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ARTICLE

Oxidation Resistance of Mg-Ca Alloys with Protective Coating Under Flame Exposure

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Abstract: To further expand the application of Mg alloys at high temperatures, the oxidation resistance of Mg-0.3Ca and Mg-3.6Ca alloys with protective coating under flame exposure was studied. Results show that the oxidation resistance of Mg-Ca alloys under flame exposure is significantly improved by the protective coating, and Mg-3.6Ca alloy shows better oxidation resistance performance. The surface temperature of Mg-Ca alloys is reduced by the coating, therefore improving the oxidation resistance under flame exposure. However, the thermal insulation effect of the coating on Mg-3.6Ca alloy is better, which can be attributed to the Ca accumulation on the surface film. In addition, the surface film with Ca accumulation layer plays a crucial role in protecting the alloy. No obvious Ca accumulation layer exists on the Mg-0.3Ca alloy surface, presenting a restricted protective effect. Nevertheless, the surface film containing Ca accumulation layer is formed on Mg-3.6 Ca alloy, which shows an excellent protective effect.

Key words: Mg-Ca alloy; oxidation; flame exposure; coating

1 Introduction

Mg and its alloys have attracted much attention due to their excellent properties[1–3], showing great application potential in aerospace, automobile, and other fields[4–6]. With the development of car seats and battery packages in the aerospace and automobile fields, the oxidation resistance of Mg alloys under flame exposure is requested[7]. For example, there is a potential risk of combustion in a car accident, which puts forward higher requirements for the anti-flammability of components of Mg alloys under flame exposure to reduce the threats to property and life safety. However, Mg shows a high affinity to O, especially at high temperatures, which creates a major drawback in the application[8–9]. The protective effect of MgO oxide film with a low Pilling-Bedworth ratio (0.80) on the substrate is inferior, leading to severe oxidation and burning, which seriously restricts the application of Mg alloys[10–12]. In addition, Mg alloys easily burn when in contact with an open flame or heat sources, and the flames are hard to extinguish[13–14], posing a serious threat to the environment and human safety.

Alloying is a simple and effective approach to improve the oxidation resistance of Mg alloys[15–19]. Mg-Ca alloys have attracted much attention due to their favorable properties[20–21]. Villegas-Armenta et al[7] indicated that the ignition temperature was increased as Ca content increased from 0wt% to 3wt%. Liu et al[22] demonstrated the improved oxidation resistance of Mg-CaO alloys with heat treatment at 400 °C in Ar atmosphere. Mg-3CaO showed the optimal oxidation resistance due to the formation of a uniform and dense thick protective MgO-CaO composite layer (thickness of 50 nm) on the surface during heat treatment. Ming et al[23] reported that Ca could enhance the oxidation resistance of Mg-*x*Ca (*x*=0.3, 0.5, 1.0, 2.0, 3.6) alloys at 515 °C, and Mg-1Ca alloy showed the optimal oxidation resistance. During oxidation, α-Mg and Mg_2Ca have different behaviour. Oxide films on α-Mg effec-

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tively improve oxidation resistance, whereas those formed on Mg_2Ca are unstable and tend to peel off from the substrate, resulting in further oxidation. Ca can significantly enhance the oxidation resistance of Mg at high temperatures due to the CaO oxide film. However, the oxidation resistance under flame exposure of Mg-Ca alloys needs further study.

Previous studies on oxidation resistance under flame exposure mainly focus on the ignition temperature. In this research, the oxidation process was primarily studied. Ming et al[24] showed that the oxidation resistance of Mg-Ca alloys under flame exposure was increased with Ca content (0.3wt%–3.6wt%). To further expand the application of Mg-Ca alloys, the protective coating was applied on the surface. In this research, the oxidation resistance under flame exposure of coated Mg-0.3Ca and Mg-3.6Ca alloys was studied.

2 Experiment

The preparation and characteristic analysis of Mg-*x*Ca (*x*= 0.3, 3.6, wt%) alloys were conducted through the procedure and devices depicted in Ref. [23]. The coating components included ammonium polyphosphate, melamine, pentaerythritol, etc. The coating was applied by spraying+standing. Each standing lasted for 6 h. After spraying+standing for 4 times, the coating thickness on the surface was 0.7 mm. The oxidation test under flame exposure was described in Ref. [24]. The surface temperature of Mg-*x*Ca alloys during the oxidation process was tested by the thermocouple wires welded on the surface.

