Protection of magnesium melt by hexafluoropropylene/air atmosphere

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Abstract. The protection of hexafluoropropylene/air mixed gas for molten magnesium at temperatures from 670 °C to 800 °C has been investigated. The morphology and the composition of the protective film formed on the surface of the melt at 700 °C for holding time of 30 min and 60 min 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 increasing of hexafluoropropylene concentration, the prolongation of holding time and the decrease of temperature. The protective film on the surface of the melt was uniform and continuous, and mainly composed of MgF₂ and small amount of MgO.

1. Introduction

Due to the low density, good damping capacity and ease manufacturing, magnesium application scope has been expanding from aerospace, automotive, biomedicine and electronic communications industries to other fields [1,2]. However, magnesium has a high affinity for oxygen, a high vapor pressure in the molten state, and an oxide layer formed on the surface of the melt in air is a loose porous structure, which causes magnesium to violently oxidize and burn at a melting temperature in air. Therefore, in order to process molten magnesium securely and validly, the melt is currently protected by many methods, such as covering with salt flux, inert gas or changing the nature of the surface oxide with a cover gas, to slow the oxidation rate down to an acceptable level [3, 4].

Many studies [5-7] have shown that during the melt handling and casting process, the cover SF₆ gas protection is the most effective method to protect molten magnesium from catastrophic oxidation or even combustion and has been widely used in industrial production. The application of SF₆ in magnesium metal casting was first investigated in 1970 by Fruehling [5]. Later, a lot of researches have been done about this gas and found that its protection effect is very good. However, the use of SF₆ has come under raised superintend in virtue of its serious greenhouse effect (GWP=23900), which has led magnesium industry to seek alternatives for SF₆. Several reports [8-11] have shown that 1,1,1,2-tetrafluoroethane (CF₃CH₂F, HFC-134a) can be used as a substitute for SF₆. But its greenhouse effect (GWP=1300) is still high. Therefore, it is necessary to find a new alternative gas to SF₆.

A new gas, hexafluoropropylene (HFP), was found suitable for this situation [12]. It was reported that HFP gas shows a well protection on molten magnesium alloy from combustion. HFP, whose chemical formula described as C₃F₆, is a colorless and tasteless gas. It is nontoxic at room temperature,
non-corrosive and security, and has a lower greenhouse effect (ODP=0, GWP=2) than SF₆. It does not burn in the air and is usually harmless to the clay [12, 13]. However, in the protection process of magnesium smelting by HFP gas, the factors affecting the protection effect is not well understood, and the composition and structure of the film formed on magnesium melts has not been characterized. In this paper, the protection of HFP/air mixed gas for molten magnesium 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 700 °C were investigated. The purpose of this paper is to provide some reference for the re-search on gas protection for magnesium melt.

2. Experiment

A magnesium rod with a purity of 99.99% was used as the raw material. The main impurities were Si 4.10 ppm, Al 5.85 ppm, Mn 6.40 ppm, Fe 7.82 ppm, Zn 8.09 ppm. The gas used for the experiment was the mixture of HFP (HFP≥99.99%, oxygen ≤ 20 ppm, water ≤ 10 ppm) and air.

An electrical resistance furnace (the working chamber size of Φ 100mm × 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 5000mL 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 0.1%, 0.3%, 0.5%, 1%, 3% and 5%, which was adjusted successively in order to determine the minimum requirement of HFP for effective protection of magnesium melts without sparks.

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. Protection effects

3.1.1. Effect of HFP concentration

Figure 1 shows the protective effects of the atmospheres containing different concentrations of HFP on magnesium melt at 700 °C for 10 min. It can be seen that in the atmospheres containing 0.1%, mars and cauliflowers appeared on the surface of molten magnesium (Figure 1a), and almost no protective film was formed on the surface of the melt. In 0.3% HFP/air, magnesium melt near the crucible wall was oxidized slightly, white particles were formed on the surface of the melt, and protective film was formed in part of the melt (Figure 1b). In 0.5% HFP/air, a surface with a partial metallic gloss appeared, which shows the formation of a protective film (Figure 1c). As the concentration of HFP rose to 1%, the whole surface presented a silvery white metallic luster (Figure 1d). Further increased the HFP concentration to 3% and 5%, the silvery white surfaces were similar (Figure 1d-f), which was relatively smooth and continuous. These results indicate the protective effects of HFP/air for
magnesium melt increased with increasing of the concentration of HFP. In this experiment, 0.3% HFP was the minimum protective concentration.

Figure 1. Protective effects of the gases containing different concentrations of HFP on magnesium melt at 700 °C for 10 min.

3.1.2. Effect of temperature
The protective effects of 1% HFP/air on magnesium melt at different temperatures for 10 minutes are presented in Figure 2. As can be seen, there was a smooth and uniform metallic luster surface on the melt at 670 °C and 700 °C. At 730 °C, the melt surface still has a certain metallic luster, but some areas produced white oxide. When temperature reached 760 °C, the metallic luster on the surface of the melt disappeared and a large amount of white oxide was produced in the central region. As temperature rose to 800 °C, the amount of white oxide in the central region increased. These results suggested that with the increase of temperature, the protective effect of HFP/air on magnesium melt became weak, and the oxidation of magnesium melt accelerated.

