Postprint: Corrosion Resistance of Novel Al-Mg Alloys

Authors: Meng Chunyan, Zhang Di, Zhuang Linzhong, Zhang Jishan

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Abstract

The effects of alloying elements and thermomechanical processing on the intergranular corrosion and exfoliation corrosion resistance of novel Al-Mg alloys were investigated through intergranular corrosion and exfoliation corrosion tests combined with scanning and transmission electron microscopy observations and analyses of the microstructure and phase structure of corroded alloys. The results indicate that with increasing Mg content, the corrosion weight loss of the alloy in concentrated nitric acid solution increases, while the intergranular corrosion resistance decreases. The increased Zn content in the alloy leads to the formation of discontinuously precipitated Mg32(Al, Zn)49 phase at grain boundaries, which reduces the corrosion weight loss and improves the intergranular corrosion resistance of the Al-Mg alloys. The corrosion resistance of the alloy is also influenced by the thermomechanical processing; appropriate stabilization treatment of the cold-deformed alloy can simultaneously enhance both intergranular corrosion resistance and exfoliation corrosion resistance compared to simple cold deformation. The residual stress, high dislocation density, and elongated grain morphology after cold deformation promote more continuous precipitation of secondary phases at grain boundaries, forming a network film that degrades the corrosion resistance of the alloy.

Full Text

Preamble

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Corrosion Performance of Newly Developed Al-Mg Alloys

MENG Chunyan, ZHANG Di, ZHUANG Linzhong, ZHANG Jishan
(State Key Laboratory for Advanced Metals and Materials, University of Science

and Technology Beijing, Beijing 100083, China)

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Correspondence author: ZHANG Di, Tel: (010)82375844, E-mail: zhangdi@skl.ustb.edu.cn

ABSTRACT

The corrosion behavior of newly developed Al-Mg alloys was investigated in terms of their alloying elements and thermo-mechanical treatments by means of intergranular corrosion test, exfoliation corrosion test, scanning electron microscopy, and transmission electron microscopy. The results show that with increasing Mg content, the mass loss of the alloys in concentrated nitric acid increased, correspondingly decreasing their intergranular corrosion resistance. Zn addition to the Al-Mg alloys led to the formation of $Mg_{32}(Al, Zn)_{49}$ phase at grain boundaries, which dramatically increased the intergranular corrosion resistance of the alloys. The corrosion resistance of the alloys was also modified by thermo-mechanical treatment. Both intergranular corrosion resistance and exfoliation corrosion resistance were dramatically increased by proper post-stabilizing treatment after cold rolling reduction. The residual stress, higher dislocation density, and morphology of elongated grains after cold rolling reduction can lead to more continuous precipitation at grain boundaries, thus decreasing the corrosion resistance of the alloys.

KEY WORDS metallic materials, Al-Mg alloys, intergranular corrosion, exfoliation corrosion, stabilizing treatment

Introduction

Al-Mg alloys exhibit excellent corrosion resistance, good formability, high strength, and weldability, making them widely used in aerospace, marine, and automotive applications. As a work-hardening alloy that cannot be strengthened by heat treatment, Al-Mg alloys rely primarily on work hardening and solid solution strengthening from Mg atoms. With the development of modern industry, the degree of alloying has gradually increased. Although Mg content exceeding 6.0 wt% significantly improves alloy strength, the high-temperature plasticity decreases sharply, which is unfavorable for industrial deformation processing. Therefore, current Al-Mg alloys typically contain no more than 6.0% Mg.

The main issue with 5xxx series aluminum alloys as marine plates is that when Mg content exceeds 3.5%, the alloys are prone to intergranular corrosion and stress corrosion cracking when used above 65°C. This occurs because supersaturated Mg atoms precipitate as Al-Mg phases (Al_3Mg_2, β phase) at grain boundaries in a continuous distribution, making Al-Mg alloys susceptible to intergranular corrosion. At room temperature, precipitation of the Al-Mg phase is very slow, so laboratory studies typically use isothermal heating (sensitization treatment) to accelerate precipitation. Another practical problem is that β phase precipitation reduces the solid solubility of Mg atoms in the Al matrix. Since the β phase is a non-hardening precipitate that mainly forms at grain boundaries, it cannot strengthen the alloy through precipitation hardening, leading to "age softening." This not only reduces corrosion resistance but also affects alloy strength. Industrially, high-Mg alloys are generally subjected to stabilizing annealing to achieve uniform precipitation of the β phase throughout the microstructure. Therefore, optimizing alloy composition and processing parameters to transform the precipitation from continuous grain boundary distribution to uniform intragranular dispersion is crucial for ensuring both strength and corrosion resistance.

