

Effect of Y and Y_2O_3 on oxidation of AZ91D Mg alloys between 400 °C and 500 °C

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Abstract: AZ91D, AZ91D+1%Y, and AZ91D+3% Y_2O_3 (mass fraction) alloys were cast, and oxidized between 400 and 500 °C in air. The oxidation resistance increased in the order of AZ91D, AZ91D+3% Y_2O_3 , and AZ91D+1%Y, indicating that Y was more effective than Y_2O_3 in increasing the oxidation resistance of the Mg alloys. However, all the alloys tested experienced ignition because the major oxide was MgO.

Key words: magnesium; yttrium; yttria; oxidation

1 Introduction

The application of magnesium alloys as light-weight structural materials is increasing due to their excellent merits such as high specific strength, rigidity, and the lowest density among metallic materials in practical use[1]. However, most Mg alloys possess poor strength and low resistance to corrosion and creep at elevated temperatures[2–3]. Hence, various alloying elements were attempted to increase the oxidation resistance of Mg alloys during casting for commercial usage.

The ignition temperature for the AZ91 alloy (Mg-8.2Al-0.7Zn, in mass fraction, %) is 580–590 °C in air[3]. However, WE43 alloy (Mg-4Y-0.6Zr-3RE with Nd, in mass fraction, %) has not burned up to 750 °C, because an Y-rich oxide quickly formed in the cracked region of the oxide layer[1]. The rare earth element, Y, increased the oxidation resistance of the pure Mg metal and, much effectively, the AZ 91D alloy because of the compact Y_2O_3 film formed on the surface[4]. When Mg-Y-Ce alloys were oxidized at 600 °C for 0.5 h, dense, compact oxide films having Y_2O_3 formed[5]. When yttrium was added to Mg-Ca alloys, the oxide layer had a double-layered structure of MgO/CaO and Y_2O_3 , playing a role of very effective barriers to improve the high-temperature oxidation resistance[6]. During the early oxidation of Mg-Y alloys ($w(Y)=0.82\%$, 1.09% ,

4.32% , 25%) at high temperatures, the increase of Y led to the decrease of the oxidation rate[7]. On the other hand, it is well established that small additions of Y_2O_3 dispersoids or Y_2O_3 -coating on the alumina-[8] and chromia-forming alloys[9] improve scale adhesion and reduce the scale-growth rate. However, it is not yet adequately confirmed whether such a beneficial effect of Y_2O_3 is operative in the Mg alloys or not. Mg alloys form the non-protective MgO scale. In this study, AZ91 alloys, AZ91 alloyed with 1%Y, and AZ91 alloys containing 3% Y_2O_3 particles were cast, and oxidized between 400 °C and 500 °C in order to find the effect of the reactive element of Y and its oxide, Y_2O_3 , on the high temperature oxidation of AZ91D alloys.

2 Experimental

Commercially available AZ91D alloys were melted at 680 °C in steel crucible under a $CO_2+1\%$ SF_6 protective atmosphere using an electric resistance furnace. While the alloy melt was rotated with a speed of 800 r/min for uniform mixing using a stirrer positioned at top of the crucible, either Y (98.5% purity, $<350\ \mu m$) or Y_2O_3 particles (99.9% purity, $6\ \mu m$) were added with a feed rate of 7 g/min[10]. Mg alloys cast were AZ91D, AZ91D+1%Y, and AZ91D+3% Y_2O_3 .

The Mg alloy samples were cut into coupons of 5 mm $\times$ 10 mm $\times$ 10 mm in size, ground to a 1 000 grit finish, degreased, and oxidized in an electrical furnace

between 400 °C and 500 °C in atmospheric air. The oxidized specimens were inspected by a scanning electron microscope (SEM), an X-ray diffractometer (XRD), and an electron probe microanalyzer (EPMA).

