Effect of grain boundary on the precipitation behavior and hardness of Al-Cu-Mg alloy bicrystals during stress-aging

Xiaobin Guo ^a, Yunlai Deng ^{a,b,*}, Jin Zhang ^{b,c}, Xinming Zhang ^{a,b}

^a School of Materials Science and Engineering, Central South University, Changsha, China

^b State Key Laboratory of High Performance and Complex Manufacturing, Central South University, Changsha, China

^c Light Alloy Research Institute, Central South University, Changsha, China

*Corresponding author. Tel.: +86 731 88876913. E-mail address: luckdeng@csu.edu.cn.

Abstract: While it is clear that precipitates near grain boundaries in aluminum alloys nucleate more easily and grow more quickly, the mechanism of how the grain boundaries influence the anisotropic distribution of S precipitates is still unknown. In this study, a bicrystal Al-Cu-Mg alloy specimen was prepared to obtain a single grain boundary. The precipitation distribution and hardness of the Al-Cu-Mg alloy bicrystal were analyzed after stress aging at 30 MPa. Transmission electron microscopy was used to analyze the precipitation behavior of S precipitates, and the hardness was tested along the location on the bicrystal specimen. The hardness of the right area around the grain boundary is lower than that of the left area around the grain boundary after stress aging. The precipitation behavior around the grain boundary is different from that in the matrix. For the left area near the grain boundary with the (1, -1, 8)_{Al} plane orientation, the anisotropic distribution of the S precipitates is inhibited. For the right area near the grain boundary with the (3, 5, 6)_{Al} plane orientation, the

anisotropic distribution of the S precipitates is even more pronounced than that in the right matrix. This difference in the influence depends on the crystallographic orientations of the matrix around the two sides of the grain boundary.

Keywords: Al-Cu-Mg alloys; Bicrystal; Crystallographic orientation; Precipitation; Grain boundary; Stress-aging

1. Introduction

An inhomogeneous distribution of precipitates is induced in the aluminum matrix when alloys are aged under applied stress [1-10]. As observed from the transmission electron microscopy (TEM) images, stresses induce precipitates to distribute more in some $\langle 100 \rangle_S$ directions and less in others. An anisotropic distribution of the precipitates leads to anisotropy of the mechanical properties of aluminum alloys [8-9]. S precipitate is the main phase in the Al-Cu-Mg series alloys and always forms in the face-centered orthorhombic structure on the $\{012\}_{Al}$ habit planes and grows along the $\langle 001 \rangle_{Al}$ directions [15]. Previous investigation [10] of the Al-Cu-Mg alloys aged under elevated compression stresses indicated that for aging under a lower stress, an obviously anisotropic S precipitate distribution is present, and the mechanical properties were degraded. Conversely, at higher applied stress such as 50 MPa, S precipitates dispersed more homogeneously due to the influence of dislocations.

In the manufacturing process, Al-Cu-Mg alloys are always polycrystalline with a large amount of grain boundaries [2]. Along the grain boundaries, the atoms are located in a disordered arrangement and lack regular bonding. The extra energy near the grain boundary makes the diffusion of the solute atoms more active [11-14]. With

the exception of the inhibiting effect of the dislocations [10], the effect of the grain boundaries in polycrystalline alloys cannot be neglected. Due to the difficulty in selecting a single grain boundary with a known orientation from the polycrystalline specimen, the mechanism of how the grain boundaries influence the anisotropic distribution of S precipitates is still unknown.

In this study, an Al-Cu-Mg alloy bicrystal specimen was prepared to obtain a single grain boundary. The effect of the grain boundary on the precipitation behavior and hardness of the alloys during stress aging was studied. Contrary to the current understanding that grain boundaries always promote precipitation and induce an inhomogeneous distribution, we found that the effect depends on the crystallographic orientations of the matrix on the two sides around the grain boundary.

