

Protection behavior of fluorine-containing cover gases on molten magnesium alloys

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Abstract: The sulphur hexa-fluoride gas (SF_6), which is commonly used as the cover gas of molten magnesium alloys in the magnesium industry today, has an extremely high global warming potential (GWP). The protection mechanism of SF_6 containing cover gases on molten magnesium alloys was presented. The cover gas protects the melt by reacting with the melt to form a coherent protective film on the melt surface. The film contains MgO and MgF_2 . Particles containing MgF_2 form on the interface between the oxide film and the bulk magnesium alloy, which correspond to the concave areas from the surface observation. These particles increase the Pilling and Bedworth ratio of surface film and enhance the protective capability of the films. Based on the understanding of the mechanism of SF_6 , a melting technology in a sealed furnace was proposed, and the protection behavior of magnesium alloys in the sealed melting furnace was investigated under the protective atmosphere containing HFC-134a. The morphology and composition of the surface film were also studied. Experiments to evaluate the protective effect of two other fluorine containing gases with low GWPs on AZ91D alloy in the sealed furnace were also carried out, and the results show that the new gases are potential substitutes for SF_6 .

Key words: magnesium alloy; melt protection; SF_6 ; surface film; protection mechanism

1 Introduction

Magnesium and its alloys are being widely used in many areas due to their excellent properties such as high specific strength and low density[1]. However, molten magnesium and its alloys oxidize rapidly in air, and magnesium oxide film does not protect the molten metal from further oxidation[2]. Protection with a cover gas mixture containing SF_6 has been commonly used in magnesium industry in the past decades, but the SF_6 gas has recognized as a very potent greenhouse gas with a high global warming potential (GWP) value of 23 900 compared with CO_2 and a long atmospheric lifetime of 3 200 years[3]. Therefore, the magnesium industry has been looking for new substitutes for SF_6 .

FRUEHLING and HANAWALT[4] firstly studied the protection effect of molten magnesium under protective atmosphere of SF_6 containing cover gases, and found that SF_6 was consumed in the protection process and proposed that the absorption of SF_6 to the MgO

surface prevented the melt from further oxidation. CASHION[5] reported that the surface film formed in protective atmosphere containing SF_6 was a mixture of MgO and MgF_2 phases and the film thickness varied between 1 μm and 2 μm . PETTERSEN et al[6] analyzed the microstructure characteristic of the surface film formed in F-containing cover gas with XRD, EPMA and TEM, and found that long-term exposure of magnesium melt to the mixture gases containing SF_6 increased the film thickness with an increasing concentration of MgF_2 . AARSTAD[7] indicated that particles containing MgF_2 formed at the interface between MgO film and bulk magnesium, and the particles would grow up until they covered 25%–50% of the total film.

In 1998, the International Magnesium Association had committed to find suitable substitutes for SF_6 , and three of them were determined to be the most possible substitutes. HFC-134a was developed by the Cooperative Research Center for Cast Metals Manufacturing in Australia[8]. GWP value of HFC-134a is 18 times lower than that of SF_6 and its atmospheric lifetime is only 14.6

years. HFE7100 and Novec 612TM were developed by 3M[9]. The GWP value and lifetime of HFE7100 are 75 times and 780 times lower than those of SF₆. Novec 612TM has the same GWP value as CO₂ and its lifetime is less than a week. However, these substitutes have not been widely used in magnesium industry.

The protection mechanism of SF₆ containing cover gases on molten magnesium has not been clearly understood and needs further studies. In this work, the protection mechanism is discussed and a vacuum assisted melting technology is presented. The potential substitutes for SF₆ are also presented.

2 Protection mechanism of SF₆ containing cover gases

2.1 Experimental methods

AM60 and AZ91D alloys were used in the study and the alloys were melted in an electric resistance furnace under a mixture of SF₆ and a diluent gas of N₂ or CO₂ that were controlled by mass flow meters. When a constant melt temperature was reached in the furnace, the original oxide film on the melt was removed to obtain a fresh melt surface, and then the melt was kept in the furnace for a period time. The crucible was then pulled out of the furnace and cooled rapidly using the compressed gases. Specimens for X-ray diffractometry, scanning electron microscopy analyses were cut from the samples. Specimens for cross-section observation of the film were coated with epoxy resin before grinding and polishing.

