Coarsening Behavior of Al₃Sc Precipitates in an Al–Mg–Sc Alloy

Chihiro Watanabe, Daizen Watanabe* and Ryoichi Monzen

Division of Innovative Technology and Science, Kanazawa University, Kanazawa 920-1192, Japan

The coarsening of Al₃Sc precipitates in an Al–1 mass%Mg–0.27 mass%Sc alloy aged at 673 to 748 K has been studied by measuring both the precipitate size by transmission electron microscopy (TEM) and the Sc concentration in the Al matrix by electrical resistivity measurements. Using the Kuehmann and Voorhees (KV) model which describes diffusion-limited coarsening in ternary systems, the values of γ and D can be calculated, independently of one another. This approach has already been applied in some ternary systems. We shall provide evidence that there exists a blended stage of growth and coarsening of Al₃Sc precipitates prior to a coarsening stage of precipitates, and the value of γ is immune to the change in coherency of the Al/Al₃Sc interfaces. In this paper, the detailed coarsening behavior of Al₃Sc precipitates in an Al–1 mass%Mg–0.27 mass%Sc alloy has been studied in the temperature range 673 to 748 K. Observations by TEM and electrical resistivity measurements were performed in order to describe the microstructural evolution and concentration of Sc in the Al matrix. The radius for the coherent/semi-coherent transition of the Al₃Sc precipitates in an Al–1 mass%Mg–0.27 mass%Sc alloy has been independently derived from data on coarsening using the LSW theory. Moreover, the Gibbs-Thompson equation has been utilized to give a value of γ using coarsening data obtained from TEM and electrical resistivity measurements. The value of γ obtained from the LSW theory is 0.22 J/m², which is nearly identical to 0.23 J/m² from the Gibbs-Thompson equation. However, we could not examine whether the value of γ is for the coherent interface or semi-coherent interface.

In this paper, the detailed coarsening behavior of Al₃Sc precipitates in an Al–1 mass%Mg–0.27 mass%Sc alloy has been studied in the temperature range 673 to 748 K. Observations by TEM and electrical resistivity measurements were performed in order to describe the microstructural evolution and concentration of Sc in the Al matrix. The radius for the coherent/semi-coherent transition of the Al₃Sc precipitates in an Al–1 mass%Mg–0.27 mass%Sc alloy has been independently derived from data on coarsening using the LSW theory. Moreover, the Gibbs-Thompson equation has been utilized to give a value of γ using coarsening data obtained from TEM and electrical resistivity measurements. The value of γ obtained from the LSW theory is 0.22 J/m², which is nearly identical to 0.23 J/m² from the Gibbs-Thompson equation. However, we could not examine whether the value of γ is for the coherent interface or semi-coherent interface.

1. Introduction

Aluminum alloys with magnesium as the major alloying element constitute a group of non heat-treatable alloys with medium strength, high ductility, excellent corrosion resistance and weldability. Unfortunately, the strength of such Al–Mg system alloys is lower than precipitation-hardening Al alloys. However, the addition of a small amount of scandium has been found to significantly improve the strength of Al–Mg alloys owing to the presence of coherent, finely dispersed L1₂ Al₃Sc precipitates that can be obtained at a high number density, thus preventing the dislocation motion. Also the Al₃Sc precipitates have modest coarsening rates at elevated temperatures, leading to the effective suppression of recrystallization and the stabilization of fine grains, at high temperatures. It is therefore important to understand the coarsening characteristics of the Al₃Sc precipitates in Al–Mg–Sc alloys since this governs the stability of the mechanical properties at elevated temperatures.

Several experiments have been performed on the coarsening behavior of Al₃Sc precipitates in Al–Sc binary alloys. Some studies by transmission electron microscopy (TEM) and electrical resistivity reports have been made at 673 to 763 K as a basis of TEM observations with a numerical model. The radius for the coherent/semi-coherent transition of the precipitates was determined from TEM images as 15 to 40 nm. By fitting the predicted curves from the numerical model to the experimental results, the energies of the coherent and semi-coherent interfaces between the Al₃Sc precipitates and the Al matrix were estimated as 0.12 and 0.17 J/m². By measuring both the Al₃Sc precipitate size by TEM and the Sc concentration in the Al matrix by electrical resistivity, we have investigated the coarsening of Al₃Sc precipitates in an Al–0.2 mass% Sc alloy aged at 673, 698 and 723 K. The Al/Al₃Sc interface energy γ and diffusion coefficient D of Sc in the Al matrix have been independently derived from data on coarsening using the LSW theory. Moreover, the Gibbs-Thompson equation has been utilized to give a value of γ using coarsening data obtained from TEM and electrical resistivity measurements. The value of γ obtained from the LSW theory is 0.22 J/m², which is nearly identical to 0.23 J/m² from the Gibbs-Thompson equation. However, we could not examine whether the value of γ is for the coherent interface or semi-coherent interface.

