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J. Boisse, Nicolas Lecoq, Helena Zapolsky, Renaud Patte. Coarsening Kinetic of Aluminium-Scandium and Aluminium-Zirconium-Scandium Precipitates. Jürgen Hirsch, Birgit Skrotzki, Günter Gottstein 11th International Conference on Aluminium Alloys (ICAA'11), Sep 2008, Aachen, Germany. Wiley, Aluminium Alloys: Their Physical and Mechanical Properties. <hal-01486150>

**HAL Id: hal-01486150**

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Submitted on 9 Mar 2017

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ICAA'11, Aachen, September 2008

**Aluminium Alloys** : Their Physical and Mechanical Properties

Edited by J. Hirsch, B. Skrotzki and G. Gottstein

Wiley-VCH GmbH & Co. KgaA, 2008

## **Coarsening Kinetic of Aluminium-Scandium and Aluminium-Zirconium-Scandium Precipitates**

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### **1 Introduction**

Al-Sc-based alloys exhibit a unique combination of high strength and plasticity, corrosion resistance and weldability [1-4]. Mechanical properties of these alloys depend on their microstructure and their phase composition, so its knowledge provides an opportunity to improve material properties by thermal treatment. The addition of Sc to aluminium is a very effective mean to form small ordered  $L_{12}$  precipitates which increase the tensile strength and inhibit recrystallisation.. Recently it was demonstrated that these precipitates remain coherent up to sizes of 40 nm in diameter [1]. To further improve the properties of Al-Sc alloys, the effects of ternary additions to Al-Sc alloys have been investigated [5]. Previous studies have shown that addition of Zr in Al-Sc alloys improve the stability these systems to coarsening [20-21]. It was determined that Zr segregates to the  $\alpha$ -Al/Al<sub>3</sub>Sc heterophase interface and acts as a barrier for the diffusion of Sc across the interface, which leads to a lowering of the coarsening rate [22-23] as compared to binary Al-Sc alloys. Harada and Dunand [7] shown that zirconium addition reduces the lattice parameter of Al<sub>3</sub>Sc and concomitantly the interface free and elastic strain energies.

The purpose of this work is to study the microstructural evolution in binary Al-Sc and in ternary Al-Sc-Zr alloys. Phase field approach based on the Cahn-Hilliard and Ginzburg-Landau equations [12-18] has been used. It is shown that  $L_{12}$  particles have a heterogeneous structure with the Al<sub>3</sub>Sc core surrounded by a Zr-rich shell .

### **2 Model description**

#### **2.1 Phase field model.**

Phase field model has been extensively used for microstructure simulation studies because of its ability to reproduce complicated microstructures without any *a priori* assumptions

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[12-14]. We consider a model for two-phase system, in which parent phase has a disordered fcc structure and the precipitates have the four variants ordered L1<sub>2</sub> structure. In this case the kinetic equations that describe the temporal evolution of the composition variable  $c(\mathbf{r}, t)$  and the long range order parameters  $\eta(\mathbf{r}, t)$  are:

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

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

where  $L$  and  $M$  are kinetic coefficients,  $F$  is a total non-equilibrium free energy functional,  $\xi$  and  $\zeta$  are the Langevin's noise terms describing the compositional and structural thermal fluctuations, respectively.

The total free energy of the system consists of the bulk free energy, the interfacial energy and the elastic energy  $E_{el}$ . Assuming an isotropic interfacial energy, the chemical energy  $F_{ch}$  in the diffuse-interface description can be written as:

$$F_{ch} = \int_V (f(c, \eta_j) + \frac{\alpha}{2} (\nabla c)^2 + \frac{\beta}{2} \sum_{j=1}^3 (\nabla \eta_j)^2) dV \quad (2)$$

where  $\alpha$  and  $\beta$  are gradient energy coefficients,  $f$  is the local free energy density which can be expressed in Landau polynomial form; in the case of ternary systems it take the following form :

$$f(c_a, c_b, \eta_1, \eta_2, \eta_3) = \frac{1}{2} A_1 (c_a + c_b - c_1)^2 + \frac{1}{2} A_2 (c_2 - c_a - c_b) \sum_{p=1}^3 \eta_p^2 + \frac{1}{3} A_3 \eta_1 \eta_2 \eta_3 + \frac{1}{4} A_4 \sum_{p=1}^3 \eta_p^4 + \frac{1}{4} A_5 (\eta_1^2 \eta_2^2 + \eta_1^2 \eta_3^2 + \eta_2^2 \eta_3^2) \quad (4)$$

where  $c_a$  and  $c_b$  are the composition variables of scandium and zirconium atoms,  $c_1$  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 and Al-Sc-Zr system at 375°C, with the constraint that for the disorder-order phase transition to be first ordered,  $A_3$  must be non-zero.

