

Precipitation sequence of η phase along low-angle grain boundaries in Al–Zn–Mg–Cu alloy during artificial aging

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Abstract: The precipitation sequence of $\eta(\text{MgZn}_2)$ phase along low-angle grain boundaries in Al–Zn–Mg–Cu alloy was investigated by examining samples aged at 135 °C for various times from 5 min to 6 h. High resolution transmission electron microscopy (HRTEM) observations and energy dispersive X-ray spectroscopy (EDX) analysis indicate that the precipitation sequence of η phase along low-angle grain boundaries should be supersaturated solid solution (SSS)→vacancy-rich clusters (VRC)→GP II zones→ η' → η . Based on the theory of non-equilibrium grain boundary segregation (NGS) and non-equilibrium grain boundary co-segregation (NGCS), the excessive solute elements gradually segregate to the grain boundaries by the diffusion of the solute–vacancy complex during aging treatment. The grain boundary segregation plays an important role in the nucleation and growth of VRC, GP II zones, η' phase as well as η phase.

Key words: Al–Zn–Mg–Cu alloy; aging; low-angle grain boundaries; grain boundary segregation; precipitation sequence

1 Introduction

Al–Zn–Mg–Cu alloys are widely used in aircraft and automotive industries due to their high strength, low density and weldability [1]. Unfortunately, Al–Zn–Mg–Cu alloys are prone to stress corrosion cracking (SCC). The major microstructure features that affect the SCC resistance are the size and dispersion of grain boundary precipitates (GBPs), the width of precipitate-free zones (PFZs) and the grain boundary segregation [2–5].

The homogeneous precipitates in Al–Zn–Mg–Cu alloys during aging treatment mainly include three phases, namely, η phase, GP zones and η' phase. The equilibrium η phase has a hexagonal lattice with $a=0.521$ nm and $c=0.860$ nm [6], which is incoherent with the Al matrix. There are 11 orientation relationships of η phase with the Al matrix termed η_1 – η_{11} [7]. Among these 11 orientation relationships, the most frequently observed ones are η_1 , η_2 and η_4 , whose specific orientation relationships with the matrix are as follows:

$$\eta_1 : (0001)_{\eta} // (110)_{\text{Al}}; (10\bar{1}0)_{\eta} // (001)_{\text{Al}};$$

$$\eta_2 : (0001)_{\eta_2} // (1\bar{1}\bar{1})_{\text{Al}}; (10\bar{1}0)_{\eta_2} // (110)_{\text{Al}};$$

$$\eta_4 : (0001)_{\eta_4} // (110)_{\text{Al}}; (\bar{1}2\bar{1}0)_{\eta_4} // (1\bar{1}\bar{1})_{\text{Al}}.$$

The GP zones and the metastable η' phase are the main strengthening phases in Al–Zn–Mg–Cu alloys [8]. Structure models for η' phase have been proposed from HRTEM [9] and precession electron diffraction [10]. The metastable phase η' is generally recognized as a hexagonal crystal structure with lattice parameters $a=0.496$ nm and $c=1.402$ nm. The crystallographic orientation relationship of η' phase with the matrix is $(0001)_{\eta'} // (1\bar{1}\bar{1})_{\text{Al}}; (10\bar{1}0)_{\eta'} // (110)_{\text{Al}}$.

The η' precipitates are semi-coherent with the matrix. Two types of GP zones appear during the early stage of aging, known as GP I and GP II, respectively [11]. The GP zones are completely coherent with the Al matrix. The spherical GP I zones were reported to be internally ordered with a structure similar to AuCu(I), with internal ordering of Zn and Al/Mg on the alternate $\{001\}_{\text{Al}}$ planes. The GP I zones are formed via solute-rich clusters, and in a wide temperature range from room temperature to 140–150 °C, independently of quenching

temperature. The plate-like GP II zones are one or a few Zn-rich atomic layers on $\{111\}_{\text{Al}}$ planes. They are believed to be related to the VRC. The GP II zones are formed after quenching from temperatures above 450 °C and aging at temperature above 70 °C.

