Quantitative Evaluation of Precipitation in an AI-Zn-Mg-Cu Alloy

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Keywords: Al-Zn-Mg-Cu Alloys, Precipitate size, Precipitate volume fraction, Precipitation kinetics, Small angle X-ray scattering.

Abstract

The evolution of microstructural parameters (mean dimension and volume fraction) of precipitates in an Al-Zn-Mg-Cu alloy during ageing has been studied by synchrotron-radiation small angle X-ray scattering (SAXS). The precipitation kinetics has been analyzed. Coarsening process of the precipitates was investigated by analyzing the curve of kinetic strength vs the cube of radius. The results show that the coarsening of precipitates is consistent with the LSW principle. In addition, the activation energy for this regime has been determined.

1. Introduction

Al-Zn-Mg(-Cu) alloys are used extensively as structural materials in aerospace industry for their high specific strength and specific modulus. Their properties can be obtained through control of the precipitation hardening process. Therefore, precipitation from the solid solution and the related hardening of the alloys is one of the most investigated areas of physical metallurgy, both from the experimental and from the theoretical viewpoint [1~4]. However, much of the research has been concentrated on qualitatively analyzing the morphology and crystallography of the precipitates [5~10]. According to C.Q. chen [11], to predict the material properties, it is very important to obtain the quantitative information such as the size and volume fraction of precipitates.

In this study we have used small angle X-ray scattering measurement to obtain the quantitative information about precipitate mean size and volume fraction at various aging conditions.

2. Experimental Procedures

The composition of the alloys in weight % is: Zn 5.14, Mg 1.35, Cu 1.76, Mn 0.35, Zr 0.10, Cr 0.24. The samples were solution treated at 490 $^{\circ}$ C for 1 hour in salt bath followed by water quenching. Artificial aging was performed at 140, 160 and 180 $^{\circ}$ C respectively for various durations and at 120 $^{\circ}$ C for 24h followed by various durations at 160 $^{\circ}$ C.

In order to quantify the evolution during aging of the size and volume fraction for the precipitates, small angle X-ray scattering measurements were performed at BSRF Division, Institute of High Energy Physics. The size of samples were 8 mm×6 mm×0.07mm.The parameters of light source near samples are as follows: energy range is 3 kev to 12 kev, Energy resolution $\Delta E/E$ about 2×10⁻⁴, Photons flux 1.0×10¹⁰ photons/sec, wavelength of X-ray 0.154 nm and facula size 3.2 mm×1.5 mm. Scattering signal is recorded by detector of image plate.

3. Experimental Results

For the experimental alloy, we mainly studied the kinetics of precipitation for the following conditions: aging at 140°C, 160°C and 180°C respectively for various durations and at 120 °C for 24h followed by various durations at 160°C. According to a TTT diagram for V95 alloy similar to the experimental alloy [12], under these aging heat treatments the precipitates are mostly the coherent metastable η' and the semi-coherent equilibrium η phase with several orientation relationship with the matrix.

3.1 Evolution of Precipitate Size

The precipitate sizes were calculated using the Guinier approximation, which gives the gyration radius for the precipitates [13].

$$I(h) = I_e N n^2 e^{-R_G^2 h^2 / 3}$$
(1)

where l(h) is the scattered intensity corrected for background, fluorescence, absorption effects and collimation error, l_e the scattered intensity of an electron, *n* the total electron number of one particle, *N* the total particle

number of one particle, N the total particle number in the field irradiated by X-ray, R_G the gyration radius of particles, $h=4\pi \sin\theta/\lambda$ the magnitude of scattering vector, λ the wavelength of X-ray, 2 θ the scattering angle.

