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Tensile creep and corrosion properties of Mg-2%Ca based cast alloys

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Abstract: The relative effect of Zn addition to Mg-2%Ca based alloy on the creep and corrosion characteristics was compared with Al addition. The creep resistance of Mg-2%Ca based alloy at 175 °C was improved by Zn addition more significantly than by Al addition. However, the Al addition showed more effective in enhancing corrosion resistance. Since the solidification range for Zn-added alloy was considerably wide, the cautious casting design may be necessary to produce high-quality castings.
Key words: magnesium; calcium; cast alloy; creep; corrosion

1 Introduction

Magnesium alloys have received considerable attention with the recent growing demand for mass reduction of vehicles since Mg alloys are virtually the lightest commonly usable metallic materials. However, the usage of greenhouse gases that are often indispensable for protecting Mg melt becomes a serious problem. Calcium is the relatively cheap alloying element that is known to increase the ignition start temperature of Mg alloys so that the Mg-Ca alloy melts can be handled without using the greenhouse gases[1].

Calcium was also added to Mg-Al alloys to improve the high temperature properties such as creep resistance[2−4]. In Mg-Al-Ca alloys, Mg_2Ca and/or Al_2Ca phases are known to form instead of $Mg_{17}Al_{12}$ that is thermally unstable, resulting in enhanced heat resistance[5−7]. Meanwhile, the corrosion resistance was observed to be increased by adding Ca to Mg-Al alloys. It was reported that the addition of Ca to AZ91 alloy up to 2% Ca reduced the corrosion rate significantly[8]. Although some research on Mg-Zn alloys containing Ca was also conducted, the creep and corrosion characteristics have not been clarified yet, especially as compared to those of Mg-Al-Ca alloys[9−12]. In this study, the relative effects of Zn addition to Mg-2%Ca (mass fraction) on the creep and corrosion resistance in comparison with Al additions were investigated.

2 Experimental

Mg-2%Ca based alloys containing various Al and Zn contents were fabricated by melting and casting under a protective SF_6+CO_2 gas atmosphere. The liquid metal was poured into a metallic mold to produce small plates with a width of 60 mm and a thickness of 24 mm. The chemical compositions of the experimental alloys are listed in Table 1. Tensile creep tests with cast specimens were carried out under various constant loads at different temperatures. The microstructural analyses were performed using optical microscope, SEM (JEOL, JSM−5610) equipped with energy dispersive X-ray spectrometer (EDS), and TEM equipped with EDS (JEM 2100F, 200 kV). TEM foil was prepared by a combination of mechanical polishing, electro-polishing, and finally ion-milling. The corrosion resistance was evaluated by measuring the corrosion potential at polarization curves obtained in the electrolytic cell containing 3.5% NaCl solution during the electrochemical tests. The surface was sealed with epoxy resin except for the area of 1 cm-diameter that was exposed for the test.

3 Results and discussion

As shown in Fig.1, the as-cast microstructure of Mg-2%Ca alloy mainly consists of primary magnesium

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Table 1 Chemical compositions of experimental alloys (mass fraction, %)

Alloy	Ca	Al	Zn	Mn	Mg
Base	1.88	−	−	0.17	Balance
3%Al	1.61	2.48	−	0.12	Balance
6%Al	1.64	5.06	−	0.17	Balance
3%Zn	1.94	−	2.70	0.14	Balance
6%Zn	1.97	−	6.16	0.13	Balance