CHEN et al [2,3] investigated the effect of recrystallization and quenching rate on the copper content, the size and distribution of GBPs in Al–Zn–Mg–Cu alloys. PENG et al [4] and RANGANATHA et al [5] researched the influence of aging treatment on the size and distribution of GBPs, and the width of PFZs in Al–Zn–Mg–Cu alloys. However, few of them paid much attention to precipitation sequence along grain boundaries. Meantime, the formation process and mechanism of precipitate along grain boundaries are still unclear. In this work, therefore, the precipitation sequence of η phase along low-angle grain boundaries is investigated by HRTEM and HAADF-STEM combined with EDX. Moreover, the mechanism of grain boundary segregation and the formation mechanism of early-stage precipitation are discussed in detail.

2 Experimental

The studies were carried out on a 7050 Al alloy, whose nominal chemical composition is Al–6.29Zn–2.22Mg–2.28Cu–0.15Zr (mass fraction, %), with a small amount of Mn, Cr, Ti, Si and Fe elements. The cast ingot of the alloy was first homogenized at 460 °C for 24 h, hot rolled to a 4 mm thin plate, then solution treated at temperature of 475 °C for 1 h, water quenched, followed by aging at 135 °C for 5 min, 20 min, 40 min, 1 h and 6 h, respectively. TEM samples were subsequently prepared by mechanical grinding and punching to 3 mm disks in diameter. The disks were finally thinned using

twin jet electropolishing with an electrolyte of 30% nitric acid and 70% methanol at 15 V below –25 °C. HRTEM and HAADF-STEM observations as well as EDX analysis were carried out by Tecnai F30 G² TEM equipped with a high-angle annular dark-field detector and an X-ray energy dispersive spectrometer. 20 low-angle grain boundaries at different aging times were studied by HRTEM as well as HAADF-STEM combined with EDX.

3 Results

Figures 1(a) and (b) present HRTEM images along $[011]_{\text{Al}}$ direction of the samples aged at 135 °C for 5 min and 20 min, respectively, showing the morphological and crystallographic features of the GP II zones [11]. The HRTEM observations show that thin planar precipitates (marked by white arrows) are fully coherent with the Al matrix, parallel to $\{111\}_{\text{Al}}$ planes, with the size of 2–6 $\{111\}_{\text{Al}}$ atomic planes thickness and 4–7 nm width. Additionally, weak diffraction streaks are observed along $\{111\}_{\text{Al}}$ in the insets of Fig. 1, indicating the GP II zones formed. As shown in Fig. 1(b), with the increase of aging time to 20 min, the sizes of GP II zones increase to 7–12 atomic layers in thickness and 6–8 nm in width. In the present study, the GP II zones along low-angle grain boundaries consist of more atomic layers parallel to the $\{111\}_{\text{Al}}$ planes, which differ from the typical GP II zones with only 1–3 $\{111\}_{\text{Al}}$ atomic planes in thickness in the interior of grains [11].

Figure 2 shows the elemental mapping images along a low-angle grain boundary obtained by HAADF-STEM combined with EDX. In Fig. 2(a), the bright contrasts along the grain boundary are treated as precipitates. Figures 2(b)–(e) show the corresponding EDX mapping

