Effect of External Stress on the Growth of Precipitates in Al-Cu and Al-Cu-Mg-Ag Alloys

Ziqiao Zheng, Daqin Chen, Shichen Li, Zhiguo Chen

School of Materials Science and Engineering, Central South University, Changsha 410083, Hunan, P.R. China

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Abstract

The effect of stress ageing on the nucleation and growth of precipitates in Al-3.88%Cu and Al-3.87%Cu-0.56%Mg-0.56%Ag was investigated by electric resistivity measurement and transmission electron microscopy observation. The results indicate that external stress promotes the formation of clusters of solute atomes or GP zones, but retards the growth of θ' and Ω phases. And the applied external stress during ageing induces preferred oriented precipitates of θ' and Ω in Al-Cu and Al-Cu-Mg-Ag alloys respectively. The reason of stress-oriented effect is understood by analyzing interaction between external stress and misfit strain by Eshelby elastic inclusion theory.

1. Introduction

The hardening effect of ageing-hardenable alloys is determined by precipitation process during ageing. It is critical to modify and control microstructure evolution finely during phase transformation in the field of materials science and engineering. Some research conclusions [1-9] showed that precipitation process could be modified dramatically on coupled elastically stress with temperature during ageing (namely, stress ageing), which helped to modify and control the species, quantity, shape, size, distribution and orientation of precipitates, and, finally, to improve the mechanical properties of materials. Stress ageing technology has been utilized in some aluminum alloys for a few years [2-10]. Those experiments were mostly focused on observation of stress-oriented effect and correlation studies in simple alloys. They did not analyze the effect of external stress on kinetics process and the mechanics of stress-oriented effect thoroughly since there were not enough quantitative data. In this paper, electrical resistively measurement and transmission electron microscopy observation were coupled to investigate the effect of external stress on nucleation and growth of precipitates in AI-Cu and AI-Cu-Mg-Ag alloys. Moreover, the reasons of stress-oriented effect were discussed through Eshelby elastic inclusion theory.

2. Experiments

Al-Cu and Al-Cu-Mg-Ag alloys were used in this study and their compositions are Al-3.88wt%Cu and Al-3.87wt%Cu-0.56wt%Mg-0.56wt%Ag respectively. The specimens were solution treated at 520°C and quenched into cold water, then artificially aged under different external stresses. Resistivity was measured by two-bridge electric-resistivity method. Foils for TEM were electropolished using a 33% nitric acid–67% methanol

solution at around -30 $^\circ\!{\rm C}$. Examination for TEM was carried out in a H-800 electron microscope with an accelerating voltage of 200kV.

3. Results and Discussion

Figure 1 provides the relative resistivity of Al-Cu binary alloy aged at 180°C with respect to ageing time during stress ageing (ρ_0 --solution treated resistivity, ρ_t -- measured instant resistivity). It is well known that, at low temperature ageing, the size of solute atoms cluster distributing heterogeneously (GP zones, clusters) is approximately a scale of nanometers, which is close to the wavelength of electron, electrons can be severely scattered and resistivity increase. Ageing kinetics process at elevated temperature is different from low temperature, in which coherent or semi-coherent metastable phases (for instance, θ "-phase or θ '-phase in Al-Cu) are directly precipitated from the solid solutions because of atomic diffusion. Thus electrical resistivity decreases in the beginning at elevated temperature [11-12]. Figure 1 indicates the electrical resistivity decreases with ageing time, which means that θ " or θ '-phases are directly precipitated from solid solution with the active atomic diffusion at 180°C. Moreover, the resistivity of stress ageing is relatively higher than that of stress-free condition in different times. Since the yield strength of Al-Cu in solid solution state is about 120Mpa[9], which is higher than external stress of experiment used, the dislocation cannot be introduced by elastically stress. Therefore, it can be concluded that the increasing resistivity is not due to the dislocation, which means the precipitating and growth of θ " or θ '-phases are retarded by external stress. After a period of time of precipitating, coherent or semi-coherent metastable phases are precipitated slowly and Ostwald ripening is occurred, which make resistivity stable.



