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# Effect of Zn/Mg ratios on SCC, electrochemical corrosion properties and microstructure of Al-Zn-Mg alloy



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#### ABSTRACT

A detailed investigations of Zn/Mg ratios on stress corrosion cracking(SCC), electrochemical corrosion properties and precipitates of Al-Zn-Mg alloy with Zn+Mg  $\approx 7$  wt% were studied by mechanical, stress corrosion cracking(SCC), electrochemical cyclic polarization together with transmission electron microscopy (TEM) microstructural examinations. It is shown that the strength, SCC and electrochemical corrosion resistance are significantly increased with the decrease of Zn/Mg ratio. The strength of the alloys are significantly increases with the decrease of Zn/Mg ratio, which was attributed to increase the volume fraction of matrix precipitates. The enhance of SCC resistance and electrochemical corrosion properties was attributed to the narrower width of PFZ and low concentration of Zn in aluminum matrix.

#### 1. Introduction

Age-hardenable Al-Zn-Mg aluminum alloys with high strength, excellent weldability and hot workability have been extensively used in aerospace and transportation [1,2]. However, the susceptibility of local corrosion, especially stress corrosion cracking (SCC), have been restricted its applications [3]. A number of investigations have been done of Al-Zn-Mg alloys in order to improve corrosion properties. Results showed that the corrosion resistance of Al-Zn-Mg alloys were relied on compositions, volume fraction of recrystallization, ageing condition and corrosion environment. For example, Cu notably improved strength and corrosion resistance while decreased welding properties due to extend solidification temperature range [4,5]. Increasing Zn+Mg content enhanced the strength while reduced the SCC resistance [6]. More recently, various literature of Al-Zn-Mg alloys have been focused on using the benefit of Zr with Sc,Yb, Er to produce Al<sub>3</sub>(Zr,Sc) [7-9], Al<sub>3</sub>(Zr,Yb) [10] or Al<sub>3</sub>(Zr,Er) [11] dispersoids in order to inhibit grain recrystallization, which were significantly improved corrosion resistance compared with Al<sub>3</sub>Zr dispersoids. Over-aged heat

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treatment increased the corrosion resistance at the expense of strength [12-17].

Zn and Mg as main compositions, are significantly affected the microstructure, strength and corrosion properties of Al-Zn-Mg aluminium alloy. It is found the high Zn/Mg ratio of Al-Zn-Mg-Cu AA7175(1.2–2.0 wt% Cu) can remarkly reduce the quenching sensitivity due to homogeneous precipitation in contrast to the low Zn/Mg ratio alloy [18]. However, the effect of Zn/Mg ratio on SCC, electrochemical corrosion properties and precipitates of over-aged Al-Zn-Mg alloy is rarely reported.

The purpose of the paper is to present a detailed characterization of the SCC, electrochemical corrosion properties and precipitates in an Al-Zn-Mg alloy with different Zn/Mg ratio under the total Zn+Mg  $\approx$  7 wt%. The susceptibility to SCC was investigated by means of slow strain rate testing. Electrochemical corrosion properties was conducted by electrochemical open circuit potential and cyclic polarization. The precipitates characterization were performed by transmission electron microscopy (TEM).

#### 2. Experimental procedures

The compositions of Al-Zn-Mg aluminum alloys with different Zn/Mg ratio are listed in Table 1. The raw materials was high purity aluminum (99.99 wt%), magnesium (99.9 wt%), zinc(99.9 wt%), and

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 Table 1

 Chemical composition of Al-Zn-Mg aluminum alloys.

No.	Mass fraction/%										
	Zn	Mg	Cu	Zr	Cr	Mn	Ti	Fe	Al	Zn+Mg	Zn/Mg
1#	6.58	0.52	0.05	0.18	0.08	0.22	0.02	0.04	Bal.	7.10	12.65
2#	6.13	0.97	0.03	0.16	0.07	0.21	0.03	0.03	Bal.	7.10	6.32
3#	5.44	1.20	0.03	0.18	0.09	0.21	0.03	0.03	Bal.	6.64	4.53

Al-Zr, Al-Cu, Al-Cr, Al-Mn and Al-Ti master alloys. The melt was held for 3 h at  $720-750\,^{\circ}\text{C}$ , stirred vigorously and then cast into  $_{\Phi}100\,\text{mm}$  graphite mould.

The cast ingots were homogenized  $24\,h$  at  $465\,^{\circ}$ C, then were extruded at  $450-460\,^{\circ}$ C into 6 mm thick section with extrusion ratio 11. The extruded samples were solution treatment 1 h at  $470\,^{\circ}$ C, followed by a cold water quench. Subsequently, the samples were immediately subjected to two stages artificial aging 5 h at  $105\,^{\circ}$ C and 6 h at  $155\,^{\circ}$ C.

Mechanical properties measurements were performed on smooth plate specimens by an Instron 3369 testing machine at room temperature with a tensile speed of 2 mm/min. The gauge length and width of the specimen were 25 mm and 6 mm, respectively.