Deschamps [1] has indicated that the Guinier plot $(Ln I(h) vs h^2)$ shows a straight large range line in а of scattering vectors(typically in the range $0.8 < h^*R < 2$, where *R* is the precipitate effective size and *h* the magnitude of the scattering vector) for the mono-disperse system. For the experimental alloy, according to our own results about precipitate morphology in the other paper, the precipitates belong to flat ellipsoid of revolution with half axes approximate to 1:1:0.4. The mean length of the unequal axes



with aging time at various temperatures.

can be approximated with the radius of a sphere with equal gyration radius to the ellipsoid. Then, the effective size of the precipitates can be written as:

$$R = \sqrt{5/3}R_G \tag{2}$$

In the following we will consider the equivalent radius as precipitate radius. It is shown in Figure 1 the evolution of the precipitate radius with isothermal aging time at different temperatures. The precipitate size is a few nanometer.

3.2 Evolution of Precipitate Volume Fraction

The volume fraction of precipitates can be derived from the integrated intensity measurements. According to P. Guyot et al. [3], in a two-phase model and for a binary alloy, integrated intensity can be written as:

$$Q = \int_0^\infty I_a(h)h^2 dh = \frac{2\pi^2}{V_{at}^2} (\Delta Z)^2 (C_p - C_m)^2 f_V (1 - f_V)$$
(3)

where $I_a(h)$ is the absolute scattered intensity, V_{at} is the atomic volume (approximate to 16.6 Å3), C_p , C_m are the concentrations of the solute in the precipitates and in the matrix, f_v the volume fraction of precipitates and ΔZ the difference of the atomic number between the solute and the matrix (approximated by Zn/Cu and Al/Mg).

Obviously to obtain f_v , the relative scattered intensity must be converted into absolute units. In this study 7050 was used as reference materials to determine conversion coefficient. The volume fraction of this alloy aged at some conditions has been given by P. Guyot [3]. Integrated intensity Q is calculated by Eq. (4).

$$Q = \int_0^{h_1} h^2 I_a(h) dh + \int_{h_1}^{h_2} h^2 I_a(h) dh + \int_{h_2}^{\infty} h^2 I_a(h) dh$$
(4)

In the range $h_1 \sim h_2$, the scattering intensity can be obtained directly from experiments. In the range $0 \sim h_1$, the scattering intensity can be obtained by extrapolation of $l_a(h)$ values from $h_1 \sim h_2$. In the range $h_2 \sim \infty$, according to Porod law, $l_a(h)h^4$ approaches a constant K_p

$$K_{p} = Lim_{h \to \infty} I_{a}(h)h^{4}$$
⁽⁵⁾

$$\int_{h_2}^{\infty} h^2 I_a(h) dh = \int_{h_2}^{\infty} K_p / h^2 dh = K_p / h_2$$
(6)

In addition, parameters C_p and C_m must be determined. To determine C_p , we neglect its dynamic variation with ageing conditions and assume that the composition of the precipitates is equal to that of the stable phase η proposed by Bigot et al. [14] with atom-probe field ion microscopy (APFIM). The matrix composition C_m is approximated by the matrix composition with η precipitate phase. The results proposed by them are as follows (in at%):

However, in the late of coarsening regime, with some large precipitates present, their composition will be near to that of equilibrium phase MgZn₂. Therefore, f_v in fact is slightly smaller than the value calculated.

Figure 2 shows the evolution of the integrated intensity for the samples aged at 140° C. After an initial increase, a plateau is observed after about 24h where integrated intensity remains approximately constant. According to Deschamps [1], the obvious decrease observed for long aging time is caused by the loss of the scattered intensity corresponding to the largest precipitates in the beam-stop. A similar behavior can be observed at other aging temperatures. Figure 3 shows the variation of volume fraction calculated by Eq. (3). The maximum of precipitate volume fraction is about 0.023- 0.028.

If we neglect the deviation caused by SAXS at long time aging, it can be seen from Figure 3 that the evolution of volume fraction is consistent with the classical two-step precipitation process, i.e. nucleation and growth of η' followed by Ostwald ripening stage. At the first stage, both integrated intensity and volume fraction increase steadily and at the second stage they keep constant.



Figure 2: Integrated intensity for the samples aged at 140° C for various durations.



