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Intergranular corrosion of spark plasma sintering assembled bimodal grain sized AA7075 aluminum alloys

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ABSTRACT

The bimodal grain sized 7075 aluminum alloys with different mass fraction of coarse and fine grains were sintered by spark plasma sintering (SPS). The effects of grain size on intergranular corrosion (IGC) were estimated by immersion tests, electrochemical measurements and complementary techniques including SEM-EDS and TEM-EDS. The results showed that the IGC depth decreased significantly with the increasing ratio of fine grains, demonstrating a less IGC susceptibility in the fine grains. The bigger size, more continuous feature and higher iron and copper content of intermetallic particles in coarse grains resulted in faster cathodic reaction rate and consequently higher IGC susceptibility.

1. Introduction

High strength aluminum alloys such as Al-Zn-Mg-Cu series alloys are widely used in aerospace industry because of their excellent combination of low density, high strength and relatively good resistance to corrosion and fatigue [1–5]. The excellent mechanical properties of these alloys are attributed to a heavy alloying elements addition and complex heat treatments. However, Al-Zn-Mg-Cu alloys contain many types of intermetallic phases, such as Al_7Cu_2Fe, $Al_{23}CuFe_4$, Al_2CuMg (S phase), Mg_2Si and $MgZn_2$ (η phase), due to the high concentration of alloying elements, and thus are very susceptible to localized corrosion, including pitting, intergranular corrosion (IGC), exfoliation and stress corrosion [6–10]. Such intermetallic particles containing Al, Zn and Mg are anodic, while those consisting of Al, Fe, Cu and Mn are cathodic relative to the surrounding matrix, leading to severe micro galvanic-coupling corrosion. The potential difference between intermetallic phases and alloy matrix is the main driving force for localized corrosion, especially at grain boundary zone [8,11–13].

Many researchers have adopted various efforts to obtain a balance between strength and corrosion resistance of high-strength aluminum alloys. These efforts were usually associated with adequate heat treatment (including solution treatment, quenching, and aging) to modify the size, density, distribution and microchemistry of grain boundary precipitates (GBP) and of precipitates free zones (PFZ) next to grain boundaries [8,14–20]. Quenching is an important factor in controlling the microstructure and microchemistry of GBP and PFZ, and thus the corrosion resistance of alloys. For Al-Zn-Mg-Cu alloys, slow quenching generally reduces the strength and corrosion resistance of the alloys owing to heterogeneous precipitation of $MgZn_2$ on grain/sub-grain boundaries [15,16,21–25]. Another reason for the deteriorated corrosion resistance of the alloys is the decreased content of Cu in GBP caused by slow quenching, especially in the alloys with a high Cu concentration [15,16,26–28]. However, some researchers achieved an increased resistance against corrosion and stress corrosion cracking by slow quenching in alloys with a low Cu concentration [29,30]. Rapid quenching from the temperature of solution treatment, on the other hand, usually leads to high residual stress which is especially critical for large scale products such as thick plate [31]. Therefore, a step-quenching and aging (SQA) treatment was adopted to enhance both the strength and corrosion resistance of alloys [15,16,32]. The GBP could precipitate homogeneously at grain boundary during SQA, then coarsen and distribute discontinuous in subsequent aging period resulting in improved corrosion resistance.

Apart from quenching, aging is another critical factor that affects the mechanical and corrosion properties of high-strength aluminum alloys. Although the highest strength can be achieved in peak-aging condition (T6 or T651 temper), the alloys usually exhibit poor corrosion resistance and become susceptible to stress corrosion and localized corrosion due to the small size and continuous distribution of GBP [15,33–36]. Therefore, over-aging treatments such as T76, T73 and T7651 are generally required to improve

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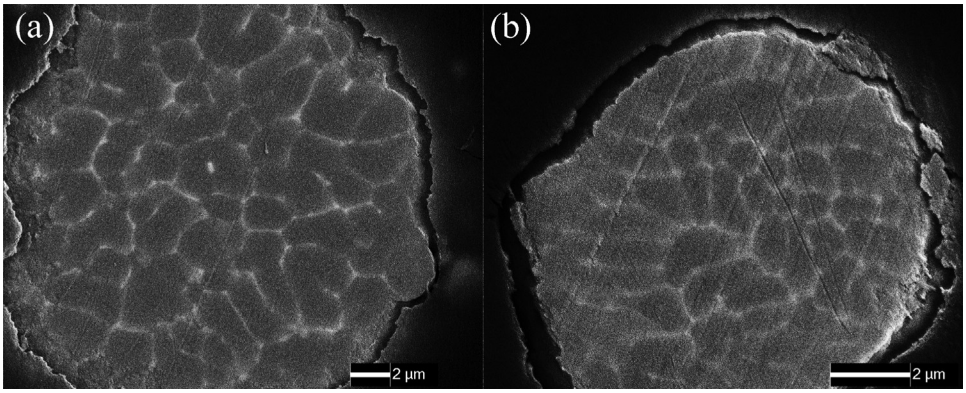

Fig. 1. BEI images of cross section for the 7075 aluminum alloy powders before sintering, (a) big powder with 100 ± 15 µm diameter (Φ100), (b) small powder with 10 ± 5 µm diameter (Φ10).

