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メタデータ	言語: eng
	出版者:
	公開日: 2017-10-03
	キーワード (Ja):
	キーワード (En):
	作成者:
	メールアドレス:
	所属:
URL	http://hdl.handle.net/2297/22580

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Coarsening of cuboidal Al$_3$Sc precipitates in an Al-Mg-Sc alloy

Chihiro Watanabe[1], Daizen Watanabe[2], Ryo Tanii[3] and Ryoichi Monzen[4]

[1] Corresponding Author, Division of Innovative Technology and Science, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

E-Mail: chihiro@t.kanazawa-u.ac.jp

TEL: +81-76-234-4677, Fax: +76-264-6424

[2] Division of Innovative Technology and Science, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

E-Mail: daizen@metal.ms.t.kanazawa-u.ac.jp

TEL: +81-76-234-4678, Fax: +76-264-6424

[3] Division of Mechanical Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

E-Mail: tanii@metal.ms.t.kanazawa-u.ac.jp

TEL: +81-76-234-4678, Fax: +76-264-6424

[4] Division of Innovative Technology and Science, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

E-Mail: monzen@t.kanazawa-u.ac.jp

TEL: +81-76-234-4678, Fax: +76-264-6495

Abstract

The coarsening of {001}-faceted cuboidal Al$_3$Sc precipitates in an Al-Mg-Sc alloy during ageing at 698, 723 and 748 K have been examined by transmission electron microscopy and electrical resistivity. Application of the theory of Kuehmann and Voorhees for coarsening of second-phase precipitates in ternary systems, generalized to any centro-symmetric precipitates, has enabled independent derivation of the {001} interface energy without assuming values of the diffusivity of solute atoms (Sc and Mg) in the Al matrix. The {001} interface energy is estimated as 0.19 J/m^2, which is excellent agreement with the value of 0.192 J/m2 obtained using the first-principles calculation method. The sphere-to-cuboidal shape change of the Al$_3$Sc precipitate during ageing is discussed by means of a simple energy consideration.

Keywords: Coarsening; Interface energy; Al$_3$Sc precipitate; Aluminium-Magnesium-Scandium alloy

1. Introduction

Kuehmann and Voorhees (KV) [1] have developed a theory for the coarsening of spherical second-phase precipitates in a ternary system. By formulating the Gibbs-Thomson equation for the ternary system, they found that the temporal power laws of the average particle radius, far-field-matrix supersaturation and particle number density were identical to those of the Lifshitz-Slyozov-Wager (LSW) [2, 3] theory on coarsening of second-phase particles in a binary system, but the amplitudes of these power laws were different from the LSW theory.

In a previous study [4], we have examined the coarsening behavior of initially coherent Al_3Sc precipitates in a ternary Al-1wt%Mg-0.27wt%Sc alloy aged at temperatures between 673 and 748 K by both of Transmission Electron Microscopy (TEM) observations and electrical resistivity measurements. The shape of Al_3Sc precipitates changed from a sphere to a cuboidal shape faceted on the matrix {001} as the precipitates grow. For the cuboidal precipitates, the radius of a sphere with volume identical to that of the cuboid was calculated. The interface energy of $\gamma \approx 0.23$ J/m^2 between the Al matrix and the Al_3Sc particles and the diffusion coefficient of Sc in the Al matrix were derived independently from data on coarsening alone using the KV theory. Although the interface energies of spherical and cuboidal precipitates are thought to be actually different from each other, the energy for faceted {001} interface was not estimated.

Recently, Watanabe et al. have extended the KV theory to a general case of second-phase particle with any centro-symmetric shape [5]. They applied the generalized KV (GKV) theory to the experimental data on the coarsening of spherical, {001}-faceted cuboidal and {111}-faceted octahedral Co, Fe and Co-Fe precipitates with a face-centred cubic (fcc) structure in a Cu-Co alloy, a Cu-Fe alloy, and three Cu-Co-Fe alloys with different Co and Fe contents during ageing at 873 to 973 K, and then estimated the values of γ for sphere, {001} and {111} interfaces.

In this study, the Ostwald ripening of {001}-faceted cuboidal Al$_3$Sc precipitates in an Al-1wt%Mg-0.27wt%Sc alloy aged at 698, 723 and 748 K is examined by TEM. The interface energy for cuboidal precipitates, namely the {001} interface energy is determined using the GKV theory with the reported data regarding solute Sc depletion in the matrix during coarsening of Al$_3$Sc precipitates in the same alloy [4].

