The early stage coarsening behaviour of $\delta'$ ($\text{Al}_3\text{Li}$) precipitates and composite precipitates, consisting of $\beta'$ ($\text{Al}_3\text{Zr}$) core enveloped by a $\delta'$ shell, in an Al–2.5% Li–0.15% Zr alloy has been studied at 443, 473 and 503 K by conventional transmission electron microscopy using superlattice dark-field images. Coarsening kinetics of $\delta'$ precipitates was found to exhibit considerable deviation from the $t^{1/3}$ law corresponding to diffusion control at 473 and 503 K. This deviation may be explained either by the operation of a surface-reaction controlled coarsening mechanism represented by $t^{1/2}$ law, or by the presence of a slower precoarsening stage preceding diffusion-controlled coarsening. The particle-size distributions of $\delta'$ precipitates were not in accordance with either the earlier theoretical predictions or the normal distribution. They were symmetrical or slightly skewed to the left, and particle sizes twice the average were observed. The coarsening kinetics of composite precipitates, was found to be rather different from that of $\delta'$; a diffusion model which yields $t^{1/n}$ law with $n$ changing from $1/4$ to $1/6$ as the coarsening progresses, was predicted. The composite precipitates have exhibited quite a narrow and rather symmetrical size distribution.

1. Introduction

Al–Li based alloys with a high technological potential in the aircraft industry due to the combination of low density and high elastic modulus also offer a scientific challenge with regard to the complex path of phase transformations involved and unexpected symmetrical particle-size distributions (PSDs) exhibited during coarsening. It is believed that, upon quenching, Al–Li solid solution almost instantaneously orders non-stoichiometrically from which non-stoichiometric $\delta'$ ($\text{Al}_3\text{Li}$) $L1_2$ ordered phase decomposes spinodally [1–3]. Such formed spherical $\delta'$ precipitates exhibit an isotropic and uniform distribution due to small coherency strains, about 0.8%. The composite precipitates formed by epitaxial nucleation of $\delta'$ phase on the already existing $L1_2$ ordered $\beta'$ ($\text{Al}_3\text{Zr}$) particles to form a uniform shell around them, is an interesting feature of zirconium-containing Al–Li alloys. The origin of the doughnut shape of the composite precipitates in superlattice dark-field transmission electron microscope images is still a matter of debate.

The coarsening kinetics of $\delta'$ in Al–Li based alloys has been found [4–10] to obey the classical relation

$$R^3 = \bar{R}_0^3 + kt$$

where $\bar{R}$ is the average particle size at time $t$, $\bar{R}_0$ is the initial average particle size, and $k$ is the rate constant that includes temperature, solute volume diffusion coefficient, surface tension and equilibrium solubility of the precipitates. The coarsening rate constant, $k$, for Al–Li based alloys was found [4] to depend on the lithium content of the alloy as well as on the temperature through the relation

$$\ln(kT) = -12946.16/T + 0.52(\text{wt\% Li}) - 19.97$$

(2)

The activation energy for coarsening of $\delta'$ in Al–Li alloys was found to be of the order of that for volume diffusion of lithium in solution, i.e. about 120 kJ mol$^{-1}$ [4, 9]. The initial particle size determined from $\bar{R}^3$ versus $t$ plots was observed to scatter around zero, ± 10 nm, with negative values as frequent as positive values [4].

The coarsening rate law given by Equation 1 is common to all contemporary theories of volume diffusion-controlled coarsening, independent of the model, diffusion geometry and mathematical approach [11–18]. The coarsening theories primarily differ in the resulting particle-size distribution (PSD), and in the magnitude of the rate constant, $k$. The mainframe of the modern theory of diffusion-controlled coarsening was developed independently by Lifshitz and Slyozov [11] and Wagner [12] in 1961, assuming negligible volume fraction of second-phase particles. Their analysis, known as the LSW theory, yielded an asymmetrical PSD with a tail on the left, i.e. negatively skewed, and cut-off radius at 1.5 $\bar{R}$. These predictions were not in full agreement with the experiments. Since then, attempts have been made to modify the LSW theory with more realistic geometries so that a better fit could be maintained between the experimental and theoretical PSDs. Ardell [13] has introduced the modified LSW (MLSW) theory which takes the volume fraction of the second-phase particles into ac-
count by modifying the diffusion geometry. PSDs predicted by MLSW theory were found to flatten and broaden with increasing volume fraction of particles but they were still asymmetrical. Comparison with the experimental data has shown that MLSW theory overestimates the effect of volume fraction on the rate of coarsening. LSW theory was further modified by adopting various diffusion geometries to rationalize the effect of volume fraction on the coarsening rate constant [14-18]. Voorhees and Glicksman [16, 17] for example, applied the multiparticle diffusion to coarsening using potential theoretic techniques. However, all the theories yielded asymmetrical PSDs except the Lifshitz and Slyozov encounter-modified (LSEM) theory presented by Davies et al. [18]. They have incorporated the effect of coalescence (encounter) of the particles at higher volume fractions to yield a broad and symmetrical PSD.

