Protective Properties of SF₆ under Various Carrier Gases for the Protection of Molten Mg

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Molten magnesium can oxidize rapidly in atmospheres containing oxygen. During the casting and handling of molten magnesium, it is essential to protect the melt from ignition. The protective gas normally contains air and/or CO₂, and with a small amount of an inhibiting agent. This study examined the minimum amount of SF₆ gas needed depending on the type of carrier gas, as well as the effects of the melt temperature, exposure time and SF₆ concentration on the surface film of molten magnesium. The analysis methods of the surface film included the XPS/depth profile and SEM/EDS. The minimum amount of SF₆ gas concentration determined over a wide a range of different carrier gases, such as air, N₂ and CO₂. The surface film thickness decreased with increasing SF₆ concentration under all conditions, such as the melt temperature, exposure time and different carrier gas. [doi:10.2320/matertrans.M2012057]

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1. Introduction

Magnesium has the lowest density among existing common alloys and is very important for reducing the weight of transportation vehicles, such as automobiles and airplanes.^{1,2)} On the other hand, its low ductility and corrosion resistance compared to other light materials has limited its use. Many of these limitations have been overcome with the advances in alloy and refining technology.³⁻⁶⁾ Recently, the automobile industry has become greatly interested in the applications of magnesium. Automobile industries around the world are developing low polluting and low mileage cars to respond to environmental restrictions. Therefore, many parts in automobiles are becoming lighter to reduce energy use⁶⁻⁸⁾ and solve environmental issues. Many materials have been developed for various automobile parts with high strength and high tenacity, such as steering wheel cores and seat frames.³⁻⁹⁾ On the other hand, magnesium exhibits poor room temperature formability because of its hexagonal close-packed (hcp) crystal structures, which limits its use.²⁾ Accordingly, magnesium is produced mostly by melting and casting. In addition, molten magnesium ignites rapidly in atmospheres containing oxygen. The ignition temperature of magnesium is approximately 3273 K and the surface of molten magnesium is ignited continuously in an oxygen containing atmosphere. Therefore, during the casting and handling of molten magnesium it is necessary to protect the melt from continuous ignition. The current method of molten magnesium protection utilizes a protective gas mixture that results in the formation of a thin surface film (oxide film) on the molten magnesium surface. The protective gas normally contains air and/or CO₂, combined with a small amount of an inhibiting agent.¹⁰⁾ Small additions of certain gases to dry air reduce the oxidation rate to an acceptable level. A number of fluorine-containing compounds for this application were suggested and patented by Reimers in 1934.¹¹⁾ The most additive commonly used in the

magnesium industry today is sulphur hexafluoride (SF₆). SF₆ gas is a protective gas with good protection performance.¹²⁾

In addition, it is non-toxic, non-corrosive and provides effective protection of molten magnesium at concentrations as low as 0.1%. On the other hand, SF₆ has a high GWP-factor (Global Warming Potential) of 23,900. Therefore, it has come under intense environmental scrutiny. By the Kyoto Protocol, the use of SF₆ was reduced from February 2005. As a result, the magnesium industry has been looking for a suitable replacement. Hydrofluorocarbon (CF₃CH₂F, HFC-134a) was recently developed for magnesium melt protection by the Research Center in Australia. GWP-factor of HFC-134a is 18 times lower than SF₆ but it is still expensive. Another replacement gas is SO₂, which was the gas most commonly employed before the introduction of SF₆ in the 1970s. SO₂ is cheap, because it is easy to extract from gas mixtures because of its high solubility in water. On the other hand, it is toxic and corrosive. Additionally it can cause acid rain. Therefore, SF₆ has been employed in the magnesium industry, and it is necessary to reduce the amount of protective gas. SF₆ should not be used alone and it needed for molten magnesium. Therefore, SF₆ is mixed with a carrier gas such as dried air and CO₂. No detailed examinations were reported on the SF₆ concentration depending on the carrier gas.

This study examined the minimum amount of SF₆ gas the melt temperature, and exposure time. The surface film was analyzed by XPS/depth profiling. Also, the microstructure and component analysis of surface film was analyzed by SEM and EDS.