2 Experimental procedures

Al-1wt%Mg-0.27wt%Sc alloy ingots were prepared in a melting furnace under an Ar atmosphere using 99.99wt%Al, an Al-5wt%Mg master alloy and an Al-2.0wt%Sc master alloy. Specimen pieces were cut from the alloy ingots, solution-treated at 923 K for 24 h, quenched into cold water and subsequently aged in air at 698, 723 and 748 K. After the desired ageing times were reached, they were quenched into cold water.

3-mm diameter discs were punched from the aged specimens, mechanically ground down to 200 μm and electro-polished using a solution of 30vol% nitric acid and 70vol% ethanol at 240 K. Microscopy was performed using a JEOL 2000EX microscope at an operation voltage of 200 kV. The average size of Al$_3$Sc precipitates was measured from dark-field images of the precipitates taken using a low-index superlattice reflection of the precipitates in the zone axis parallel to the matrix [001]. To obtain statistically reliable data, more than 200 precipitates were analyzed for each ageing condition.

3 Results and discussion

3.1 Coarsening kinetics of cuboidal Al$_3$Sc precipitates

Figures 1(a) and 1(b) show dark-field images of Al$_3$Sc precipitates in an Al-1wt%Mg-0.27wt%Sc alloy aged at 723 K for 30 min and 27 h, respectively. The insets at

the lower right in Figures 1(a) and 1(b) are selected-area diffraction patterns (SADPs) taken from the areas containing the precipitates. Similar to the previous studies [4, 6], small Al$_3$Sc precipitates were first coherent and spherical, as exemplified in Figure 1(a). When the radius of precipitates was over about 20 nm, the precipitates were semi-coherent with the Al matrix [4] Moreover, as the precipitates size increased, Al$_3$Sc precipitates gradually changed from sphere to the nearly cuboidal shape with flat interfaces parallel to {001}, as clearly seen in Figure 1(b). Similar change in the shape of precipitates have been reported in some Ni-based super alloys [x] and Cu-Co system alloys[x], and explained by the energy analysis based on elastic strain energy and isotropic interface energy of the precipitates using the super sphere concept, which can describe continuously the shape transition from sphere to cuboid [x]. Even after the shape change occurred, the cube-on-cube orientation relationship was satisfied between the matrix and the Al$_3$Sc precipitates, as seen in the inset of Figure 1(b). In the case of cuboidal precipitates, the distance λ between the centre of a precipitate and {001}-faceted interface is measured as size of the precipitate. When r is taken as the radius of equivalent-volume sphere (EVS), the spherical-to-cuboidal shape transition took place at $r \approx 30$ nm.

The GKV mathematical treatment of coarsening predicts that the cube of the average size of precipitates, $\overline{\lambda^3}$, increases with ageing time t, as follows [5]:

$$\overline{\lambda^3} = Kt \qquad (1)$$

where K is the coarsening rate constant and given by

$$K = \left(\frac{\eta}{3\omega}\right)\frac{8\gamma V_m}{9\Lambda} . \qquad (2)$$

Here, η and ω are particle-shape-dependent constants (for cuboid, $\eta = 6$ and $\omega = 1$), γ is the interface energy between the Al$_3$Sc phase and the Al matrix, and V_m is the atomic volume per mol of the Al$_3$Sc phase, calculated from $V_m = N_a a^3/4$, where N_a is the Avogadro's number and a is the lattice constant of Al$_3$Sc (= 0.4106 nm [7]). The coefficient Λ is given as

$$A = \frac{\Delta c_{Sc}}{D_{Sc}} \left(\Delta c_{Sc} G_{ScSc}^{"} + \Delta C_{Mg} G_{ScMg}^{"} \right) + \frac{\Delta c_{Mg}}{D_{Mg}} \left(\Delta c_{Sc} G_{ScMg}^{"} + \Delta c_{Mg} G_{MgMg}^{"} \right), \qquad (3)$$