This study investigates the effects of Mg and Zn content on intergranular and exfoliation corrosion resistance of Al-Mg alloys, as well as the influence of different process combinations including cold rolling, stabilizing treatment, and sensitization treatment. The corrosion morphologies and microstructures of the newly developed Al-Mg alloys under various conditions were observed and analyzed.

Experimental Procedures

The experimental Al-Mg alloys were prepared by conventional resistance furnace melting and steel mold casting, with nominal chemical compositions listed in . The Mg content was controlled within 5.0-6.0 wt%, aiming to achieve high corrosion resistance under high Mg conditions through optimization of Zn content and processing parameters. After homogenization, hot rolling, recrystallization annealing (370°C for 75 min), and cold rolling (15% reduction), the alloy specimens were divided into four groups: Group A tested directly for corrosion performance (cold-worked condition), Group B tested after stabilizing treatment at 250°C for 1 h (stabilized condition), Group C tested after sensitization treatment at 100°C for 7 days (cold-worked + sensitized condition), and Group D tested after stabilizing treatment followed by sensitization at 100°C for 7 days (stabilized + sensitized condition). The specific processing routes are shown in .

Intergranular corrosion testing was conducted using the ASTM G67 nitric acid mass loss test (NAMLT), which evaluates intergranular corrosion resistance by comparing mass loss after immersion in concentrated nitric acid. Specimen dimensions were 50 mm × 6 mm × 4-5 mm. The procedure involved grinding specimen surfaces with 320-grit sandpaper, acid cleaning, alkali cleaning, drying, and weighing; then immersing dried specimens in 30°C concentrated nitric acid (76%) for 24 h; finally removing, washing, drying, and reweighing to determine mass loss per unit surface area under different processing conditions.

Exfoliation corrosion testing followed the ASTM G66 standard, with corrosion levels determined by comparison with standard rating charts. Test specimen dimensions were 40 mm × 100 mm, with the rolling direction (L direction) as 40 mm and the transverse direction (LT direction) as 100 mm. Non-test surfaces were sealed with epoxy resin before testing. Sealed specimens were immersed in 80°C 3.5% NaOH solution for 1 min, water-rinsed, then placed in concentrated nitric acid for 30 s, water-rinsed and dried. Dried specimens were immersed in 65°C acidic solution (ammonium chloride, ammonium nitrate, ammonium tartrate, and hydrogen peroxide) for 24 h, after which macroscopic corrosion morphology was observed.

After intergranular corrosion testing, surface micro-morphology was examined using a Zeiss Supra 55 scanning electron microscope (SEM). Microstructure and phase characterization were performed using a transmission electron microscope (FEI Tecnai F20). Samples were first ground to 80 m thick foils, punched into 3 mm diameter discs, and then twin-jet electropolished. The electrolyte was a 1:3 volume ratio of HNO_3 to CH_3OH, with a voltage of 28 V at -28°C.

2.1 Intergranular Corrosion Performance

The mass loss per unit area of alloys under different processing conditions obtained by ASTM G67 standard is shown in [Figure 1: see original paper]. With the same Zn content, mass loss from intergranular corrosion increased correspondingly with increasing Mg content. With the same Mg content, mass loss decreased significantly with increasing Zn content. Alloys also exhibited different intergranular corrosion susceptibility after various heat treatments: mass loss was lowest in the stabilized condition, showing the best intergranular corrosion resistance; after cold working and sensitization treatment, mass loss increased significantly, indicating reduced intergranular corrosion resistance.

Intergranular corrosion is a localized corrosion caused by potential differences between precipitates and the matrix or depleted zones near grain boundaries. In traditional Al-Mg alloys, it is primarily caused by continuous precipitation of Al_3Mg_2 phase at grain boundaries. After cold deformation, the distortion energy of grains increases, enhancing the driving force for phase precipitation. Simultaneously, increased dislocations in the microstructure facilitate Mg atom diffusion to grain boundaries or subgrain boundaries through pipe diffusion, rapidly forming an extremely thin β-phase network that reduces intergranular corrosion resistance. A proper stabilizing annealing treatment after cold deformation can eliminate internal defects such as dislocations and vacancies, reducing diffusion channels and driving force for Mg atoms. Low-temperature stabilizing treatment only causes partial recovery, with β phase still precipitating continuously at grain boundaries, which cannot achieve ideal intergranular corrosion resistance. Excessively high stabilizing temperatures cause β phase coarsening and dissolution, leading to age softening during service and failing to achieve stabilization. Our previous work found that isothermal annealing at 250°C ensures uniform distribution of β phase in the microstructure, providing good intergranular corrosion resistance with minimal strength reduction.

