

Ca and Ce Effect on the Corrosion Resistance of Hot-Rolled AZ31 Mg Alloys

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Abstract—In this study, AZ31 Mg alloys with added Ca and Ce were produced by low pressure die casting and were rolled at 400°C. The corrosion properties of the materials were determined by immersion test for 72 hours at a 3.5% NaCl solution. The microstructure of the samples was investigated by light optical microscopy (LOM) and scanning electron microscopy (SEM) before the corrosion test. Twins, dynamic recrystallization (DRX), and the alloying elements have an important role in imparting the final corrosion resistance of the investigated materials.

Keywords—Mg alloys; Ca; Ce; hot rolling; corrosion

I. INTRODUCTION

Because of their low density and high specific strength, magnesium alloys have received great interest as structural materials for applications in the automotive and aerospace industries [1]. However, low corrosion resistance is still the main deficiency of Mg alloys which could be solved by alloying, coating, or heat treatment processes [2, 3]. To get finer grains, rolling is especially utilized to form the billet from high thickness to thin sheets. The twins are the main deformation mechanism of rolling which deteriorates the corrosion resistance of wrought Mg alloys because of the fact that stresses resulted from twin boundaries impart site to cathodic corrosion [3, 4]. Moreover, the secondary phases of $Mg_{17}Al_{12}$ are the second cathodic corrosion contributor for Mg alloys finer formed and non-homogenous distributed inside the matrix and on grain boundaries [2]. Alloying with Ca is suggested to improve the oxidation resistance of Mg alloys due to its more affinity to oxidation than Mg which acts as a barrier during the corrosion of Mg [5]. Rare earth elements (REMs) are another option to change secondary phases. The Ce is more electronegative than Mg to compound with Al which results in more stable corrosion phase while non-homogeneously distribution of $Mg_{17}Al_{12}$ could be replaced by Ce-Al including secondary phases mostly showing regular shapes on grain boundaries [6, 7]. In this study, to improve the commercially widespread Mg alloy of AZ31, Ca and Ce elements were added

to the composition and hot rolling was utilized to get finer grains and homogeneous secondary phases on the microstructure. The corrosion resistance of the produced materials was tested at 3.5% NaCl solution at room temperature. To understand the Ce contribution on the corrosion resistance of AZ31 LOM, and SEM characterization methods were used.

II. EXPERIMENTAL PART

AZ31 Mg alloys containing 1% Ca (wt.%) were produced by low pressure die casting. In argon gas protected environment, pure Mg alloys were allowed to melt at 750°C for 1 hour and then Ca-Mg and Ce-Mg master alloys were added to the ladle and alloyed. In SF₆-CO₂ protective atmosphere, the alloy was transferred to a stainless steel 36×36×200mm mold, heated at 350°C by applying 2atm pressure. The billets with dimensions of 36×12×80mm were cut from the alloys and were left to cool in the molds. The billets were used in the homogenization process before rolling. The surfaces of the billets which were homogenized for 24 hours at 400°C were sanded with 800 sanding sheets and made ready for rolling after pre-rolling at 400°C for 30 minutes. The samples were reduced at 400°C rolling temperature from 12mm wall thickness to 2mm wall thickness in 5 passes and were allowed to cool in the air after the last pass. In this study, the rolling parameters were 30% cross-sectional reduction per pass and the rolling speed was 1.5m/min and 10m/min. The rollers of the rolling machine used are made of stainless steel with a diameter of 110mm. No lubricant was used in the rolling process. The 2mm sheet materials were exposed to corrosion in 3.5% NaCl environment for 72 hours. After corrosion, the materials were cleaned in chromic acid solution by an ultrasonic cleaning device and then the surface materials were dried with alcohol and their weight was measured on a sensitive balance machine. After the corrosion test, microstructure images of the samples were taken by optical microscope (Nikon Eclipse MA200 + Clemex software) and SEM (Carl Zeiss Ultra Plus Gemini Fesem).

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TABLE I. ALLOY CHEMICAL COMPOSITION (%WT.)

Alloys	Al	Zn	Mn	Ca	Ce	Mg
AZ31-1Ca	2.69	0.92	0.14	0.80	-	Bal.
AZ31-1Ca-0.5Ce	2.99	0.90	0.24	0.96	0.43	Bal.

III. RESULTS AND DISCUSSION

A. Microstructure Results

Figure 1 shows the LOM images of the studied alloys. It can be seen that the grains of all samples were mainly formed after the rolling process. However, the average grain size varies, depending on rolling speed. Lower rolling speed gives larger grains and more black points are distributed mainly inside the grains when the rolling speed is 4.7m/min (Figure 1(a)). On the other hand, the twins activated during rolling occur more often in the microstructure at higher rolling speeds of AZ31-1Ca alloy (see Figure 1(b)). Regarding the Ce addition to AZ31-1Ca alloy, larger grains were formed. The Ce added alloy deformed at 10m/min shows larger grains and contains more twins.