2. Experimental Procedure

2.1 Experiment apparatus

Figure 1 shows a schematic diagram of the apparatus. A mild steel crucible was located in center of the furnace. The feeding pipe for SF₆ gas was located at the top of the crucible. Several mass flow meters were used to control the composition and flow rate of the protective gas.

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Fig. 1 A schematic diagram of the experiment apparatus for the melt protection of molten magnesium: (a) furnace and (b) crucible (mm).

Table 1 Experimental conditions on the protection properties of molten magnesium.

Temp. [K]	Gas species			Exposure time [ks]
	Total mixture gas: 83 mL/s		Concentration [%]	
	Protective gas	Carrier gas		
953	SF ₆	N ₂	0.02, 0.03, 0.04,	0.6, 1.2, 1.8, 3.6, 7.2
973		CO ₂	0.05, 0.075, 0.1,	
1003		Dry air	0.125, 0.15	

2.2 Experimental conditions and procedure

The protection behavior of SF₆ on the surface film of molten magnesium under different atmospheres was evaluated using pure magnesium. Pure magnesium (~350 g) was melted in a crucible. The surface area of the molten magnesium was 100 mm². The molten magnesium was exposed to 0.02–0.15% SF₆ gas in air, N₂ and CO₂ mixtures. The exposure time (injection time of SF₆) was counted after removing the initial surface film from the top of molten magnesium by using scraper. The surface film formation in the top of molten magnesium was examined by changing the exposure time (0.6, 1.2, 1.8, 3.6 and 7.2 ks) of SF₆. Table 1 lists the experimental details in this study. After the end of experiment, molten magnesium was solidified carefully to obtain a surface film under air cooling conditions. For depth profile of XPS and SEM/EDS analyses, the specimens were cut from the ingot, which were located at the top of the solidified magnesium. The specimens were cut to a slice of 3 mm × 3 mm × 3 mm using a micro cutting machine. The specimens were removed from relatively flat areas because cross-sections of the samples by depth profiling requires a flat surface. The chemical characterization of the surface films was performed using X-ray photoelectron spectroscopy (XPS) and the film thickness was determined by depth profiling in conjunction with Auger electron spectroscopy (AES). XPS was performed using a K-alpha model (Thermo Fisher, UK Co.). The XPS was set

Fig. 2 Surface films formed on molten magnesium at 973 K for 0.6 ks of exposure to (a) 0.1%SF₆ with CO₂ carrier gas and (b) 0.01%SF₆ with CO₂ carrier gas.

at an energy of 117.4 eV and the step size of 0.05 eV was applied. The depth profile was analyzed at intervals of 90 s and the sputter rates of 1 nm/s. In addition, SEM/EDS analyses were performed using the S-4300 model of HITACHI Co.

3. Results and Discussion

3.1 Protection properties of molten magnesium

As shown in Fig. 2, a high SF₆ concentration is needed for the effective protection of molten magnesium at the higher temperature. The protection properties of molten magnesium were analyzed by varying of carrier gas. The research was performed with the aim of reducing the consumption of SF₆. As shown in Fig. 2, a high SF₆ concentration is needed for the effective protection of molten magnesium at the higher temperature. This is due to the vapor pressure of magnesium. The vapor pressure of magnesium increased from 602 Pa at 953 K to 1220 Pa at 993 K. In addition, the protection properties of surface layer on the molten magnesium differed depending on the carrier gas, even when a constant SF₆ concentration was used.

Fig. 3 For protecting ignition of molten Mg, minimal concentrations of SF_6 under different carrier gases and melt temperatures; (a) 953 K (b) 973 K, and (c) 1003 K.

For example, the ignition of molten magnesium was examined according to the changing carrier gas under constant conditions with 0.2% SF_6 and a melt temperature of 973 K. When melting magnesium, the use of dry air as a carrier gas resulted in an intense ignition reaction, such as white light, whereas local ignition occurred in both sides of the crucible when N_2 was used as the carrier gas. On the other hand, CO_2 carrier gas had a good protective effect on molten magnesium.

