Protective behavior of an \( \text{SO}_2/\text{CO}_2 \) gas mixture for molten AZ91D alloy

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Abstract: The protective behavior for a molten AZ91D alloy in an open melting furnace was investigated under a protective gas mixture containing 3% \( \text{SO}_2 \) and 97% \( \text{CO}_2 \), and the protection mechanism was discussed. Experimental results show that the gas mixture provides effective protection for AZ91D melt in the temperature range from 680 °C to 730 °C. The microstructure, chemical composition and phase composition of the surface film formed on the molten AZ91D alloy were analyzed using scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). The SEM results demonstrate that the surface films with an average thickness between 0.5 μm and 2 μm are dense and coherent in the protected temperature range. The EDS results reveal that the surface film mainly contains elements S, C, O, Al and Mg. The XRD results show that the surface film consists of MgO, MgS and a small amount of C phase.

Key words: AZ91D alloy; protective behavior; \( \text{SO}_2/\text{CO}_2 \) gas mixture; surface film


Molten magnesium and magnesium alloys oxidize rapidly in air, and the magnesium oxide film does not protect the molten metal from further oxidation \(^1\). It is necessary to protect the melt from extensive oxidation during melting and casting of magnesium alloys. In order to prevent the oxidation of the melt, gas protection and covering protection for the molten alloys are mainly used. However, fluxes have a tendency to be mixed into the melt and the resultant occlusions accelerate the molten metal from further oxidation. Pettersen et al. \(^6\) investigated the protection of ZK60 alloy and molten magnesium in (0.1% \( \text{SO}_2 \), 0.99% \( \text{N}_2 \))/air atmospheres. The results showed that the film formed in air containing 0.1% 1,1,1,2-tetrafluoroethane or higher provided a protective effect, which was composed of MgO and C with small amounts of Mg. Zeng et al. \(^10\) researched the protective behavior of molten magnesium in the shielding gas containing 1,1-difluoroethane (CH\(_2\)F\(_2\), HFC-152a), and pointed out that the film had a shiny metallic appearance and only contained MgO and MgF\(_2\) phases. Wang and Xiong \(^11\) explored the protective behavior of AZ91D alloy and molten magnesium in (0.1%–4%)\( \text{SO}_2/\text{N}_2 \)/air atmosphere in the sealed furnace, and discussed the formation process and the protection mechanism of the net-like two layers of surface film, suggesting that MgS or MgSO\(_4\) increased the density of the surface film and enhanced its protective capability. They pointed out that increasing the \( \text{SO}_2 \) content can partly enhance the protective effect. Pettersen et al.\(^6\) researched the protective effect of 1% \( \text{SO}_2/\text{air} \) on molten magnesium, indicated that the surface film consisted of small MgO grains with some sulfur dissolved.

Much research had been done on some fluorine-containing gases, and each gas had a certain global warming potential (GWP) value. \( \text{SO}_2 \) gas has not any greenhouse effect, and it can be used to protect molten magnesium alloy\(^{12}\). So, \( \text{SO}_2 \) becomes a possible replacement for SF\(_6\) gas. However, the mechanism of protection of molten magnesium alloy against oxidation and combustion by \( \text{SO}_2 \)-containing cover gases has not yet been well understood \(^6,11,13\). It is very important to study the protective mechanism of \( \text{SO}_2 \) gas for magnesium alloy melt through advanced analytical techniques to obtain an ideal substitute for SF\(_6\) gas. In this study, the protection...
behavior of SO$_2$/CO$_2$ cover gas for a molten AZ91D alloy was investigated in an unsealed melting furnace by analyzing the morphologies and composition features of the surface film formed on the melt.

1 Experimental procedure

The experimental alloy used in the study was AZ91D. The chemical composition of the main elements in AZ91D alloy was 9% Al, 0.7% Zn, 0.3% Mn and Mg balance (by weight percent). Base on actual protective results, a dried gas mixture with 3.0% SO$_2$ and 97.0% CO$_2$ (by volume percent) was used as the protective gas in this experiment.

The metal materials were firstly melted in an unsealed electric resistance furnace containing a graphite crucible. When the melting temperature was raised to 450 °C, the gas mixture of 3.0% SO$_2$ and 97.0% CO$_2$ was introduced into the graphite crucible. The flow rate of the gas mixture was between 0.05 and 1 L·min$^{-1}$, which was controlled by a mass flow meter according to the material’s temperature. When pure magnesium began to melt in the graphite crucible, the gas mixture was continuously fed into the furnace chamber at 0.5 L·min$^{-1}$. The melt temperature was adjusted by a silicon temperature controller (error band ±2 °C).