3 Results and Discussion

3.1 Microstructure of Mg-*x*Ca alloys

The chemical composition, X-ray diffraction (XRD) patterns, and microstructure of as-cast Mg-*x*Ca alloys are described in Ref. [23]. Only α-Mg exists in Mg-0.3Ca alloy, and α-Mg and Mg_2Ca exist in Mg-3.6Ca alloy. The melting temperature of the phases in Mg-*x*Ca alloys is displayed in Ref. [24]. The melting temperature of Mg_2Ca (522.7 °C) is lower than that of α-Mg (652 °C of Mg-0.3Ca; 637.5 °C of Mg-3.6Ca), and the melting temperature of α-Mg is decreased with the increase in Ca content.

3.2 Oxidation resistance of Mg-*x*Ca alloys under flame exposure

The ignition time in this research is defined as the time when the alloy begins to burn, and the results are shown in Table 1. It can be seen that the Mg-*x*Ca alloys with coating show longer ignition time than those without coating, particularly for Mg-3.6Ca alloy. The ignition time of Mg-0.3Ca alloy with coating is 123 s, and that of Mg-3.6Ca alloy with coating is beyond 600 s. Based on the difference of ignition time (Δt), the oxidation resistance under flame exposure is greatly improved by coating, and Mg-3.6Ca alloy shows better oxidation resistance.

Table 1 Ignition time of different Mg-*x*Ca alloys

Alloy	Ignition time/s		
	Without coating[24]	With coating	Difference of ignition time, Δt
Mg-0.3Ca	24	123	99
Mg-3.6Ca	35	>600	>565

3.3 Surface morphology

The surface morphology of coated Mg-0.3Ca alloy under flame exposure for 120 s is shown in Fig. 1. Because of its brittleness, the coating on surface peels off after the test. After the coating peels off, the alloy surface is not smooth, and the cross-section morphology indicates a slight amount of deformation and melting, as shown in Fig. 1a–1c. The surface is uneven, as in Fig. 1d. Many small particles are distributed on the surface, as shown in Fig. 1e. According to EDS mappings in Fig. 1g, the particles constitute the coating. The tear-like area in Fig.1f is speculated to be α-Mg based on EDS mappings in Fig. 1h. Obvious oxidation can also be observed, as shown in Fig.1i–1j.

However, Mg-3.6Ca alloy under flame exposure for 600 s shows different morphologies, as shown in Fig. 2. After the coating peels off, the surface is still smooth, as shown in Fig. 2b. As shown in Fig. 2c, the Mg-3.6Ca alloy presents a small amount of deformation and significant melting. The surface is uneven, as shown in Fig. 2d. According to the microstructure of area A and corresponding EDS mappings, the network of Ca accumulation can be observed, which is speculated to be Mg_2Ca. Many small round particles can be observed in area B in Fig.2f, and they are identified as coating based on EDS mappings in Fig.2h.

3.4 Surface film

For Mg-0.3Ca alloy under flame exposure for 120 s, the surface film is thick, as shown in Fig.3a. According to Fig.3b, the surface film is rich in O, P, and C. In addition, a little Ca is found on the surface film, which is consistent with the EDS results in Table 2. For Mg-3.6Ca alloy under flame exposure for 600 s, Mg_2Ca can be observed on the substrate, according to Fig.3d. The thickness of the surface film on Mg-3.6Ca alloy is smaller than that on Mg-0.3Ca alloy, which is rich in Ca, O, P, and C. Combined with the EDS results, the Ca accumulation layer is formed on the surface, and the average Ca content is 4.47at%. A small amount of molten Mg-3.6Ca alloy releases some surface-active element Ca, which promotes the outward diffusion of Ca, thus forming the Ca accumulation layer and showing a superior protective effect.