2.2 Experimental results and discussion

2.2.1 Film appearance and structure

Fig.1 shows the cross-section view of the sample with 0.3% (volume fraction, the same below if not mentioned) SF₆ held at 680 °C for 10 min. It can be seen from Fig.1 that the surface film is dense and uniform in thickness with some semicircular particles formed at the interface between the oxide film and bulk magnesium, and these particles combine closely with the protective film and are embedded into bulk magnesium alloy. Fig.2 shows the surface morphology of a sample in 0.1% SF₆ held at 680 °C for 10 min. It can be seen from Fig.2 that there are many concavities on the surface film inside which the grain size is smaller compared with that of the other flat areas.

2.2.2 Composition of surface film

The EDS results listed in Table 1 and Table 2 indicated that the concavities in Fig.2 are mainly composed of magnesium and fluorine elements with a small amount of oxygen, which is in accordance with the composition of those particles on the interface view. It can be concluded that these particles from the interface

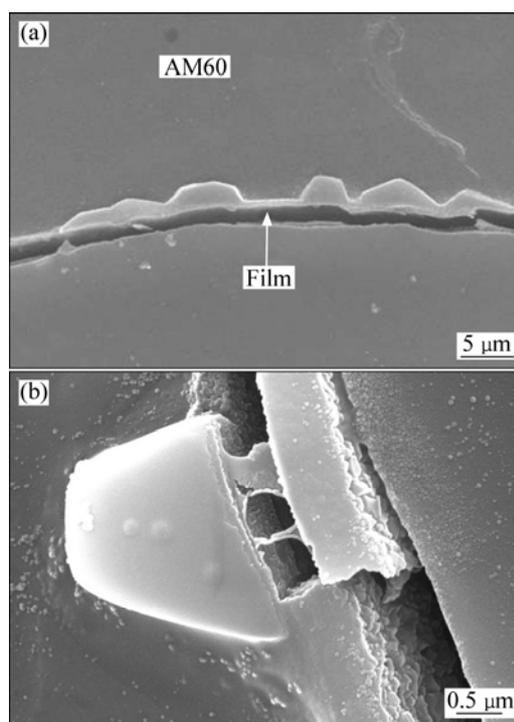


Fig.1 SEM images of cross-section sample with 0.3% SF₆ held at 680 °C for 10 min (a) and particles between bulk magnesium alloy and MgO film (b)

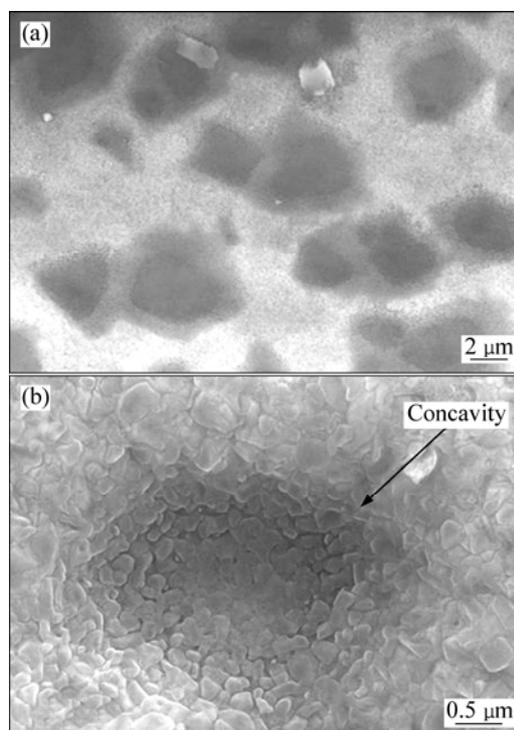


Fig.2 SEM images of surface morphology of sample in 0.1% SF₆ held at 680 °C for 10 min (a) and concavity with finer grains (b)

view are MgF₂ corresponded to the concavities (dark areas) from surface observation as shown in Fig.3.

However, the EDS results also show that the compositions of other areas (bright areas) from surface observation are Mg, O and F with large concentration of oxygen element, and all XRD patterns of the samples contain the peaks of MgF_2 and MgO compounds, which indicates that these films are composed of MgF_2 and MgO phases with some particles contained MgF_2 form at the interface between the oxide film and the bulk magnesium.