3 Results and discussion

When Mg alloys were exposed to hot air, they suffered from severe oxidation or even burning after certain time. This resulted in the complete disintegrating into oxide powders. The time when local burning began to occur in the specimen was defined as the oxidation limit, and the values for AZ91D, AZ91D+1%Y and AZ91D+3%Y₂O₃ alloys are listed in Table 1. As expected, the oxidation rate increased rapidly with an increase in the oxidation temperature. It is seen that the addition of Y is more effective than that of Y₂O₃ in increasing the oxidation resistance. The oxide scales formed initially was thin and protective. But, they were eventually destroyed sooner or later during oxidation testing.

Table 1 Oxidation limit of prepared Mg alloys

Temperature/ °C	Oxidation limit/h		
	AZ91D	AZ91D+1%Y	AZ91D+3%Y ₂ O ₃
400	85	>100	90
425	45	85	70
450	1	6	3
475	<1	3	1
500	0.67	1	0.83

Fig.1 shows the XRD patterns of AZ91D+1%Y before and after oxidation in air. AZ91D+1%Y consisted primarily of α -Mg and a small amount of Al₁₂Mg₁₇ (Fig. 1(a)), being analogous to the AZ91D alloy. This is consistent with the fact that the Mg-9%Al melt solidifies into α -Mg and Al₁₂Mg₁₇(s) by the eutectic reaction upon cooling, according to the Mg-Al binary phase diagram. Yttrium was not detectible in Fig.1. However, Y is believed to exist as Al₂Y, owing to its strong binding energy with Y[11]. The oxide scale formed before ignition was too thin to detect using XRD, as shown in Fig.1(b). Generally, initially formed, thin oxide scales became thick, and loosely-adherent as oxidation progressed. The ignition of the alloy led to the formation of MgO-rich oxide scales, as shown in Fig.1(c). Since the amount of Mg was the largest, predominantly the MgO scale formed, regardless of the oxidation temperature and time.

Fig.2 shows XRD patterns of AZ91D+3%Y₂O₃ before and after oxidation in air. As did AZ91D+1%Y, AZ91D+3%Y₂O₃ also consisted primarily of α -Mg and a small amount of Al₁₂Mg₁₇ (Fig.2(a)). Here, a faint

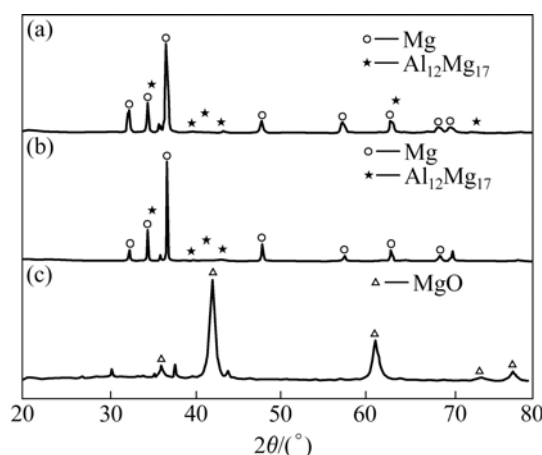


Fig.1 XRD patterns of AZ91D+1%Y: (a) As-cast; (b) Oxidized at 400 °C for 100 h; (c) Oxidized at 450 °C for 20 h

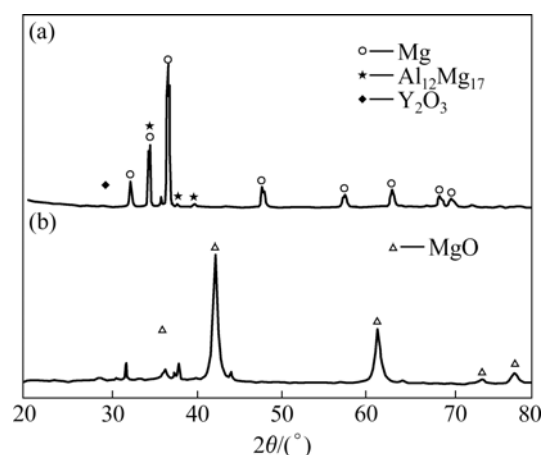


Fig.2 XRD patterns of AZ91D+3%Y₂O₃: (a) As-cast; (b) Oxidized at 450 °C for 25 h

indication of Y₂O₃ particles added is seen. In Fig.2(b), a strong MgO pattern is seen, resulting from the ignition of the alloy. The ignition resulted in the formation of thick, porous oxide scales. In this study, Y and Y₂O₃ added have not improved the oxidation resistance significantly. This must be originated from the inherently highly poor oxidation resistance of Mg alloys.