2. Experimental

Al–1 mass%Mg–0.27 mass%Sc alloy ingots were prepared in a melting furnace under an Ar atmosphere using 99.99 mass%Al, an Al–5 mass%Mg master alloy and an Al–2.0 mass%Sc master alloy. Specimens cut from the alloy ingots were solution-treated at 923 K for 24 h, quenched into cold water and subsequently aged in air at 673, 698, 723 and 748 K. After the desired aging times were reached, they were quenched into cold water. The specimens for electrical resistivity measurements were cut to the size of 200 mm × 12 mm × 0.3 mm. After aging, resistivity measurements were made at liquid nitrogen temperature (77 K) using a standard four-point potentiometric technique. The measure-
ments were repeated ten times to obtain one data point, reversing the current direction to eliminate the stray electro motive force. The cross-sectional area of specimens was measured at different positions and the average value was evaluated.

3 mm diameter discs were punched from the aged specimens, mechanically ground down to 200 μm and electropolished using a solution of 30 vol% nitric acid and 70 vol% ethanol at 240 K. Microscopy was performed using a JEOL 2000EX microscope at an operation voltage of 200 kV. The average radii of precipitates were measured from dark-field images of the Al₃Sc precipitates taken using a low-index superlattice reflection of the Al₃Sc precipitates in a low index zone axis, typically parallel to matrix [001]. The precipitate coherency was judged from the Ashby and Brown contrast15,16 which appears around a spherical coherent precipitate in bright-field images. The details of the principle and process for the judgment of precipitate coherency are described in the literature.8,17) The ratio of semi-coherent precipitates was determined from a pair of the dark-field and bright-field images from the same region. To obtain statistically reliable data, more than 200 precipitates were analyzed for each aging condition. In order to test the presence of Mg in the Al matrix and Al₃Sc precipitates, TEM foils were examined in a JEOL 2010 FE microscope operated at 200 kV and equipped with an energy dispersive X-ray spectroscopy system. The electron beam diameter used was 0.5 nm and the foil thickness examined was about 20 nm.

3. Results

3.1 Coarsening behavior of Al₃Sc precipitates

The Al–Mg–Sc ternary equilibrium phase diagram18) shows that Mg in the present Al–1 mass%Mg–0.27 mass%Sc alloy does not form any compounds at aging temperatures examined. In fact, aging of the alloy at 673 to 748 K produced only Al₃Sc precipitates in the Al matrix.

The precipitate size and distribution were examined from dark-field TEM images. Figure 1 shows the effect of aging time on the precipitate size and distribution. As would be expected, the size of precipitates increases and the number density of precipitate decreases as the aging time increases.

Small Al₃Sc precipitates were nearly spherical and coherent with the Al matrix, as shown in Figs. 1(a) and 2(a). However, the Ashby and Brown contrasts became irregular, as revealed in Fig. 2(b), when the precipitate radius was over about 20 nm. According to the literature,8,17) we judged the smallest Al₃Sc precipitate labeled C in Fig. 2(b) is coherent, but other precipitates in Fig. 2(b) are semi-coherent. This indicates that the interface between the Al₃Sc precipitate and Al matrix became semi-coherent with precipitate growth. Large semi-coherent precipitates larger than about 30 nm in radius tended to become a nearly cuboidal shape with flat interfaces parallel to {100}, as clearly recognized in Fig. 1(b). These observations are similar to those of our previous work.9) The nearly cuboidal shape is assumed to be a supersphere, and the supersphere is reduced to a sphere which has the same volume as the supersphere, as in the previous study.9)