3.5 Mechanism

3.5.1 Surface temperature

Because the alloy was molten and the thermocouple wires fell off during the experiment, only a few data points are available. As shown in Fig. 4, the surface temperature of the alloys without coating is increased sharply with time, and the maximum surface temperature of Mg-0.3Ca and Mg-3.6Ca alloys reaches 526.7 and 505.8 °C, respectively. However, the temperature of the coated alloys is increased slowly with time. As the temperature increases, for the uncoated Mg-3.6Ca alloy, a small platform appears around 520.3 °C, which is

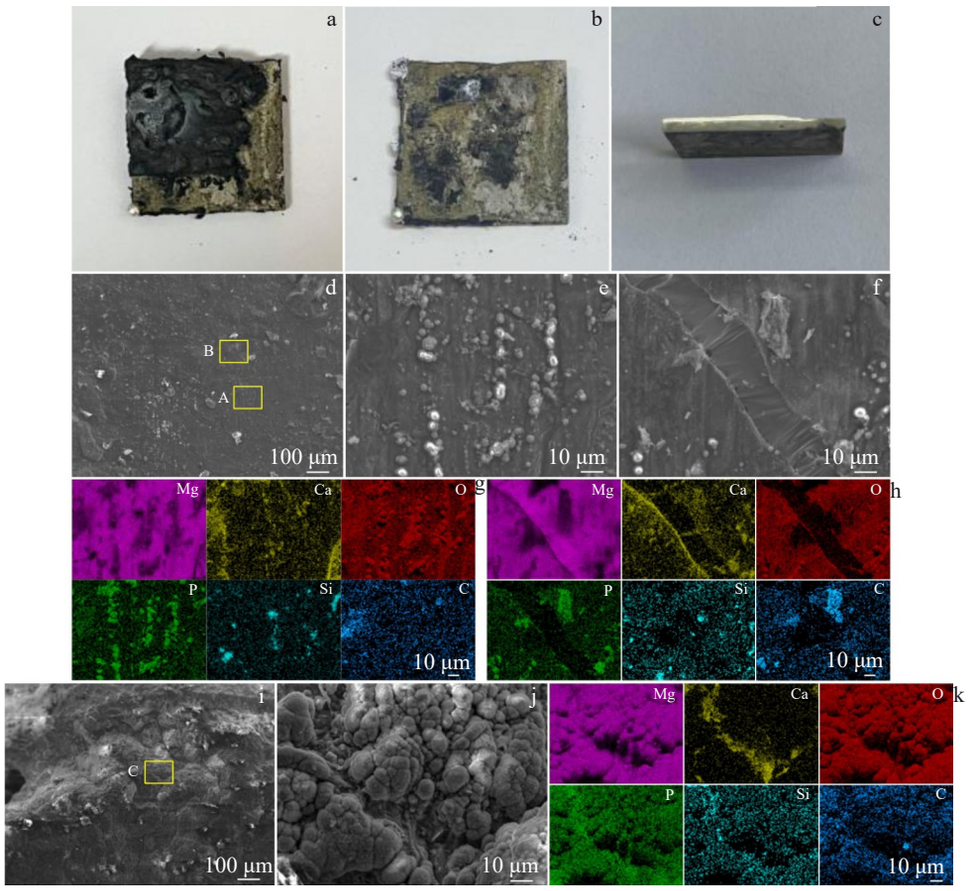

Fig.1 Appearances (a–b), cross-section morphology (c), and microstructures (d, i) of Mg-0.3Ca alloys with (a, d, i) and without (b–c) coating under flame exposure for 120 s; magnified images of area A in Fig. 1d (e), area B in Fig. 1d (f), area C in Fig. 1i (j); EDS mappings corresponding to Fig.1e (g), Fig.1f (h), and Fig.1j (k)