2. Experimental procedures

The chemical composition of the Al-Cu-Mg alloy in this work is given in Table 1. An Al-Cu-Mg alloy plate with a thickness of 8 mm was used to prepare the bicrystal specimen. The bars cut from the plate were pulled to 0.5~1.0% strain, followed by annealing at 525°C for 24 hours, and the strain-annealing cycle was repeated 8~10 times. Finally, bar specimens with macro-grains up to 10 mm in diameter were prepared. The bicrystal specimen was cut from the macro-grains bars using a spark-erosion cutting machine. The optical micrograph of the Al-1.23Cu-0.43Mg alloy bicrystal is shown in Fig. 1(a).

Table 1. Composition of Al-1.23Cu-0.43Mg alloy in weight percent

Alloys	Cu	Mg	Si	Fe	Zn	Al
Al-Cu-Mg	1.23	0.43	0.02	0.03	0.01	Balance

The orientation of the bicrystal specimen was determined by electron backscatter diffraction (EBSD) in the Helios NanolabTM 600i using a Field Emission Gun LEO 1530 operated at 20 kV. Prior to the examination, the bicrystal samples were electrolytically polished using 10% perchloric acid + 90% ethanol at 21 V and -15°C. The mapping and orientation analysis of the bicrystal were performed using the OIM Analysis 6.0 software, with the Inverse Pole Figure (IPF) shown in Fig. 1(b). The plane orientation of the left matrix in the bicrystal is $(1, -1, 8)_{Al}$, while that of the right matrix is $(3, 5, 6)_{Al}$. The rotation axis of the grain boundary is $[16, -7, -6]$, and the rotation angle is 44.6° .

Fig. 1. Macrograph (a) and orientation map (b) of Al-1.23Cu-0.43Mg alloy bicrystal specimen.

The bicrystal specimen was sliced into two parts, and both parts were first solution treated at 525°C for 2 hours then quenched with water. The aging of the two specimen parts was performed at 180°C for 66 h, with one part under conventional free-stress conditions and another under an applied compressive stress of 30 MPa. The stress was applied perpendicular to the plane orientation of the bicrystal samples.

Fig. 2. Sampling location and sample numbers of three types of TEM foils.

Transmission electron microscopy (TEM) foils were examined using a Titan G2 60-300 with an image corrector microscope operated at 300 kV. The sampling location of three areas in the bicrystal is shown in Fig. 2. For the two sides of the matrix of the bicrystal, Sample 1 is on the left with the $(1, -1, 8)_{\text{Al}}$ plane orientation, and Sample 2 is on the right with the $(3, 5, 6)_{\text{Al}}$ plane orientation; disks with a diameter of 3 mm were punched from the aged samples, ground to a thickness of ~ 0.1 mm, and then twin-jet electro polished in a solution of 25% nitric acid + 75% methanol at 20 V and -25°C . To accurately detect the grain boundary, TEM foils near the grain boundary (Sample 3) were prepared by focused ion beam (FIB) techniques in the Helios NanolabTM 600i using a Ga ion beam. The Vickers hardness of the aged specimen was measured in a Huayin[®] HV-5 micro-hardness tester.

3. Results

3.1 Hardness in stress-aged Al-Cu alloy bicrystal

The hardness results of the Al-1.23Cu-0.43Mg alloy bicrystal obtained after stress-aging at 180°C for 66 h under 30 MPa are shown in Fig. 3. To study the change in the hardness along the location on the bicrystal, the hardness was tested along two lines. Twenty hardness points were chosen, with one part sampled by points 1-9 and

another by points 11-19; points 6, 7, 13 and 14 were tested near the grain boundary, as shown in Fig. 4a. The hardness test direction and crystallographic orientation of the bicrystal specimen are also shown in Fig. 4b.

Fig. 3. Hardness results along the location on Al-1.23Cu-0.43Mg alloy bicrystal specimen after aging at 180°C for 66 h under 30 MPa of applied stress.

Fig. 4. Schematic of the twenty hardness points in bicrystal specimen. (a) Two hardness test lines shown in bicrystal specimen macrograph; (b) crystallographic orientation of bicrystal and hardness test points positions.

With different plane orientations, the hardness values of the two sides of the matrix in the bicrystal remain distinct. The effect of the grain boundary on the hardness of the stress-aged bicrystal is apparent in Figs. 3a and 3b; the hardness values at points 6 and 13 are higher than the values in the matrix, but the values at points 7 and 14 are lower.

