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ARTICLE

High-Temperature Oxidation Resistance of Mg-Ca Alloys in Air and Under Flame Exposure

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Abstract: The oxidation behavior and mechanism of Mg-Ca alloys in air and under flame exposure were studied. Results show that for the oxidation in air, the Mg-Ca-O oxide film with Ca accumulation and low Mg vapor pressure on the surface of Mg-Ca alloys with high Ca content shows good protective effect. However, the falling off phenomenon of the oxide film on Mg_2Ca results in the further oxidation. Hence, the Mg-Ca alloys with high Ca content only show good protective effect. For the oxidation in flame, the molten alloys release the Ca atoms to diffuse outward. The Mg-Ca-O oxide film with high Ca accumulation layer forms in Mg-Ca alloys with high Ca content. Despite the high Mg vapor pressure in the molten alloy, the Mg-Ca-O oxide film with high Ca accumulation layer shows excellent protective effect.

Key words: oxidation; air; flame; Mg-Ca alloys

1 Introduction

Magnesium and its alloys show excellent potential application in automotive, aerospace, and other industries, due to their excellent properties[1–4]. However, the high affinity between Mg and oxygen[5–7], notably at high temperatures, seriously restricts the widespread application of Mg alloys[8–10]. In the application of automobile, aerospace, and other industries, the demands for high-temperature oxidation resistance in air and under flame exposure are both proposed, such as the battery pack shell and aircraft seat. For example, there is a potential risk of combustion in the battery of new energy vehicles, especially in the car accident. Higher requirements for the anti-flammability of the battery package shell for Mg alloy under flame exposure are put forward, which can reduce the threats to property and life safety.

Alloying has been verified as an effective way to improve the oxidation resistance of Mg alloys[11–15]. Mg-Ca alloys have drawn much attention due to the low cost and the improved oxidation resistance[16–19]. Villegas-Armenta et al[20] studied the ignition temperature of Mg-Ca alloys, and found that the ignition temperature increases with Ca content at different heating rates. Han et al[21] found that the ignition temperature of Mg-Al-Ca-Mn alloys increases with Ca content, reaching up to approximately 1040 °C, due to the composite oxide layer consisting of CaO and MgO. Our previous study also focused on the oxidation behavior of Mg-Ca alloys in air and under flame exposure, and the mechanism had been described. Results showed that Mg-Ca alloys exhibit distinct oxidation behavior in air and under flame exposure, and the MgO-CaO oxide film plays an important role in the improvement of oxidation resistance[22–23]. However, comparative analysis on oxidation resistance of Mg-Ca alloys in different environments has been rarely discussed. In this study, different behavior and mechanisms on high-temperature oxidation resistance of Mg-Ca alloys in air and under flame exposure were analyzed.

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2 Experiment

Mg-xCa alloys (x=0.3, 0.5, 1.0, 2.0, 3.6, wt%) used in this experiment were produced by pure Mg (99.95wt%) and Mg-20wt%Ca master alloy. The raw materials were melted in an electric resistance furnace using a graphite crucible as the vessel under the protection of a mixed atmosphere of N_2 and SF_6. The molten material was then poured into a columniform steel mould with a size of Φ80 mm. The chemical composition of the Mg-Ca alloys in terms of the Ca content was tested using X-ray fluorescence (XRF-1800 CCDE), and the result is listed in Table 1. The microstructure of the oxide layers was observed using scanning electron microscope (SEM, JEOL JSM-7800F). Furthermore, the element distribution of the alloys was obtained by energy dispersive X-ray spectroscope (EDS).

An isothermal oxidation test was conducted using the thermal gravimetric analysis (TGA, Mettler Toledo 1/1100 SF) apparatus. Specimens were cut from the cast ingots with a size of Φ5 mm×3 mm and then mechanically polished. TGA test was conducted at 515 °C under synthetic air (79vol% high-purity N_2 and 21vol% high-purity O_2) atmosphere with a heated rate of 15 °C/min for 1.5 h.

Because there is no standard for the oxidation test under flame exposure, the test in this study was conducted at laboratory scale referred to previous researches. The specimen (25 mm×25 mm×2 mm) was clamped and fixed using a chemical bench. The polished specimen was subjected to a liquefied butane gas flame at a temperature of approximately 1300 °C with the nozzle placed 20 mm from the specimen surface.

