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INFLUENCE OF ALUMINUM CONTENT ON CORROSION RESISTANCE OF Mg–Al ALLOYS CONTAINING COPPER AND ZINC

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Abstract

The corrosion resistance of Mg–Al alloys deteriorates significantly with increasing copper content. Consequently, the tolerance limit of copper is commonly fixed at less than 300 ppm in Mg–Al alloys to ensure they have sufficient corrosion resistance. However, it is desirable to use higher copper tolerance limit in actual operations. To realize this, it is very important to prevent the deterioration in the corrosion resistance with increasing copper content. In this study, Mg–Al alloys with different aluminum, zinc, and copper contents were casted by high-pressure die casting and the corrosion resistances of the castings were investigated. The corrosion resistance of Mg–9% Al alloys decreased significantly with increasing copper content. However, adding zinc to copper-rich alloys prevented the reduction in the corrosion resistance due to copper. The corrosion rate of Mg–Al alloys containing 0.5% copper and 3% zinc was minimized at an aluminum content of 9%. The corrosion resistance of Mg–Al alloys containing copper and zinc was highest at a zinc content of over 3% and an aluminum content of about 9%.

Introduction

Magnesium alloys are used in automobile lighting. In manufacturing processes, biscuits and runners of die castings are put into furnaces and are remelted. Magnesium alloys sometimes become contaminated with impurities during this process. Copper is one of the impurities. The corrosion resistance of Mg–Al alloys deteriorates significantly with increasing copper content, because copper forms copper-based intermetallic compounds [1–2]. Consequently, copper concentrations of less than 300 ppm are commonly used in Mg–Al alloys to ensure they have sufficient corrosion resistance [3]. To enable remelting, this limitation on the copper content needs to be lifted. To realize this, it is very important to prevent the deterioration in the corrosion resistance with increasing copper content.

In this study, the corrosion resistance of Mg–Al alloys containing copper and zinc was investigated. We determine the optimum zinc and aluminum contents for realizing a high corrosion resistance.

Experimental

Mg–9% Al–(0–6)% Zn–(0–1)% Cu–0.3% Mn alloys were prepared to determine the effect of the copper and zinc contents on the corrosion resistance of Mg–Al alloys. Mg–(5–13)% Al–3% Zn–0.5% Cu–0.3% Mn alloys were then prepared to investigate the influence of the aluminum content on the corrosion resistance of Mg–Al alloys containing copper and zinc. Alloys containing more than 0.7% zinc were casted with commercial AZ91D alloy ingots and grains of pure zinc and copper. Alloys containing less than 0.7% zinc were casted with ingots of pure magnesium and aluminum, Mg–3.3% Mn alloy ingots, and grains of pure zinc and copper. These raw materials were melted at 1023 K and were casted by high-pressure die casting. The cast samples had dimensions of $3\times40\times150$ mm^3. The casting temperature was 50 K above the liquidus temperature, the shot pressure was 64 MPa, and the shot velocity was 0.4 m/s. The microstructures of the castings were observed by scanning electron microscopy (SEM) and electron microprobe analysis (EPMA). Samples with dimensions of $2\times25\times25$ mm^3 were prepared for corrosion tests by scraping casts. They were polished with #600 waterproof abrasive papers and purified with acetone. For the corrosion test, they were soaked in 5% NaCl aqueous solution. Corroded samples became lighter through the evolution of hydrogen. The corrosion rate was calculated from the weight loss after soaking for 100 h. In addition, alloys were casted at 1023 K by gravity die casting and the cast samples had dimensions of $25\times35\times300$ mm^3. The microstructures of the castings were observed by SEM and image analyses of them were performed.

Results and Discussion

Influence of copper and zinc contents

Figure 1 shows the relationship between the copper content and the corrosion rate of Mg–9% Al–(0–5)% Zn–(0–1.2)% Cu–0.3% Mn alloys. The corrosion rate increased with increasing copper content irrespective of the zinc content. The rate of increase in the corrosion rate with increasing copper content (i.e., the gradient of the curve) decreased with increasing zinc content for zinc contents between 0 and 2%, whereas it remained almost constant for zinc contents higher than 3%. Thus, the corrosion resistance of Mg–9% Al alloys decreased significantly with increasing copper content. However, adding zinc (preferably more than 3%) to copper-rich alloys prevented the reduction in the corrosion resistance due to copper.