Fig.3 shows the SEM top view and cross-sectional image of the oxide scale formed on AZ91D+1%Y. The scale formed initially was generally thin and uniform. Oxide nodules formed locally (Fig.3(a)). A thin, compact scale formed on the alloy, consisting of the α -Mg grains and the eutectic Mg/Al₁₂Mg₁₇ mixture (Fig.3(b)). As the oxidation progressed, a porous, non-adherent, thick, and fragile scale or nodules having a cauliflower morphology formed. Oxide nodules formed by local ignition, and spread over the whole surface as oxidation progressed.

Fig.4 shows the SEM top view of the oxide scale formed on AZ91D+3%Y₂O₃. Usually thin scales formed before ignition (Fig.4(a)). However, such scales were destroyed after ignition, forming porous, non-adherent,

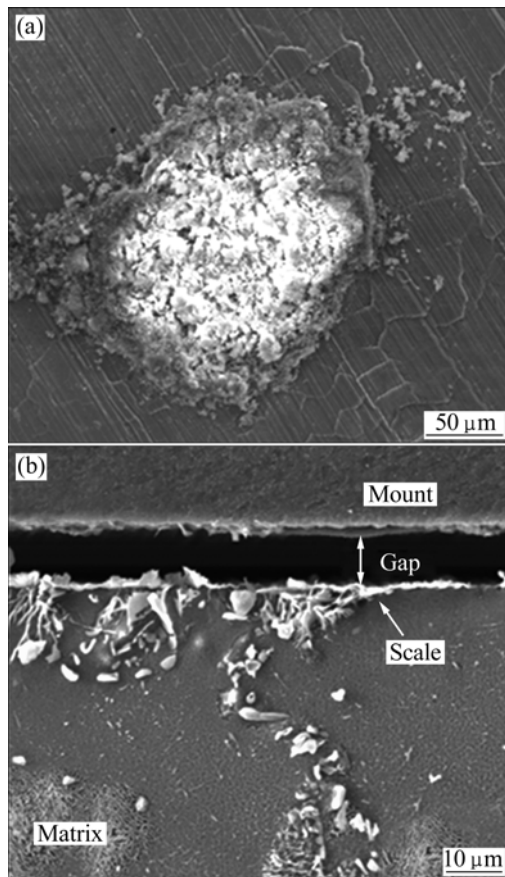


Fig.3 SEM images of scale formed on AZ91D+1%Y after oxidation at 400 °C for 100 h in air: (a) Top view; (b) Cross-sectional image

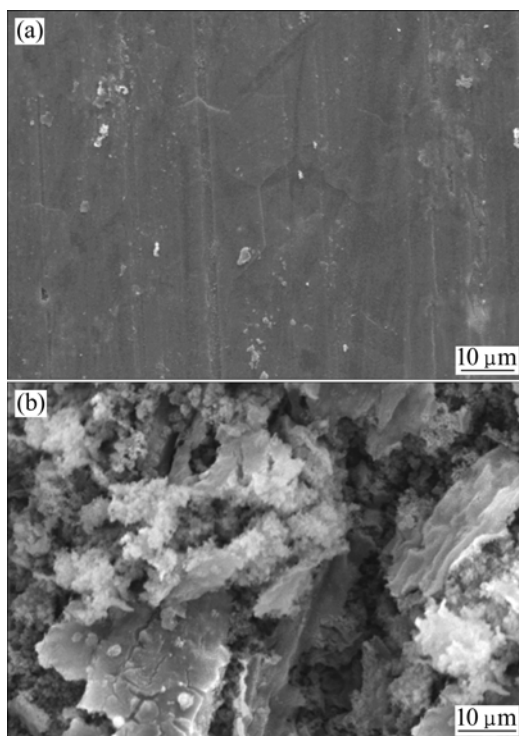


Fig.4 SEM top view of scale formed on AZ91D+3%Y₂O₃ after oxidation: (a) 425 °C for 10 h; (b) 475 °C for 1 h