Therefore, to minimize the economic and environmental damage, the concentration of SF_6 gas was quantified depending on the type of carrier gas. The protective effects of surface layer on the molten magnesium were in the following order: $\text{CO}_2 > \text{N}_2 > \text{dry air}$ in a state mixed with SF_6 , as shown in Fig. 3. Figure 3 shows the minimum amount of SF_6 depending on the type of carrier gas and the temperature of molten magnesium. The grey part in Fig. 3 shows that magnesium was ignited during melting. When the molten magnesium was partially ignited during melting, the graph was displayed as an diagonal line. Finally, the straight line was displayed as good protection properties of molten magnesium during melting.

Magnesium could be successfully melted using the proper protective gas. Figure 2(a) showed that the surface of the specimen was clean. On the other hand, surface of the ignited specimen was quite rough, as shown in Fig. 2(b). Table 2 lists the effects of these parameters on the protective effect and film thickness. Figure 4 shows SEM/EDS and XPS

Table 2 Properties of the surface film in molten magnesium.

Parameters	Surface film thickness	Order of surface film thickness	Protective effect
Increasing temp.	Increasing	$\text{Air} > \text{N}_2 > \text{CO}_2$	Similarity at SF_6 gas concentration of over 0.075%
Increasing SF_6 concentration	Decreasing		
Increasing exposure time	Increasing		

binding energy under a 0.6 ks of exposure time and 1.5% SF_6 concentration. The surface was covered by a uniform and dense surface film consisted of magnesium oxygen, fluorine and carbon. Surface compositional analysis by EDS revealed Mg, O and F. In addition, carbon was observed when CO_2 was used as a carrier gas. The existence of carbon indicates to a reaction of Mg with carbon dioxide in the carrier gas.

For the more detailed study, the film composition and distribution of magnesium was examined using different carrier gas and various SF_6 concentrations.

3.2 Surface film properties of molten magnesium at different temperatures

Analyses of the surface films produced under controlled conditions showed that only the chemical species present were carbon, oxygen, magnesium and fluorine. To examine the depth characteristics of surface films, the film thickness

Fig. 4 Micrographs of the surface films formed under a 1.5%SF₆ concentration and exposure time for 0.6 ks. (a) Carrier gas is air, (b) carrier gas is N₂ (c) carrier gas is CO₂, and (d) binding energy of CO₂ carrier gas.

was analyzed by depth profiling through ion-beam etching in conjunction with AES. The AES depth profile of the surface film revealed the existence of magnesium, fluoride, oxygen and carbon. With the changes in depth, the relative element concentrations changed at the interface between the film and bulk magnesium interface. For example, Fig. 5 shows the EDS and AES results for the sample produced under a protective gas containing N₂ and 1% SF₆ at 973 K for 0.6 ks. Depth profile analysis showed that the concentration of each element remained relatively constant from the outer surface

of the films to the interface between the films and bulk magnesium. According to Fig. 5, the magnesium and oxygen concentration was very high at the outer surface of the protective film, and decreased sharply to a very low level after approximately 1.2 ks sputtering. When the ion-beam sputtering technique was used to profile the film, the thickness was calculated by multiplying the sputtering time by the sputtering rate. The sputtering rate in this experiment was 1.67 nm/s. The sample thickness was approximately 1.5–2 μm, which is consistent with SEM analysis.

Fig. 5 Film concentration vs. film exposure time profiles. The sample was produced under a protective gas N_2 and 1% SF_6 at 973 K for 0.6 ks. (a) EDS and (b) AES analysis.

Fig. 6 Film thickness vs. film exposure under different melt temperature: (a) 953 K (b) 973 K, and (c) 1003 K.

In this protection experiment, the compositions of the protective gas, melting temperature and exposure time were the most important factors that could affect the surface films. The trend of the reaction was determined by keeping two of the three parameters constant and changing the other in the experiments. Figure 6 shows the change in surface film thickness depending on the exposure time. The surface film thickness was determined by depth profile and it decreased with increasing SF_6 concentration, whereas the surface film thickness increased with increasing melt temperature and exposure time. These data showed the same tendencies regardless of the carrier gas. There was no segregation of

particular elements from the bulk to the surface of the protective film. The rate of surface film growth decreased with increasing film thickness. As shown in Fig. 7, the linear relationship indicates the parabolic rate of film growth as follows:

$$(\text{thickness})^2 = kt$$

where, k is the parabolic rate constant ($\mu m^2/ks$) and t is the time exposed to protective gas.