Figure 2 shows the microstructures and EPMA maps of Mg–9% Al–(0.7, 3)% Zn–0.5% Cu–0.3% Mn alloys. Three phases were observed in both alloys. Based on the observed magnesium, aluminum, copper, and zinc distributions, the matrix phase is the α-Mg phase, the gray regions in the secondary-electron (SE) image are β phases ($Mg_{17}Al_{12}$ compounds), and the white regions in the SE image are copper-based intermetallic compounds.

Figure 3 shows the appearance of the surfaces of Mg–9% Al–(0.7, 3)% Zn–0.5% Cu–0.3% Mn alloys after the corrosion test. Both samples appeared porous after the corrosion test. The remains of the alloy containing 3% zinc were thicker than those containing 0.7% zinc. In general, the centers of the α-Mg phases corroded away, whereas the β phases and aluminum-rich regions of the α-Mg phase adjacent to the β phases remained in AZ91D alloys [4–5]. α-Mg phases are anode portions and copper-based intermetallic compounds are cathode portions in Mg–Al alloys containing copper. The centers of α-Mg phases corroded away, whereas the β phase, aluminum-rich zones of α-Mg phases adjacent to the β phase, and copper-based intermetallic compounds remained. Therefore, samples subjected to corrosion test were porous, as shown in Figs. 3(a) and (b).

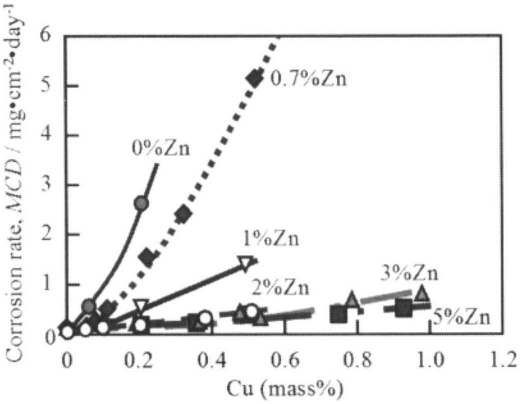

Figure 1. Relationship between copper content and corrosion rate of Mg–9% Al–(0–5)% Zn–(0–1.2)% Cu–0.3% Mn alloys.

Table I shows the chemical compositions of the copper-based intermetallic compounds of Mg–9% Al–(0.7, 3)% Zn–0.5% Cu–0.3% Mn alloys. The zinc content of the intermetallic compounds increased and the copper and aluminum contents decreased when the zinc content was increased from 0.7 to 3%.

For the reasons stated above, the copper-based intermetallic compounds in the alloys containing 0.7% and 3% zinc were cathode portions. However, the copper-based intermetallic compounds in the two alloys had different chemical compositions, which resulted in different cathode reactions. Consequently, the two alloys exhibited different corrosion resistances.

Influence of aluminum content

Figure 4 shows the relationship between the aluminum content and the corrosion rate of Mg–(5–13)% Al–3% Zn–0.5% Cu–0.3% Mn alloys. The corrosion rate of the alloys was minimized when the aluminum content was 9%.

Figure 5 shows SEM-backscattered electron (BSE) images of microstructures of Mg–(5–13)% Al–3% Zn–0.5% Cu–0.3% Mn alloys. α-Mg phases and copper-based intermetallic compounds, which appear white in SEM images, were observed at an aluminum content of 5% (Fig. 5(a)). In addition to α-Mg phases and copper-based intermetallic compounds, β phases, which appear gray in SEM images, were observed at aluminum contents higher than 7% (Figs. 5(b)–(e)). Increasing the aluminum content of the alloys increased the amount of β phases and caused fine dispersion of copper-based intermetallic compounds.