The coherency of the Al/Al₃Sc interfaces was judged from the Ashby-Brown contrast in bright-field images. Figure 3 shows the ratio of semi-coherent Al₃Sc precipitates to the total number of precipitates at each average radius. The ratio rapidly increases from about 20 to 56 nm, and no clear dependence on aging temperature and time was observed. Similar to the result for an Al–0.2 mass%Sc alloy by Iwamura and Miura,8) the precipitation process of Al₃Sc in the present ternary alloy is divided into three stages: (1) coherent stage (r < 20 nm), with almost all precipitates coherent, (2) intermediate stage (20 < r < 56 nm), with coexisting coherent and semi-coherent precipitates and (3) semi-coherent stage (r > 56 nm), with almost all precipitates semi-coherent. It should be, however, noted that the critical radius for coherent/semi-coherent transition of the Al₃Sc precipitates in the present ternary alloy is larger than that (15 < r < 40 nm) for the Al–Sc binary alloy obtained by Iwamura and Miura.9) This can be understood, because the lattice parameter of Al₃Sc is larger than that of Al and the solute Mg makes the lattice parameter of Al matrix slightly larger.17) The addition of 1 mass%Mg causes an increase in the lattice parameter of Al matrix from 0.40496 to 0.40538 nm19) and thus a decrease in the lattice misfit between the Al₃Sc precipitate and Al matrix from 0.014 to 0.012.

In the KV mathematical treatment of coarsening, the time dependence of the average precipitate radius r is described by12)
\[ r^n - r_0^n = Kt, \]  

where \( n = 3 \) is the predicted exponent, \( r_0 \) is the average radius of precipitates at the onset of coarsening and \( K \) is the rate constant which is dependent on the interfacial energy and the diffusion coefficient of Mg or Sc in Al. Equation (1) exhibits the same time dependence for both binary and ternary systems, but the \( K \) is significantly different, as shown later.

Log-log plots of \( r \) versus \( t \) yield slopes of \( 1/n \). Figure 4 displays the average precipitate radius \( r \) against aging time \( t \) on logarithmic scales. Figure 4 indicates that the experimental slopes are nearly identical to the value \( 1/3 \) excepting at early times. Slopes smaller than \( 1/3 \) in the initial stage of aging could be an indication that the system is in a transient regime before reaching a coarsening stage. Figure 5 shows the coarsening curves of the Al\(_3\)Sc precipitates in the present ternary alloy aged at 673, 698, 723 and 748 K. Hereafter, the data for an Al–0.2 mass\%Sc alloy will be taken from the literature. A linear relationship exists between \( r^3 \) and \( t \), except for the early stage of aging. As shown in the upper right of Fig. 5, the growth rate decreases gradually and reaches a constant value above about \( 3 \times 10^5 \), \( 6 \times 10^4 \), \( 10^4 \) and \( 3 \times 10^3 \) s at 673, 698, 723 and 748 K respectively. The cause of the growth rate change will be discussed later.

Experimental values of \( K \) were determined from the slopes of the straight lines using experimental points above these times in Fig. 5, and Table 1 lists the values of \( K \). The addition of Mg does not significantly change the coarsening rate.
3.2 Change in Sc concentration in Al

The electrical resistivity showed first a rapid decrease and then a gradual decrease with increasing aging time. This is similar to previous results of electrical resistivity measurements of aged Al–Sc alloys.\(^7\)\(^,9\)

The KV model of coarsening for a ternary alloy predicts that the solute concentration \(C\) in solid solution after coarsening time \(t\) varies as\(^2\)

\[
C - C_e = kt^{-1/3},
\]

where \(C_e\) is the solid-solubility of Sc in the Al matrix and \(k\) is a coarsening parameter.

An energy-dispersive X-ray analysis of Al\(_3\)Sc precipitates at the edge of TEM foils revealed that the concentration of Mg was less than 0.2 mass%, indicating that the Al matrix contains nearly 1 mass% Mg, since the equilibrium volume fraction of the Al\(_3\)Sc precipitates is about 0.006. Thus, the values of \(C\) in the Al matrix were determined by applying the experimental data in the literature,\(^7\) after the resistivity increment caused by 1 mass% Mg in the matrix was removed using the data in the literature.\(^20\)

Following eq. (2), plots of \(C\) against \(t^{-1/3}\) are shown in Fig. 6. Hereafter, the concentration will be represented by atomic fraction. For each aging temperature, \(C\) rapidly decreases at the initial stage of aging and, over a time, a linearity is observed between \(C\) and \(t^{-1/3}\). Table 1 lists the values of \(k\) obtained from the slopes of the straight lines, determined by the least-squares method. Table 2 summarizes the values of \(C_e\), obtained directly by extrapolation to \(t^{-1/3} = 0\). The quasi-binary Al–2 mass%Mg–Sc phase diagram exhibits much smaller Sc solubility than the Al–Sc binary system.\(^13\) However, the addition of 1 mass% Mg does not significantly affect the values of \(C_e\), as shown in Table 2.