where $\Delta c_i = c_i^{Al_3Sc} - c_i^{Al}$; $c_i^{Al_3Sc/Al}$ is the concentration of the i with i = Sc or Mg in the Al_3Sc and matrix near the precipitate interface. During coarsening, the system is very close to equilibrium. This allows us to presume an approximation that $\Delta c_i = c_i^{Al_3Sc} - c_i^{Al} \approx c_i^{Al_3Sc}(\infty) - c_i^{Al}(\infty)$, where $c_i^{Al_3Sc/Al}(\infty)$ is the concentration far from the Al/Al$_3$Sc interfaces. The Sc concentration in the Al matrix is negligibly small at any ageing time compared to that in the Al$_3$Sc precipitates [4], $c_{Sc}^{Al_3Sc}$ = 0.25, and thus we obtain $\Delta c_{Sc} \approx c_{Sc}^{Al_3Sc}$. The Mg concentration in the Al$_3$Sc precipitates is assumed to be equal to zero, since first principles calculations predict the absence of Mg in the Al$_3$Sc phase [7]. The D_{Sc} or D_{Mg} is the diffusion coefficient of Sc or Mg in the Al matrix. The $G_{pq}^{"}$ are the second derivatives of the Gibbs free energy with respect to the concentration of p and q, with p, q =Sc, Mg. Assuming that the Al matrix phase is described by the dilute ideal solid-solution theory, the $G_{pq}^{"}$ can be written as

$$G_{ScSc}^{"} = \frac{RT\left(1 - c_{Mg}^{Al}(\infty)\right)}{c_{Sc}^{Al}(\infty)\left(1 - c_{Sc}^{Al}(\infty) - c_{Mg}^{Al}(\infty)\right)}, \qquad (4)$$

$$G_{ScMg}^{"} = \frac{RT}{1 - c_{Sc}^{Al}(\infty) - c_{Mg}^{Al}(\infty)} \quad \text{and} \qquad (5)$$

$$G_{MgMg}^{"} = \frac{RT\left(1 - c_{Sc}^{Al}(\infty)\right)}{c_{Mg}^{Al}(\infty)\left(1 - c_{Sc}^{Al}(\infty) - c_{Mg}^{Al}(\infty)\right)}. \qquad (6)$$

Equation (1) indicates that log-log plots of $\bar{\lambda}$ versus t yield time exponents. Figure 2 displays the $\bar{\lambda}$ against t on logarithmic scales. The experimental slopes are almost identical to the value of 1/3, predicted by the GKV theory. Figure 3 shows the coarsening curves of Al$_3$Sc precipitates in the alloy aged at 698, 723 and 748 K. For each temperature, a linear relationship exists between $\bar{\lambda}$ and t. Experimental values of the rate constant K were determined from the slopes of the straight lines by the least-squares method. Table 1 lists the

Watanabe et al.

values of K, together with the values of K obtained in the previous study by assuming the cuboidal shape of precipitate to be an EVS [4]. The values of K in the previous study were unaffected by the changes in coherency and shape of the precipitates. The present values of K are smaller than those obtained in previous study.

The GKV theory also predicts that the solute concentration C in solid solution after coarsening time t varies as [5]

$$C - C_{\mathrm{e}} = kt^{-1/3},\qquad (7)$$

where C_{e} is the solid-solubility of Sc in the Al matrix and k is a coarsening parameter given by

$$k = \left(\frac{3\omega}{\eta}\right)^{1/3} \frac{(3\gamma V_{\mathrm{m}})^{2/3}\Lambda^{1/3}\Delta c_{\mathrm{Sc}}}{\Delta c_{\mathrm{Sc}}\left(\Delta c_{\mathrm{Sc}}G''_{\mathrm{ScSc}} + \Delta c_{\mathrm{Mg}}G''_{\mathrm{ScMg}}\right) + \Delta c_{\mathrm{Mg}}\left(\Delta c_{\mathrm{Mg}}G''_{\mathrm{MgMg}} + \Delta c_{\mathrm{Sc}}G''_{\mathrm{ScMg}}\right)}.\qquad (8)$$

Following equation (7), C versus $t^{-1/3}$ was plotted for the Al-1wt%Mg-0.27wt%Sc alloy aged at 698, 723 and 748 K. For each temperature, C rapidly decreased at the initial stage of ageing and, over a time, a linearity existed between C and $t^{-1/3}$. The slopes and intercepts ($t^{-1/3} \rightarrow 0$, i.e. $t \rightarrow \infty$) yielded values of k and C_{e}, respectively. Table 1 also lists the values of k and C_{e}, thus obtained, for the alloy aged at 698, 723 and 748 K in our previous study [4].

