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Characterisation of protective surface films formed on molten magnesium protected by hexafluoropropylene/air atmosphere

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Abstract

The characterisation of protective surface films formed on molten magnesium protected by hexafluoropropylene/air atmosphere at temperatures between 670 °C and 800 °C has been investigated. The morphology and the composition of the protective film formed on the surface of the melt at different temperatures were investigated by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). The results showed that the protective effect of the mixed gas on molten magnesium increased with the prolongation of holding time and the decrease of temperature. The surface film of the melt was uniform and continuous, and mainly composed of MgF2 and small amount of MgO.

Keywords

Magnesium, Hexafluoropropylene, Oxidation, Gas protection.

1. Introduction

Magnesium alloys have excellent properties and are commonly used in aerospace, biomedicine, electronic communications, and automotive industries[1-3]. However, magnesium alloys, especially pure magnesium, are very susceptible to oxidation, combustion and even explosion during the melting process[4]. SF_6 gas has a good protective effect on the smelting of magnesium alloys, but it has been banned due to its strong greenhouse effect[5]. Therefore, it is a challenge for magnesium alloy smelting researchers to find a protective gas with excellent protection effect and little impact on the ecological environment. It was reported[6] that a new, environmentally friendly and green gas hexafluoropropylene (HFP), whose chemical formula described as C_3F_6, can be used for magnesium metal smelting. Hexafluoropropylene is a colorless and odorless gas. It is non-corrosive at room temperature. The greenhouse effect is very low (GWP = 2, ODP = 0), and our preliminary research showed that the mixed gas containing HFP could perform a well protection on molten magnesium from further oxidation in the sealed furnace[7, 8], which shows that HFP gas could be potentially used as a substitute for SF_6 in the magnesium industry. However, the morphological characteristics of the surface film of pure magnesium at 670 °C-800 °C in a mixed atmosphere containing hexafluoropropylene are still unclear.

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In this work, the protective effect of pure magnesium melt in air containing 1% HFP has been studied from 670 °C to 800 °C. The surface film of the melt has been characterized by SEM, XRD, EDS, and the protective effect was also discussed.

2. Experiment

A magnesium rod was used as the raw material. The chemical composition of pure magnesium in weight percent is 0.004%Si, 0.004%Mn, 0.0006%Al, 0.0008%Fe, 0.0008%Zn and Mg balance. The chemical composition of HFP gas was 99.99 vol.% HFP, 0.0011vol.% O_2 and 0.0004 vol.% H_2O.

An electrical resistance furnace (the working chamber size of Φ100mm × 150mm) was employed to smelt the magnesium. A cover of low carbon steel (with the size of Φ270 mm×150 mm) with an inlet and exit hole and an observation port was placed above the electrical resistance to prevent air from entering. The gases of HFP and air mixed evenly through a 5 L gas cylinder entered the electrical resistance furnace by the inlet channel. A low carbon steel crucible (the inside diameter of 60 mm and the depth of 75 mm) coated with boron nitride was put into the resistance furnace and preheated to 300 °C for 30 min. Then, about 120 g of pure magnesium specimens were added to the low steel crucible and a certain concentration of HFP/air mixture gases were introduced into the working chamber of the resistance furnace at a flow rate of 3 L/min. After purging the gas mixture inside the chamber for at least 60 min, the specimens were heated. When temperature reached the desired temperature, an original oxide film on the surface of melt magnesium was removed by use of a surface-film-pick-up device and the fresh protective film was formed in the atmosphere, which was recorded by camera after 10 min, 30 min, 60 min, 90 min and 120 min, respectively. After reaching the required holding time, the sample with a new surface protective film was taken out and cooled down for analysis of its composition and microstructure. The melt temperature was 670 °C, 700 °C, 730 °C, 760 °C and 800 °C, the concentration of HFP in mixed gases was 1%.

X-ray diffraction (X Pert Pro MPD) with a Cu-Kα source operated at 40 kV and 40 mA was used to identify the phases in the surface film. The surface morphology and elemental composition of the surface films were studied by using a Quanta FEG 250 field emission scanning electron microscope equipped with an EDAX Genesis APEX energy dispersive spectroscopy system.

3. Results and Discussion

3.1. Macro-morphology of the surface film

Fig. 1 shows the macro-morphology of the surface film when 1% HFP/air mixed gas was held at different temperatures for 30 min of magnesium melt. Fig. 1(a) shows metallic luster on the entire surface at 670 ℃, and three places near the crucible wall were metallic Bubbles, which may be caused by the oxidation of the melt remaining on the crucible wall. But these oxidation nodules did not show a trend of continued oxidation, indicating that the protective effect of HFP on the melt inhibits the oxidation of the melt, making the melt other part of it had a smooth metallic luster. The surface was also silver-white metallic color when the temperature was 700 ℃ in Fig. 1(b), and basically flat. The melt surface was also appears on the right side in addition to the metallic color white at 730 ℃ in Fig. 1(c), the oxidation of the melt was accelerated. This oxidation phenomenon was more obvious at 760 ℃ and 800 ℃ in Fig. 1 (d) and (e), and the protective effect of HFP on the melt was weakened with the increase of temperature.