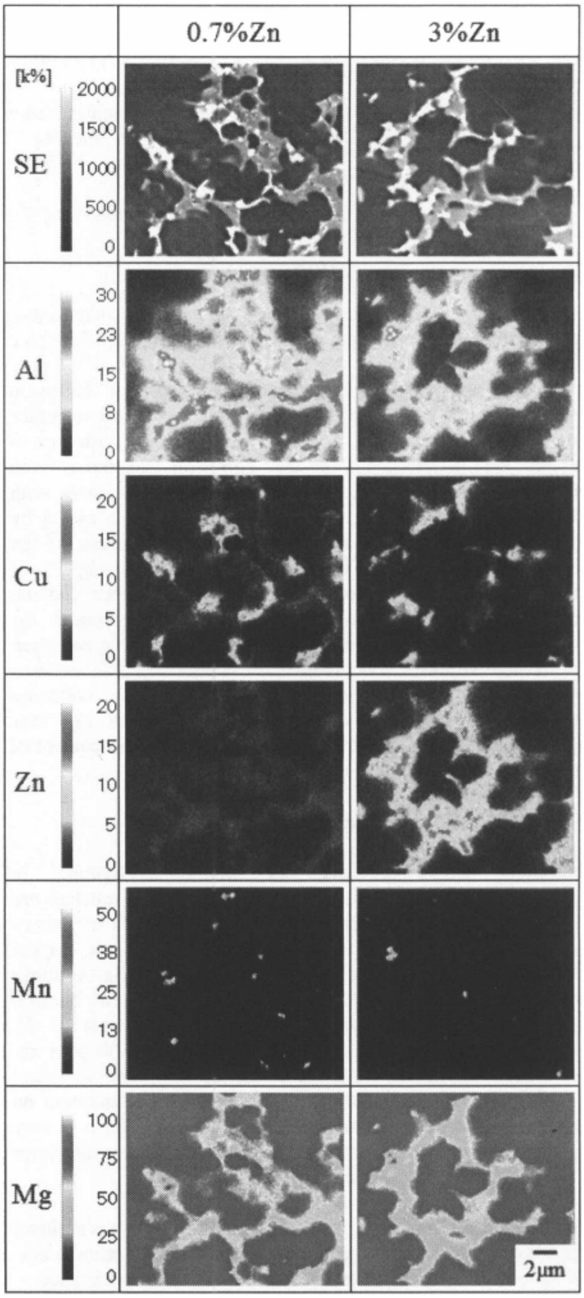

Figure 2. Microstructures and EPMA maps of Mg–9% Al–(0.7, 3)% Zn–0.5% Cu–0.3% Mn alloys.

Figure 6 shows the relationship between the aluminum content and the areas of β phases and copper-based intermetallic compounds. These areas were determined by performing image analysis of the images of the microstructures shown in Fig. 4. The β phase area increases linearly with aluminum content of the alloys. In contrast, the copper-based intermetallic compound area was almost independent of the aluminum content. Aluminum contributes to the formation of β phases and copper-based intermetallic compounds in the alloys. The alloys had the same copper content (0.5%). Consequently, increasing the aluminum content increased only the β phase; the copper-based intermetallic compound areas remained constant.

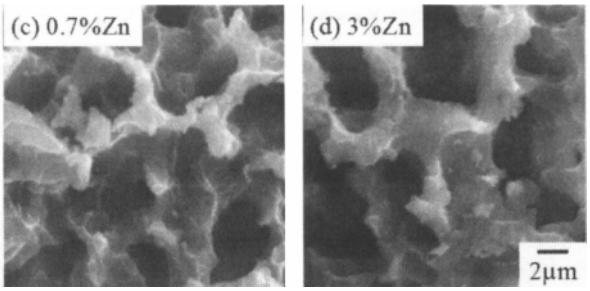

Figure 3. Appearance of surfaces of Mg–9% Al–(0.7, 3)% Zn–0.5% Cu–0.3% Mn alloys after corrosion tests.

Table I. Chemical compositions of copper-based intermetallic compounds of Mg–9% Al–(0.7, 3)% Zn–0.5% Cu–0.3% Mn alloys (mass%)

Alloy	Al	Zn	Cu	Mg
Mg-9%Al-0.7%Zn -0.5%Cu-0.3%Mn	31.1	3.8	12.5	Bal.
Mg-9%Al-3%Zn -0.5%Cu-0.3%Mn	26.1	12.5	10.6	Bal.