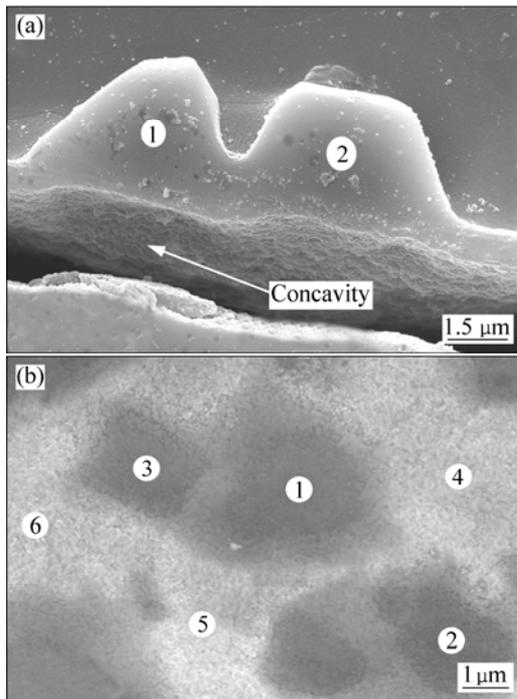


Fig.3 EDS analyses for concavities and particles as well as flat areas on surface

Table 1 Particle composition (mole fraction, %)

Point in Fig.3(a)	Mg	F	O
1	31.6	64.1	4.4
2	34.1	63.7	2.1

Table 2 Film composition (mole fraction, %)

Point in Fig.3(b)	Mg	F	O
1	28.2	66.6	5.2
2	32.4	62.6	5.0
3	34.9	59.6	5.5
4	59.3	23.6	17.1
5	53.4	29.5	17.0
6	58.2	26.2	15.6
Macro	44.0	44.8	11.3

2.2.3 Film appearance at different exposure time

Fig.4 shows the surface morphology of samples in

0.1% SF_6 held at 680 °C for different exposure time. It can be seen from Fig.4 that the surface morphology changes greatly with the increase of the holding time. At 3 min, the surface film contains mainly MgO with a small concentration of MgF_2 . As the holding time increases to 30 min, the number of particles containing MgF_2 in the film increases greatly and keeps almost unchanged even as the holding time increases to 60 min.

It is known that magnesium oxide film does not protect the molten magnesium from further oxidation due to the mismatch of the mole volume of magnesium oxide and the mole volume of the equivalent amount of magnesium (the Pilling-Bedworth ratio) [10–11]. Since the Pilling-Bedworth ratio of the magnesium oxide film is 0.73 [12], magnesium ion can still react with oxygen on the surface of samples by diffusing through the porous oxide film. When some particles containing MgF_2 with a Pilling-Bedworth ratio of 1.29 [12] formed in the film, the film becomes dense and can protect the melt effectively.

In the early stage of the experiment, the film only containing MgO forms on the surface of samples by the prior reaction between magnesium and oxygen in the atmosphere. However, since MgF_2 is a more stable phase than MgO in the system from thermodynamic point of view [13], magnesium ion can continually react with fluorine to form MgF_2 and the concentration of MgF_2 in the film increases with the increase of the holding time. The fluorine atoms can also diffuse through the surface film to the interface between the oxide film and bulk magnesium to form MgF_2 particles until the diffusion is stopped by the particles. Meanwhile, the diffusion of magnesium ion to the film surface is also prevented.

3 Vacuum assisted melting technology for magnesium alloys in sealed furnace

3.1 Introduction

Magnesium and magnesium alloys are usually protected under an open condition with the cover gases continually flowed through the melting furnace. It wastes a large quantity of cover gases and has a bad impact on the atmosphere and the operator. Based on the understanding of the protection mechanism of the cover gases containing SF_6 , a vacuum assisted melting technology for magnesium alloys in a sealed furnace was proposed to directly form a layer of MgF_2 during the melting process.

3.2 Experimental method

Fig.5 shows a schematic diagram of the melting furnace. Pressure in the furnace can be pumped to below 6 Pa and the pressure rising rate is below 0.67 Pa/h.