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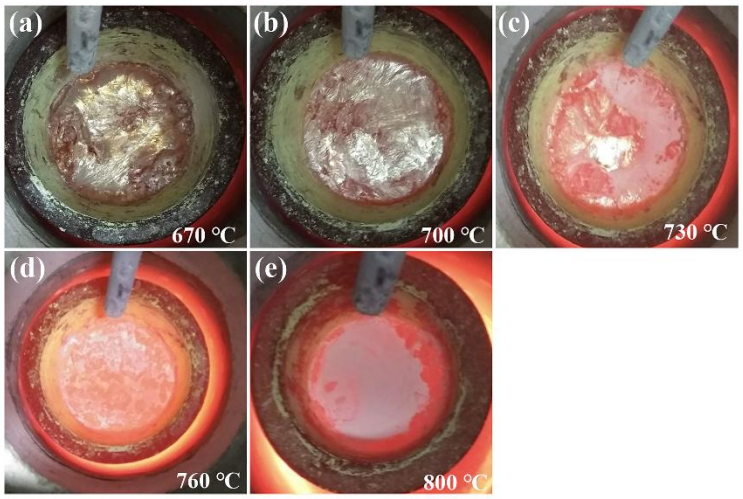

Figure 1. Macro-morphology of the melt surface film at different melting temperatures in 1% HFP/air for 30 min.

3.2. SEM and EDS Analysis of Surface Film

Fig. 2 shows the morphology of the surface film at 670 ℃-800 ℃ in 1% HFP/air mixed gas for 30 min. With the increased of temperature, the continuity of the surface film gradually deteriorated after 730 ℃, and the compactness weakened. The roughness increases and the magnesium melt oxidation intensifies.

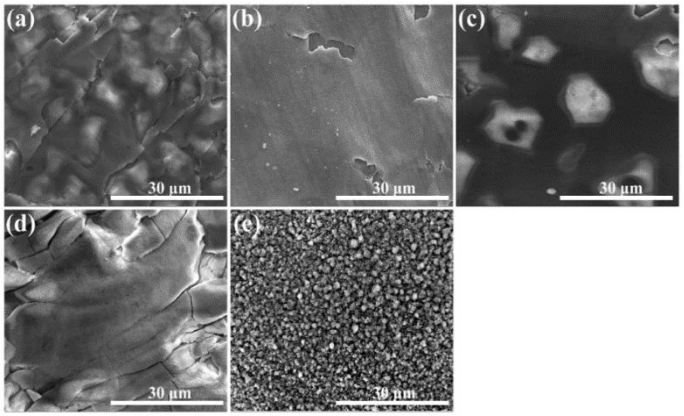

Figure 2. SEM morphology of the surface film at 30 min in 1% HFP/air : (a) 670 ℃ ; (b) 700 ℃ ; (c) 730 ℃ ; (d) 760 ℃ ; (e) 800 ℃.

The EDS surface characterization analysis of the surface film under the conditions of Fig.2, the results were shown in Table 1. There were mainly five elements Mg, F, O, C and Si in the surface film, and the content of Mg element decreases with the increase of temperature. The content of F element was the highest at 700 ℃, and the content of O element remained basically unchanged before 730 ℃, which showed that HFP had a good protection effect on the melt before this temperature, which is consistent with Table 1.The topographic results of the mask were the same. However, when the temperature increased to 760 °C, the content of F element decreased, and the content of O element suddenly increased, indicating that the oxidation degree of the surface film increased at this time. At 800 ℃, the content of O element is still increasing, while the content of F element continues to decrease. The large amount of white matter in the surface film may be the result of the accelerated oxidation rate of the melt and the increase of the content of O element. The mass ratio of F/O elements in Table 1 increases when the temperature increases from 670 ℃ to 700 ℃. The mass ratio of F/O elements decreases gradually when the temperature is between 700 ℃ and 800 ℃, especially at 760 ℃ and 800 ℃ The decreasing trend is obvious, indicating that with the increase of temperature, the content

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of O in the melt surface increases and the oxidation rate accelerates. The existence of a small amount of C in Table 1 may be caused by the formation of carbon element after the gas is decomposed at high temperature or the adsorption of CO_2 on the surface of the film. The existence of Si element may be an impurity introduced during the sample preparation process.