The rate-controlling step in the coarsening process, although less frequently encountered, may be the atom transfer across the particle–matrix interface, i.e. surface reaction, rather than volume diffusion. In the case of surface reaction-controlled coarsening, the rate equation is shown [11, 12] to be

$$\bar{R}^2 = \bar{R}_0^2 + kt$$

where the rate constant, $k$, now also includes a surface reaction-rate parameter. The driving force of the coarsening process is still the concentration gradient between the particles due to interfacial curvature-dependent solubility of the particles. PSDs expected from a surface reaction-controlled coarsening was found [11-13] to be identical to that predicted by MLSW theory for volume diffusion-controlled coarsening at a volume fraction of one. Shiflet et al. [19] have proposed a coarsening model based on a ledge mechanism which gives a rate law with the exponent changing from 2 to 3 as the coarsening progresses.

The coarsened $\delta'$ precipitates in Al–Li alloys were observed to exhibit a particle-size distribution broader and more symmetrical than that predicted by LSW or MLSW or the other modified theories, neglecting particle coalescence. The symmetrical PSDs observed in Al–Li alloys are reminiscent of the coalescence (encounter) of particles as predicted by LSEM theory, but particle aspect ratio measurements on Al–Li alloys [6] have shown that the majority of the coarsened particles have aspect ratios greater than 0.8, negating the possibility of particle coalescence. The origin of the symmetrical shape of PSDs in Al–Li alloys is not yet fully understood. Mahalingam et al. [8] have shown that the PSDs broaden, i.e. standard deviation of the distribution increases, the skewness of the distribution changes from negative to positive, i.e. from a tail on the left to a tail on the right, and the coarsening rate accelerates with increasing lithium content of the alloy. The normalized PSDs in Al–Li alloys were observed to achieve a steady state, independent of coarsening time and temperature in a short time. The presence of composite precipitates in zirconium-containing Al–Li alloys has caused some confusion because of the duplex nature of the PSDs with smaller $\delta'$ precipitates and larger composite precipitates. In addition, the larger initial average size, $\bar{R}_0$, of the composite precipitates, the coarsening rate constant, $k$, was also greater than that for $\delta'$ precipitates [7, 9].

The purpose of the present study was to contribute to the understanding of the coarsening behaviour of $\delta'$ and composite precipitates in Al–Li based alloys during the early stages of ageing where classical diffusion-controlled coarsening behaviour has, possibly, not yet dominated.

2. Experimental procedure

A commercial alloy received as 1.7 mm thick sheet with composition 2.52% Li, 1.22% Cu, 0.68% Mg and 0.15% Zr by weight, was used. The alloy solution treated in the range 743–863 K were quenched to room temperature and then aged at 443, 473 and 503 K for various periods. Thin foils for transmission electron microscopy were prepared using a twin-jet polisher with a 40% CH3COOH, 30% H3PO4, 20% HNO3 and 10% H2O solution at 273 K and were examined in Jeol 100 CXII transmission electron microscope operated at 100 kV. The particle size measurements were carried on recorded [1 001] and [1 1 0] superlattice dark-field images with deviation parameter, $s$, set to zero by locating the [2 00] and [2 2 0] fundamental Kikuchi lines to the positions 3/2 [1 00] and 3/2 [1 1 0], respectively. The micrographs were evaluated manually using an enlarger.

3. Results and discussion

Transmission electron microscopy studies on the alloy in the quenched state showed very small, about 4 nm diameter, uniformly distributed $\delta'$ domains with low contrast and a diffuse interface in a matrix which also exhibited some contrast [3]. In the quenched state, almost all of the $\beta'$ particles were observed to be decorated with heterogeneously nucleated $\delta'$ precipitates, either as individually distinguishable particles or in the form of a thin shell, constituting the initial stages of composite precipitate formation. Upon ageing, in addition to the increase in the average particle size, the contrast of $\delta'$ precipitates was intensified while that of the matrix disappeared [3]. As coarsening progressed, the composite precipitates took their classical doughnut shape with a core of almost no contrast. Typical microstructures observed by TEM during the progress of coarsening are shown in Fig. 1.

3.1. Coarsening of $\delta'$ precipitates

In the present study, the coarsening behaviour of $\delta'$ precipitates and composite precipitates was considered separately. The coarsening data for $\delta'$ precipitates involving the particle sizes and statistical parameters are given in Table I. The average particle-size data were plotted in Fig. 2 as $\bar{R}^3$ versus $t$ curves according to Equation 1, for temperatures of 443, 473 and 503 K, and the corresponding regression coefficients and coarsening parameters $\bar{R}_0$ and $k$ obtained