In addition, the surface film thickness was varied by the type of carrier gas. The use of a carrier gas with dry air resulted in the thickest surface film, whereas the CO_2 carrier

Fig. 7 Film thickness vs. exposure time: protective gas of CO₂ containing 1%SF₆ at 973 K.

gas resulted in the thinnest surface film. The order of the thickness was CO₂ < N₂ < dry air. Therefore, when the longer time is required for the refining and melt process of magnesium, an increase of the SF₆ concentration in the gas, is needed to decrease the surface film thickness.

Recently, as a new magnesium production, a continuous process from the Pidgeon to the refining process was examined to produce high-quality magnesium with the mass production. Because the refining process requires a large amount of protective gas, the use of CO₂ and N₂ as the carrier gas in the refining process will offer good protection to molten magnesium and reduce the consumption of SF₆. The selection of the appropriate protective gas and concentration are important because the thicker surface film causes a loss of molten magnesium.

3.3 Surface film composition

The peak positions from the XP spectra were used to determine the chemical binding between the elements in the surface film. The measured values correspond to the peak position for MgO and MgF₂.¹³⁾ Figures 8 and 9 show the fluorine, oxygen, carbon and magnesium content of the surface film melted under N₂ and CO₂ carrier gas, respectively. Figure 8(a) shows the fluorine, oxygen, carbon and magnesium contents. The film melted at various temperatures under N₂ carrier gas and a constant SF₆ concentration of 1.25% for 0.6 ks. The magnesium content decreased with increasing the temperature. On the other hand, the oxygen and fluorine content increased with increasing temperature but the decrease in oxygen content was minor and insignificant. This shows that the reaction of MgF₂ increased at the higher temperature. Therefore, the thickness of surface film increases at the higher temperature. Figures 8(b) and 8(c) showed an increase in fluorine content for the linear exposure time and at the higher SF₆ concentration. This shows that the MgF₂ content is affected by the melt temperature, exposure time and SF₆ concentration. This result is similar to results reported by Cashion *et al.*,¹⁰⁾ who showed that the fluorine content of the surface film increased with increasing SF₆ concentration. Nevertheless, there were some differences in the fluorine content in the surface film with increasing exposure time and SF₆ concentration, which were attributed to differences in the experimental conditions, such as the type of carrier gas, humidity of laboratory, total gas mixture etc.

Fig. 8 Composition of the surface films produced under carrier gas of N₂. (a) The exposure time was 0.6 ks and SF₆ concentration was 1.25%, (b) Mg was melted at 1003 K and the SF₆ concentration was 1.5%, and (c) Mg was kept at 973 K for 0.6 ks.

Figure 9 shows the fluorine, oxygen, carbon and magnesium content in the surface film melted under carrier gas of CO₂. This is similar to a study of N₂ carrier gas. Therefore, Figs. 9(a)–9(c) show that the fluorine content increased with increasing melt temperature,^{11,12)} exposure time and SF₆ concentration. There were some differences between the N₂ and CO₂ carrier gases. In addition, no carbon was found in the case of carrier gas N₂. On the other hand, the carbon, fluorine and oxygen contents in the case of the CO₂ carrier gas were generally lower than those with N₂ carrier gas.

From these observations, the following can be suggested as a mechanism for surface film formation in oxidizing fluorine-containing atmospheres. Owing to the rapid kinetics and abundance of oxygen in the protection gas, magnesium reacts rapidly with oxygen to form a thin MgO film on the surface. The reaction is considered as:

In addition, the existence of carbon is explained by a reaction of Mg with carbon dioxide in the carrier gas.

Fig. 9 Composition of the surface films produced under CO₂ carrier gas and different conditions. (a) Exposure time was 0.6 ks and the SF₆ concentration was 1.25%, (b) Mg melting temp. was 1003 K and the SF₆ concentration was 1.5%, and (c) Mg melting temp. was 973 K and the Exposure time is 0.6 ks.

Finally, the reaction between magnesium and magnesium fluoride can occur according to the following reaction:¹³⁾

- (1) Concentration of SF₆ gas is low: there are no reactions between Mg and SF₆.