Khachaturyan's model [13] is used for the description of elastic energy arising from the lattice misfit, with a homogeneous modulus approximation. In our calculations we assumed that the lattice parameter  $a_\gamma$  and  $a_\alpha$  of the disordered and ordered phases, respectively, has a linear dependence on solute composition (Vegard's law).

The kinetic coefficient  $M$  in equation (1a) corresponds to the chemical mobility of elements in alloys. In many cases, for simplicity, the chemical mobility is assumed to be constant and is calculated on the average concentrations in the system. But in facts,  $M$  is related to the atomic motilities  $\beta_{Sc}$  and  $\beta_{Al}$  of each system's elements and is defined in the lattice refer-

ICAA'11, Aachen, September 2008

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ence frame as a composition and temperature-dependent function. In the case of an Al-Sc binary alloy the chemical mobility can be expressed by the following equation:

$$M = c_{Sc}(1 - c_{Sc})[(1 - c_{Sc})\beta_{Sc} + c_{Sc}\beta_{Al}] \quad (5)$$

where  $c_{Sc}$  is the mole fraction of Sc. The atomic mobility  $\beta_i$  of species  $i$  can be written as:

$$\beta_i = D_i \exp(-Q_i / RT) \quad (6)$$

where  $R$  is the gas constant,  $D_i$  and  $Q_i$  are diffusion factor and diffusion activation energy of species  $i$  in the disordered phase. These two constants can be generally obtained from atomic mobility databases.

There is not enough experimental databases for atomic mobilities for ternary Al-Sc-Zr system, this is why in our simulation we chose constant mobility for Zr and Sc atoms for ternary alloys. However, we took into account that at 375°C Zr diffuse 100 times slowly than Sc atoms in Al.

In addition, in our model, we also integrated the concentration dependence of misfit between two coexisting phases.

### 3 Numerical simulations and results.

Simulations were performed by numerically solving the four nonlinear equations (1a) and (1b), one for each field variable, using the semi-implicit Fourier-Spectral method [18]. In 3D computer simulations,  $128^3$  discrete grid points are used and periodic boundary conditions are applied. The initial state was a homogeneous solution with small composition fluctuations around the average composition. The Langevin's noises were introduced during the beginning of each simulation to ensure the nucleation of small precipitates. Particles with a radius greater than the critical nucleation radius can then grow. 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 randomized Langevin's noises.

The parameter  $\varepsilon_0$  used in the elastic energy term may be estimated from the  $\gamma/\gamma'$  lattice misfit,

$$\frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma}} \approx 0.0098$$

and  $a_{\gamma}$  at 375°C [10]. If Vegard's law for the misfit is assumed, at this temperature  $c_{\gamma} = 0.0001$  and  $c_{\gamma'} = 0.25$ , the estimation for  $\varepsilon_0$  gives 0.039.

To determine the influence of the volume fractions of  $Al_3Sc$  precipitates on the coarsening rate and on the microstructure, three alloys with different volume fraction of the  $L1_2$  phase, 0.35, 0.39 and 0.42, were studied. Therefore, for each alloy, two kinds of simulations were performed : with and without concentration dependent atomic mobilities.

Figure 1 show the morphological evolution of  $L1_2$  ordered precipitates. We can conclude that including the concentration dependence mobility doesn't induce large influence on the morphology of microstructure in Al-Sc binary alloys. However, our statistical analyze of