[Figure 2: see original paper] shows the corrosion morphologies of Al-5.5%Mg-1.0%Zn alloy after stabilizing treatment and stabilizing plus sensitization treatment. In the stabilized condition, the alloy surface remained relatively flat without grain dropping (Figures 2a, b). After sensitization treatment at 100°C, surface flatness decreased significantly, with obvious gaps appearing between grains (Figures 2c, d). Grain dropping in Al-Mg alloys results from reduced bonding strength caused by continuous grain boundary corrosion, which is related to continuous precipitation of Al_3Mg_2 at grain boundaries. Since the Al_3Mg_2 phase is more active than the matrix, it corrodes preferentially in corrosive environments. Under prolonged sensitization at 100°C, Mg atoms not only segregate at grain boundaries but also precipitate as β phase. β phase nucleates preferentially at triple junctions and grain boundaries, then at precipitate-matrix interfaces. With extended holding time, Mg atoms continuously transport from subgrain boundaries to grain boundaries, forming coarse β-phase particles at grain boundaries. Meanwhile, β phase at grain boundaries grows. When the growth direction of β phase aligns with the grain boundary orientation, it forms a continuous network along the grain boundary. The gaps between grains shown in Figure 2 resulted from corrosion and dropping of continuously precipitated Al_3Mg_2 phase.

During the study, different specimen surfaces exhibited varying degrees of corrosion. To illustrate the effect of grain morphology on intergranular corrosion susceptibility, morphologies from different surfaces of Alloy #3 were compared. [Figure 3: see original paper] shows the corrosion morphology of Al-5.8%Mg-0.6%Zn alloy after stabilizing and sensitization treatment. The surface perpendicular to the rolling plane (LT-ST plane) showed poor flatness, with deep holes indicated by arrows. The rolling plane (L-LT plane) exhibited relatively uniform grain structure with a flatter surface after corrosion, showing obvious corrosion gaps but no corrosion pits. These different corrosion morphologies indicate that grain morphology affects intergranular corrosion susceptibility, with elongated grains being more prone to intergranular corrosion. On the LT-ST plane, the grain aspect ratio is much larger than in other directions. Precipitation of Al_3Mg_2 phase at grain boundaries requires Mg atom diffusion to the boundaries, with diffusion time depending on temperature and distance. Elongated grains shorten the diffusion path for Mg atoms to reach grain boundaries, facilitating Mg segregation at grain boundaries. Severe intergranular corrosion on the LT-ST plane significantly reduces grain boundary bonding strength, causing grain dropping and surface roughening. Thermo-mechanical processing breaks up large intermetallic compounds while making them distribute more densely on the LT-ST plane. When severe corrosion occurs in the matrix around these phases in Al-Mg alloys, the densely distributed intermetallic compounds along the rolling direction drop out, forming deep corrosion pits.