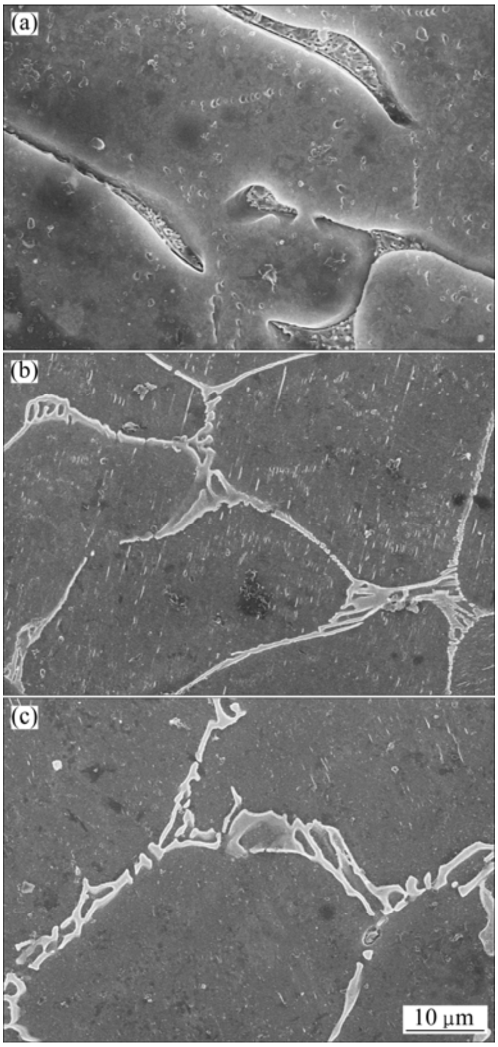

Fig.1 SEM images showing as-cast microstructure of Mg-2%Ca based alloys: (a) Base; (b) 3%Al; (c) 5%Al

(matrix) and the second phase. Microanalysis performed on the specimens suggested that the second phase observed in Mg-2%Ca based alloy is Mg_2Ca. In case of Al-added alloys, Al is partly dissolved in the matrix and is also used to form the second Al_2Ca or $(Mg, Al)_2Ca$ phase[3−6]. Zn is also dissolved to some degree in the Mg matrix and MgZnCa phase is formed as the second phase (Fig.2). SEM-EDS analysis results are summarized in Table 2. Although it is uneasy to clearly identify phases precisely based on small peaks in XRD analysis,

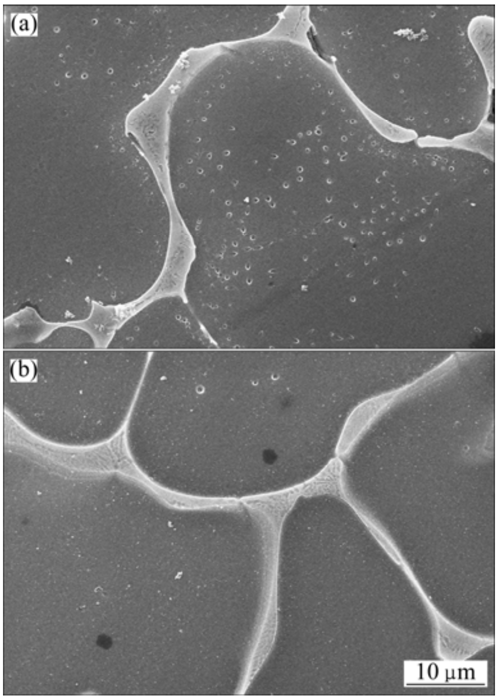

Fig.2 SEM images showing as-cast microstructure of Mg-2%Ca base alloys: (a) 3%Zn; (b) 6%Zn

Table 2 SEM-EDS results for second phases in Mg-2%Ca base alloys (molar fraction, %)

Alloy	Ca	Al	Zn	Mg
Base	6.2−9.0	−	−	Balance
3%Al	5.7−6.6	11.6−12.3	−	Balance
5%Al	5.7−10.1	22.5−31.3	−	Balance
3%Zn	4.3−17.0	−	2.6−6.8	Balance
6%Zn	7.7−10.4	−	10.8−13.7	Balance

some peaks for Mg_2Ca, Al_2Ca, and $Ca_2Mg_6Zn_3$ were detected in Fig.3[13−14].