Figure 1: Relative electrical resistivity-ageing time curves for Al-Cu alloy aged at 180 $^\circ\!C$ under different external stresses.

Figure 2(a) shows the evolution of the relative resistivity of Al-Cu-Mg-Ag alloy aged at 180 $^{\circ}$ C with respect to ageing time during stress ageing. It can be found that each curve exhibits a peak value, which means GP zones or clusters can be found at this time. The addition of small amounts Mg and Ag into Al-Cu alloy with high Cu:Mg ratio will modify the sequence of precipitation and induce a precipitation of Ω phase of disc shape on {111} planes rather than on {001} planes.

Suh and Park [13] have calculated that the addition of Mg and Ag into Al-Cu alloy induced Mg clusters or Mg-Ag co-clusters on {111} planes which gives rise to minimum strain

energy on {111} planes, therefore, it can be believed that these clusters could be mainly responsible for the formation of Ω phase in Al-Cu-Mg-Ag alloy. This prediction is confirmed by a recent result of atom probe of Ringer et al [14].

Therefore, the GP zones or clusters as above mentioned are actually Mg clusters or Mg-Ag clusters or {111} GP zones etc. Figure 2 (b) shows the evolution of the relative resistivity of Al-Cu-Mg-Ag at different stress ageing conditions. Combined with figure 2(a) and (b),it can be concluded that the variation of relative resistivity as time can be divided three stages(as noted number in fig2(a)): in the first stage the increasing resistivity corresponds to the formation of clusters/co-clusters or {111}GP zones; in the second stage the decreasing resistivity corresponds to the precipitation of Ω phase; in the third stage the gentle changing resistivity corresponds to the stable existence of Ω phase(because Ω phase has excellent thermal stability at temperatures up to 200°C [15-16]).

It can be found from figure 2(a) that a higher peak value is detected in the relative resistivity curves and that the evolution patterns of the resistivity curves are perfectly similar when the external stress is equivalent to or more than a critical value (50Mpa).

These phenomena are attributed to the more formation of clusters/co-clusters or {111} GP zones in the matrix due to the external stress equivalent to or more than threshold value. The decreasing resistivity is due to the precipitation and growth of Ω phases. Compared with the resistivity of stress-free ageing, the decreasing of the resistivity of stress ageing is slow, which means that external stress will retard the precipitation and growth of Ω phases.

Figure 2(b) shows the evolution of the relative resistivity with respect to the longer ageing time at 180° C or 300° C by stress ageing (the external stress is about 150 MPa) or stress-free ageing. As above-mentioned, if we increase the ageing time, we can find that the platform of the resisitivity curves also occurs during stress ageing and the value corresponds to the platform is similar to that of stress-free ageing.

Therefore, compared with the relative resistivity of stress-free ageing, it can be shown that the external stress promote the formation of clusters but retard the precipitation of Ω phases in Al-Cu-Mg-Ag alloy.

Another point we should take care is that the relative resisitivity at 300 $^{\circ}$ C ageing which do not have obvious peak value in the relative resisitivity curve, is completely different to that at 180 $^{\circ}$ C. This may be due to clusters or {111} GP zones dissolving or directly precipitating of Ω phases at higher temperature.



Figure 2: (a) Relative electrical resistivity-ageing time curves for Al-Cu-Mg-Ag alloy aged at 180°C under different external stresses; (b) Comparison curves for Al-Cu-Mg-Ag alloy aged for long time under stress-free or external stress at different temperatures.

