Effects of aging treatment on the intergranular corrosion behavior of Al–Cu–Mg–Ag alloy

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ABSTRACT

The effects of aging treatment on the corrosion behavior of Al–Cu–Mg–Ag alloy were studied by means of intergranular corrosion (IGC) testing, potentiodynamic polarization combined with optical microscopy (OM) and transmission electron microscopy (TEM). Corrosion testing results suggest that, the intergranular corrosion resistance properties of Al–Cu–Mg–Ag alloy decreased with increasing aging time, which is also corroborated by the potentiodynamic polarization test results for under-aged, peak-aged and the over-aged Al–Cu–Mg–Ag alloys. TEM results reveal that precipitations on the grain boundary became coarsened and distributed discontinuously with increasing aging time; widening of precipitation free zones (PFZ) is also observed. The PFZ with the lowest self-corrosion potential is preferentially attacked, and corrosion progresses along the PFZ. The corrosion resistance of over-aged Al–Cu–Mg–Ag alloy decreased because of its wider PFZ in comparison with those in other samples.

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1. Introduction

Al–Cu–Mg alloys with trace amounts of Ag have attracted considerable research interest as novel heat-resistant aluminum alloy because of their excellent mechanical properties and creep resistance at elevated temperatures [1–6]. These alloys are thus a promising material for aircraft applications.

Corrosion damage is one of the main failure forms of Al alloys. However, as an aviation Al alloy, little attention has been given to the research on the corrosion resistant behavior of Al–Cu–Mg–Ag alloy, which is also of particular importance for the development of heat-resistant Al alloy.

Factors affecting the microstructure of alloys, such as their chemical composition and the aging treatment, perform important functions in determining the corrosion behavior of Al alloys [7–12]. Shi et al. [13] reported that the discontinuity of precipitate distribution along the grain boundary is enhanced by introduction of Sc and Zr, which may result in improvements in the corrosion resistance property of Al–Zn–Mg–Cu–Sc–Zr alloys. Li et al. [14] found that the improved corrosion resistance of Al–Zn–Mg–Sc–Zr alloy is duo to the coarsening of separated precipitates η on the grain boundary, as well as the increased spacing of grain boundary precipitates with increasing the aging temperature. However, Lin et al. [15] reported the opposite results in 2024 alloy. The corrosion resistance of 2024 alloy decreases with increasing creep-aging

temperature. Lin et al. ascribed this result to the formation of local galvanic cells on the surface of the alloy by the growth of the S phases [15]. These controversial results may be due to the different chemical compositions of the precipitations. In order to clarify the localized corrosion mechanism associated with different precipitations in Al alloys, including θ (Al$_2$Cu), η (MgZn$_2$) and T$_1$ (Al$_2$CuLi), Li et al. [16] prepared the simulated bulk phase through melting and casting according to their designed chemical proportions. Potentiodynamic scanning results show that the corrosion potential (E_{corr}) of θ precipitation is more positive with respect to that of α (Al), whereas those of T$_1$ and η precipitations are negative. These results could be used to explain the various phenomenons observed in Al alloys after immersion in NaCl solution for 1–2 h. Precipitations of η and T$_1$ in the 7075 and 2195 alloys are preferentially attacked at the beginning of corrosion, whereas the alloy base at the adjacent periphery of θ precipitation in the aged Al–Cu alloy is preferentially attacked.

All of these results reveal that corrosion resistance behaviors are sensitive to the variation in the chemical composition or the heat treatment of Al alloys. Thus, electrochemical analysis and microstructural observation are important means to clarify the corrosion mechanism of Al alloys. As no evidence could be used to forecast the corrosion resistance of the new heat resistant alloy, in the present work, the corrosion behavior of Al–Cu–Mg–Ag alloy was investigated by intergranular corrosion testing, potentiodynamic polarization, and optical microscopy (OM). The microstructure of the grain boundaries was observed by transmission electron microscopy (TEM) to support the corrosion results.

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The simulated matrix, θ (Al$_2$Cu), and the precipitations free zones (PFZ) were prepared and their open circuit potentials were also measured.

2. Experimental

The experimental material Al–5.3Cu–0.8Mg–0.5Ag–0.3Mn–0.15Zr (in wt.%) was prepared with pure Al, pure Mg, pure Ag and Al–Cu, Al–Zr, Al–Mn master alloys by ingot metallurgy in a crucible furnace. The ingot was homogenized at 500 °C for 24 h [17], hot rolled to 6 mm and then cold rolled to a 3 mm thin plate. The samples were solid solution treated at 515 °C for 1.5 h [18], subsequently water quenched and then immediately aged at 185 °C for different time.

The intergranular corrosion tests were performed according to ASTM G110 [19]. The solution temperature is maintained at 35 ± 2 °C by thermostat. The surface area and the solution volume ratio is 6 mm^2/mL.

Electrochemical measurement was carried out by three-electrode system. A saturated calomel electrode was used as reference electrode, a Pt sheet as counter-electrode and the tested sample with a square surface of 1.0 cm^2 as working electrode. All of the measurements were performed in intergranular corrosion solution.

The anodic and cathodic polarization curves were performed with a scan rate of 1 mV/s. The simulated bulk phases θ (Al$_2$Cu) was prepared through melting and casting according to its chemical proportion. The as quenched Al–Cu–Mg–Ag alloy was selected as the simulated matrix in this work and pure Al was selected as the simulated PFZ. The open circuit potentials of the simulated θ (Al$_2$Cu), the matrix and PFZ were tested ranging from 1.0 V to −1.0 V with a scan rate of 1 mV/s.