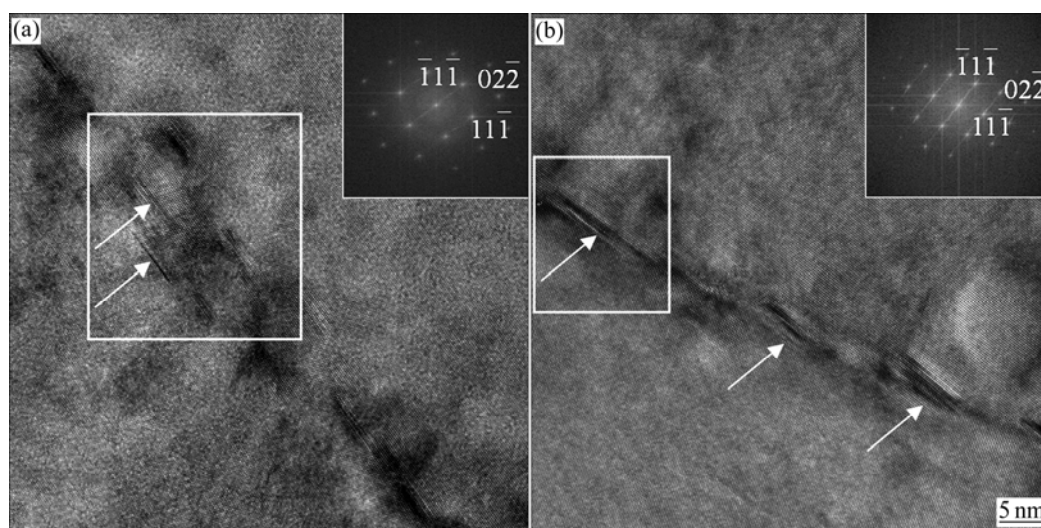


Fig. 1 HRTEM images in $[110]_{\text{Al}}$ projection with corresponding fast Fourier transform (FFT) spectra of white rectangular regions, showing GP II zones along low-angle grain boundaries: (a) Aged at 135 °C for 5 min; (b) Aged at 135 °C for 20 min

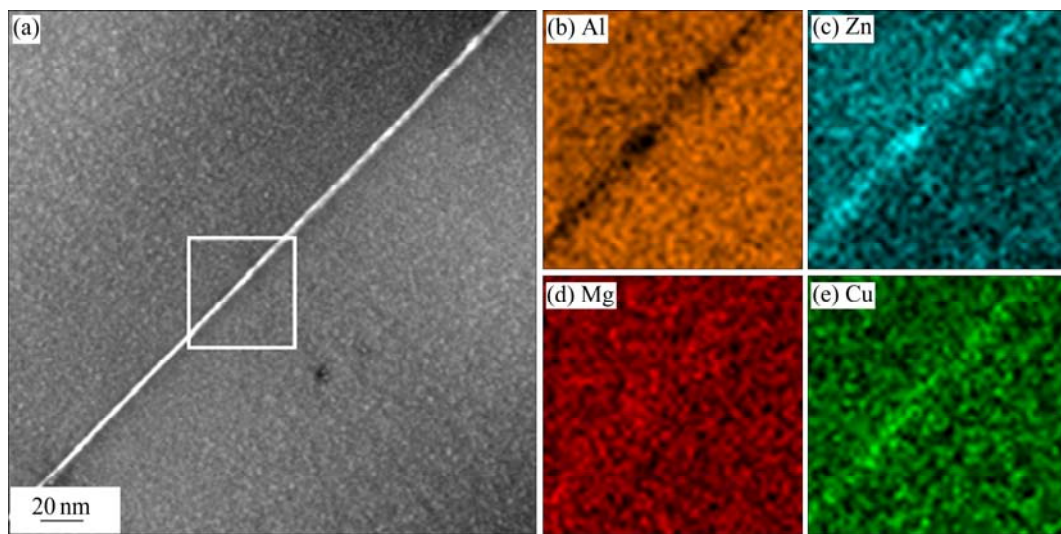


Fig. 2 HAADF-STEM image of 7050 Al alloy aged at 135 °C for 20 min (a) and corresponding EDX mapping images of white rectangular regions related to Al (b), Zn (c), Mg (d) and Cu (e)

images of Al, Zn, Mg, and Cu, respectively. These mapping images clearly show that elements Zn and Cu are enriched. The element Mg is slightly enriched next to the Zn-rich region, and element Al is obviously depleted at the locations of precipitates. HRTEM image (Fig. 1(b)) and EDX analysis (Figs. 2(b)–(e)) can confirm that the precipitates along low-angle grain boundaries are GP II zones that exhibit several Zn-rich atomic layers (some Zn atoms substituted by Cu atoms) on $\{111\}_{\text{Al}}$ planes.