TEM micrographs and corresponding SAED patterns of Al-Cu and Al-Cu-Mg-Ag specimens of stress ageing or stress-free ageing to peak values are shown in Figure 3. The incident electron beam for (a)-(b) is close to $<001>_a$, and the other is close to $<110>_a$. Three different variants of θ' -phase in Al-Cu alloy are precipitated in {100} planes with equal-probability (figure 3(a)). One of the θ' variants is invisible due to its orientation paralleling to the incident electronic beam. And the stress ageing specimens show the preferential formation of particular variants of θ' (figure 3(b)). Figure 3(c) and 3(d) provide the bright field TEM images and corresponding selected area electron diffraction patterns taken from <011> zone axes of Al-Cu-Mg-Ag alloy for different thermal treatment. The diffraction from the {111}, plate like phases produce reflection at the 1/3 and $2/3g{220}$ position in Figure 3(c,d) shows that Ω phase is also precipitated. It can be seen that the microstructure is dominated by homogeneous distribution of Ω phases and small amount perpendicular θ' phases in figure 3(c). However in figure 3(d), the preferential formation of particular variants of (111) Ω can be observed. It is worth to point out that the preferential formation of particular variants of precipitates in Al-Cu-Mg-Ag allov is not more complete than that in Al-Cu binary alloy. And the stress ageing specimen shows the finer dispersion of Ω precipitates, which confirms the above results analysis of resistivity measurement.

Although the value of the applied stress in Al-Cu-Mg-Ag alloy is much more than that in Al-Cu alloy, the stress-oriented effect is not obvious, which is in agreement with the experimental results of Skrotzki et al [5]. They suggested that the different misfit strains (experiments have determined that Ω has a large negative misfit of –9.3 pct [17] or –8.3 pct [18] and is twice as high as that of θ') and the different habit planes between Ω and θ' required a higher stress to induce the stress oriented effect of quaternary alloy than that of binary alloy.



Figure 3: Bright field transmission electron micrographs and corresponding selected area electron diffraction patterns of: (a) Al-Cu alloy: 0MPa/32h/180°C; (b)Al-Cu alloy: 80MPa/32h/180°C; (c) Al-Cu-Mg-Ag alloy: 0MPa/8h/180°C; (d)Al-Cu-Mg-Ag alloy: 120MPa/8h/180°C.

4. Theoritical Calculation and Analysis

With the assumption of the directly precipitating of θ' from the matrix, we employ the Eshelby elastic inclusion theory [19-21] to analyze the reason of stress-oriented effect. The precipitation process is determined by the misfit strain between the second phase and the matrix. The misfit strain energy of the precipitates in unit volume, lying perpendicular to and parallel to the stress axis (see figure 4), e_1^e and e_{II}^e , with the applied stress, $\sigma^A = \sigma_{33}^A = 80 \text{MP}a$, are calculated as below:

$$e_{\mathrm{I}}^{e} = -\sigma^{\mathrm{A}}\varepsilon_{\mathrm{33}}^{\mathrm{T}}, e_{\mathrm{II}}^{e} = -\sigma^{\mathrm{A}}\varepsilon_{\mathrm{11}}^{\mathrm{T}}$$
(1)

We can calculate:

$$e_I^e = 36.15 \text{J/m}^3, e_{II}^e = 1.91 \text{J/m}^3$$
 (2)



From equation (2), we can find that the increasing of the strain energies of variant 1 is much more than that of variant 2 and thus variant 2 will preferentially precipitate at the cost of variant 1. The reason for different experimental results [2-3] can be explained by

using the above analysis. The variation of misfit strain can naturally affect the interaction energy and then induce the different stress oriented effects.

5. Conclusions

- 1. During stress ageing, the precipitation and growth of θ''/θ' are retarded for Al-Cu binary alloy and the formation of Mg clusters or Mg-Ag co-clusters or {111} GP zones is promoted and the growth of Ω are also retarded for Al-Cu-Mg-Ag alloy.
- 2. With applied stress of 80Mpa,the preferential orientation of θ' is observed after about 32 hours of ageing at 180°C for Al-Cu alloys. With applied stress of 120Mpa,the preferential orientation of Ω is also observed for Al-Cu-Mg-Ag alloys but not completely as Al-Cu alloy.
- 3. Calculated by Eshelby elastic inclusion theory, the variations of the system elastic strain energy of different variants under applied stress is the reason of the stress oriented effect.

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