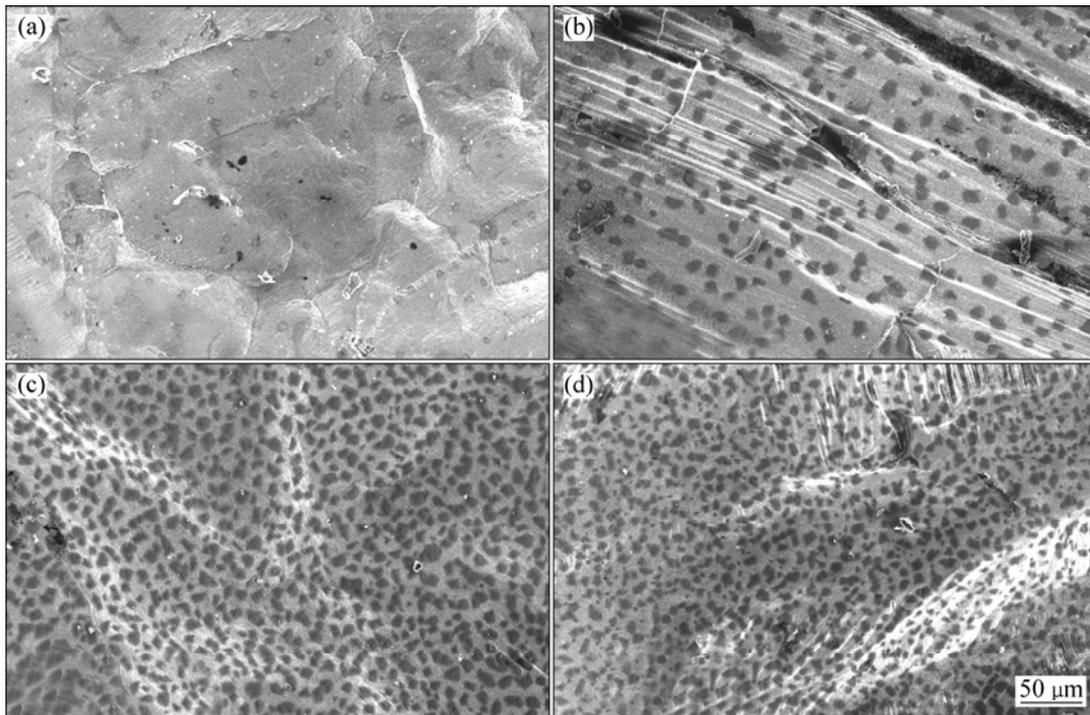


Fig.4 SEM images of surface morphology of samples in 0.1% SF₆ held at 680 °C for different exposure time: (a) 3 min; (b) 10 min; (c) 30 min; (d) 60 min

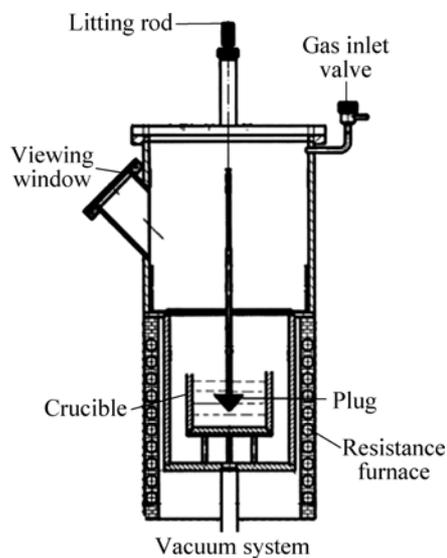


Fig.5 Schematic diagram of melting furnace

Firstly, the pressure in the furnace was pumped to a vacuum level of 6 Pa, and then, the gas mixture of HFC-134a or SF₆ and N₂ controlled by flow meters was filled into the furnace. Finally, the gas inlet valve and the flow meter were closed when the pressure in the furnace was increased to 10⁵ Pa. When the protective effect of gas mixture of HFC-134a, N₂ and air was considered, the gas mixture of HFC-134a and N₂ would be filled into the furnace first to a certain pressure level, and then the air

was filled until the pressure in the furnace was increased to 10⁵ Pa. The protection effect on molten magnesium alloys and the impact of adding air into the atmosphere on the surface morphology and composition in the film were studied.

3.3 Experimental results and discussion

3.3.1 Protective effects

Table 3 lists the protection effects on molten magnesium alloy at different melting temperatures and cover gases contents. It can be seen from Table 3 that, all the protective atmospheres containing different cover gases can perform excellent protection on molten magnesium alloy at 760 °C, and the minimum concentration of HFC-134a in the protective atmosphere for protection on the molten magnesium is 0.003%.

Table 3 Protective effect of melting temperature and cover gases content on molten magnesium alloy

Temperature/°C	Volume fraction of HFC-134a/%	Protective effect
760	0.003,0.01,0.1, 0.25,0.5,1.0	Protected
800	0.01	Protected
830	0.01	Protected
845	0.01	Protected
856	0.01	Little evaporation
856	0.01	Protected

Protective effect is reduced by the increase of melting temperature when the concentration of cover gases is fixed at a constant value, and when the concentration of cover gases is increased, the effective protective temperature on melt is increased with the highest protective temperature up to 856 °C.