3.2 Precipitation behavior of *S*-plates in bicrystal

TEM images were observed from the $\langle 112 \rangle_{Al}$ axis, and three *S* precipitate variants $[100]_S$, $[010]_S$ and $[001]_S$ could be seen, as shown by the white arrows in Figs. 5 and 6. TEM images of Sample 1 in the left matrix, Sample 2 in the right matrix, and Sample 3 on the grain boundary were observed in the bicrystal after free-stress aging (as shown in Fig. 5) and stress aging at 30 MPa (as shown in Fig. 6). Sample 3 has been tilted twice in TEM in order to observe the *S* precipitates' behavior in two orientation planes around the grain boundary, and therefore, the TEM images of Sample 3 were shown from the left and right of the grain boundary.

For conventional free-stress aging, *S*-variants of all three $\langle 100 \rangle_S$ appear, with sufficient amounts for each one. The distributions of the *S* precipitates in the left matrix with the $(1, -1, 8)_{Al}$ plane orientation and the right matrix with the $(3, 5, 6)_{Al}$ plane orientation are almost identical, and around the grain boundary, the distribution is sparse compared to that of the matrix of each side. After stress aging at 30 MPa, the *S* precipitates distributions in the matrix on the two sides of the matrix are different. Few $[001]_S$ precipitates appeared in the left matrix, and the distribution is significantly

anisotropic (Fig. 6a), while in the right matrix (Fig. 6b), precipitates were distributed homogeneously on all three $\langle 100 \rangle_s$, and the S -variants were more finely dispersed than in the free-stress aged specimen (Fig. 5b). After aging under applied stress, the distribution of precipitates on the left of the grain boundary is much denser, and more S precipitates distribute on $[001]_s$ and $[010]_s$ compared to the left matrix (Fig. 6c). However, precipitates to the right of the grain boundary are much sparser, and the number of $[001]_s$ variants decreased compared to the right matrix (Fig. 6d).

Fig. 5. $\langle 112 \rangle$ Al TEM images of three S precipitates variants $[100]_s$, $[010]_s$ and $[001]_s$ in Al-1.23Cu-0.43Mg alloy bicrystal specimen after conventional free-stress aged. (a) Sample 1 of bicrystal (Left matrix); (b) Sample 2 (Right matrix); (c) Precipitation behavior on left of the grain boundary in Sample 3; (d) Right of the grain boundary in Sample 3.

Fig. 6. $\langle 112 \rangle_{\text{Al}}$ TEM images of three S precipitates variants in bicrystal after stress aged at 30 MPa. The cases of (a), (b), (c) and (d) are the same as in Fig. 5.

4. Discussion

The distributions of three S precipitates variants on all $\langle 100 \rangle_s$ directions have been quantitatively measured. More than five TEM images of each condition were examined, and the statistical results are listed in Table 2. For the specified aging conditions, the number fraction of the S -plates variants on each $\langle 100 \rangle_s$ direction should be constant. The statistical results for the free-stress aged Al-Cu-Mg alloys bicrystal specimen presented in Table 2 show that the number proportion of $[100]_s$: $[010]_s$: $[001]_s$ equals 1.1 : 1.1 : 1 in the matrix and around the grain boundary. After

conventional free-stress aging, the homogeneous distribution of S precipitates in the matrix is considered as a reference. A parameter α is introduced to describe the degree of the anisotropy of the distribution that could be calculated by the difference between the number proportion of the three S -variants and the results after free-stress aging, namely, 1.1 : 1.1 : 1. The values of α should be greater than 0 and less than 1. The value is 1 for the free-stress aged conditions, and as the distribution becomes more anisotropic, the value decreases to less than 1. The expression for α is shown in equation (1).

$$\alpha = 10 \cdot \left(\frac{32}{11} \left(\frac{f_{[100]}}{f_v} \cdot \frac{f_{[010]}}{f_v} \cdot \frac{1.1f_{[001]}}{f_v} \right)^{\frac{1}{3}} - 0.9 \right) = 30 \frac{(f_{[100]} \cdot f_{[010]} \cdot f_{[001]})^{\frac{1}{3}}}{f_v} - 9 \quad (1)$$

where $f_{[100]} / f_v$ is the number fraction of the S -variants on $[100]_S$, $f_{[010]} / f_v$ is the number fraction of the S -variants on $[010]_S$, and $f_{[001]} / f_v$ is the number fraction of the S -variants on $[001]_S$. The calculated values of α are also listed in Table 2.