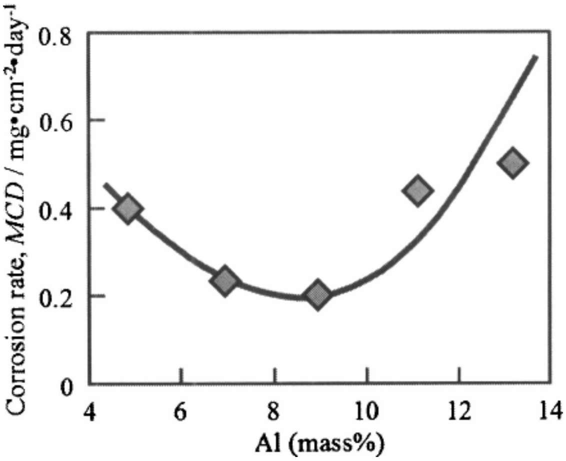

Figure 4. Relationship between aluminum content and corrosion rate of Mg–(5–13)% Al–3% Zn–0.5% Cu–0.3% Mn.

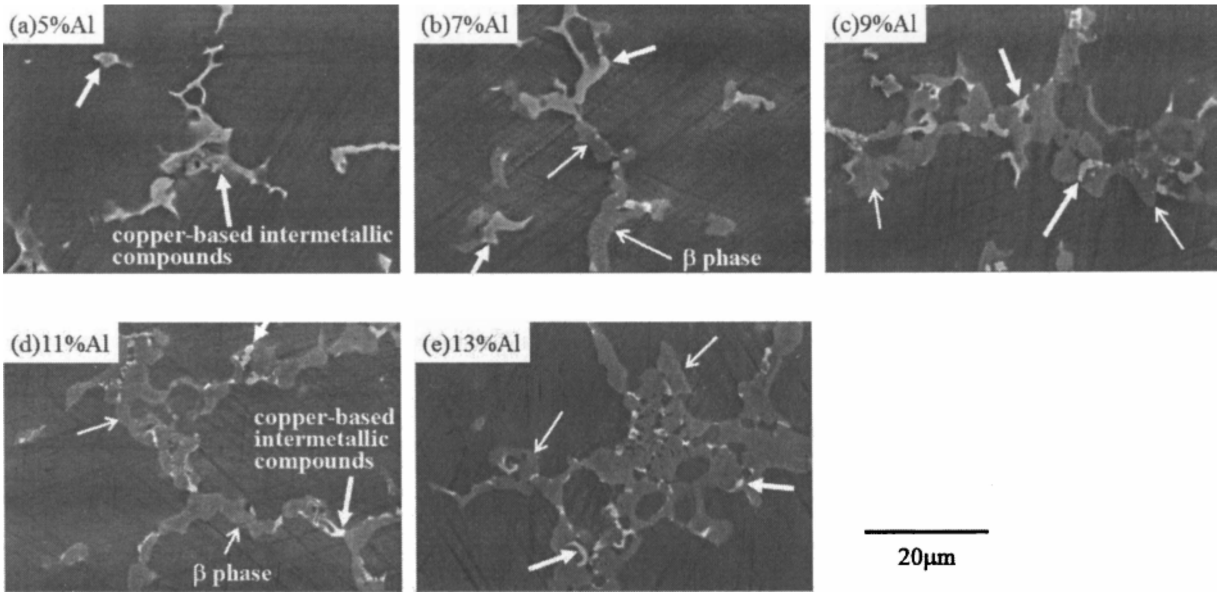

Figure 5. SEM-BSE images of microstructures of Mg–(5–13)% Al–3% Zn–0.5% Cu–0.3% Mn alloys.

Figure 7 shows the relationship between the aluminum content and the number of copper-based intermetallic compounds and their average area per 1 mm2. The number of copper-based intermetallic compounds increased and the average area of the compounds decreased with increasing aluminum content. This indicates that with increasing aluminum content, copper-based intermetallic compounds were finely dispersed while their total area remained constant. During solidification, copper-based intermetallic compounds precipitated in residual liquid phases after the α-Mg phase solidified. With increasing aluminum content, the α-Mg phase grains became finer and residual liquid phases were dispersed more finely. Consequently, copper-based intermetallic compounds were finely dispersed while their total area remained constant.

