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Preparation of bimodal grain size 7075 aviation aluminum alloys and their corrosion properties

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Abstract The bimodal grain size metals show improved strength and ductility compared to traditional metals; however, their corrosion properties are unknown. In order to evaluate the corrosion properties of these metals, the bimodal grain size 7075 aviation aluminum alloys containing different ratios of coarse (100 μm in diameter) and fine (10 μm in diameter) grains were prepared by spark plasma sintering (SPS). The effects of grain size as well as the mixture degree of coarse and fine grains on general corrosion were estimated by immersion tests, electrochemical measurements and complementary techniques such as scanning electron microscope (SEM) and transmission electron microscope-energy disperse spectroscopy (TEM-EDS). The results show that, compared to fine grains, the coarse grains have a faster dissolution rate in acidic NaCl solution due to the bigger size, higher alloying elements content and larger area fraction of second phases in them. In coarse grains, the hydrogen ions have a faster reduction rate on cathodic second phases, therefore promoting the corrosion propagation. The mixture of coarse and fine grains also increases the electrochemical heterogeneity of alloys in micro-scale, and thus the increased mixture degree of these grains in metal matrix accelerates the corrosion rate of alloys in acidic NaCl solution.

1. Introduction

Al-Zn-Mg-Cu (7xxx series) alloys are ultra-high strength aluminum alloys and widely used in aerospace industry because of their excellent mechanical properties and relatively good resistance to corrosion and fatigue.[1–6] The 7xxx series alloys have a remarkably increased strength compared to pure aluminum because of the high amount of alloying elements addition. Many types of strengthening particles, such as $MgZn_2$ (η-phase), Al_2CuMg (S-phase), Al_7Cu2Fe, $Al_{23}CuFe_4$ and Mg_2Si precipitated in metal matrix during aging and thus enhanced the strength of alloys. Even though Al-Zn-Mg-Cu alloys have a superficial oxide (passive) film to resist corrosion, their corrosion resistance still deteriorates significantly compared to pure aluminum, and are very susceptible to localized corrosion, including pitting, intergranular corrosion (IGC)

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and exfoliation corrosion (EXCO),[7–10] because of the electrochemical heterogeneity caused by second (strengthening) phases. Both the anodic particles (usually containing Al, Zn and Mg) and the cathodic particles (usually containing Al, Fe, Cu and Mn) can induce severe micro galvanic-coupling corrosion, because they exhibit different electrochemical activity and passivation ability compared to surrounding matrix.[8,10–12]

Some kinds of heat treatments such as quenching and aging have been employed to improve both the strength and corrosion resistance of Al-Zn-Mg-Cu alloys. These heat treatments usually include several adequate steps to modify the distribution, density, size and microchemistry of strengthening particles.[10,13–15] Quenching is an important step usually performed after solution treatment on Al-Zn-Mg-Cu alloys, and has great effects on microstructure and microchemistry of alloys matrix (including strengthening precipitates and precipitates free zone), therefore affecting alloys' corrosion resistance remarkably. Slowing quenching could deteriorate both the strength and corrosion resistance of alloys owing to the heterogeneous precipitation of more continuous and bigger η-phase ($MgZn_2$) on grain/sub-grain boundaries.[13,14,16–18] The Cu element content in η-phase also decreases with slowing quenching rate, therefore increases the electrochemical activity of particles and thus deteriorates corrosion resistance of alloys.[19,20] However, rapid quenching from solution treatment temperature always leads to high residual stress in metal matrix which usually causes cracks, deformation and exfoliation on thick plates.[21] Therefore, the step-quenching and aging (SQA) treatments were developed to deal with the shortcomings of traditional quenching treatments.[13,14]