To illustrate the effect of Zn content on corrosion resistance, microstructures of Al-5.7%Mg-0Zn and Al-5.8%Mg-0.6%Zn alloys were examined. [Figure 4: see original paper] shows grain boundary morphologies of these two alloys in the stabilized and sensitized condition. Figure 4a shows the grain boundary morphology of Al-5.7%Mg-0Zn alloy, where the white contrast at grain boundaries in the TEM image indicates that grain boundary precipitates have dropped out. Figure 4b shows the grain boundary morphology of Al-5.8%Mg-0.6%Zn alloy, exhibiting discontinuous precipitation without precipitate dropping. During TEM sample preparation, grain boundary precipitates are easily corroded and drop out due to poor corrosion resistance to the strong acid used in twin-jet polishing. Zn has very low solid solubility in Al matrix at room temperature, and $MgZn_2$ or $Mg_{32}(Al, Zn)_{49}$ phases typically precipitate in 7xxx aluminum alloys. In the new Al-Mg alloy microstructure, besides Al_3Mg_2, Mg_2Si, and Al-Fe-Mn phases, rectangular-shaped phases were observed as shown in [Figure 5: see original paper]. High-resolution TEM imaging and inverse Fourier transform diffraction results identified this phase as body-centered cubic $Mg_{32}(Al, Zn)_{49}$ with a lattice spacing of 1.422 nm. 5xxx aluminum alloys are prone to intergranular corrosion due to continuous β-phase precipitation at grain boundaries. The electrode potential of β phase is significantly lower than that of the matrix, forming micro-galvanic cells with the surrounding matrix that cause anodic dissolution and corrosion. In Al-Mg-Zn alloys, the electrode potential of $Mg_{32}(Al, Zn)_{49}$ phase (-1009 mV) is higher than that of β phase (-1124 mV), and its precipitation at grain boundaries reduces the potential difference between grain boundary phases and the matrix, thereby mitigating intergranular corrosion. Higher Zn content in 5xxx aluminum alloys leads to more Zn combining with Mg atoms, forming more $Mg_{32}(Al, Zn)_{49}$ phase and reducing Al_3Mg_2 phase content, thus improving intergranular corrosion resistance. Additionally, $Mg_{32}(Al, Zn)_{49}$ precipitation at grain boundaries breaks the continuity of Al_3Mg_2 phase, occupying nucleation sites for Al_3Mg_2 at grain boundaries and further enhancing corrosion resistance.

2.2 Exfoliation Corrosion Performance

[Figure 6: see original paper] shows macroscopic morphologies of alloys after exfoliation corrosion testing in the stabilized and sensitized condition. By comparing specimen corrosion morphologies with the rating charts in ASTM G66 standard, the corrosion level of all five alloys was rated as pitting corrosion (PC) level. This indicates that after stabilizing and sensitization treatments, only pitting corrosion occurred without exfoliation corrosion. The pitting corrosion resistance of alloys is related to large intermetallic compounds such as Al_3Fe and $Al_6(Mn, Fe)$, which have higher electrode potentials than the matrix. Therefore, in corrosive environments, these intermetallic compounds act as cathodes while the matrix acts as anode, forming micro-cells that cause localized pitting corrosion. Variations in Mg and Zn content have minimal effect on the formation of these intermetallic compounds, thus having little influence on pitting performance. The exfoliation corrosion rating did not change significantly with Mg and Zn content.

[Figure 7: see original paper] shows exfoliation corrosion morphologies of alloys after cold working and sensitization treatment. Obvious grain structure loosening and exfoliation were observed on specimen surfaces, with corrosion level rated as exfoliation corrosion (EC) level, indicating severe exfoliation corrosion. During heavy hot and cold rolling, grains become flattened, causing exfoliation corrosion in aluminum alloys without complete recrystallization. After cold deformation and sensitization treatment, specimens were in the recovery stage without recrystallization, with elongated grains and weak exfoliation corrosion resistance. Exfoliation corrosion in aluminum alloys is related to intergranular corrosion susceptibility, which depends on the distribution and amount of anodic dissolution phases. After cold deformation and sensitization treatment, large amounts of supersaturated Mg atoms precipitated as Al_3Mg_2 at grain boundaries, causing intergranular corrosion. Under cold deformation, insoluble corrosion products from intergranular corrosion propped up the flattened, uncorroded grains above, leading to metal exfoliation.

Conclusions

1. For the newly developed Al-Mg alloys, increased Mg content leads to greater mass loss in nitric acid and reduced intergranular corrosion resistance. Increased Zn content improves intergranular corrosion resistance because the higher electrode potential $Mg_{32}(Al, Zn)_{49}$ phase precipitates at grain boundaries, reducing the potential difference between precipitates and matrix.
2. Alloys in the stabilized condition exhibit the strongest intergranular corrosion resistance, while cold working and sensitization treatment both reduce this resistance.
3. Different surfaces of alloy specimens exhibit varying degrees of corrosion in nitric acid. The rolling plane shows better intergranular corrosion resistance than the plane perpendicular to the rolling plane (side plane).
4. After cold deformation, the high dislocation density and elongated grains in the microstructure reduce the alloy’ s exfoliation corrosion resistance.
5. Through alloying and different processing treatments, the Al-5.5%Mg-1.0%Zn alloy in the stabilized condition demonstrates optimal intergranular and exfoliation corrosion resistance.

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