Figure 3 shows the $[\bar{1}12]_{\text{Al}}$ HRTEM image, which was taken from the sample aged at 135 °C for 40 min. The HRTEM observation shows that the precipitates (marked by white arrows) are semi-coherent with the Al matrix, consisting of more atomic layers (>6 layers) parallel to the $\{111\}_{\text{Al}}$ planes, and some precipitates have ring-like image contrasts. One can observe diffuse streaks and diffraction spots at the 1/3 and 2/3 $\{220\}_{\text{Al}}$ positions in the FFT spectrum (inserted in the top-right of Fig. 3), indicating that η' precipitates have been formed. Some η' precipitates with ring-like image contrast in our observations differ from the η' precipitates with the separate ring chains seen between two wave-like lines in Ref. [9]. HRTEM observations taken from the sample aged at 135 °C for 1 h (not shown here) indicate that the precipitates are still η' phase.

After aging at 135 °C for 6 h, equilibrium η precipitates can be observed at low-angle grain boundaries. Figure 4 shows the $[\bar{1}12]_{\text{Al}}$ HRTEM image of the η precipitate which is incoherent with the Al matrix. It can be seen that the orientation relationship between the η precipitate and the matrix is $(0001)_{\eta} // (1\bar{1}\bar{1})_{\text{Al}}$; $(1010)_{\eta} // (110)_{\text{Al}}$, namely variant η_2 . Diffraction spots at the 1/3 and 2/3 $\{220\}_{\text{Al}}$ positions in the FFT spectrum

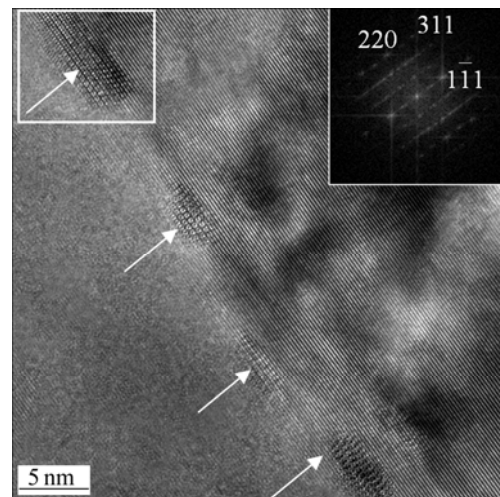


Fig. 3 HRTEM image in $[\bar{1}12]_{\text{Al}}$ projection, showing η' precipitates along low-angle grain boundary in sample aged at 135 °C for 40 min (The inset is the corresponding FFT spectrum of white rectangular region)

(inserted in the top-left of Fig. 4) indicate that η precipitates have been formed. Moreover, the measured c parameter along the $\langle 111 \rangle_{\text{Al}}$ direction is close to 0.860 nm in the enlarged portion of the white rectangular region (inserted in the bottom-right of Fig. 4), so these precipitates are identified as η phase. It is generally believed that η_2 precipitates are formed by direct transformation of η' phase, since these two phases η_2 and η' have similar orientation relationships and morphologies [7].

4 Discussion

4.1 Non-equilibrium grain boundary segregation

The diffusion of solute atoms from the vicinity of

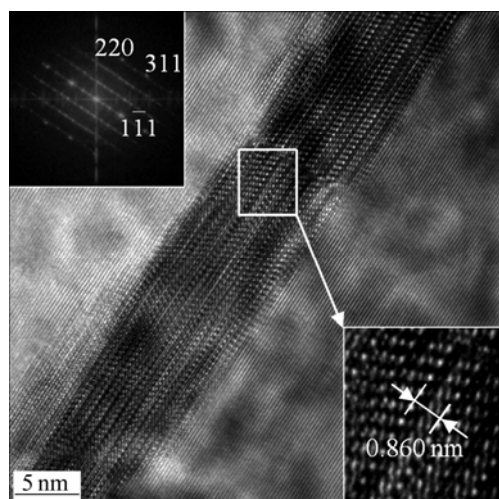


Fig. 4 HRTEM image in $[112]_{\text{Al}}$ projection, showing η precipitate along low-angle grain boundary in sample aged at 135 °C for 6 h (The insets are the corresponding FFT spectrum and magnification of the rectangular region, respectively)

grain boundaries to grain boundaries will occur in Al–Zn–Mg–Cu alloys during aging treatment because of the occurrence of NGS. The mechanism of NGS relies on the diffusion of the vacancy–solute complex toward grain boundary. Quantification analysis of NGS has been investigated by JIANG et al [12] and XU and CHENG [13].