3 Results

3.1 Oxidation resistance of Mg-*x*Ca alloys

The oxidation resistance of Mg-xCa alloys at 515 °C in air for 1.5 h and under flame exposure was studied, respectively. Fig. 1 shows the oxidation trend in different environments. It can be seen that the oxidation resistance in air increases firstly and then slightly decreases with Ca content, and Mg-1.0Ca alloy shows the best oxidation resistance[22]. However, the oxidation resistance under flame exposure is improved with Ca content increasing. All alloys are ignited in the molten state, and the alloys remain molten state for a longer time with the increase in Ca content[23].

Table 1 Measured Ca content of Mg-*x*Ca alloys (wt%)

Alloy	Mg-0.3Ca	Mg-0.5Ca	Mg-1.0Ca	Mg-2.0Ca	Mg-3.6Ca
x	0.33	0.49	1.06	1.95	3.65

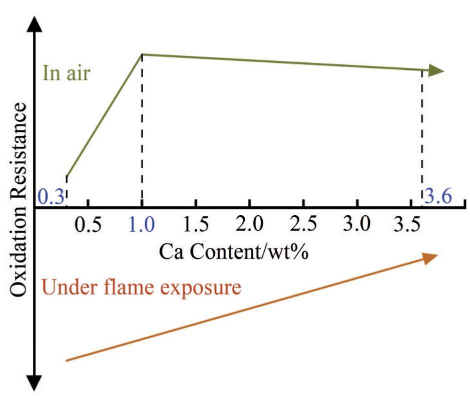

Fig.1 Oxidation resistance trend of Mg-xCa alloys in different environments

3.2 Microstructure analysis of Mg-*x*Ca alloys

3.2.1 Microstructure

The microstructure analysis in Ref. [22] showed that only α-Mg is found in Mg-0.3Ca alloy, Mg_2Ca and α-Mg are detected in other alloys, and the amount of Mg_2Ca increases with Ca content increasing.

Ref. [23] showed that the melting temperature of α-Mg is higher than that of Mg_2Ca. In other words, Mg_2Ca melts preferentially over α-Mg.

3.2.2 Oxide film

Ref. [22] showed that for the oxidation in air, a partial Ca accumulation layer is observed on Mg-0.3Ca alloy, while an obvious Ca accumulation layer is found in other alloys, and the thickness of Ca accumulation layer is increased with Ca content increasing. Meanwhile, oxide films varying with time on Mg-0.3Ca and Mg-3.6Ca alloys were analyzed for oxidation under flame exposure. No obvious Ca accumulation layer is observed on Mg-0.3Ca alloy during the oxidation. However, the Ca accumulation layer is observed on Mg-3.6Ca alloy in the melting state, and its thickness increases with time[23].

Fig.2 shows the Ca content in oxide film of Mg-xCa alloys. Ref.[22] reported that the isothermal oxidation kinetics curves for oxidation in air show two parabolic oxidation stages. The first platform is observed on the oxidation curve from 800 s to

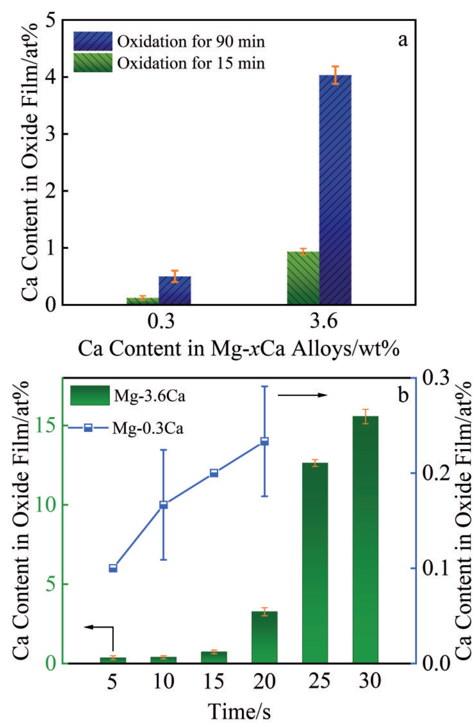

Fig.2 Ca content in oxide film of Mg-xCa alloys: (a) in air; (b) under flame exposure

1000 s, and the second platform is observed from 70 min to 90 min. Therefore, the Ca content at 15 and 90 min in air was analyzed. As shown in Fig.2, a small amount of Ca content is found in Mg-0.3Ca alloy, and Mg-0.3Ca alloy oxidized in air shows higher Ca content than that under flame exposure due to the longer oxidation time. However, Mg-3.6Ca alloy shows high Ca content in oxide film. It is worth noting that the increase in Ca content under flame exposure is much higher than that in air. The molten Mg-3.6Ca alloy promotes the outward diffusion of surface-active element Ca, leading to the high Ca content of oxide film.