Table 1 Values of the coarsening rate constant \(K\) and coarsening parameter \(k\) for Al–1 mass%Mg–0.27 mass%Sc and Al–0.28 mass%Sc\(^9\) alloys.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(K) (m(^3)s(^{-1}))</th>
<th>(k) (s(^{1/3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>(8.40 ± 0.79) \times 10^{-30}</td>
<td>(1.60 ± 0.09) \times 10^{-3}</td>
</tr>
<tr>
<td>698</td>
<td>(4.13 ± 0.04) \times 10^{-29}</td>
<td>(1.52 ± 0.14) \times 10^{-3}</td>
</tr>
<tr>
<td>723</td>
<td>(1.82 ± 0.09) \times 10^{-28}</td>
<td>(1.22 ± 0.13) \times 10^{-3}</td>
</tr>
<tr>
<td>748</td>
<td>(5.57 ± 0.14) \times 10^{-28}</td>
<td>(1.15 ± 0.10) \times 10^{-3}</td>
</tr>
</tbody>
</table>

Table 2 Values of the equilibrium solubility \(C_e\) of Sc in the Al matrix for Al–1 mass%Mg–0.27 mass%Sc alloy, and Al–0.28 mass%Sc\(^9\) and Al–0.25 mass%Sc alloys.\(^7\)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(C_e) (mass%)</th>
<th>Al–1Mg–0.27Sc</th>
<th>Al–0.28Sc</th>
<th>Al–0.25Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>(1.62 ± 0.02) \times 10^{-2}</td>
<td>1.58 \times 10^{-2}</td>
<td>1.97 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>698</td>
<td>(2.59 ± 0.03) \times 10^{-2}</td>
<td>2.57 \times 10^{-2}</td>
<td>2.38 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>723</td>
<td>(3.65 ± 0.03) \times 10^{-2}</td>
<td>3.74 \times 10^{-2}</td>
<td>3.45 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>748</td>
<td>(5.17 ± 0.07) \times 10^{-2}</td>
<td>—</td>
<td>4.90 \times 10^{-2}</td>
<td></td>
</tr>
</tbody>
</table>
These times are identical to those above which, in Fig. 6, the kinetics of the decay of supersaturation with r on aging at the temperatures obey the prediction of the KV model. Therefore, the coarsening of the Al3Sc precipitates begins over about 3 × 10^5 s at 673 K, 6 × 10^4 s at 698 K, 10^4 s at 723 K and 3 × 10^3 s at 748 K. On the other hand, Nc keeps falling and the slopes show the expected theoretical value of −1 for precipitate coarsening in a binary system and a ternary system. These results indicate that the growth and coarsening take place simultaneously before the coarsening starts.

Figure 8 presents the age hardening curves of the present alloy aged at 673, 698, 723 and 748 K. The hardness shows a rapid decrease with aging time for each aging temperature. This rapid decrease in the hardness can be understood, since the yield stress of an Al–2 mass%Mg–0.2 mass%Sc alloy containing Al3Sc precipitates larger than r ≈ 2.4 nm is controlled by the Orowan mechanism in room temperature, and the number density of the Al3Sc precipitates rapidly decreases with t, as shown in Fig. 7. It is usually assumed that the coarsening of precipitates begins as soon as the hardness or the number density of precipitates starts to decrease. However, comparison between Figs. 7 and 8 reveals that the hardness already decreases before the beginning of the coarsening of Al3Sc precipitates. Therefore, it is actually difficult to judge the commencement of precipitate coarsening, if the change in the volume fraction of precipitates is not examined.