Table 2. Number and proportion of three S precipitates variants $[100]_S$, $[010]_S$ and $[001]_S$ for different conditions shown in Figs. 5 and 6, and values of α , which describe the degree of the anisotropy of the distribution.

Conditions	Sample number	$[100]_S : [010]_S : [001]_S$	$[100]_S : [010]_S : [001]_S$	α
Free-stress aging (As shown in Fig. 5)	Sample 1	211 : 214 : 191	1.10 : 1.10 : 1	1.0
	Left of Sample 3	147 : 159 : 130	1.13 : 1.22 : 1	1.0
	Right of Sample 3	161 : 153 : 145	1.11 : 1.06 : 1	1.0
	Sample 2	223 : 221 : 200	1.11 : 1.10 : 1	1.0
Stress aging at 30 MPa (As shown in Fig. 6)	Sample 1	174 : 114 : 94	1.86 : 1.22 : 1	0.6
	Left of Sample 3	170 : 139 : 191	0.89 : 0.73 : 1	0.9
	Right of Sample 3	231 : 152 : 99	2.33 : 1.54 : 1	0.4
	Sample 2	240 : 203 : 222	1.08 : 0.91 : 1	1.0

The values of the degree of the distribution anisotropy α in the 30 MPa stress-aged bicrystal specimen were calculated and compared to those obtained in the free-stress aging condition, as shown in Fig. 7. The distributions of the precipitates on the different positions of the stress aged bicrystal specimen are different. It was found that the value of α in the left area around the grain boundary (Left of Sample 3) is 0.9, indicating a more homogeneous distribution compared to that indicated by the 0.6 value of the left matrix (Sample 1). While the value of α in the right area around the grain boundary (Right of Sample 3) is 0.4, the S precipitates distribution is more anisotropic than that in the right matrix (Sample 2), with α equal to 1.0.

First, we consider the precipitate behavior in the left and right matrix. During stress aging, the anisotropic precipitate distribution depends on the direction of the applied stress. If the direction of stress is perpendicular to the matrix, the crystallographic orientations of the grains are the main factors. To discuss the effect of the crystallographic orientation on the distribution of the S -plates during stress aging, we assume the plane orientation of one side matrix to be (hkl) , and a stress σ is applied perpendicularly on the (hkl) plane so that the axis of the stress is $[hkl]$. We assume that the threshold value of the applied stress required to induce an anisotropic distribution in Al-1.23Cu-0.43Mg alloys is σ_m . The criterion for the appearance of an anisotropic distribution of the S -plates is that the stress components on the (120) , (012) or (201) habit planes exceed σ_m , represented as

$$\left\{ \begin{array}{l} \frac{h+2k}{\sqrt{5} \cdot \sqrt{h^2+k^2+l^2}} \cdot \sigma \geq \sigma_m \\ \frac{k+2l}{\sqrt{5} \cdot \sqrt{h^2+k^2+l^2}} \cdot \sigma \geq \sigma_m \\ \frac{2h+l}{\sqrt{5} \cdot \sqrt{h^2+k^2+l^2}} \cdot \sigma \geq \sigma_m \end{array} \right. . \quad (2)$$