When the melt in the crucible was heated to a desired experimental temperature (680, 710, 730, and 750 °C), the primitive surface film was removed by a home-made carbon steel scraper, and then a fresh surface film appeared. In the meantime, a small amount of melt with the fresh surface was taken out from the bulk melt using a preheated carbon steel sampling cup and hung in the protective gas. Thus, the protective gas might react with the AZ91D melt surface for 10 min at different temperatures (680, 710, 730 and 750 °C), and then the sampling cup was cooled rapidly outside the furnace using a stream of industrial CO$_2$ gas. The surface film sample in the cup (which had a diameter of 25 mm and a length of 20 mm) was taken out. The inside of the cup and the surface of the scraper had been coated with boron nitride to avoid any AZ91D melt sticking to them. The morphology and chemical composition of the surface film formed on the molten AZ91D alloy were examined using an FEI Sirion SEM operated at 20 kV with a resolution of 1.5 nm, equipped with EDS. The phase composition of the surface film was identified using a D/MAX-RB diffractometer with Cu-K$_\alpha$ ($\lambda = 1.5405$ Å) as a radiation source.

2 Results

2.1 Phase composition of protective film

X-ray diffraction analysis was carried out to confirm the phase components of the protective film. Figure 1 presents the XRD patterns of AZ91D alloy at 680 °C and 750 °C after 10 min in an atmosphere containing 3.0% SO$_2$ + 97.0% CO$_2$, respectively. At 680 °C, the surface film consists of Mg, MgO, C and MgS, as shown in Fig. 1(a). Figure 1(b) is the magnified zone in Fig. 1(a). However, at 750 °C, no appreciable C diffraction peaks can be observed, only those for Mg, MgO and MgS phases, see Fig. 1(c). The appearance of a large amount of Mg phase in the analysis of XRD patterns is attributed to the X-ray radiation penetrating the thin film into the substrate metal [9]. This implies that the main phases in the surface film are MgO and MgS at different temperatures. The reason why carbon was not observed by XRD in the film formed at 750 °C may be that its amount is too little to produce a sufficient X-ray signal.

2.2 Cross-sectional morphology and composition

By examining the sample cross-section using SEM we can obtain the surface film thickness and its chemical composition information. Figure 2 shows the SEM images and EDS analysis results of cross-section samples held for 10 min under protective gas at 680 °C and 750 °C, respectively. It can be seen from Fig. 2(a) that the surface film formed on AZ91D melt exposed to protective gas at 680 °C for 10 min is dense and continuous. The average thickness of the film is about 2 μm. However, when the melt temperature was increased to 750 °C, the protective film was less compact and thinner, with an average thickness that was estimated to be 0.5 μm (Fig. 2(c)). This result suggests that the increase of the melt temperature leads to a decrease in compactness of the surface film formed on the molten AZ91D alloy.

Figure 2(b) and (d) present the cross-sectional element composition of the surface films formed on AZ91D melt...
at 680 °C and 750 °C, respectively. It is clear that elemental compositions in the surface film are very different from those in the AZ91D matrix. The surface film formed in SO₂/CO₂ mixture gas contains mainly oxygen, carbon, magnesium and sulfur elements. A comparison of Figs. 2(b) and (d) reveals that the increase in melt temperature results in an increase in the amount of Mg and a decrease in the amount of S in the film.

2.3 Surface film morphology characterization

The surface film morphology exhibits the gas mixture protective effects for magnesium alloys at different temperatures. Figure 3 gives the SEM images of the surface film on AZ91D alloy exposed to protective gas in the temperature range from 680 °C to 750 °C for 10 min.
respectively. It is evident that the surface film morphology varies considerably with increasing the melt temperature. When the melt temperature was at 680 °C, a net-like structure protective film appeared on the surface of the AZ91D melt, where a few white granules were observed, as shown in Fig. 3(a). These white granules were confirmed by EDS results to be MgO. The similar structure was also observed in the study of the oxidation behavior of molten magnesium in atmospheres containing SO2. With the melt temperature rising to 710 °C, the surface was smooth and uniform, with few white granules showing (Fig. 3(b)). As the melt temperature was increased to 730 °C, several bands (see arrows in Fig. 3(c)) with thinner surface film occurred, which were believed to be crack sites of the surface film. There were still a few white granules on the surface film. With further increase of the melt temperature to 750 °C, there were a larger number of rounded granules uniformly distributed on the cracked surface film. In addition, larger-sized irregular white granules still existed on the surface film (Fig. 3(d)). These results reveal that the protection effect of 3.0% SO2 + 97.0% CO2 gas mixture for AZ91D alloy obviously decreases with the increase in the melt temperature, presenting the weakening compactness of the surface film, which is consistent with the cross-sectional SEM analysis results of the surface film.

Figure 4 shows the EDS results of the surface film on AZ91D alloy exposed to protective gas at 680 °C and 750 °C for 10 min, respectively. The EDS results indicate that the surface film formed in the SO2/CO2 gas mixture contain mainly oxygen, carbon, magnesium aluminum, sulfur, and tiny amounts of zinc elements. The existence of aluminum element is attributed to the X-ray radiation penetrating the surface film into the AZ91D matrix. It can be seen that the increase in the melt temperature leads to a rise of oxygen and sulfur content in the surface film. In addition, the growth rate of oxygen is faster than that of sulfur, indicating that the amount of MgO is larger than that of MgS. Since MgS has a porous structure, the results reveal that the higher the melt temperature, the lower the compactness of the surface film.