In Ref. [13], it was reported that the influence of the vacancy–solute binding energy, E_b , on the non-equilibrium grain boundary segregation is the most significant, and the segregation effect is large when E_b lies in the range from 0.15 to 0.6 eV.

The values of E_b can be calculated by an elasticity theory. According to the ideas of COTTRELL [14], the following formula describes approximately the binding energy E_b of a vacancy with a foreign atom:

$$E_b = 8\pi\mu r_0^3 \varepsilon^2 \quad \varepsilon = \pm(r_1 - r_0)/r_0 \quad (1)$$

where ε is the misfit of the foreign atom with the matrix lattice, μ is the shear modulus of the matrix, r_0 is the matrix atom radius, and r_1 is the foreign atom radius. Therefore, the binding energy of a vacancy with a solute atom in 7050 Al alloy can be calculated as $E_b^{\text{Mg}} = 0.28$ eV, $E_b^{\text{Zn}} = 0.06$ eV, and $E_b^{\text{Cu}} = 0.22$ eV. The calculated results show that solutes Mg and Cu respectively have a binding energy with a vacancy in suitable range for NGS, from 0.15 to 0.6 eV.

According to the NGS theory [13], it is postulated that in 7050 Al alloys there is an equilibrium between solute atoms (Mg and Cu), vacancy (hereafter denoted as V) and their recombined complex described as Mg–V and Cu–V, respectively.

Based on the NGS theory, in the conditions that 7050 Al alloy was first held at a solution treatment temperature 475 °C for 1 h and then rapidly water quenched, immediately aged at lower temperature 135 °C for a reasonably long time, solute atoms gradually segregate to the grain boundaries.

The vacancy equilibrium concentration in the matrix at 475 °C is obviously higher than that at 135 °C. When the samples are aged at 135 °C, vacancy gradients develop between the grain boundary and the interior of grain due to grain boundary being an ideal sink of vacancy. The complexes (Mg–V and Cu–V) are decomposed into vacancies and solute atoms (Mg and Cu) because of the decrease of the vacancy concentration near the grain boundaries. As a result, the complexes (Mg–V and Cu–V) gradients generate between the grain boundary and the interior of grain far away from the grain boundary. The complexes (Mg–V and Cu–V) diffuse from the interior of grain to the grain boundary owing to the gradients of the complexes (Mg–V and Cu–V). This diffusion causes excessive solute atoms (Mg and Cu) to segregate to the grain boundaries.

XU and CHENG [13] proposed a model for thermodynamic calculation of NGS. The maximum NGS segregation concentration, $C_m(T_{i+1})$, of a solute is

$$C_m(T_{i+1}) = K[C_i]_g \frac{E_b}{E_f} \exp\left(\frac{E_b - E_f}{kT_i} - \frac{E_b - E_f}{kT_{i+1}}\right) \quad (2)$$

where $C_m(T_{i+1})$ is the maximum NGS segregation concentration for cooling from T_i to T_{i+1} ; T_i is solution treatment temperature; T_{i+1} is a lower temperature; $[C_i]_g$ is the equilibrium concentration of solute i within grains; E_f is the vacancy formation energy; E_b is the vacancy–solute binding energy; and k is the Boltzmann's constant.

The interaction energy between vacancies and solute atoms Zn is rather weak (~ 0.06 eV), why can Zn atoms be also largely transported to grain boundaries? The reason may be that NGCS takes place, which was put forward by XU and CHENG [13]. In 7050 Al alloy, solute Mg has a binding energy (0.28 eV) with vacancy in a suitable range for NGS to occur in solvent Al, while solute Zn has a binding energy (0.06 eV) with a vacancy beyond the range for NGS to occur. Both the electronegativity difference and the atomic radii difference between Mg and Zn, between Mg and Al, and between Zn and Al are respectively 0.34 and 0.025 nm, 0.3 and 0.017 nm, 0.04 and 0.008 nm. Therefore, the attraction between Mg and Zn is stronger than that between Mg and Al, and between Zn and Al. According to the model, the non-equilibrium segregation of solute Zn occurs along with the non-equilibrium segregation of solute Mg. This implies that the diffusion of Zn atoms to grain boundaries in the 7050 Al alloy occurs via Mg–V complexes.