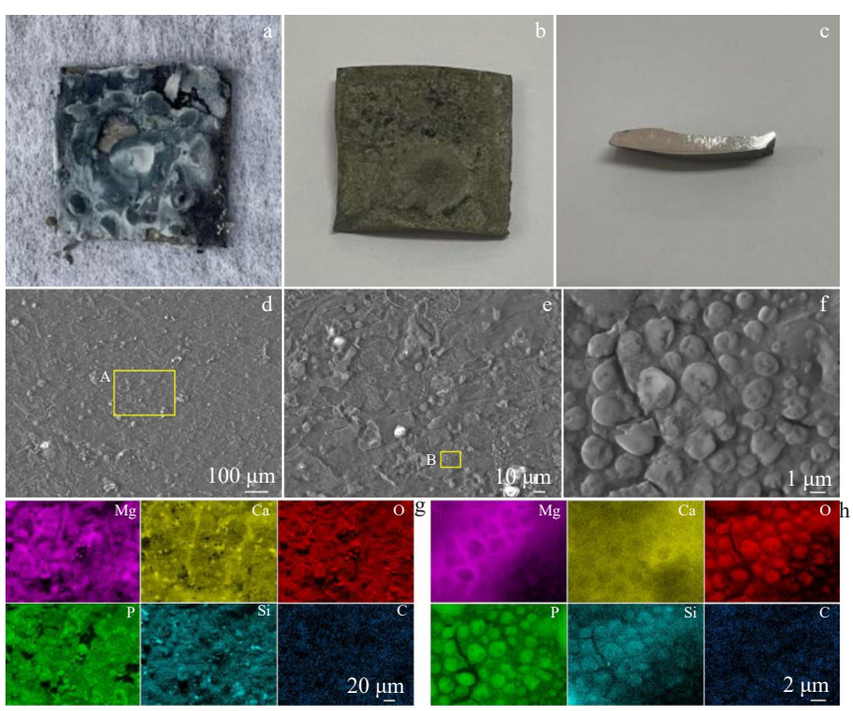

Fig.2 Appearances (a–b), cross-section morphology (c), and microstructure (d) of Mg-3.6Ca alloys with (a, d) and without (b–c) coating under flame exposure for 600 s; magnified images of area A in Fig.2d (e) and area B in Fig.2e (f); EDS mappings corresponding to Fig.2e (g) and Fig.2f (h)

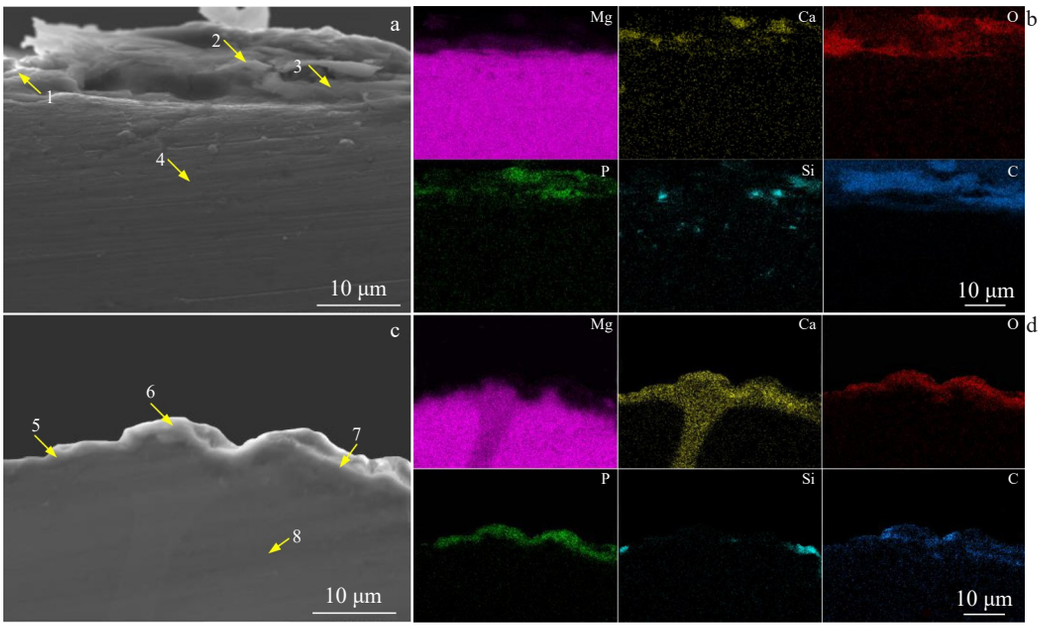

Fig.3 Cross-section morphologies of surface film on Mg-0.3Ca alloy under flame exposure for 120 s (a) and Mg-3.6Ca alloy under flame exposure for 600 s (c); EDS mappings corresponding to Fig.3a (b) and Fig.3c (d)

Table 2 EDS results of points marked in Fig.3 (at%)