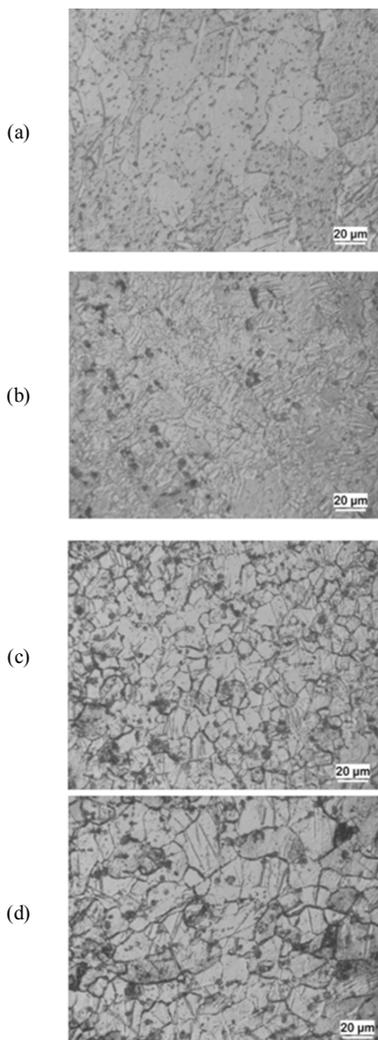


Fig. 1. LOM images of AZ31-1Ca alloys deformed with (a) 1.5m/min and (b) 10m/min and AZ31-1Ca-0.5Ce alloys deformed with (c) 1.5m/min and (d) 10m/min rolling speeds

The investigated samples show that higher rolling speeds activate more twin formations for both alloy groups (Figures 1(d) and 3(b)). The formation and distribution of the secondary phases were examined by the SEM images of the alloys presented in Figure 2.

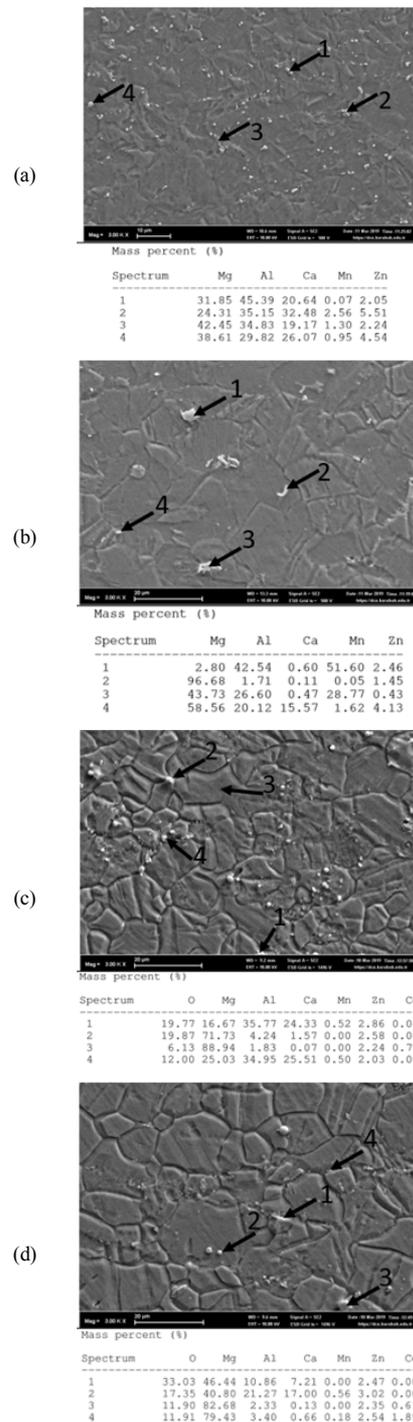


Fig. 2. SEM images and EDX results of AZ31-1Ca alloys deformed with: (a) 1.5m/min and (b) 10m/min, and AZ31-1Ca-0.5Ce alloys deformed with: (c) 1.5m/min and (d) 10m/min rolling speeds