Apart from quenching, aging is another important heat treatment to 7xxx series aluminum alloys, which can also change the mechanical performance and corrosion susceptibility of alloys significantly. The Al-Zn-Mg-Cu alloys usually get the highest strength under peak-aging condition, but they are susceptible to stress corrosion and localized corrosion under this condition, because of the small size and continuous distribution of second phases in grain boundaries.[13,22,23] In order to improve the service life of Al-Zn-Mg-Cu alloys and enhance the safety of aircraft, over-aging treatments are usually performed on alloys to improve the corrosion resistance, however with a 10%-15% decrease in strength. The increased content of Cu as well as decreased content of Zn, bigger size and more separated features of η-phase particles along grain boundaries are the main reasons of increased corrosion resistance of alloys after over-aging.[10,21–25] A so-called three-step aging treatment termed as retrogression and re-aging (RRA) was developed in recent years to obtain the balance between strength and corrosion resistance. After this treatment, the high density and small sized second phases distributed homogeneously in metal matrix; therefore, the alloys obtained high strength as peak-aging and good corrosion resistance as over-aging.[13,14]

A so-called core-shell structure was developed by Ameyama et al.[26–28] in recent years to improve both the ductility and strength of traditional metals. In this kind of structure, the fine (small) grains assembled a three-dimensionally connected network as the shell, while the coarse grains were embedded in this network as the core. However, up to now, this interesting structure was seldom carried out on Al-Zn-Mg-Cu ultra-high strength aluminum alloys. Besides, the effects of the bimodal grain size structure on corrosion were never investigated thoroughly. In this work, the bimodal grain size AA7075 aluminum alloys containing different mass fraction of coarse and fine grains are sintered by spark plasma sintering (SPS). The corrosion behavior of these alloys in acidic NaCl solution is also investigated.

2. Experiment

2.1. Materials and preparation

Two kinds of rotating disk centrifugal atomized 7075 aluminum alloy powders were used to prepare bulk alloys. The 100 μm diameter powders simulate coarse grains, while the 10 μm diameter powders simulate fine grains in metal matrix; these two kinds of powders were wetly blended in an acetone ultrasonic bath for 2 h, and then dried in vacuum at 50 °C for 12 h. The dried mixed alloy powders were loaded in a cylindrical graphite die for SPS sintering. The sintering temperature was 450 °C with 1 min dwell time and a heating rate of 50 °C/min in vacuum. A uniaxial pressure of 60 MPa was applied during the sintering. The sintered alloys were cooled naturally in vacuum after sintering.[29] Six kinds of 7075 alloys named as AL1-AL6 were sintered by SPS, and these alloys contained different mass fraction of coarse and fine grains as shown in Table 1. The mixture degree of coarse and fine grains increased with the decreasing content difference between them, i.e., AL3 and AL4 had relatively high mixture degree of coarse and fine grains. The chemical composition (wt%) of the alloys and unsintered powders was measured by Optima-7000DV inductively coupled plasma atomic emission spectrometer (ICP-AES). The element content (wt%) of AL1-AL6 and powders is the same and listed as follows: Zn 5.6, Mg 2.8, Cu 1.8, Fe 0.4, Si 0.2, Mn 0.05, Ti 0.05, Cr 0.05, Zr 0.05 and Al balance.

2.2. Microstructure measurements

Leica-4000 optical microscope was used to obtain the metallographic morphologies of alloys. The back-scattered electron images (BEI) of alloys and unsintered powders were revealed by Apollo-300 scanning electron microscope (SEM). JEOL-2100F transmission electron microscope (TEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to analyze the detailed morphologies and composition of second phases in metal matrix. The high angle annular dark field (HAADF) images of alloys were taken by TEM. The area fraction of second phases in metal matrix was calculated by ImageJ software. The corroded surface of alloys was observed by KH-7700 three-dimensional video microscope.

Table 1 Mass fraction of coarse and fine grains in alloys AL1-AL6.

Alloy	Mass fraction of coarse grains	Mass fraction of fine grains
AL1	100%	0%
AL2	80%	20%
AL3	60%	40%
AL4	40%	60%
AL5	20%	80%
AL6	0%	100%

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