### 3.3 Calculation of $\gamma$ and $D$

The coarsening rate constant $K$ for the KV coarsening model for ternary systems is given as\(^{12}\)

$$K = \frac{8\gamma V_m}{9\Lambda}.$$  

(4)

Here, $\gamma$ is the interface energy between the Al3Sc phase and the Al matrix and $V_m$ is the atomic volume per mol of the Al3Sc phase, calculated from $V_m = N_A a^3/4$, where $N_A$ is Avogadro’s number and $a$ is the lattice constant of Al3Sc (= 0.4106 nm\(^{17}\)). The coefficient $\Lambda$ is given as

$$\Lambda = \frac{\Delta c_{Sc}^r}{D_{Sc}}(\Delta c_{Sc}G_{ScSc}^{\prime} + \Delta c_{Mg}G_{ScMg}^{\prime})$$

$$+ \frac{\Delta c_{Mg}}{D_{Mg}}(\Delta c_{Sc}G_{ScMg}^{\prime} + \Delta c_{Mg}G_{MgMg}^{\prime}),$$

(5)

where $\Delta c_i = c_i^{Al3Sc} - c_i^{Al}$, $c_i^{Al3Sc/Al}$ is the concentration of the i with i = Sc or Mg in the Al3Sc and matrix near the precipitate interface. During coarsening, the system is very close to equilibrium. This allows us to assume an approximation that $\Delta c_i = c_i^{Al3Sc} - c_i^{Al} \approx c_i^{Al3Sc}(\infty) - c_i^{Al}(\infty)$, where $c_i^{Al3Sc/Al}(\infty)$ is the concentration far from the Al/Al3Sc interfaces. At any aging time, the Sc concentration in the Al matrix is negligibly small compared to that in the Al3Sc precipitates, $c_{Sc}^{Al3Sc} = 0.25$, and thus we obtain $\Delta c_{Sc} \approx c_{Sc}^{Al3Sc}$. The Mg concentration in the Al3Sc matrix is approximately a constant. The Mg concentration in the Al3Sc precipitates is assumed to be equal to zero, since first principles calculations predict the absence of Mg in the Al3Sc phase.\(^{23}\) The $D_{Sc}$ or $D_{Mg}$ are 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 $G_{pq}^{\prime}$ can be written as

$$G_{ScSc}^{\prime} = \frac{RT(1 - c_{Mg}^{Al3Sc}(\infty))}{c_{Sc}^{Al3Sc}(\infty)(1 - c_{Sc}^{Al3Sc}(\infty) - c_{Mg}^{Al}(\infty))},$$

(6)

$$G_{ScMg}^{\prime} = \frac{RT}{1 - c_{Sc}^{Al3Sc}(\infty) - c_{Mg}^{Al}(\infty)}$$

(7)

$$G_{MgMg}^{\prime} = \frac{RT(1 - c_{Sc}^{Al3Sc}(\infty))}{c_{Mg}^{Al3Sc}(\infty)(1 - c_{Sc}^{Al3Sc}(\infty) - c_{Mg}^{Al}(\infty)).}$$

(8)

The coarsening parameter $k$ describing the Sc concentration in the matrix during coarsening is given by the equation\(^{14}\)

$$k = \frac{(3\gamma V_m)^{2/3} A^{1/3} \Delta c_{Sc}}{\Delta c_{Sc}(\Delta c_{Sc}G_{ScSc}^{\prime} + \Delta c_{Mg}G_{ScMg}^{\prime} + \Delta c_{Mg}G_{MgMg}^{\prime} + \Delta c_{Sc}G_{ScMg}^{\prime})},$$

(9)

By combining eqs. (4) to (9), the Al/Al3Sc interface energy $\gamma$ can be expressed as

$$\gamma = \frac{K^{1/3}[\Delta c_{Sc}(\Delta c_{Sc}G_{ScSc}^{\prime} + \Delta c_{Mg}G_{ScMg}^{\prime} + \Delta c_{Mg}G_{MgMg}^{\prime} + \Delta c_{Sc}G_{ScMg}^{\prime})]}{2V_m \Delta c_{Sc}},$$

(10)

and the diffusion coefficient $D_{Sc}$ of Sc in the Al was also deduced with the relations of $\Delta c_{Sc} \gg \Delta c_{Mg}$ and $D_{Sc} \ll D_{Mg}$\(^{23,24}\) that

$$D_{Sc} = \frac{9}{4} K^{2/3} k^{-1} \frac{\Delta c_{Sc}^r(\Delta c_{Sc}G_{ScSc}^{\prime} + \Delta c_{Mg}G_{ScMg}^{\prime})}{\Delta c_{Sc}(\Delta c_{Sc}G_{ScSc}^{\prime} + \Delta c_{Mg}G_{ScMg}^{\prime}) + \Delta c_{Mg}(\Delta c_{Sc}G_{ScMg}^{\prime} + \Delta c_{Mg}G_{MgMg}^{\prime}).}$$

(11)
Using experimental values of $K$, $k$, and $C_c$, the values of $\gamma$ and $D_{sc}$ are calculated by eqs. (10) and (11). The resulting values of $\gamma$ and $D_{sc}$ are listed in Table 3. The values of $\gamma$ range from 0.225 to 0.235 J/m$^2$ and the average of the values is 0.231 J/m$^2$.