thick scales. The loosely adherent oxide layer shown in Fig.4(b) progressively became non-adherent, thick oxide powders.

Fig.5 shows the cross-sectional image and the corresponding EPMA line profiles of the AZ91D+3%Y₂O₃ after oxidation at 500 °C for 40 min. In Fig.5(a), the thin oxide layer is partially embedded in the mounting epoxy, because it is loosely adherent. In Fig.5(b), it is seen that the MgO-rich oxide layer was incorporated with a large amount of Al, and a small amount Zn and Y. Since the oxide layer was neither dense nor impervious, oxygen transported into the matrix rather easily along the phase boundaries of the Y₂O₃. Internally formed oxides consisted primarily of Mg, Al, Zn, and Y₂O₃. Further oxidation resulted in the sudden ignition, completely destroying the alloy.

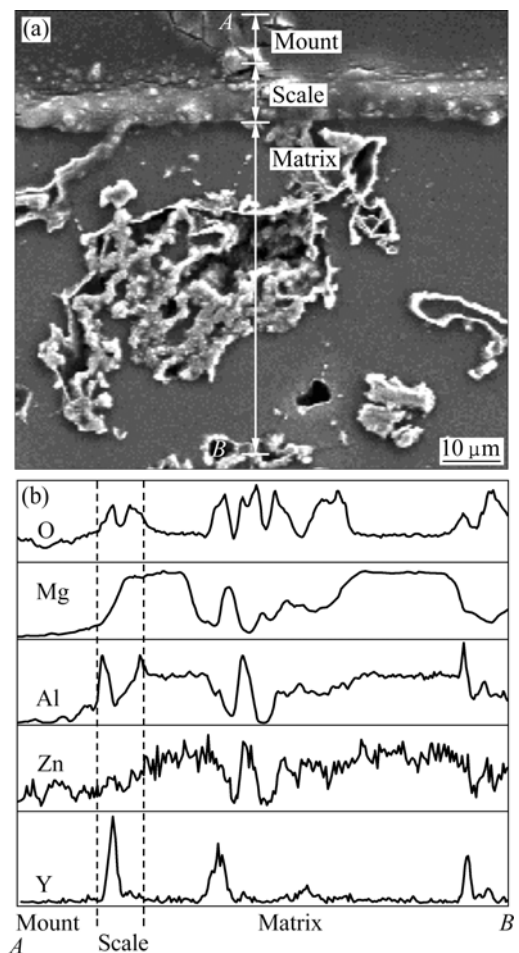


Fig.5 EPMA analytical results of AZ91D+3%Y₂O₃ after oxidation at 500 °C for 40 min: (a) Cross-sectional image (etched); (b) Line profile along A-B of (a)

4 Conclusions

The principal oxidation mode of AZ91D, AZ91D+1%Y, and AZ91D+3%Y₂O₃ alloys was similar. Before ignition, thin, uniform oxide scales formed on the

surface. Oxide nodules continuously developed, as oxidation progressed. Finally, ignition occurred, forming non-protective oxides. Y_2O_3 and, moreover, Y were beneficial to increasing the oxidation resistance of Mg alloys to a certain extent. Apparently, Y_2O_3 scattered in the alloy provided short-diffusion paths such as phase boundaries. This favored the dissolution and transport of oxygen beyond the oxide scale. This may be one of the reasons for the less effectiveness of Y_2O_3 compared with Y in improving the oxidation resistance of Mg alloys.

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