For stress aging at 30 MPa, when the (hkl) plane is in the {100} orientation, two {012} habit planes are under a compressive stress, and the stress components are $1/\sqrt{5}\sigma$ and $2/\sqrt{5}\sigma$, so the *S*-plates on the habit plane under $2/\sqrt{5}\sigma$ compressive stress distribute preferentially, and the degree of anisotropy is more significant. For the (hkl) plane in the {101} orientation, the three {012} habit planes are under the stress components $1/\sqrt{10}\sigma$, $2/\sqrt{10}\sigma$ and $3/\sqrt{10}\sigma$, so the habit plane with $3/\sqrt{10}\sigma$ will distribute more *S*-plates and an anisotropic distribution will appear. For the {111} plane orientation, the stress components on the three {012} habit planes are $3/\sqrt{15}\sigma$, the applied compressive stress is divided uniformly on the habit planes, and an anisotropic distribution does not appear. Thus, the degree of anisotropy of the distribution of the matrix with {111} orientation is minimal. According to equation (2), a parameter q describing the effect of crystallographic orientation on the distribution of *S*-plates is introduced as

$$q = \cos \lambda \quad (3)$$

where λ is the minimum angle between the plane orientation of the matrix and the (111)_{Al} orientation. For the (1, -1, 8)_{Al} plane orientation, q is 0.711. For the (3, 5, 6)_{Al} plane orientation, q is 0.907. The values of the parameter q for the two side matrix in a bicrystal specimen are close to α that described the anisotropic distribution of the

precipitates observed in the TEM images.

Fig. 7. Values of the degree of distribution anisotropy α calculated according to the proportion of three S precipitates variants $[100]_S$, $[010]_S$ and $[001]_S$ listed in Table 2.

Second, the effect of the grain boundary on the distribution of the S precipitates during stress aging is complex. Because the applied stress induces an extra shear stress near the grain boundary, the precipitation behavior around the grain boundary is different from that in the matrix. For the left area near the grain boundary with the $(1, -1, 8)_{Al}$ plane orientation, the anisotropic distribution of the S precipitates is inhibited. For the right area near the grain boundary with the $(3, 5, 6)_{Al}$ plane orientation, the anisotropic distribution of the S precipitates is even more pronounced than that in the right matrix. The mechanical properties of the aged Al-Cu-Mg alloy bicrystal depend

on the S precipitates distribution. Once the applied stress induces the lath-like S precipitates to distribute more on some direction, the macro-mechanical properties become anisotropic, and thus, the mechanical properties such as hardness decline. Therefore, the hardness of the right area around the grain boundary (Points 7 and 14 in Fig. 3) is lower than that of the left area around the grain boundary (Points 6 and 13 in Fig. 3). The grain boundary has a significant influence on the distribution of the precipitates during stress aging, depending on the crystallographic orientations of the two side's matrix around the grain boundary. In this work, the distribution of the precipitates near the grain boundary with the $(1, -1, 8)_{Al}$ orientation is more homogeneous, while the distribution near grain boundary with the $(3, 5, 6)_{Al}$ orientation is significantly anisotropic.

5. Conclusions

(1) Precipitation behavior is different in the matrix with different crystallographic orientations after stress aging at 30 MPa. Few $[001]_S$ -variant precipitates appeared in the left matrix with the $(1, -1, 8)_{Al}$ orientation, and the distribution is significantly anisotropic, while in the right matrix with the $(3, 5, 6)_{Al}$ orientation, precipitates distributed homogeneously on all three $\langle 100 \rangle_S$ and S -variants were more finely dispersed than in the free-stress-aged specimen.

(2) A parameter q describing the effect of the crystallographic orientation on the S -plates distribution is introduced. For the left matrix with the $(1, -1, 8)_{Al}$ plane orientation, q is 0.711. For the right matrix with the $(3, 5, 6)_{Al}$ plane orientation, q is 0.907. The values of parameter q for the two sides of the matrix in the bicrystal

specimen are close to the degree of distribution anisotropy of the precipitates seen in the TEM images.

(3) Following stress aging, the precipitation behavior around the grain boundary is different from that in the matrix. For the left area near the grain boundary with the (1, -1, 8)_{Al} plane orientation, the anisotropic distribution of *S* precipitates is inhibited. For the right area near the grain boundary with the (3, 5, 6)_{Al} plane orientation, the *S* precipitates distribution is even more significantly anisotropic than in the right matrix. The hardness of the right area around the grain boundary is lower compared to that of the left area around the grain boundary. The different influences depend on the crystallographic orientations of the two sides of the matrix around the grain boundary.

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