Figure 9 presents the Arrhenius plot of $D_{sc}$ obtained as a function of $T^{-1}$, together with the data for the Al–Sc alloy obtained by Watanabe et al. The Mg addition does not significantly change the $D_{sc}$ values. The pre-exponential factor $D_0$ and the activation energy $Q$ can be determined from the intercept and slope of the straight line fitted to the $D_{sc}$ data. The estimated values of $D_0$ and $Q$ were $(8.8 \pm 2.9) \times 10^{-4} \text{m}^2/\text{s}$ and $177 \pm 7 \text{kJ/mol}$, which agree well with $5.3 \times 10^{-4} \text{m}^2/\text{s}$ and $174 \text{kJ/mol}$ for impurity diffusion of Sc in Al obtained using a tracer diffusion technique by Fujikawa.

### Table 3: Values of the interface energy $\gamma$ and diffusion coefficients of Sc in Al calculated for Al–1 mass%Mg–0.27 mass%Sc alloy. Also shown are values of $\gamma$ for Al–0.28 mass%Sc alloy.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\gamma$ (J/m$^2$)</th>
<th>$D$ (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>$0.225 \pm 0.022$</td>
<td>$(1.45 \pm 0.17) \times 10^{-17}$</td>
</tr>
<tr>
<td>698</td>
<td>$0.235 \pm 0.024$</td>
<td>$(4.42 \pm 0.40) \times 10^{-17}$</td>
</tr>
<tr>
<td>723</td>
<td>$0.227 \pm 0.031$</td>
<td>$(1.48 \pm 0.19) \times 10^{-16}$</td>
</tr>
<tr>
<td>748</td>
<td>$0.228 \pm 0.024$</td>
<td>$-(3.31 \pm 0.31) \times 10^{-16}$</td>
</tr>
</tbody>
</table>

Fig. 9 Comparison of the diffusivity values obtained in the present study with those available in the literature by Fujikawa and Watanabe et al.

### 4. Discussion

The obtained value of $\gamma \approx 0.23 \text{J/m}^2$ is nearly identical to the average value of $\gamma \approx 0.221 \text{J/m}^2$ for the Al–Sc alloy. Marquis et al. reported using three-dimensional atom probe microscopy that Mg atoms segregate at the Al/Al$_3$Sc interface by a factor of 2 to 3 in an Al–2 mass%Mg–0.2 mass%Sc alloy aged at 573 K, even when the Al$_3$Sc precipitates are perfectly coherent with the Al matrix. If this is also the case in the present study, the interface segregation of Mg should lead to at most 0.011 J/m$^2$ reduction in $\gamma$, and should reduce the coarsening rate of the Al$_3$Sc precipitates by approximately 5%, according to the prediction by Marquis et al. However, such a small reduction in the coarsening rate and interface energy cannot be detected in this study.

Iwamura and Miura have investigated the coarsening behavior of Al$_3$Sc precipitates in an Al–0.2 mass%Sc alloy in the temperature range 673 to 763 K on the basis of TEM observations with a numerical model. The radius for coherent/semi-coherent transition of the precipitates has been determined from TEM images as 15 to 40 nm. It has also been shown that the average radius $r$ of the Al$_3$Sc precipitates obeys the $r^3$ growth law both in the coherent stage ($r < 15$ nm) and in the semi-coherent stage ($r > 40$ nm) but the coarsening is delayed in the intermediate stage (15 $r < 40$ nm). Similar to the observation by Iwamura and Miura, the growth rate of Al$_3$Sc precipitates decreases gradually and reaches a constant value after a certain aging time, as shown in the upper right of Fig. 5. It should be, however, recalled that the Ostwald ripening begins over about $3.0 \times 10^5$, $6.5 \times 10^4$, $10^4$, and $3 \times 10^3$, namely, over 18, 15, 11, and 10 nm in average radius on aging at 673, 698, 723, and 748 K respectively (Figs. 5, 6, and 7). The radii at the beginning of coarsening are smaller than the transition radius $r \approx 20$ nm from the coherent stage to the intermediate stage in Fig. 3. In the mixed stage of growth and coarsening before the coarsening stage, supersaturated Sc atoms in the Al matrix tend to be captured by the Al$_3$Sc precipitates. This may explain the faster growth of the Al$_3$Sc precipitates in the mixed stage. Therefore, the change in growth rate cannot be attributable to the loss in coherency of the Al$_3$Sc precipitates but the transition from the growth and coarsening stage to the coarsening stage.