4.2 Vacancy-rich clusters formation

At the early stages of artificial aging, the vacancy–solute complexes (Mg–V, Mg–Zn–V and Cu–V) gradually migrate to the grain boundaries due to NGS and NGCS. In the vicinity of grain boundary, frequent collisions between these solute–vacancy complexes release vacancies which finally annihilate at the grain boundaries leaving behind mobile complexes of solute atoms which may or may not also include vacancies. As a result, vacancy-rich Zn clusters are formed, which is known to occur in most Al–Zn–Mg–Cu alloys, in which the number of Mg atoms is reduced due to the reduction in the number of vacancies [15]. In addition, Zn atoms are partially replaced by Cu atoms in VRC.

4.3 GP II zones formation

At the beginning of artificial aging (5 to 20 min at 135 °C), the GP II zones could be imaged quite readily by HRTEM in $\langle 110 \rangle_{\text{Al}}$ projections which appear as thin layers on $\{111\}_{\text{Al}}$ planes (see Fig. 1). These zones are identified as Zn and Cu by EDX analysis in STEM mode, as shown in Fig. 2. Therefore, the combination of the HRTEM observations and EDX analysis can show that the GP II zones with a high content of Zn have probably started to form on $\{111\}_{\text{Al}}$ planes in the early stage of the decomposition of the supersaturated solid solution along low-angle grain boundaries.

The fine vacancy-rich Zn clusters are formed at the beginning of artificial aging, which act as GP II zones nuclei on subsequent aging. It is suggested that a possible mechanism of GP II zone growth along low-angle grain boundaries involves the diffusion of Mg–Zn–V complexes to the GP II zones boundary where the complexes dissociate, releasing Zn atoms.

The GP II zones, which are fully coherent with the matrix, therefore, have a lower interfacial energy than intermediate or equilibrium precipitate phases. As a result, the nucleation barrier for GP II zones is significantly smaller than η' phases as well as η phases. Subsequent evolution of the microstructure involves the replacement of the GP zones with more stable phases [16].

5 Conclusions

1) The precipitation sequence of η phase along low-angle grain boundaries in Al–Zn–Mg–Cu alloys aged at 135 °C is $\text{SSS} \rightarrow \text{VRC} \rightarrow \text{GP II} \rightarrow \eta' \rightarrow \eta$.

2) Quenched-in vacancies play critical roles in the processes of the grain boundary segregation. Solute atoms (Mg and Cu) gradually segregate to grain

boundaries by the diffusion of the solute–vacancy complexes (Mg–V and Cu–V) in Al–Zn–Mg–Cu alloys during aging treatment. Meanwhile, solute atoms Zn segregate to grain boundaries via Mg–Zn–V complexes.

3) The grain boundary segregation of precipitate-forming elements will affect the nucleation and growth of VRC, GP II zones, η' phase as well as η phase along grain boundaries in Al–Zn–Mg–Cu alloys during aging treatment.

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Al–Zn–Mg–Cu 合金在时效过程中 η 相沿小角晶界的析出序列

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摘 要: 采用高分辨透射电子显微镜和高角环形暗场扫描透射电子显微镜结合 X 射线能谱仪, 研究 Al–Zn–Mg–Cu 合金 η 相沿小角晶界的析出序列。试样在 135 °C 分别时效 5 min 到 6 h。结果表明, η 相在小角晶界的析出序列是: SSS→VRC→GP II 区→ η' → η 。基于非平衡晶界偏析和非平衡晶界共偏析理论, 在 Al–Zn–Mg–Cu 合金时效过程中, 通过溶质–空位对的扩散, 大量的沉淀形成元素偏析到晶界。这种晶界偏析在 VRC、GP II 区、 η' 相和 η 相的形核和生长中起重要作用。

关键词: Al–Zn–Mg–Cu 合金; 时效; 小角晶界; 晶界偏析; 析出序列

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