The creep resistance, measured as total creep strain under a constant load of 75 MPa at 175°C, was found to increase with Al addition (Fig.4). The resistance tended to further improve with increasing Al content. Zn addition to the base alloy was observed to be more effective in improving the creep resistance as compared to Al addition. However, increasing Zn content more than 3% didn’t show clear effect on the resistance. As shown in Table 3, the stress exponent for creep of base alloy was observed to be about 10, and it was reduced to approximately 7 when 5%Al was added. Meanwhile, the stress exponent for Zn-added alloys was about 5. Therefore, it is postulated that the creep process in the Al or Zn-added alloys is mainly controlled by dislocation glide and climb[15−16].

Figure 5 shows the polarization curves for the cast alloys. Because the corrosion resistance is generally

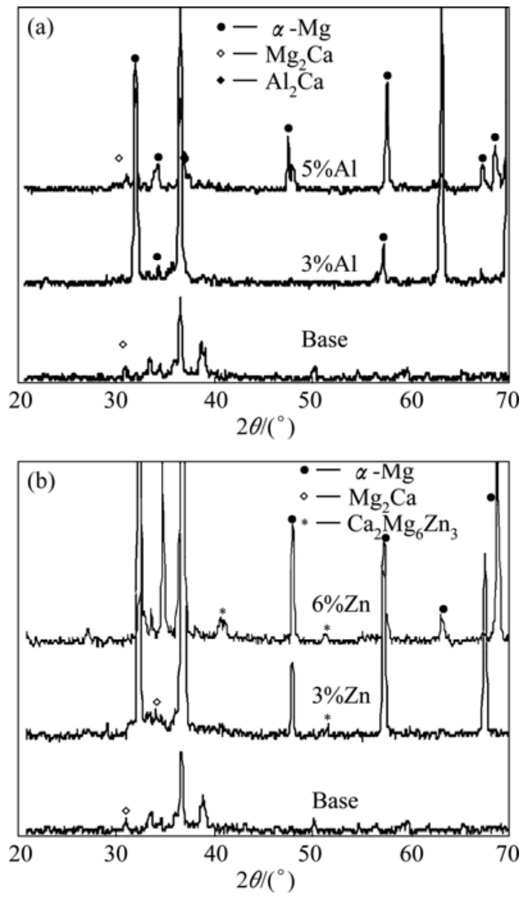

Fig.3 XRD patterns of Mg-2%Ca alloys

Table 3 Tensile creep characteristics of Mg-2%Ca base alloys at 175 °C under constant load of 75 MPa for 100 h

Alloy	Total strain/%	Stress exponent n
Base	9.29	10.38
3%Al	6.16	10.20
5%Al	5.91	7.21
3%Zn	1.70	5.43
6%Zn	1.81	5.08