3.2 **Calculation of γ from experimental data**

Combination of the K and k enables the matrix / precipitate interface energy γ to be calculated without having to assume the values of D_{Sc} and D_{Mg}:

$$\gamma = \frac{K^{1/3}k\left[\Delta c_{\mathrm{Sc}}\left(\Delta c_{\mathrm{Sc}}G''_{\mathrm{ScSc}} + \Delta c_{\mathrm{Mg}}G''_{\mathrm{ScMg}}\right) + \Delta c_{\mathrm{Mg}}\left(\Delta c_{\mathrm{Mg}}G''_{\mathrm{MgMg}} + \Delta c_{\mathrm{Sc}}G''_{\mathrm{ScMg}}\right)\right]}{2V_{\mathrm{m}}\Delta c_{\mathrm{Sc}}}\qquad (9)$$

Using experimental values of K, k and $C_{\mathrm{e}} \approx c_{\mathrm{Sc}}^{\mathrm{Al}}(\infty)$, values of γ are calculated by equation (9). The resulting values of γ are listed in Table 2. The values of γ range from 0.184 to 0.205 J/m^2 and the average of the values is 0.19 J/m^2. This value is smaller than the value of $\gamma \approx 0.23$ J/m^2

for the EVS precipitates obtained in our previous study [4]. Interestingly, this value of $\gamma \approx 0.19$ J/m^2 is in good agreement with the values of $\gamma = 0.192$ J/m^2 for the {001} plane at 0K obtained using the first-principles calculation by Asta *et al.* [8].

In a previous study [9], we have examined the coarsening behaviour of Al$_3$Sc precipitates in the same Al-Mg-Sc alloy aged at a temperature of 573K by TEM and electrical resistivity. On ageing at 573 K, the average radius of precipitates was only 7 nm even in the case that the longest ageing time (5000 h) was applied, and the precipitates were perfectly coherent with the Al matrix and had a sphere shape. The interface energy γ_s of spherical precipitates obtained by the application of the KV theory is 0.23 J/m^2, which agrees well with the interface energy for the EVS precipitates [4]. Even when the shape of precipitate changed from a sphere to a cube, the coarsening rates of the EVS precipitates were unchanged [4]. Moreover, we have shown in the previous study [5] that the coarsening rate of second-phase precipitates at a given temperature is dependent upon the interface energy alone, even when the precipitates have internal stress and corresponding elastic strain energy: that is, the Wluff construction [x] that the shape of a particles is determined by minimization of the interface energy does not hold true in actual systems. Therefore, the relation $\gamma_s = g_{001}\gamma_{001}$ must be satisfied. Here g_{001} and γ_{001} are the ratio of the interfacial area of the cube to that of EVS and the energy for {001} interface, respectively. Using the average values of $\gamma_{001} \approx 0.19$ J/m^2 in Table 2 and $g_{001} = 1.24$, we have $g_{001}\gamma_{001} \approx 0.236$ J/m^2, which is identical to the value of γ_s.

3.3 Energy consideration on precipitate shape transition

Onaka et al. [10] and Satoh and Johnson [11] have shown that, in some cases of coherent precipitates in cubic materials, the precipitate shape is controlled by minimization of the sum of the elastic strain energy and interface energy of a precipitate. Moreover, Onaka et al. [12] have calculated the elastic strain energies E_v per unit volume of cubic materials containing spherical and {001}-cuboidal precipitates with a purely dilatational misfit strain, using the

supersphere concept. In their energy calculations, the elastic anisotropy of the matrix has been taken into consideration. In the present and previous studies [4, 6], the spherical-to-cuboidal shape change of Al_3Sc precipitates took place as the precipitate size increases. We will consider the sum of the elastic strain and interface energies of a precipitate so as to discuss the shape transition.