The susceptibility of SCC was evaluated by using the slow strain rate test (SSRT) with strain rate of  $6.67 \times 10^{-6}~\text{s}^{-1}$  in air and in 30 g/L NaCl+10mL/L HCl aqueous solution. Rectangular tensile specimens with a gauge length of 30 mm and a width 6 mm were used. The susceptibility of SCC was calculated by the ratio of I<sub>SSRT</sub>. The expression was defined as follows [19–21]:

$$I_{SSRT} = 1 - \left[ \sigma_{fw} \times \left( 1 + \delta_{fw} \right) \right] / \left[ \sigma_{fA} \times \left( 1 + \delta_{fA} \right) \right]$$
 (1)

where  $\sigma_{fA}$  is the fracture strength in air, MPa;  $\sigma_{fW}$  is the fracture strength in corrosion aqueous solution, MPa;  $\delta_{fA}$  is the elongation in air, %,  $\delta_{fW}$  is the elongation in corrosion aqueous solution, %.

Electrochemical open circuit potential and cyclic polarization were used by CHI600C electrochemical system. A saturated calomel electrode (SCE) was used as the reference electrode, platinum sheet was served as the counter-electrode and the alloy being studied was used as the working electrode. The 5 mm-thick specimens were polished using abrasive papers from 600 # to 1400 #, polished with diamond paste, rinsed with distilled water and dried in air. The 5 mm-thick specimens were connected to a copper wire, and then mounted in epoxy with only 1 cm² surface exposed. The test solution was 3.5 wt% NaCl aqueous solution at  $25\pm2\,^{\circ}\text{C}$ .

Microstructures were studied by transmission electron microscope (JEOL-2100F) operated at 200 kV. Thin foils for TEM were prepared by mechanical polishing to 100  $\mu$ m and final twin-jet electro polishing in 25% HNO<sub>3</sub>+75% CH<sub>3</sub>OH solution at  $-25\,^{\circ}$ C.

#### 3. Results

#### 3.1. Mechanical properties

Fig. 1 shows the mechanical properties of Al-Zn-Mg alloy with different Zn/Mg ratios. The tensile strength and yield strength increased with the decrease of Zn/Mg ratios. The tensile strength and yield strength of Zn/Mg = 4.53 and Zn/Mg = 12.65 were 435.3 MPa,394.3 MPa and 344.5 MPa,301.4 MPa,respectively, which increases of 27.1% and 30.8% for the Zn/Mg = 4.53 alloy compared with Zn/Mg = 12.65 alloy. The elongation of Zn/Mg = 4.53 was slightly lower compared with other Zn/Mg ratios. Therefore, it is can conclude that the significant improvement in strength of low Zn/Mg ratio alloy with respect to the high Zn/Mg ratio alloy.

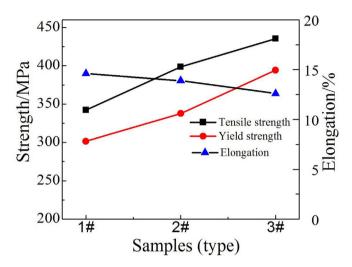


Fig. 1. Mechanical properties of Al-Zn-Mg alloy with different Zn/Mg ratios.

#### 3.2. SCC

The slow strain rate SCC testing of Al-Zn-Mg alloys with different Zn/Mg ratios in air and 30 g/L NaCl + 10 mL/L HCl corrosion aqueous solution conditions are revealed in Fig. 2. Fig. 2(a) shows the slow strain rate testing tensile curves in air. Fig. 2(b) shows the slow strain rate testing tensile curve in 30 g/L NaCl + 10 mL/L HCl corrosion aqueous solution. The tensile strength increased with the decrease of the Zn/Mg ratios in air and corrosion aqueous solution. With Zn/Mg ratio from 12.65 to 4.53, the tensile strength in air increased 27.8% from 328.4 MPa to 419.7 MPa.However, in corrosion aqueous solution, the tensile strength of Zn/Mg = 4.63 is 75.4% higher than that of Zn/Mg = 4.63Mg = 12.65. It is indicated the Al-Zn-Mg alloy suffered from the SCC compared the result of the strength in air and in corrosion aqueous solution. In addition, the fracture time in air of Zn/Mg ratio of 12.65 was 27.3 h while Zn/Mg ratio of 4.53 was 36.9 h, which is 135% higher than that of Zn/Mg ratio of 12.65. Furthermore, it is showed that the fracture time in corrosion aqueous solution is remarkly lower than that of in air environment. In corrosion aqueous solution, the fracture time of Zn/Mg = 4.53 is about 8.4 h higher than that of Zn/Mg = 12.63. Above all, the SCC resistance of the lower Zn/Mg = 12.63. Mg ratio can be obviously improved on the basis of the results from the strength and fracture time, especially in corrosion aqueous solution.

In order to obtain the susceptibility of SCC resistance, the SCC index ( $I_{SSRT}$ ) of Al-Zn-Mg alloy with different Zn/Mg ratios has been shown in Fig. 3. The SCC susceptibility with Zn/Mg ratio of 12.65 ( $I_{SSRT}=0.486$ ) was the highest compared with the others Zn/Mg ratios. The  $I_{SSRT}$  of Zn/Mg ratio = 4.53 alloy ( $I_{SSRT}=0.034$ ) was about 93% lower than that of Zn/Mg ratio = 12.65 alloy. It was indicated the low Zn/Mg ratio alloy was lower susceptible to SCC compared to the high Zn/Mg ratio alloy with Zn+Mg  $\approx 7$  wt%.

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