Point	Mg	Ca	O	P	Si	C
1	3.7	0.5	18.1	0.3	0.1	77.3
2	3.2	0.2	15.6	1.3	0.1	79.6
3	3.8	0.0	7.8	0.1	0.1	88.0
4	90.7	0.0	0.8	0.0	0.0	8.4
5	10.6	2.5	57.3	7.6	0.8	21.2
6	3.0	8.1	52.0	6.9	0.2	29.8
7	11.4	2.8	54.4	6.8	0.4	24.2
8	96.4	0.3	2.5	0.0	0.0	0.8

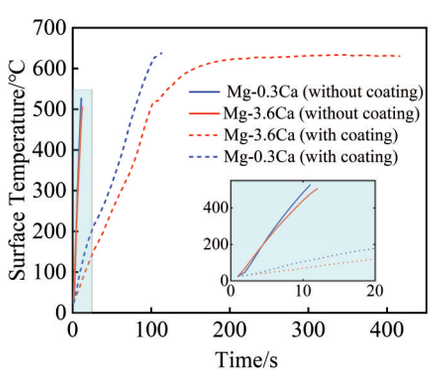

Fig.4 Change of surface temperature of Mg-*x*Ca alloys with time

related to the Mg_2Ca. After the melting of Mg_2Ca, the surface temperature rises continuously and tends to be stable at around 630 °C, which is lower than the melting point of α-Mg, so Mg-3.6Ca alloy can maintain the state of partial melting. However, for the coated Mg-0.3Ca alloy, the final surface temperature is 637.6 °C, which is lower than the melting temperature of Mg-0.3Ca alloy (652 °C), indicating that the coated Mg-0.3Ca alloy is solid.

The protective coating on the surface isolates the alloy from the flame. Comparing the surface temperature curves of Mg-0.3Ca and Mg-3.6Ca alloys with and without coating, it is found that the coating can greatly reduce the temperature increasing rate and the final surface temperature, hence slowing down the oxidation reaction. Besides, the thermal insulation effect of the coating on Mg-3.6Ca alloy is better, which may be related to the Ca accumulation layer on the surface film.

3.5.2 Protective effect of surface film

For Mg-0.3Ca alloy, no obvious Ca accumulation is found on the surface film, indicating a limited protective effect. For Mg-3.6Ca alloy, the coating reacts with O_2, the partial melting alloy simultaneously promotes the outward diffusion of surface active element Ca, and the surface film with Ca layer is formed on the surface, which jointly shows an excellent protective effect.

4 Conclusions

1) The protective coating can significantly improve the oxidation resistance of Mg-0.3Ca and Mg-3.6Ca alloys under flame exposure, and Mg-3.6Ca alloy shows better oxidation resistance.

2) The coating reduces the surface temperature and thereby improves the oxidation resistance under flame exposure. The thermal insulation effect of the coating on Mg-3.6Ca alloy is better, which can be attributed to the Ca accumulation layer on the surface film.

3) No obvious Ca accumulation layer can be observed on the surface film of Mg-0.3Ca alloy, resulting in a limited protective effect, whereas the surface film on the Mg-3.6Ca alloy containing a Ca accumulation layer shows an excellent protective effect.

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具有保护涂层的Mg-Ca合金在火焰环境下的抗氧化性能

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摘　要：为了进一步扩大镁合金在高温环境下的应用，研究了Mg-0.3Ca和Mg-3.6Ca合金在火焰环境下的抗氧化性。结果表明，保护涂层显著提高了Mg-Ca合金在火焰环境下的抗氧化性，且Mg-3.6Ca合金的抗氧化性更佳。涂层降低了Mg-Ca合金的表面温度，最终提高了合金在火焰环境下的抗氧化性。然而，涂层对Mg-3.6Ca合金的隔热效果更好，这与表面膜上的钙聚集层有关。此外，具有钙聚集层的表面膜在保护合金方面起着至关重要的作用。Mg-0.3Ca合金表面没有明显的钙积累层，保护作用有限；而在Mg-3.6Ca合金上形成了含有Ca积聚层的表面膜，显示出优异的保护效果。

关键词：Mg-Ca合金；氧化；火焰环境；涂层

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