Assuming that the precipitate shapes are perfect sphere and cube, the total free energy G of a precipitate can be written as [10]

$$G = S \cdot \gamma + V \cdot E_v, \tag{10}$$

where S and V are the interface area and the volume of the precipitate, respectively. According to Onaka et al. [12], $E_v = \Phi C_{44} \varepsilon^2$, where Φ is a shape-dependent constant, C_{44} is the shear modulus of the matrix and ε is the purely dilatational misfit strain of precipitate phase. For the present system, $\varepsilon = 0.015$ calculated from the lattice constants of Al [13] and Al_3Sc [7], $C_{44} = 2.85 \times 10^{10}$ Pa [14] and $\Phi = 3.81$ and 3.73 for sphere and cube [12] are employed to obtain values of E_v. Using the averages of γ for both shapes in Table 2, values of G_s and G_c for sphere and cube are calculated from equation (10) as a function of r. Figure 4 shows $G_s - G_c$ against r. In the rage of $0 < r < 33$ nm, $G_s - G_c < 0$, but when $r > 33$ nm, $G_s - G_c > 0$. This means that the spherical shape is energetically favourable when the precipitate is smaller than 33 nm. This corresponds to the experimental result that the spherical-to-cuboidal transition of Al_3Sc precipitates occurs at $r \approx 30$ nm.

6. Conclusions

The Ostwald ripening of Al_3Sc precipitates in an Al-1wt%Mg-0.27%Sc alloy has been investigated by transmission electron microscopy observations. Al_3Sc precipitates smaller than about 30 nm in radius r of equivalent volume sphere are spherical, while larger Al_3Sc precipitates have a cuboidal shape faceted on {001}. The average size of the cuboidal precipitates increases with ageing time t as $t^{1/3}$, as predicted by the generalized Kuehmann and

Voorhees (KV) theory [5]. By applying the generalized KV theory to the experimental data on coarsening of the cuboidal precipitates together with the reported data in literature [4], the energy γ for $\{001\}$ interface has been determined. The estimate of $\gamma \approx 0.19$ J/m^2 is in good agreement with the reported value of 0.192 J/m^2 calculated using the first-principles calculation [8]. The sphere-to-cube shape transition of Al$_3$Sc precipitates at $r \approx 30$ nm can be well explained by a simple energy analysis based on the elastic strain and interface energies of the precipitate.

Watanabe et al.

Acknowledgements

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Tables with captions

Table 1 Rate constants K for cuboidal Al$_3$Sc precipitates in an Al−1wt%Mg−0.27wt%Sc alloy aged at 698, 723 and 748 K. Also shown are values of K for equivalent-volume sphere (EVS) precipitates, coarsening parameter k and equilibrium concentrations C_e of Sc in the Al matrix obtained in the previous study [4].

Temperature (K)	K (m³/s)		k (s$^{1/3}$) [4]	C_e (wt%) [4]
	cuboid	EVS [4]		
698	$(2.35 \pm 0.01)\times10^{-29}$	4.13×10^{-29}	1.52×10^{-3}	1.41×10^{-2}
723	$(9.68 \pm 0.63)\times10^{-29}$	1.82×10^{-28}	1.22×10^{-3}	1.99×10^{-2}
748	$(4.03 \pm 0.20)\times10^{-28}$	5.57×10^{-28}	1.15×10^{-3}	2.82×10^{-2}

Table 2 Energy γ for {001} interface of Al$_3$Sc precipitates, obtained using Equation (9) and calculated using the first-principles method by Asta et al. [8]. Also shown are values of γ for EVS precipitates obtained in the previous study [4].

Temperature (K)	γ (J/m^2)		EVS [4]
	{001} interface		
	experimental	calculated [8]	
698	0.195 ± 0.018		0.235
723	0.184 ± 0.024	0.192	0.227
748	0.205 ± 0.021		0.228

Figure captions

Fig. 1 Dark-field images of Al$_3$Sc precipitates in an Al−1wt%Mg−0.27wt%Sc alloy aged at 723 K for (a) 30 min and (b) 27 h. The zone axis is [001].
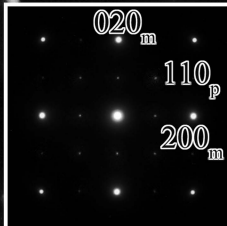
Fig. 2 Variation in the average precipitate size $\bar{\lambda}$ with ageing time t for an Al−1wt%Mg−0.27wt%Sc alloy aged at 698, 723 and 748 K. Dashed lines with slope = 1/3 are superimposed.

Fig. 3 Coarsening plots of cuboidal Al$_3$Sc precipitates in an Al−1wt%Mg−0.27wt%Sc alloy aged at 698, 723 and 748 K.

Fig. 4 Plot of the $G_s − G_c$, calculated from Eq. (10), as a function of radius r of equivalent-volume sphere (EVS).

(a)

100 nm

020$_m$

110$_p$

200$_m$

(b)

200 nm

020ₘ

110ₚ

200ₘ