Ref. [22] indicated that for the oxidation in air, no continuous supply of Ca atoms diffuses outward during the oxidation of Mg_2Ca, while Ca atoms in α-Mg can diffuse outward for oxidation. Hence, the Ca accumulation mainly depends on the oxidation of α-Mg. Moreover, the oxide film formed on Mg_2Ca is not stable and easily peels off from the substrate, resulting in further oxidation. But oxide film formed on α-Mg is stable and effective[22].

3.3 Mg vapor

Mg vapor is an important characteristic for oxidation. The saturated vapor pressure of Mg and Ca can be calculated by the following equations[24]:

$$\lg P_{Mg} = 5.006 + 8.489 - \frac{7813}{T} - 0.8253 \lg T = 13.495 - \frac{7813}{T} - 0.8253 \lg T \quad (1)$$

$$\lg P_{Ca} = 5.006 + 10.127 - \frac{9517}{T} - 1.4030 \lg T = 15.133 - \frac{9517}{T} - 1.4030 \lg T \quad (2)$$

where P is the saturated vapor pressure (Pa) and T is the temperature (K). Mg vapor is one of the important factors for evaluating the oxidation resistance of Mg alloys. High Mg vapor will exert a significant force on the oxide film, resulting in the cracks on the oxide film. Mg vapor diffuses through cracks, and reacts with O_2 to form oxide ridges, accelerating the oxidation of Mg alloys. The saturated vapor pressures of Mg and Ca are shown in Fig. 3. At high temperature, the saturated vapor pressure of Mg is much higher than that of Ca, which causes high stress on oxide film and serious oxidation.

3.4 Oxidation resistance of Mg-*x*Ca alloys in different environments

Mg_2Ca is observed on Mg-*x*Ca alloys and the amount of Mg_2Ca increases with the increase in Ca content. Mg-1.0Ca alloy possesses the best oxidation resistance in air, and the oxidation resistance decreases with the increase in Ca content. Therefore, Mg_2Ca is unfavorable for the oxidation resistance at 515 °C in air. The oxidation resistance of Mg-*x*Ca alloys under flame exposure is improved with the increase in Ca content. Therefore, Mg_2Ca is beneficial to the oxidation resistance under flame exposure.

Mg-*x*Ca alloys show different oxidation behavior due to the difference in alloy composition and oxidation temperature. The Ca content in the alloy determines the microstructure, and the oxidation temperature determines whether the alloy is melted or not. There are three factors affecting the oxidation process, including oxide film, Mg vapor pressure, and the state of Mg_2Ca, as described in Table 2.

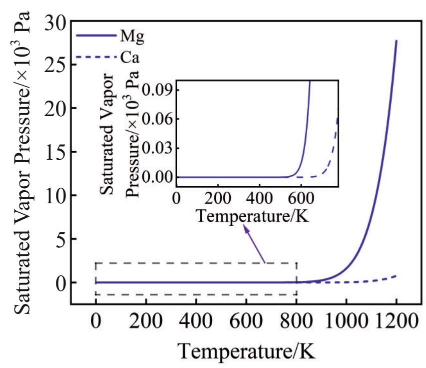

Fig.3 Saturated vapor pressures of Mg and Ca

Table 2 Comparison of oxidation resistance of Mg-*x*Ca alloys under different environments and influencing factors