The secondary phases of 1Ca deformed at 1.5m/min rolling speed are finer and homogeneously distributed inside the grains and grain boundaries in surface and cross-section. However, the size of the secondary phases was larger when the rolling speed was 10m/min and the distribution of the larger secondary phases was especially placed on grain boundaries (Figure 2). The Ce added materials contain more homogeneously distributed equiaxed grains, although the secondary phases of the samples rolled at 1.5m/min were formed at a larger size and placed on grain boundaries. The EDX examination shows that the secondary phases of Ca-added deformed alloy at 1.5m/min rolling speed were formed as small spherical shapes which are dominantly Al-Ca rich. However, the rising of rolling speed to 10m/min dissolved the generally smaller sized secondary phases in the matrix where the Al-Mn rich secondary phases that occurred mostly on grain boundaries have a larger size and complex or rectangular shapes. However, a small number of the finer and spherical shaped secondary phases were detected on twins' boundaries. When we examine the Ce added AZ31-1Ca alloys, the Ce mostly has been solved in the matrix of 1Ca-0.5Ce alloy deformed at 1.5m/min rolling speed due to the chemical composition of secondary phases. However, the same alloy contains spherical shaped secondary phases that contain Ce, when the rolling speed is 10m/min, more than when rolled at 1.5m/min. The average grain size results show that finer grains of $7.8\mu\text{m}$ were obtained for 1Ca alloy deformed at 10m/min rolling speed. Higher rolling speed imparts finer grains to 1Ca added alloys, although the finer grains were obtained in 1Ca-0.5Ce added alloys after 10m/min rolling speed. As for the twins, both alloys showed an increase in twins fraction along with the rising of rolling speed. Moreover, the highest twins' density is introduced on 1Ca-0.5Ce added alloy deformed at 10m/min rolling speed (Figure 3).

B. Immersion Corrosion Results

The immersion test results of the investigated alloys are exhibited in Figure 4. At the first test period the inclinations of corrosion rate belonging to alloys are similar for 9 hours. Rising of metal loss after 9 hours was observed, and the higher amount was detected on 1Ca alloy deformed at 1.5m/min rolling speed. The increased inclination of corrosion rate endured up to 12 hours. Afterwards the inclination did not show any higher rising. Most alloys illustrated a similar trend between 12 and 48 hours. However, the inclination line of corrosion rate decreased until the end of the test for all samples. During the immersion tests, the highest corrosion resistance was obtained with 1Ca-0.5Ce alloy deformed at 1.5 m/min. As mentioned above, Ce mostly diffuses into the matrix where the solutes of Ce have a significant influence on the corrosion behavior of the material due to the galvanic effect occurring softly between the matrix and the grain boundaries [5, 8]. On the other hand, the poorest resistance to corrosion was detected in 1Ca alloy deformed at 1.5 m/min which has fine and continuously distributed Al-Ca rich secondary phases highly accelerate corrosion. Ce compounds with Al, thus eliminates the stable $\text{Mg}_{17}\text{Al}_{12}$ secondary phases from the structure which are replaced by AlRE_3 types [9].

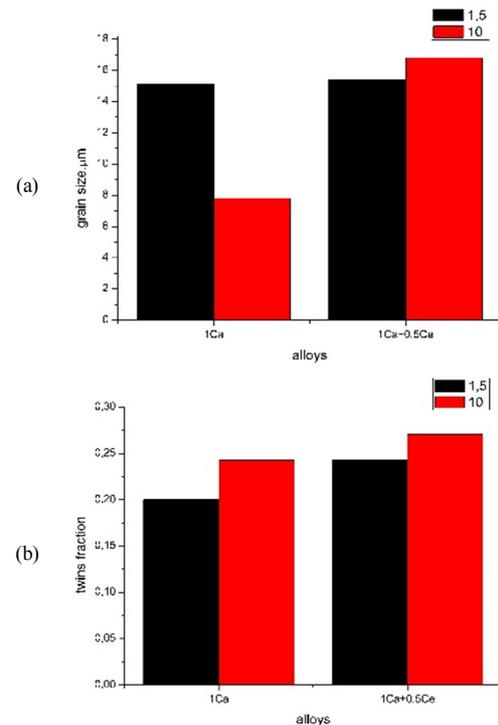


Fig. 3. a) Average grain size, b) twins fractions of investigated alloys

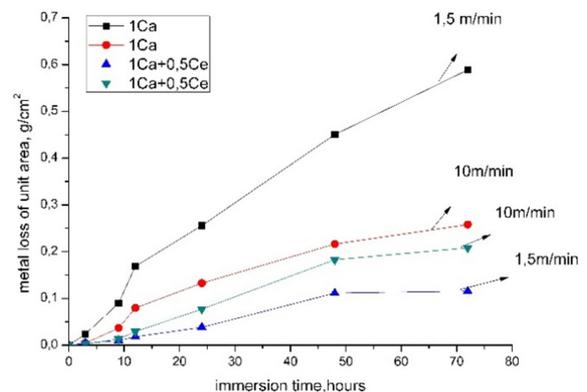


Fig. 4. Immersion corrosion test results of the investigated alloys

IV. CONCLUSION

In this study, Ce and rolling speed effects on the corrosion resistance of AZ31-1Ca alloys were proved by microstructure analysis, where the solid solution of Ce element in a matrix held an important role as a dominant stability determiner in 3.5% NaCl solution. Moreover, the rolling speed changed the size and shape of the secondary phases distributed on grain boundaries when the rolling speed was 1.5m/min, controlling the corrosion resistance positively.

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