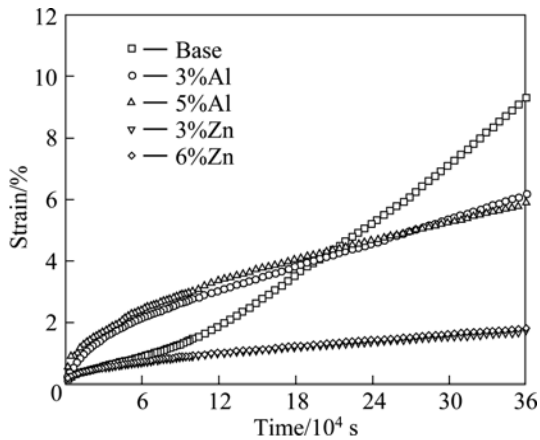

Fig.4 Creep curves of Mg-2%Ca alloys at 175 °C under constant load of 75 MPa

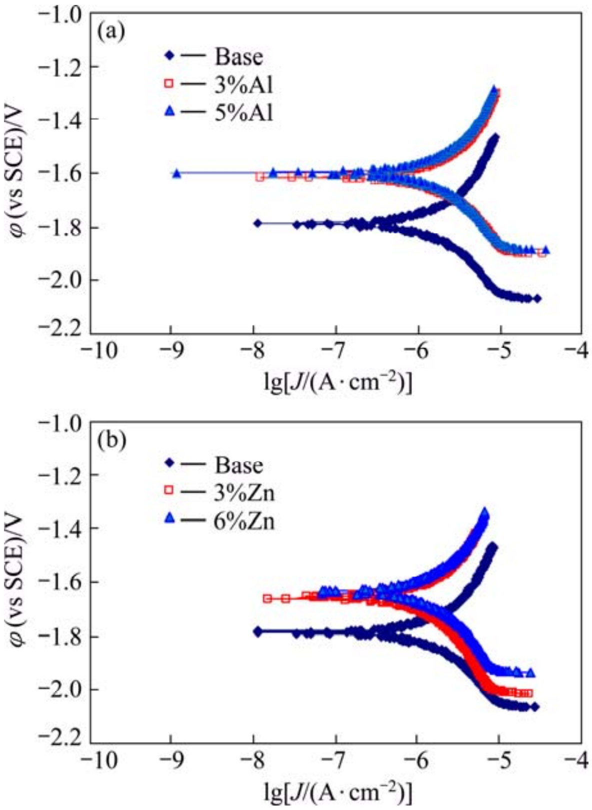

Fig.5 Polarization curves for as-cast Mg-2%Ca base alloys with Al (a) and Zn (b) additions

inversely proportional to the corrosion potential, Al addition is believed to increase the corrosion resistance of Mg-2%Ca alloy. Zn addition also enhances the corrosion resistance but not as much as Al addition. The corrosion current density was also measured and is indicated in Table 4, however its accuracy may not be high due to the lack of linearity of plots. Figure 6 shows typical morphology and thickness of oxide film formed on the electrochemically tested specimens. Apparently thicker oxide layer was formed in the base alloy as compared to Al or Zn added alloys. In case of the base alloy the interface between oxide film and Mg matrix is not clear and there exists transition layer between them.

Mg alloy parts are mostly fabricated by casting process such as die-casting, and the high casting capability is necessary for Mg alloys. Table 5 shows

Table 4 Polarization characteristics of Mg-2%Ca alloys

Alloy	φ_{corr}(vs SCE)/V	J_{corr}/(μA·cm^{-2})
Base	−1.786	5.981
3%Al	−1.616	5.924
5%Al	−1.599	5.964
3%Zn	−1.663	6.010
6%Zn	−1.637	5.989