- (2) Concentration of SF₆ gas is increased: there are some reactions.

The rate of oxidation is reduced once a dense fluorine-containing MgO film is formed, as shown in Fig. 10. In addition, a small amount of SF₆ was consumed. Figure 11 shows the Ellingham diagram of compounds for the protection of molten magnesium at 101325 Pa. The diagram gives the Gibbs free energy for formation of the various species in Table 3 as a function of temperature. The data of

Fig. 10 Comparison on variation of thickness and composition of surface film with exposure time under carrier gas N₂ and 0.15% of SF₆ at 973 K.

Fig. 11 Ellingham diagram of magnesium compounds (pressure: 101325 Pa).

Table 3 Physical properties of magnesium and magnesium compounds, d = decomposed.

Compound	Molar mass (g/mol)	Melting point (K)	Density (g/cm ³) at 300 K	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔH_m° (kJ/mol)
Mg (s)	24.3	923	1.7	0	0	9
MgF ₂	62.3	1669	3.0	-1123	-1070	58
MgO	40.3	3073	3.6	-601	-570	77
Mg ₃ N ₂	101.0	d800	2.7	-461	-401	

the diagram was calculated using the FactSage package (version 6.2).¹⁴⁾ In Table 3, the physical properties of magnesium and various magnesium compounds are presented. The values for ΔG_f° are given for the formation of the compounds from standard states at 298 K. The values vary in different data collections, however the values presented here are taken from the identical data source.¹⁵⁾ From the Ellingham diagram, fluoride was found to be the most stable compound in the Mg-based binary systems.

Therefore, the thickness of a surface film on molten magnesium decreased in the case of CO₂ carrier gas. A layer of MgO is formed on the melt surface when molten magnesium was exposed to a protective gas mixture containing SF₆ and oxygen, N₂ and CO₂, due to the initial reaction between oxygen and magnesium. The immersion

experiments showed that under an SF₆ gas environment, the molten magnesium wets the solid magnesium oxide. When MgO particles float on surface, this wettability causes the effect that the magnesium metal is drawn up to the MgO particles by capillary action.^{16,17)} Capillary forces act on the adjacent oxide particles, pulling them together to form a cohesive “raft” of MgO particles on the melt surface. This minimizes the exposed surface area of the melt, reducing further magnesium vaporization and halting the subsequent rapid oxidation and ignition. The decomposition of SF₆ provides the fluorine needed for the formation of MgF₂. This fluoride can also occupy sites within the product layer. The concept of a surface layer consisting of solid phases (MgO and MgF₂) bound in a liquid matrix (molten magnesium) is consistent with the flexibility exhibited by the protective film formed on molten magnesium exposed to an air, N₂ and CO₂/SF₆ protective gas.^{16,17)} Because, the CO₂ carrier gas is denser than N₂ and air carrier gases, it reacts effectively with Mg melt to form MgO particles. They are effective in protecting molten magnesium.

In this study, the composition of protective gas, melting temperature and exposure time were found to be the three most important factors on melt protection with different carrier gases.

4. Conclusions

This study examined the protective properties of molten magnesium using SF₆ gas in the carrier gas. The minimum SF₆ gas concentration was determined using air, N₂ and CO₂. The composition of the protective gas, melting temperature and exposure time were the three most important factors for melt protection with carrier gases. The surface film thickness decreased with increasing SF₆ concentration under all the conditions, such as temperature, exposure time and carrier gas. In particular, air as a carrier gas produced the thickest surface film, whereas CO₂ produced the thinnest. The exposure time had a significant effect on the surface film thickness. Higher temperature resulted in an increase in surface film thickness and a higher fluorine content in the film. Because a high temperature will accelerate the reaction between magnesium and fluoride, leading to an increase in MgF₂ concentration in surface films, these results show that

the protective film consisted of MgO and MgF₂, and the concentrations of these elements are affected by the SF₆ gas concentration and melt temperature. The surface film thickness causes the evaporation loss of molten magnesium. Therefore, selection of the appropriate protective gas and concentration depending on the process is important. The concentration of SF₆ in CO₂ can be reduced to a level of approximately 0.025, 0.03 and 0.04% at 953, 973 and 1003 K, respectively.

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