Figure 2. Protective effects of 1% HFP/air on magnesium melt at different temperatures for 10 min.

3.1.3. Effect of holding time
The protective effects of 1% HFP/air on magnesium melt for different times at 700 °C are shown in Figure 3. It can be found that when molten magnesium was exposed to the atmosphere within 60 min, its surface had a shiny metallic appearance and became flatter with increasing time (Figure 3a-d). As the holding time increased to 120 min (Figure 3e), the surface turned dark red and its metallic luster disappeared. This may be due to the thickening of the film over time.
3.2. Morphologies and composition of the protective film

Figure 4 is the SEM image and EDS mapping results of the surface film produced in 1% HFP/air at 700 °C for 30 min. It shows that the surface was basically flat and uniform, but there were also some pores and cracks in the film. These pores and cracks may act as channels for transporting magnesium vapor outward to react with HFP and oxygen. The EDS analysis displayed that the surface chiefly included Mg, F, O and Si elements. Mg and F were the dominant elements and the contents were 57.392% and 36.233%, respectively. The content of O element was 6.028%, which was relatively small, and the content of C element was 0.347%. The results indicate that there was a relatively flat and uniform protective film on the surface of magnesium melt in HFP/air atmosphere, which was consisted of MgF₂ and a bit of MgO. It can be seen from the mapping diagram that the overall distribution of Mg, O, C and F elements on the surface film was relatively uniform, which also indicates that the surface film was homogeneous and a composite film. However, the local distribution of Mg and F elements was not very even.

Figure 5 is the cross-sectional view of the sample after held in 1% HFP/air at 700 °C for 30 min and 60 min. The EDS line scanning results of the cross-section of the sample after held in 1% HFP/air at 700 °C for 60 min are shown in Fig. 5(c) and (d). It indicates that there was a protective film on the magnesium surface. The continuity of the film was not very good and there were some holes in the film for 30 min. For 60 min, there was a continuous film on the surface of magnesium and the film seems to be uniform in thickness. Further observation showed that the thickness of the film was between 2.011 and 2.448 μm. The reason why the film became uniform with time may be that with the increase of the holding time, the magnesium vapor from the pore continuously reacted with HFP, which made the surface film more continuous and denser. The fluorine element was not uniformly distributed in the film, and its content had a maximum near the matrix.
For the sake of identifying the reaction products on the surface of molten magnesium, X-ray diffraction analysis was carried out. Figure 6 indicates the XRD analysis results of magnesium after melted in air containing 1% HFP at 700 °C for 30 min. It can be seen that there were the diffraction peaks of MgF₂, MgO and Mg on the surface. MgO peak was not very obvious and the intensity of the peak was very weak. The intensity of MgF₂ peaks was high. The appearance of Mg peaks may be due to the X-ray breakdown of the film to the matrix. Therefore, it can be considered that the surface film consisted of MgF₂ and a bit of MgO.

Based on the descriptions above, the protection mechanism of HFP/air atmosphere for molten magnesium can be described as follows: Due to the large amount of oxygen present in the protective atmosphere, and oxidation does not require complex decomposition processes, magnesium will first react with oxygen to form a thin MgO film on its melt surface, which is loose and porous, at the melt surface according to the reaction:

$$\text{Mg (l)} + \frac{1}{2}\text{O}_2(\text{g}) = \text{MgO (s)}$$  \hspace{1cm} (1)

When the concentration of HFP in the atmosphere is low, there are no reactions between magnesium and HFP. The loose and porous MgO film cannot prevent further oxidation of magnesium, so in this case, the mixed gas has little protection on magnesium melt. When the concentration of HFP
in the atmosphere is increased, magnesium will react with HFP or F₂, a decomposition product of HFP, to form MgF₂ in the pores of MgO film. The reactions are as follows:

\[
3\text{Mg(l)} + \text{C}_3\text{F}_6(g) + 3\text{O}_2(g) = 3\text{MgF}_2(s) + 3\text{CO}_2(g) \quad (2)
\]
\[
\text{Mg(l)} + \text{F}_2(g) = \text{MgF}_2(s) \quad (3)
\]

The formation of MgF₂ makes the film on the surface of the magnesium melt dense, which prevents further oxidation of magnesium. Therefore, the mixed gas of high HFP concentration can provide effective protection to magnesium melt, and the higher the HFP concentration is, the better the protection of the magnesium melt will be.

4. Conclusions
The protection of HFP/air mixed gases for molten magnesium at temperatures between 670 °C and 800 °C has been investigated. The results show that molten magnesium can be protected from excessive oxidation and burning by the mixed gases of HFP/air. With the increase of the concentration of HFP, 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 MgF₂ and MgO. The thickness of the film was between 2.011 and 2.448 μm in 1% HFP/air at 700 °C for 30 min.

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