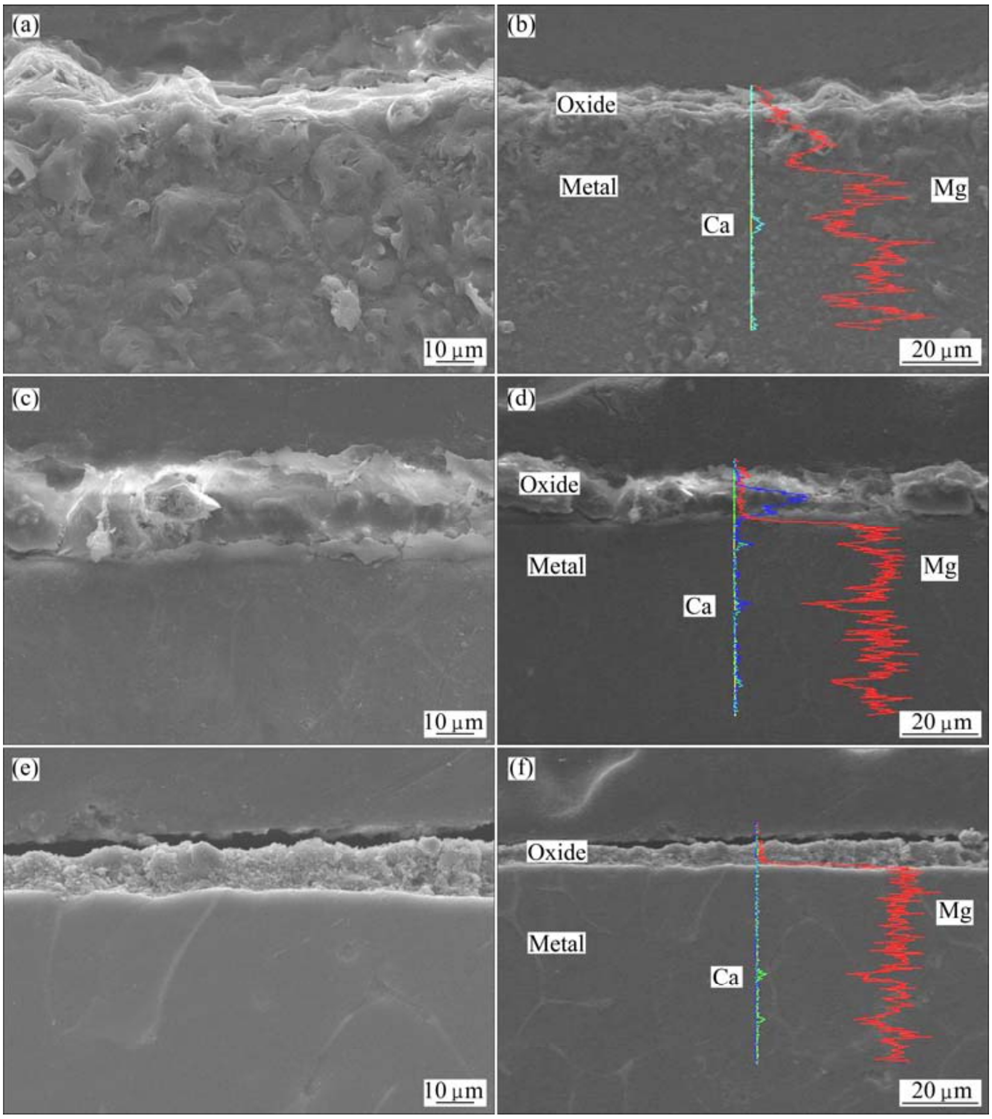

Fig.6 SEM micrographs and EDS line-profiles showing oxide/metal interface of electrochemically tested Mg-2%Ca based alloy specimens: (a), (b) Base; (c), (d) 3%Al; (e), (f) 3%Zn

Table 5 Solidification range for Mg-2%Ca alloys measured by DSC at heating rate of 5 °C/min

Alloy	Liquidus/°C	Solidus/°C	Solidification temp./°C
Base	644	527	117
3%Al	632	536	96
5%Al	613	544	69
3%Zn	636	422	214
6%Zn	626	417	209

solidification ranges for the experimental alloys that were measured by DSC analyses. Although the casting capability including fluidity and feed metal transfer is a very complicated phenomenon, it is generally inversely proportional to the solidification range[17]. Therefore, Al-added alloys are expected to possess better casting capability than the base alloy whereas Zn-added alloys may have lower capability.

4 Conclusions

Various phases such as Mg_2Ca and $Ca_2Mg_6Zn_3$ were found in the Zn-added Mg-2%Ca alloys, while Al_2Ca or $(Mg, Al)_2Ca$ phase was observed in the Al-added alloys. The creep resistance of Mg-2%Ca alloy at 175 °C was enhanced more significantly by the Zn addition as compared to the Al addition, but the corrosion resistance was somewhat higher in case of Al addition.

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铸造Mg-2%Ca合金的拉伸蠕变和抗腐蚀性能

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摘　要：对分别添加Zn和Al的Mg-2%Ca合金的拉伸蠕变和抗腐蚀性能进行比较。结果表明：添加Zn比添加Al能更加显著地提高Mg-2%Ca合金在170 °C下的蠕变性能。然而，添加Al对提高合金的耐腐蚀性能更为有效。由于添加Zn的合金的凝固区间更为宽大，因此，为了生产高质量的铸件产品，对铸造工艺的控制要求更加严格。

关键词：镁；钙；铸造合金；蠕变；腐蚀

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