Figure 3:. Evolution of the precipitate volume fraction with isothermal aging time at various temperatures.

4. Discussion

From the mean radius and volume fraction deduced from the SAXS measurements, it appears that the precipitation kinetics follows classical two-step regime. The first regime is the nucleation-growth, where R increases smoothly. However, the variation of fv is very complex. It increases before a plateau appears, but it decreases obviously after about 18h for one-step aging and about 24h for two-step aging. This maybe results in the partial reversion of the η' . Therefore, it is difficult to quantify the kinetics. In this study we mainly describe the kinetics for coarsening regime. To quantify the kinetics, firstly, we determine the activation energy and then explain the variation of precipitate size with kinetic strength *K*s.

4.1 Determination of the Activation Energy from SAXS Measurements

After the isothermal aging heat treatments for various conditions, the coarsening process of precipitates can be described by LSW (Lifshitz-Slyozov-Wagner) model [3]. The LSW model for coarsening kinetics is given by Eq. (7), which predicts the time dependence of the precipitate radius. The growth coefficient K is given by Eq. (8)

$$R^{3} - R_{0}^{3} = Kt$$
 (7)

$$K = \frac{8 V_{at} \gamma c_{eq} D}{9 k_{B} T} = \frac{8 V_{at} \gamma c_{eq} D_{0}}{9 k_{B} T} \exp(-\frac{Q}{k_{B} T})$$
(8)

Where γ is the precipitate-matrix interface energy, V_{at} the average atomic volume, c_{eq} the equilibrium solute concentration, D the solute diffusion coefficient expressed by $D = D_0 e^{-Q/k_b T}$, Q the activation energy and T the aging temperature.

In the narrow temperature range 140° C ~ 180° C, it is assumed that the change in the concentration and the interface energy can be neglected. Then the growth coefficient Kcan be written as

$$K = \frac{c}{T} \exp(-\frac{Q}{k_B T})$$
(9)

where *c* is approximated as an constant. For each aging temperature *K* was determined by plotting curves of R^3 vs isothermal time t (see for instance Figure 4). Then the activation energy Q for the Ostwald ripening stage was obtained using a plot ln(KT) vs 1/T (Figure 5). The activation energy estimated from Eq. (9) is about 1.45eV, this value is intermediate between those of Cu (1.4 eV), Mg (1.17-1.34), Zn (1.25-1.34) for diffusion in aluminum, as well as the activation energy for self-diffusion in AI (1.47 eV) [3].



aged at various temperatures.

4.2 Variation of Precipitate Radius with Kinetic Strength

To gather all experimental results, for various times t and temperature T, on a master plot, we use here a integrated variable as given by

$$K_{s} = \int \frac{dt}{T(t)} e^{-Q/k_{B}T(t)}$$
(10)

it was called "kinetic strength" by Shercliff and Ashby [3]. The kinetic strength characterizes the advance of coarsening that results from a given aging treatment.

By using the kinetic strength K_s , we can describe the coarsening process given by Eq. (7) in a modified LSW model for various times t and temperature T.

$$R^{3} - R_{0}^{3} = cK_{s}$$
 (11)

As shown in Figure 6, the increase of R^3 with variable K_s follows a linear behavior. So the coarsening of precipitates conforms to the principle of LSW with R_0 =1.93 nm and c=1.37e16 nm³K/s.

5 Conclusion

- The evolution of precipitate size and volume fraction at different aging conditions has been determined by means of SAXS measurements. The precipitate size is a few nanometers. The maximum of precipitate volume fraction is about 0.023- 0.028.
- 2) The coarsening behavior of the precipitate has been quantified with LSW model.
- 3) The activation energy of coarsening regime has been determined to be about 1.45 eV.



Figure 6: Diagram of R^3 vs kinetic strength *K*s for different aging treatments.

Acknowledgements

This research was supported by National Key Fundamental Research Project of China (No. G19990649) and National 863 High Technology project of China (No. 2001AA332030).

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