Iwamura and Miura have been estimated the coherent-interface and semi-coherent-interface energies as 0.12 and 0.171 J/m$^2$, by fitting the predicted curves from the numerical model to the experimentally obtained coarsening curves. This increase of the interface energy for coherency loss was understood by the introduction of an interfacial dislocation network. The energy $\gamma_{\text{dis}}$ of the interfacial dislocation network per unit area is expressed as follows:27

$$\gamma_{\text{dis}} = \frac{Gb}{2\pi^2} \left[ 1 + \beta^2 - \frac{(1 + \beta^2)^{1/2}}{\beta} \left( 2\beta^2 - 1 \right) \right], \tag{12}$$

$$\beta = \frac{\pi \delta}{1 - v}, \tag{13}$$

where $b$ is the magnitude of the Burgers vector, $\delta$ is a lattice misfit between the precipitate and matrix, $G$ is the shear modulus of the matrix and $v$ is the Poisson ratio of the matrix. In the present case, substitution of $G = 26.5 \text{GPa}$, $b = 0.287 \text{nm}$, $\delta = 0.012$ (calculated from the lattice constants of the matrix and Al$_3$Sc) and $\nu = 0.347$ in eqs. (12) and (13) produces $\gamma_{\text{dis}} = 0.077 \text{J/m}^2$. Equation (4) indicates that the introduction of an interfacial dislocation network should increase the coarsening rate of the Al$_3$Sc precipitates by approximately 30%. However, the increase in growth rate corresponding to the transition from the intermediate stage to the semi-coherent stage as observed by Iwamura and Miura is never detected in the growth curves on aging at 723 and 748 K in Fig. 5. Thus, the value of $\gamma \approx 0.23 \text{J/m}^2$ in Table 3 is insensitive to the coherency of the Al$_3$Sc/Al interfaces.
5. Conclusions

(1) The size of Al1Sc precipitates, during growth and coarsening of the precipitates in an Al–1 mass% Mg–0.27 mass% Sc alloy aged at 673, 698, 723 and 748 K, has been determined by transmission electron microscopy, and the Sc concentration in the Al matrix has been measured by electrical resistivity. In the early stage of aging, the growth rate of the precipitates decreases gradually and, over a time, the average radius r of the precipitates follows the $r^3$ growth law. Over the same time, the kinetics of the decay of supersaturation with aging time $t$ obeys the predicted $t^{-1/3}$ time law.

(2) Before the commencement of coarsening, the growth and coarsening of Al1Sc precipitates take place simultaneously. The transition from the mixed stage of growth and coarsening to the coarsening stage causes the change in growth rate of the Al1Sc precipitates. The hardness already starts to be reduced at the mixed stage.

(3) Independent values of the energy $\gamma$ of the interfaces between the coherent and semi-coherent Al1Sc precipitates and the Al matrix, and the diffusivity $D$ of Sc in the Al matrix have been derived from a coarsening model developed by Kuehmann and Voorhees for ternary systems using data on coarsening. The estimates of $\gamma$ and $D$ are nearly identical to those obtained by the application of the LSW theory from data on coarsening of Al1Sc precipitates in an Al–0.28 mass% Sc alloy. The experimentally obtained value of $\gamma \approx 0.23 J/m^2$ is immune to the change in coherency between the Al1Sc precipitate and Al matrix.

Acknowledgments

This work has been partially supported by a Grant-in-Aid for Young Scientists (B) from Japan Society for Promotion of Science (JSPS) under Grant No. 15760489. The authors are grateful to Dr. T. Eto, Kobe steel Ltd., for supplying the present alloy. We thank Professor K. Tazaki, Kanazawa University, for use of the JEOL 2000EX and 2010FEF. We also acknowledge Mr. K. Higashimine of the Center for Nano Materials and Technology, Japan Advanced Institute of Science and Technology, for the TEM observation.

REFERENCES