Alloy	Environment	Microstructure		Oxide film	Mg vapor pressure	Oxidation resistance
		α-Mg	Mg_2Ca			
Mg-0.3Ca	Air	Solid	-	Mg-Ca-O oxide film with partial Ca accumulation	Low	-
Mg-1.0Ca			Solid	Mg-Ca-O oxide film with thin Ca accumulation layer	Low	The best
Mg-2.0Ca			Solid	Mg-Ca-O oxide film with Ca accumulation layer of medium thickness	Low	-
Mg-3.6Ca			Solid	Mg-Ca-O oxide film with thick Ca accumulation layer	Low	-
Mg-0.3Ca	Flame	Molten	-	Mg-Ca-O oxide film without obvious Ca accumulation	High	-
Mg-1.0Ca			Molten	-	-	-
Mg-2.0Ca			Molten	-	-	-
Mg-3.6Ca			Molten	Mg-Ca-O oxide film with high amount of Ca accumulation	High	The best

For Mg-*x*Ca alloys oxidized in air, the temperature is relatively low, and the alloys remain solid state. (1) Oxide film: the solid alloy enables a small number of Ca atoms in α-Mg to diffuse to the surface for oxidation, resulting in a relative low Ca content in the oxide film. As the Ca content in the alloy increases, the Ca content in the oxide film also increases, and the Ca accumulation layer becomes thicker and thicker, resulting in the Mg-Ca-O oxide film with good protective effect. (2) Mg vapor pressure: the solid alloys result in the low Mg vapor pressure and low stress on the oxide film. (3) The state of Mg_2Ca: the oxide film formed by Mg_2Ca is easy to peel off, and the amount of Mg_2Ca increases with Ca content, thus promoting the further oxidation. Combined with the above three factors, the oxide film on Mg-Ca alloys shows protective effect.

For Mg-*x*Ca alloys oxidized under flame exposure, the oxidation temperature rises rapidly above the melting point and the alloy begins to melt. (1) Oxide film: the free Ca atoms in molten alloy diffuse to the surface for oxidation, leading to the Mg-Ca-O oxide film formation. For Mg-Ca alloys with low Ca content, the alloy burns shortly after melting, and Ca does not have enough time to diffuse outward. While for Mg-Ca alloys with high Ca content, the alloys maintain the molten state for a period of time. Thus, an obvious Ca accumulation layer is formed on the oxide film, showing an excellent protective effect. (2) Mg vapor pressure: the molten alloy causes the high vapor pressure and high stress on oxide film. Hence, the oxidation resistance mainly depends on the protective effect of oxide film. (3) The state of Mg_2Ca: The priorly melted Mg_2Ca releases Ca atoms to diffuse outward, and the following complete melting allows the Ca atoms to diffuse outward and form the obvious Ca accumulation layer. Combined with the above three factors, the oxide film on Mg-*x*Ca alloys with high Ca content shows excellent protective effect.

4 Conclusions

1) Mg_2Ca is unfavorable for the oxidation resistance in air, but beneficial to the oxidation resistance under flame exposure.

2) For the oxidation in air, the Mg-Ca-O oxide film with Ca accumulation layer in Mg-*x*Ca alloy shows good protective effect, and the low Mg vapor pressure exerts small force on the oxide film. However, the formation of Mg_2Ca results in the further oxidation. Hence, the Mg-*x*Ca alloys in air show good protective effect.

3) For the oxidation under flame exposure, the released Ca atoms in molten alloy diffuse outward for the formation of Mg-Ca-O oxide film with Ca accumulation layer in Mg-Ca alloys with high Ca content. In spite of the high Mg vapor pressure, the Mg-Ca-O oxide film with Ca accumulation layer shows an excellent protective effect.

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Mg-Ca合金在空气和火焰环境下的高温抗氧化性

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摘　要：研究了Mg-Ca合金在空气和火焰环境下的氧化行为和机理。结果表明，对于空气中的氧化，高Ca含量Mg-Ca合金表面形成的具有Ca积聚层的Mg-Ca-O氧化膜和低的Mg蒸汽压，表现出良好的保护效果。然而，Mg_2Ca上氧化膜的脱落导致了进一步的氧化。因此，高Ca含量的Mg-Ca合金仅显示出良好的保护效果。对于在火焰环境下的氧化，熔融合金释放出了Ca原子并向外扩散，在高Ca含量的Mg-Ca合金中形成具有高Ca含量积聚层的Mg-Ca-O氧化膜。尽管熔融合金中Mg蒸汽压很高，但具有高Ca积聚层的Mg-Ca-O氧化膜仍显示出优异的保护效果。

关键词：氧化；空气；火焰；镁钙合金

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