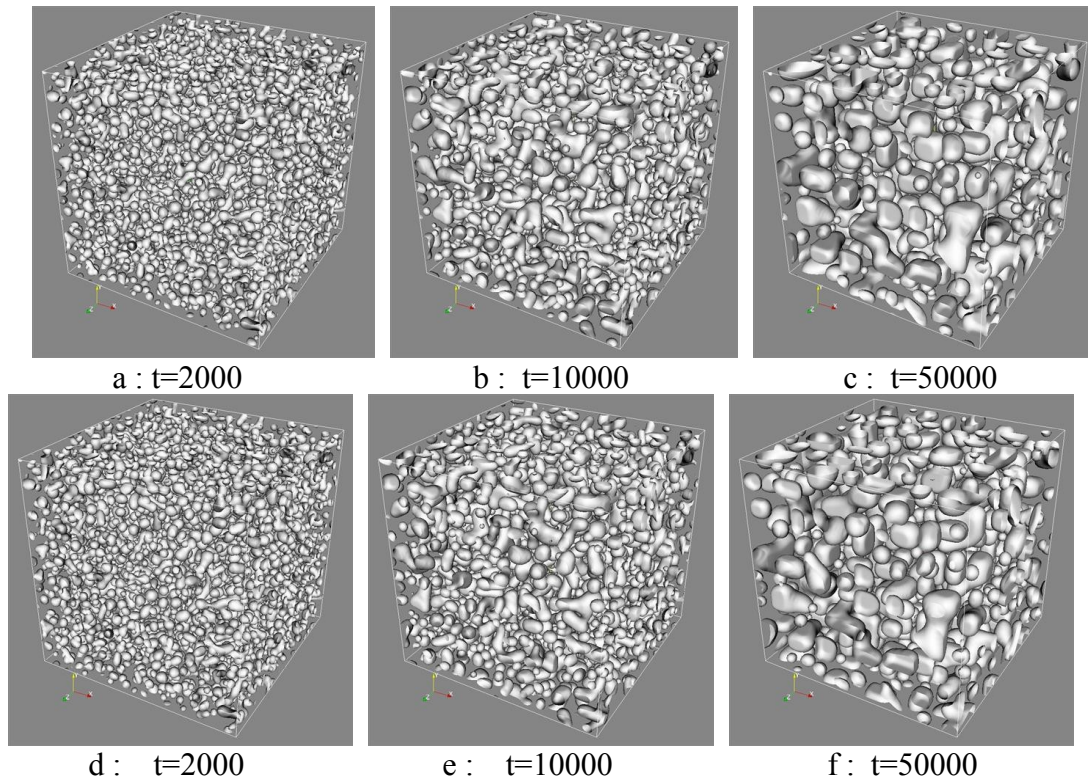
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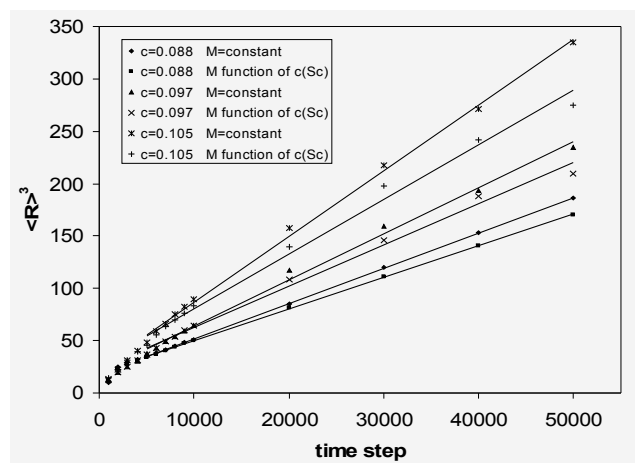
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temporal evolution for the mean radius of precipitates indicates differences between these two simulations.



**Figure 1:** Temporal microstructural evolution for Al-Sc alloys during coarsening for different reduced time  $t$  with : (a-c) constant atomic mobility ; (d-f) concentration dependent atomic mobility. The coherent ordered  $Al_3Sc$  precipitates are shown in white, the matrix is transparent.



**Figure 2:**  $\langle R \rangle^3$  versus reduced time step for different concentrations and for constant and concentration dependent atomic mobilities. Solid lines are linear fits of the data from the simulations.

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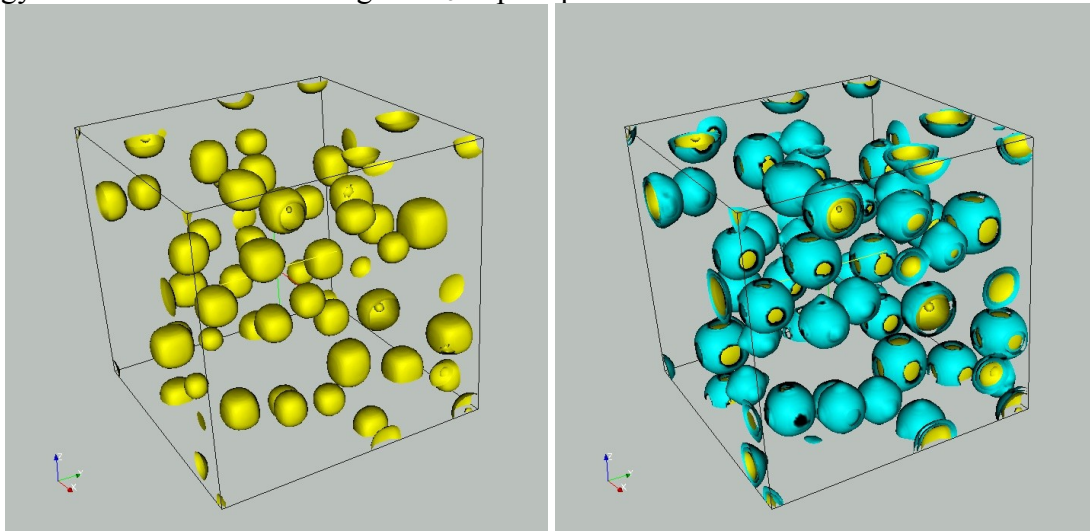
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We find that the cubic growth law provides reasonably good fits in all cases. It is apparent in figure 2 that the slope of the curves, i.e. the value of the coarsening rate constant  $K$ , increases with increasing volume fraction which is also in good agreement with experimental data. This behavior was predicted in the modified LSW theory proposed by Ma and Ardell [16]. But, we observe that coarsening rate in the case of simulations with concentration dependent mobility is smaller than with constant mobility for each volume fraction. It can be understood by the fact that during growth and coarsening of precipitates, atomic mobility decreases with the decrease of Sc atomic concentration in the matrix.