3.3.2 Film appearance and structure

Fig.6 shows the surface morphologies of samples with 0.01% HFC-134a and different air pressures held at

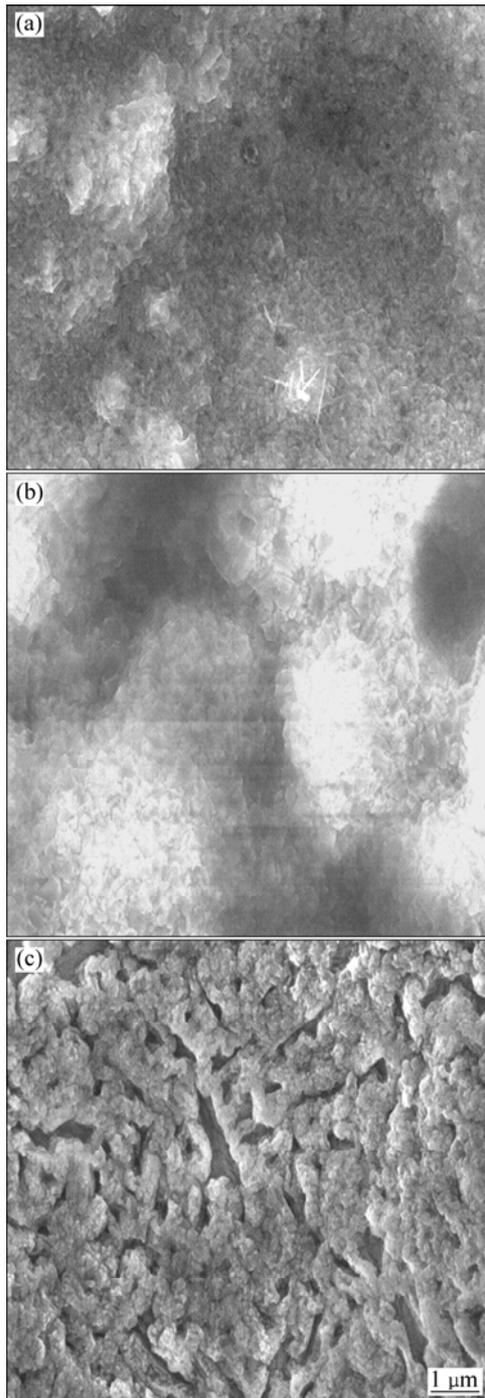


Fig.6 SEM images of surface morphology of samples with 0.01% HFC-134a under different air pressures at 760 °C for 2 h: (a) 2.3 kPa; (b) 8 kPa; (c) 80 kPa

760 °C for 2 h. It can be seen from Fig.6 that the roughness of the surface film is increased with the increase of air concentration in the cover gases, and finally the surface film presents irregular net structure under atmosphere with 80% air.

3.3.3 Composition of surface film

Table 4 lists the EDS results of the surface film in Fig.6. The oxygen concentration in the film increased with the reduction of the carbon content when the air concentration in the gas mixture was increased, as more reactions happened between magnesium and oxygen, and the carbon in the film further reacted with oxygen to form CO and CO₂, which went into the atmosphere. Fig.7 shows the cross-section view and element backscattered electron image of a sample in 0.3% SF₆ and N₂ held at 690 °C for 2 h in the sealed furnace. Table 5 lists the EDS results of the surface film. It can be seen from Table 5 that a surface film of pure MgF₂ is formed on the surface of magnesium alloy, having excellent protection performance on molten magnesium alloy.

Table 4 EDS results of surface films in Fig.6 (mole fraction, %)

Pressure/kPa	Mg	F	O	C	Al
2.3	32.78	52.96	11.58	0.98	2.7
8	31.84	52.77	14.53	–	0.86
80	33.08	39.49	26.62	–	0.81

Table 5 EDS results of surface films in Fig.7 (mole fraction, %)

Position	Mg	F	Al
1	60.62	–	39.38
2	30.72	69.28	–

4 Studies on substitutes for SF₆

Table 6 lists the global warming potential values of SF₆ and potential substitutes for SF₆. It can be seen from Table 6 that HF-134a and HFE7100 gases still have a high GWP value and can only be used as the transitional substitutes for SF₆. The magnesium industry is urgent to find new substitutes for SF₆ with low GWP value and short atmospheric lifetime. As shown in Table 6, two kinds of F containing gases have a low GWP values and relatively short atmospheric lifetime. Their protecting effects on molten magnesium alloys were studied and the results showed that the cover gas mixture containing either of the two gases could perform a well protection on molten magnesium alloy from further oxidation in the sealed furnace, which shows that these two gases could be potentially used as substitutes for SF₆ in magnesium industry.