Table 1. Elemental composition and its mass fraction of the surface film at different temperatures in 1% HFP/air atmosphere for 30 min.（wt. %）

Element	Mg	F	O	C	Si	F/O
670 ℃	61.09	31.37	5.73	0	1.81	5.47
700 ℃	57.55	35.71	5.18	0.42	1.14	6.89
730 ℃	56.82	35.18	5.87	0.88	1.25	5.99
760 ℃	51.13	33.44	13.47	0.49	1.47	2.48
800 ℃	50.88	33.27	14.22	0.29	1.34	2.34

Fig. 3 shows the surface and cross-sectional morphological characteristics of the film at different holding times in a 1% HFP/air mixture at 700 °C. As shown in Figure 3(a)-(d), the roughness of the surface film increases with the increase of the holding time, and the surface film gradually becomes a flower-shaped sheet, which is different from the macroscopic morphology of the film. The content of EDS elements in Table 2 is corresponding to Figure 2. The surface film mainly contains Mg, F, C, O and Si elements. With the increase of holding time, the content of Mg element in the film decreases, and the content of F element increases, which means that with constant temperature With the extension of time, more HFP gas reacted with the melt, and the content of O element first increased and then decreased. This may be due to the influence of the flow of air in the semi-closed system. On the other hand, it reflects the excellent protective effect of HFP. , with the continuous increase of F element, even though the film is being oxidized, HFP rapidly reacts with the melt to form a new protective film, so the reduction of O element is seen at 120 min, and the oxidation trend is controlled; from Fig. 2(e)-(h) The cross-sectional morphology of the surface film and the thickness of the cross-section film in Table 2 show that with the increase of the holding time, the surface film becomes denser, and the average film thickness shows an increasing trend, and the film thickness is between 2.12 μm and 3.30 μm.

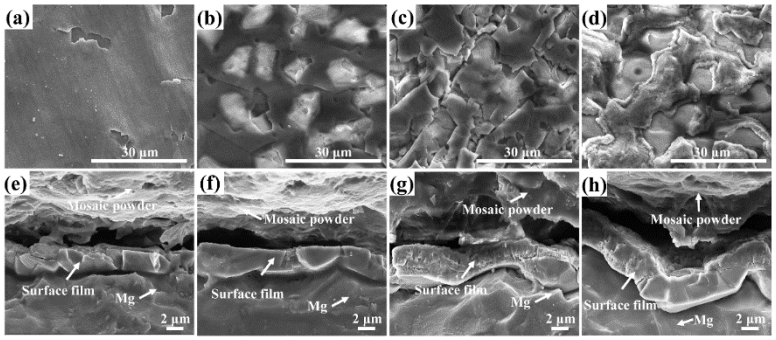

Figure 3. Surface and cross-sectional morphologies of the surface film at different holding times in 1% HFP/air at 700 ℃: (a), (e) 30 min; (b), (f) 60 min; (c), (g) 90 min; (d), (h) 120 min

Table 2. Elemental composition and its mass fraction of the surface film with different constant temperature in 1% HFP/air atmosphere at 700 ℃.（wt. %）

Element	Mg	F	O	C	Si	F/O
30 min	57.55	35.71	5.18	0.42	1.14	6.89
60 min	52.09	37.79	9.10	0	1.02	4.15

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90 min	49.59	38.36	10.41	0	1.64	3.68
120 min	46.66	45.81	5.71	0	1.82	8.02

3.3. XRD Analysis of Surface Film

Fig. 4 shows the XRD patterns of the surface films at different temperatures in a 1% HFP/air mixture for 30 min. The surface film in the figure was mainly a composite film composed of MgF_2 and MgO. The phase in the film did not change with the increase of temperature. The peak intensity of MgF_2 increased with the increased of temperature. Because the content of MgO in the film was less, the temperature When the temperature was lower than 760 ℃, the peak of this substance did not appear, and the intensity of the peak was obviously enhanced at 760 ℃ and 800 ℃, and the peak of Mg element was the magnesium matrix.

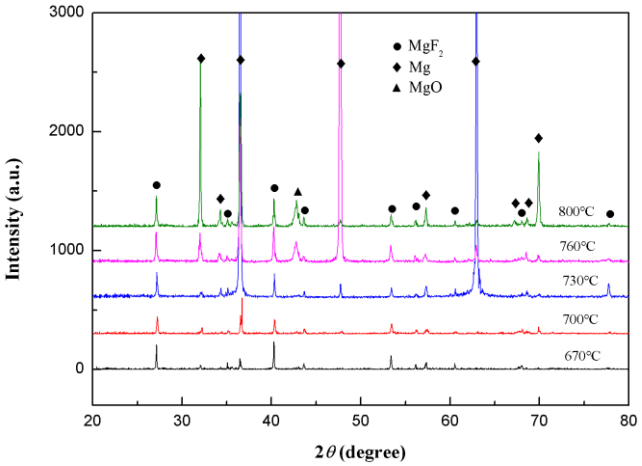

Figure 4. XRD patterns of surface films at different temperatures in 1% HFP/air for 30 min

4. Conclusion

The characterisation of protective surface films formed on molten magnesium protected by hexafluoropropylene/air atmosphere at temperatures between 670 °C and 800 °C has been investigated. The results showed that with the increase of the holding time and the decrease of melt temperature, the protective effectiveness of HFP/air mixed gases increased. There was a uniform coherent film on the surface of molten magnesium, which contained MgF_2 and MgO. The film thickness is between 2.12 μm and 3.30 μm in 1% HFP/air at 700 °C from 30 min to 120 min.

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