Dealing with the Al-Sc-Zr alloys, it was demonstrated that the ordered  $\text{Al}_3\text{Sc}$  particles appear firstly and exhibit a cuboidal shape which is result of the minimization of strain energy (figure 3). The Zr atoms diffuse slowly and precipitate on the interface between matrix and  $\text{Al}_3\text{Sc}$  particles. The main effect is due to the strain energy and not on the diffusion velocities of the components.

Figure 4 is shown the influence of misfit dependent of concentration. On the later case, precipitates are smaller, zirconium forms shells around the Sc rich cores to minimize the strain energy and blocks the coarsening of  $\text{Al}_3\text{Sc}$  precipitates.



**Figure 3.** Microstructural evolution from 3D simulation at reduced time  $t^*=10000$ , showing the heterogeneous structure of  $\gamma'$  precipitates in a  $\gamma$  (transparent) disordered matrix. Left : Iso-concentration of  $\text{Al}_3\text{Sc}$  (yellow); Right : Zr rich-shell (blue) surrounding the previous  $\text{Al}_3\text{Sc}$  precipitates.

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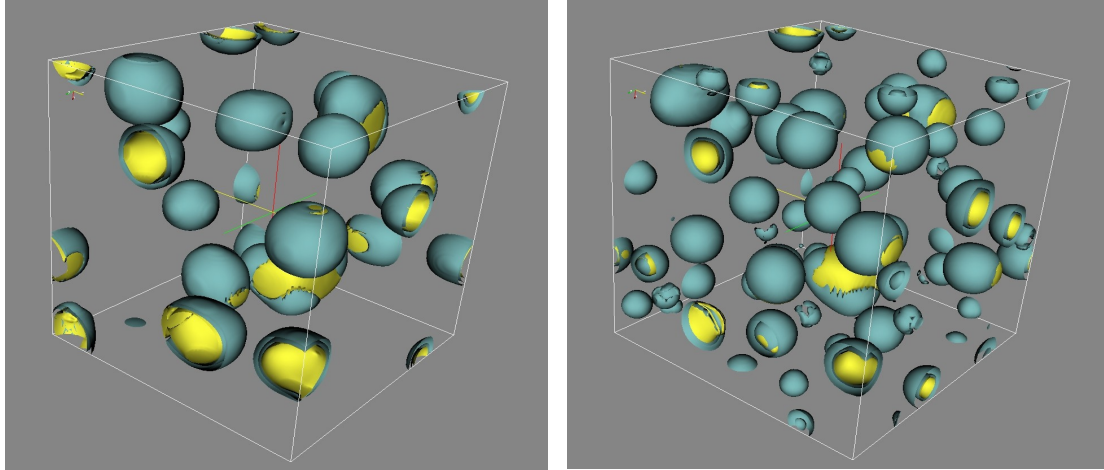


Figure 4. Microstructural evolution from 3D simulation at reduced time  $t^*=10000$ , showing the heterogeneous structure of  $\gamma'$  precipitates in a  $\gamma$  (transparent) disordered matrix. Left : without the misfit dependent of concentration; Right : misfit depends on concentration.

The precipitation of  $Al_3(Sc,Zr)$  particles has been successfully studied by means of transmission electron microscopy [24] and 3D atom probe analysis [20-24]. It has been shown that ordered precipitates contain a Sc-rich core and a Zr enriched outer shell. These works confirm the hypothesis of an intense initial precipitation of  $Al_3Sc$  nuclei, favored by the fast Sc-diffusion rate, followed by later Zr segregation. Our simulation results are in very good agreements with these experimental data.

## 5 Conclusion.

Our simulation show that phase field model can successfully reproduce the microstructural evolution in binary and ternary system. The concentration dependence of atomic mobility and misfit was integrated in our calculations. It was shown that elastic interaction is responsible to heterogeneous structure of  $L1_2$  precipitates in Al-Sc-Zr alloys.

## Acknowledgements

The simulations were performed at the CRIHAN center under project 2006007.

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