On the other hand, before SF₆ was widely used in

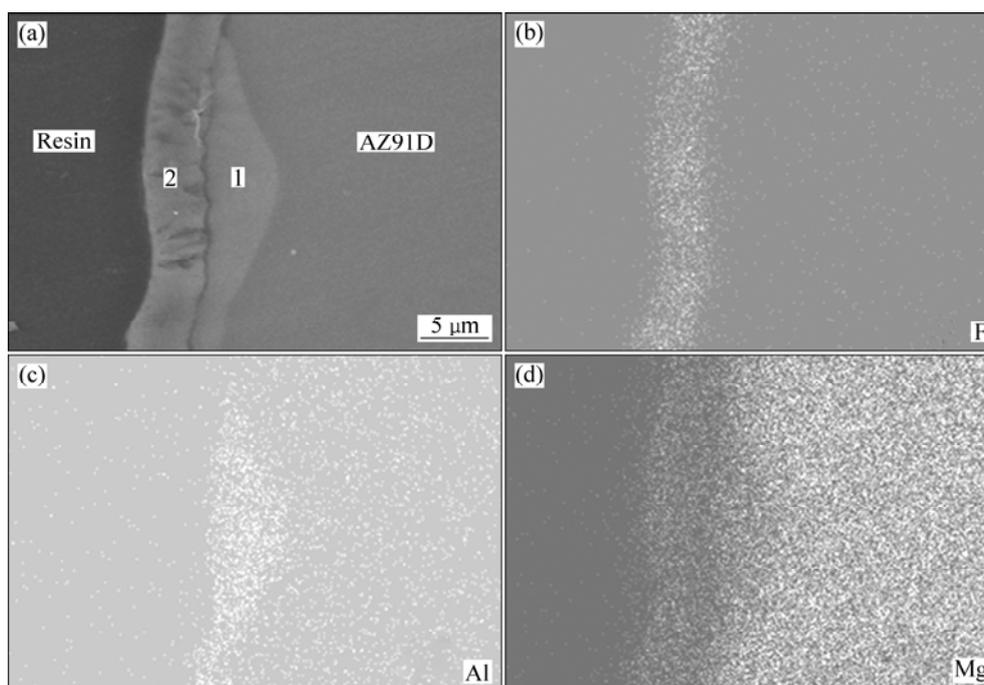


Fig.7 Mapping results of surface film: (a) SEM image of cross section; (b) Mapping result of fluoride; (c) Mapping result of aluminium; (d) Mapping result of magnesium

Table 6 GWP value of SF₆ and potential substitutes for SF₆[14–16]

Substitute	Compound	Lifetime/a	GWP (per 100a)
Benchmarks	CO ₂	100–150	1
	SF ₆	3 200	23 900
Alternatives	CF ₃ CH ₂ F-HFC134a	13.6	1 600
	C ₄ F ₉ OCH ₃ -HFE7100	4.1	320
New gases studied	CF ₃ I	20	5
	CF ₂ =CFCF ₃	< 10	~1

magnesium industry, SO₂ was commonly used as the protective cover gas, but the protective mechanism of SO₂ on molten magnesium alloy has not yet been clearly understood. Therefore, studies on protective mechanism of SO₂ on molten magnesium alloy will provide positive theoretical basis for finding new substitutes for SF₆.

5 Conclusions

1) Compact and coherent surface film containing MgO and MgF₂ forms on the molten magnesium alloy in the protective atmosphere containing SF₆. The protective film is composed of MgO, and with the increase of the holding time, particles containing MgF₂ forms on the interface between the oxide film and bulk magnesium by fluorine ion diffusing through the porous magnesium oxide film and reacting with magnesium ion, which makes the oxide film protective.

2) A vacuum assisted melting technique in a sealed furnace to directly form a layer of MgF₂ was presented. HFC134a/N₂ atmosphere is suitable for protecting AZ91D magnesium alloy in the sealed furnace. The minimum concentration to protect magnesium melt at 760 °C is 0.003% and no continuous inlet of the cover gas mixture is needed in the sealed furnace.

3) CF₃I and C₃F₆ have low GWP value and short atmospheric lifetime, and could also perform excellent protection on magnesium and magnesium alloy in the sealed furnace, which shows that they are potential substitutes for SF₆ in magnesium industry. The protection mechanism of SO₂ on magnesium melt needs further study for other substitutes of SF₆.

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