the corrosion resistance, however with a 10–15% decrease in the strength compared to peak-aging. After over-aging, η-phase particles become larger and more dispersed, therefore resulting in improved corrosion resistance [1,35,37–41]. The structural changes of PFZ adjacent to the grain boundary also play an important role, where a wider PFZ always promotes the IGC propagation [15,26]. Besides the microstructure, the changes of chemical composition in GBP and PFZ during aging also have a critical effect; the increase of Cu content and decrease of Zn content in η-phase (GBP) tend to enhance the IGC resistance [9,26,41–43]. Meanwhile, a depletion of Cu within PFZ can also increase the resistance of stress corrosion cracking [44]. However, the depletion of alloying elements especially Cu in PFZ will promote the propagation of IGC in many cases due to PFZ usually acts as anode during corrosion [1–4,42–44]. In recent years, a three-step aging treatment termed retrogression and re-aging (RRA) was adopted to achieve the balance between strength and corrosion resistance, which can produce high strength as peak-aging and low corrosion susceptibility similar to over-aging. These treatments modify the size, distribution, nearest neighbor and chemistry of the GBP and PFZ [15,16,26,43–46].

The heat treatments and relative GBP mentioned above usually relate to $MgZn_2$ (η-phase) which is anodic relative to aluminum matrix in corrosion. In fact, some kinds of cathodic particles (such as Al_7Cu_2Fe, Al_3Fe and $Al_{23}CuFe_4$) usually exist in high-strength aluminum alloys, because of the existence of Fe and Cu in metal matrix [1–4,8,11–15,19]. In some cases (such as aerated solution), the cathodic particles have a greater effect on corrosion than anodic particles. Oxygen is easily reduced on cathodic particles in aluminum alloys, which increases the amount of hydroxyl ions and the pH value of localized solution, therefore leading to the breakdown of passive film and consequent dissolution of adjacent aluminum matrix [1,4,8,11–13,19,34,47]. Burstain found that Al_3Fe could facilitate pitting initiation and propagation surround it in aluminum alloys [48]. Burstain and Guan also studied the current transients caused by pitting initiation, and proved that localized cathodic reaction could occur on cathodic particles even at a very high anodic polarization potential in both aerated and deaerated solutions [48–51].

In recent years, Ameyama [52–54] developed a new core-shell structure to improve mechanical properties of traditional metals, which contains a small-grains-assembled shell and a big-grains-assembled core. This interesting structure improves both the ductility and strength of traditional metals. However, up to now, the understanding of the effects of this bimodal grain sized core-shell structure on corrosion is lacking, especially for the high-strength aluminum alloys. In this study, the bimodal grain sized AA7075 aluminum alloys with different ratios of coarse grains to fine grains were prepared by SPS. The IGC susceptibility of these alloys was also tested and discussed with the corresponding microstructures.

2. Experimental

2.1. Materials and processing

Two kinds of rotating disk atomized 7075 aluminum powders with diameters of 100 ± 15 µm (Φ100) and 10 ± 5 µm (Φ10) (provided by HaoTian company) were used to prepare bulk metal. Six kinds of bulk alloys with different weight ratios (100%Φ100, 80%Φ100 + 20%Φ10, 60%Φ100 + 40%Φ10, 40%Φ100 + 60%Φ10, 20%Φ100 + 80%Φ10, and 100%Φ10) of these two kinds of powders were sintered by spark plasma sintering (SPS), and named as AL1 to AL6, respectively. Prior to sintering, the Φ100 and Φ10 powders of different weight ratios were wet blended in a acetone ultrasonic bath for 2 h, and followed by vacuum drying at 50 °C for 12 h. Then the dried mixed powders were loaded in a cylindrical graphite die with an inner diameter of 15 mm for SPS processing. The SPS experiments were carried out at 450 °C with a 1 min dwell time and a heating rate of 50 °C/min under vacuum. A uniaxial pressure of 60 MPa was applied during the whole SPS process. The sintered samples were cooled naturally in vacuum after sintering period. The whole sintering period (including heating and cooling time) was less than 30 min.

The chemical composition (wt.%) of the sintered 7075 alloys was 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, which was measured by Optima-7000DV inductively coupled plasma atomic emission spectrometer (ICP-AES), and was the same as that of the original powders.

2.2. Electrode preparation and immersion test

The sintered 7075 aluminum alloys were cut into cylinders of 5 mm diameter and cubes of 5 × 5 × 5 mm for electrochemical experiments and IGC tests, respectively. For the electrochemical experiments, the working electrode (cylindrical specimen) was inlaid in phenolic resin, and its electrical contact was made by spot welding a copper lead on to the back of it. The nonworking surface of the working electrode was sealed using epoxy resin. In the IGC test, the cubic specimen was also inlaid in phenolic resin, with just one surface exposed. The working surface of each specimen was ground with a series of emery papers from 600 to 6000 grit, and subsequently polished using 250 nm diamond spay suspension, and then cleaned thoroughly with deionized water and alcohol in turn.

The IGC susceptibility of sintered 7075 alloys was evaluated using immersion test in a solution of 1.0 M NaCl + 0.01 M H_2O_2 at