The lengthwise sections of the intergranular corrosion sample were observed by optical microscopy (OM). Transmission electron microscopy (TEM) observations were carried out on TECNAI G220 transmission electron microscopy. The specimens for TEM observation were prepared by the standard twin-jet electropolishing method using 75% methanol and 25% nitric acid solution at −30 °C.

3. Results

3.1. Intergranular corrosion behavior

Fig. 1 displays the optical microstructure of the aged Al–Cu–Mg–Ag alloy immersed in intergranular corrosion solution for 6 h. The under-aged, peak-aged and over-aged samples were aged at 185 °C for 1 h, 4 h and 24 h, respectively. The under-aged, peak-aged and over-aged is distinguished by the aging hardening curves of Al–Cu–Mg–Ag alloy revealed in our previous work [20]. All of the samples were evidently damaged to a certain extent by intergranular corrosion.

The damage corrosion extent could be described in terms of maximum corrosion depth and global corrosion condition. The maximum intergranular corrosion depths and the intergranular corrosion levels of the samples were given in Table 1. Although the intergranular corrosion level of the three samples was fairly consistent at 4, their damaged conditions differed significantly. The maximum corrosion depth of the under-aged sample was 173 μm (Fig. 1a), which is similar to that of the peak-aged sample at 178 μm (Fig. 1c). The global corrosion conditions of the two samples were also markedly different. As can be seen from Fig. 1, the average corrosion depth of the under-aged sample was less than that of the peak-aged alloy. Only one section with relatively serious corrosion was found in the former (Fig. 1b), whereas at least three existed in the latter (Fig. 1d). Thus, the intergranular corrosion resistance property of the under-aged Al–Cu–Mg–Ag is better than that of the peak-aged alloy. The over-aged sample was seriously damaged globally and showed a maximum corrosion depth of 266 μm. A considerable amount of grains were etched out from its surface during immersion (Fig. 1e and f).

The results of the corrosion testing show that the intergranular corrosion sensitivities of the aged Al–Cu–Mg–Ag alloys follow the order: under-aged < peak-aged < over-aged.

3.2. Microstructure

Fig. 2 illustrates the TEM images of the aged Al–Cu–Mg–Ag alloys and the corresponding selected area electron diffraction patterns as given in Fig. 2c. Only little precipitation Ω with an average size of 10 nm (arrow in Fig. 2a) was observed in the grains of the under-aged sample. The phases on the grain boundaries were larger than those in the grains and distributed continuously along these grain boundaries (Fig. 2b). The precipitations coarsened both the grains and grain boundaries of the peak-aged sample with increasing aging time, accompanied by the appearance of a PFZ with an average width of 90 nm (Fig. 2c). The phase distribution on the grain boundaries eventually became discontinuously. With further increases in aging time up to 24 h, precipitations especially those on the grain boundary, became extremely large and were distributed separated (Fig. 2d). The PFZ width of the over-aged sample was approximately 120 nm.

As the intergranular corrosion usually begins at the grain boundaries, the corrosion resistance property of an alloy is determined by the intergranular microstructure. As can be seen from Fig. 2, the precipitations of Al–Cu–Mg–Ag alloys coarsened on the grain boundaries and their distribution varied from continuous to discontinuous with increasing the aging time. As reported by Li et al. [14], the discontinuous distribution of phases on the grain boundary could be favorable to the corrosion resistance of Al–Zn–Mg alloy. However, contrastive results were obtained in the present work. The intergranular corrosion resistance of over-aged Al–Cu–Mg–Ag alloy was the worse among the samples studied; this alloy also showed discontinuous distribution phases on its grain boundaries. These differences in findings may be due to the different phases precipitated on the grain boundaries and will be discussed in detail in Section 4.

3.3. Electrochemical analysis

The polarization curves of Al–Cu–Mg–Ag alloys in the intergranular corrosion solution and their corresponding electrochemical parameters, such as corrosion potential E_{corr}, corrosion current density I_{corr}, and polarization resistance R_p are shown in Fig. 3 and Table 2, respectively. The negative E_{corr} and the increase of I_{corr} with increasing aging time indicate a strong effect of the heat treatment on the electrochemical response of Al–Cu–Mg–Ag alloy. The largest E_{corr} and R_p and the smallest I_{corr} were achieved for the under-aged sample, suggesting its excellent corrosion resistance, which is in good accordance with the results of the intergranular corrosion tests.

4. Discussion

The aging heat treatment performs important functions in determining the microstructure and the corrosion resistance of Al–Cu–Mg–Ag alloys. The size and quantity of strengthening phases precipitate from the matrix both increase with increasing aging time. The coarsening rate of the precipitations on the boundary is larger than that in the grains, which may be due to the distortional strain energy of the grain boundaries. Several phases preferentially precipitate on the grain boundary. Consumption of the solution atoms to form precipitations on the grain boundaries leads to formation of PFZ along these boundaries. With increasing aging time, precipitations on the grain boundaries grew and coarsened, and eventually became discontinuously distributed in these areas, accompanied by widening of the PFZ. The intergranular corrosion results show that the corrosion resistance of Al–Cu–Mg–Ag alloy deteriorated with increasing aging time. Therefore, combined microstructure and intergranular corrosion results implies that the discontinuous distribution of precipitations on the grain boundaries or widening of the PFZ may be detrimental to the corrosion resistance of the alloys. However, this finding contrasts the results reported by Li et al. [14] regarding Al–Zn–Mg alloys, likely