![Figure 4: EDS results of the surface film on AZ91D alloy exposed to protective gas for 10 min (a) at 680 °C and (b) at 750 °C](image)

### 3 Discussion

From the results obtained above, it can be seen that the surface film contains mainly MgO, MgS and C and has a net-like structure morphology at a lower melt temperature. The increase in the melt temperature changes the relative content of MgO, MgS and C and the morphology, as well as the thickness of the surface film. This change in temperature also causes the change in the protective behavior of the SO2/CO2 gas mixture towards the molten AZ91D alloy.

As the molten AZ91D alloy is protected by the gas mixture containing 3.0% SO2 + 97.0% CO2, the following reactions between the melt and the gas mixture may happen:

\[
2\text{Mg(l)} + \text{O}_2(g) = 2\text{MgO(s)} \quad (1)
\]

\[
2\text{Mg(l)} + \text{CO}_2(g) = 2\text{MgO(s)} + \text{C(s)} \quad (2)
\]

\[
3\text{Mg(l)} + \text{SO}_2(g) = \text{MgS(s)} + 2\text{MgO(s)} \quad (3)
\]

According to the thermodynamic theory calculation made by Liang and Che, the standard Gibbs free energies for reactions (1), (2) and (3) at 1,000 K are -986.07 kJ·mol\(^{-1}\), -590.22 kJ·mol\(^{-1}\) and -1012.11 kJ·mol\(^{-1}\), respectively. So, the reaction (3) is favorable, suggesting that MgO and MgS will first form in the melt surface film. So, the MgO and MgS phases were detected in the XRD analysis. Since the standard Gibbs free energy for reaction (2) is larger than those for reactions (1) and (3), the reaction (2) is not thermodynamically favorable compared with reactions (1) and (3), leading to the absence of carbon in the film. This is inconsistent with the XRD and EDS analysis results because both the XRD and EDS analyses discovered the presence of carbon in the film. Therefore, the carbon must have been formed by the reaction (2) for dynamic reasons. Since a mass of CO is in the protective gas mixture, magnesium will react with CO2 to form carbon and MgO in the surface film. Meanwhile, reaction (1) perhaps takes place in the surface film for the same reason.

From the above analysis, it can be seen that the protective film formed on AZ91D alloy in the gas mixture of 3.0% SO2 + 97.0% CO2 contained mainly MgO and MgS as well as a small amount of carbon. Although plentiful MgO and MgS appear
in the protective film, the MgO does not protect the molten magnesium from further oxidation due to the mismatch of the mole volume of MgO and the mole volume of the equivalent amount of magnesium (the Pilling-Bedworth ratio) \(^{12, 16}\). As the Pilling-Bedworth ratio of MgO and MgS are 0.73 and 1.40 \(^{12, 17}\), respectively, the MgS increases the Pilling-Bedworth ratio of the surface film. It can be concluded that the formation of MgS in surface film plays a major role in enhancing the protective effect of the SO\(_2\)/CO\(_2\) gas mixture on AZ91D melt. Further, the presence of carbon also contributes to an improved protection behavior of the surface film. Because the atomic radius of carbon is smaller, carbon atoms can fill the gaps between the MgO and MgS particles in the film, resulting in a further increase of the Pilling-Bedworth ratio of the surface film and enhancement of the protection effect of the film.

Based on the above analysis, it is clear that promoting the formation of a surface film containing MgS will enhance the protecting effect for the AZ91D melt. According to Wang and Xiong \(^{14}\), it is evident that the activity for Mg in the reaction (1) is much smaller than that in the reaction (3). As the melt temperature increases, the reaction rate of molten AZ91D alloy with O\(_2\) is higher than that of AZ91D melt with SO\(_2\), which will result in more MgO to be formed on the surface of the melt. The analysis result is consistent with the EDS experimental result because the content of oxygen in the film increases quickly as the temperature increases. Due to the amount of MgO increasing, the compactness of the surface film will reduce, leading to the appearance of the tiny crack structure in the film at 750 °C.

4 Conclusions

1. The 3.0% SO\(_2\) + 97.0% CO\(_2\) mixture gas provides an effective protection for the AZ91D alloy during melting by forming a dense and compact film on the melt surface. The protection effect of the SO\(_2\)/CO\(_2\) gas mixture obviously decreases with the increase of the melt temperature, suggesting that the surface film’s thickness decreases from 2.0 μm to 0.5 μm.

2. The 3.0% SO\(_2\) + 97.0% CO\(_2\) gas mixture reacts with the molten AZ91D alloy to produce MgO, MgS and a small amount of C phase, which form the protective film on the melt surface. The MgS increases the compactness of the surface film, resulting in an enhanced protective capability of the film. The element C fills the gaps between the MgO and MgS particles in the film and further enhances the protective performance of the surface film.

References


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