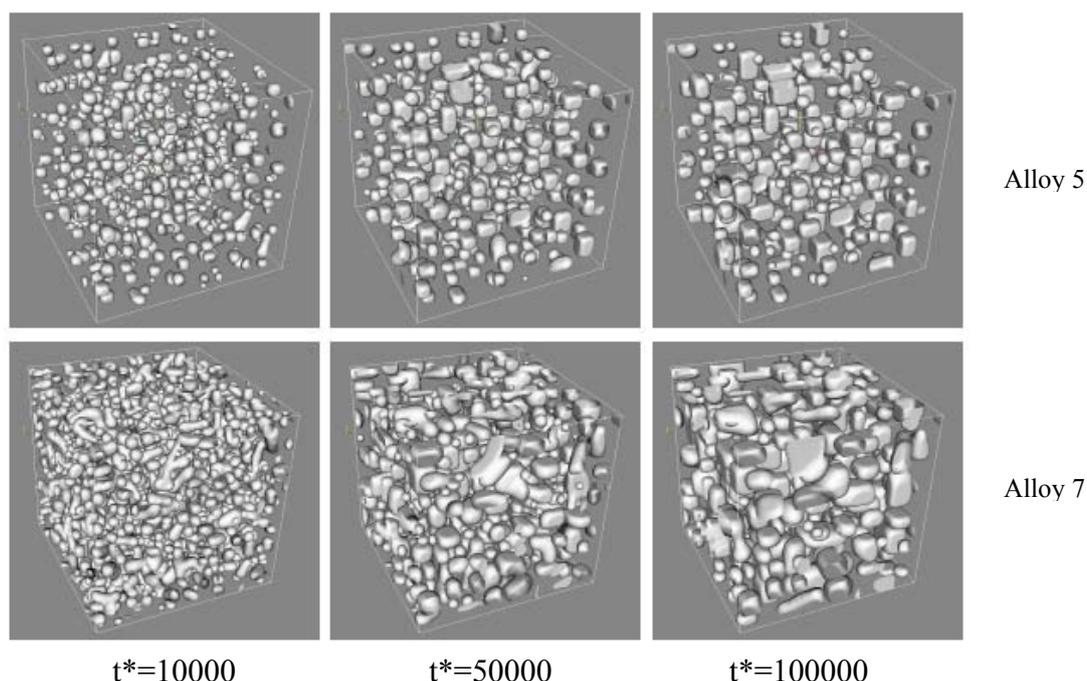


Fig.1 Simulated microstructural evolution in Al-Sc alloys at 350°C. Each line represents the different alloys. Each colon corresponds to the different reduced times.

At later stages of coarsening for all volume fractions the particle shapes transform from spherical to cuboidal,. For Alloy 2, 4, 5 and 7 we observe the alignment of precipitates along to elastically soft $\langle 100 \rangle$ directions. This microstructure minimizes the elastic energy of system. As was discussed previously [8] for high volume fraction of γ' particles the nearest precipitates which correspond to the same translation variant can coalesce. Since in the case of the $L1_2$ ordered structure there are four translation variants, the probability that neighboring precipitates are the same variant structure is $1/4$. In reality, this probability is considerably less because of the correlation between the types of the neighboring precipitates due to the presence of elastic interaction in system. However, this probability should be not negligible for the high volume fraction of ordered phase. This phenomenon is clearly observed in Alloy 7 (Fig. 1). In this alloy, some irregular forms of precipitates due to the coalescence of neighboring γ' particles appear. We can note also that this phenomenon is observed at different stages of coarsening.

The most interesting aspect of coarsening kinetics is growth law. Following to classic LSW theory the kinetic coarsening equation is:

$$\langle R(t) \rangle^3 - \langle R(0) \rangle^3 = Kt \quad (6)$$

where $\langle R(0) \rangle$ is the average precipitate radius at the start of coarsening and K is the coarsening rate constant. The modified LSW theory proposed by Ardell and independently by Marquisee and Ross [11,13] predict that K is function of volume fraction of precipitates. We find that the cubic growth law provides reasonably good fits for all alloys. In Fig. 2 the coarsening rate constant $K(f_v)$ is represented for different volume fraction. It normalize on the value of the coarsening rate constant in LSW theory $K(0) = 9/4 \text{ m}^3 \cdot \text{s}^{-1}$. In the same figure we present the curves predicted by different theory. We can see that our simulation results can't be reproduced by all these models. However our simulation results are in good agreement with experimental results obtained by Ardell and Novotny [4]. We can conclude that finite volume fraction of precipitates and strong elastic interaction between precipitates have a big influence on the coarsening rate in Al-Sc alloys.

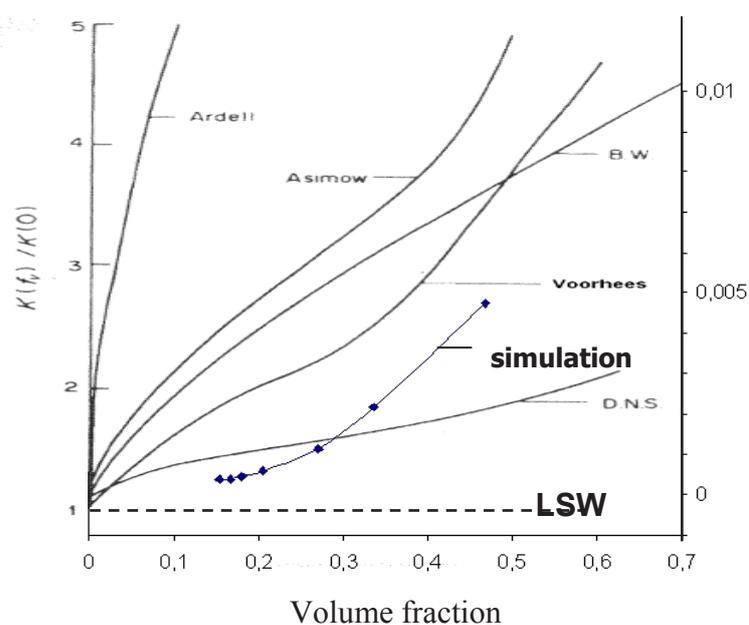


Fig. 2. Coarsening rate as function of volume fraction of ordered precipitates. The simulated results are shown in blue. The theoretical predictions are shown in black and correspond to the next references : Davies et al.(D.N.S [9]), Brailsford and Wynblatt (B.W. [10]), Ardell et al.[11] et Voorhees [12].

4. Conclusions

A phase field simulations of coarsening kinetics in Al-Sc alloys with different volume fraction of $L1_2$ ordered precipitates has been performed. Our simulations results have demonstrated the capability of model to capture the main features of microstructural evolution during coarsening stages. It was found that coarsening rate is strongly depends from the volume fraction of precipitates. However, the cubic growth law provides reasonably good fits for the temporal evolution of the average radius of precipitates for all studied alloys.

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