We now consider the influence of aluminum on the corrosion resistance of the alloys in terms of the above-described structural changes. In Mg–Al alloys containing copper, α-Mg phases form the anode portion and copper-based intermetallic compounds compose the cathode portion. While the centers of α-Mg phases corrode away, β phases and aluminum-rich regions of the α-Mg phase adjacent to a β phase inhibit the progress of corrosion-like barriers. Thus, the corrosion resistances of the alloys will increase with increasing β phase area.

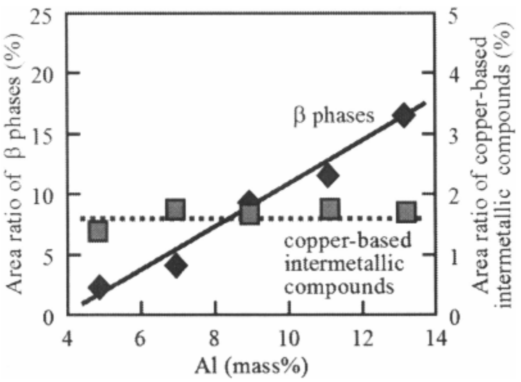

Figure 6. Relationship between aluminum content and areas of β phases and copper-based intermetallic compounds.

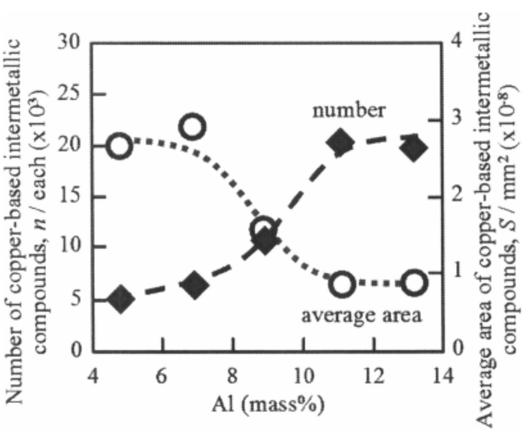

Figure 7. Relationship between aluminum content and the number of copper-based intermetallic compounds and average area.

On the other hand, fine dispersion of copper-based intermetallic compounds, which are cathode portions, increases the corrosion portion and increases the anode–cathode reaction, reducing the corrosion resistance. Thus, increasing the aluminum content in the alloys simultaneously enhances the corrosion resistance by increasing of the amount of β phase and deteriorates the corrosion resistance due to fine dispersion of copper-based intermetallic compounds. At aluminum contents below 9%, the increase in the corrosion resistance due to the increase in the β phase is greater than the reduction in the corrosion resistance due to fine dispersion of copper-based intermetallic compounds. The opposite is true at aluminum contents greater than 9%. Therefore, the corrosion resistance is maximized at an aluminum content of 9%.

Summary and conclusions

The corrosion resistance and microstructures of Mg–Al alloys with different aluminum, zinc, and copper contents were investigated. The results obtained are summarized as follows:

1. The corrosion resistance of Mg–9% Al alloys decreased significantly with increasing copper content. However, adding zinc to copper-rich alloys prevented the corrosion resistance reduction due to copper. In Mg–Al alloys containing copper and zinc, α-Mg phases were anode portions and copper-based intermetallic compounds were cathode portions. The copper-based intermetallic compounds in alloys with different zinc contents had different chemical compositions and this gave rise to different cathode reactions. Therefore, the alloys had different corrosion resistances.
2. Increasing the aluminum content of the alloys containing 0.5% Cu and 3% Zn resulted in a linear increase in the β phase area and increased the fine dispersion of copper-based intermetallic compounds while their total area remained constant.
3. The corrosion rate of Mg–Al alloys containing 0.5% Cu and 3% Zn was smallest at an aluminum content of 9%. For aluminum contents less than 9%, the improvement in the corrosion resistance due to the increase in the β phase is larger than the reduction in the corrosion resistance due to fine dispersion of copper-based intermetallic compounds. The opposite is true for aluminum contents greater than 9%.
4. In Mg–Al alloys containing copper and zinc, the optimum zinc and aluminum contents for corrosion resistance are more than 3% and about 9%, respectively.

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