

Oxidation of MgF₂ Particles in SF₆/Air Atmosphere at High Temperatures

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Abstract. High temperature oxidation of MgF₂ particles in the atmosphere of air containing different concentrations of SF₆ were studied by using XRD and EDS. The results show that the oxidation of MgF₂ in SF₆/air atmosphere was mainly related to the concentration of SF₆, temperature and reaction time. In the atmosphere of air containing higher SF₆ concentration, MgF₂ underwent a very weak oxidation. With the decrease of SF₆ concentration, the increase of temperature and the prolongation of reaction time, the degree of MgF₂ oxidation increased. The particle size of MgF₂ and the mixed gas flow have little effect on the high temperature oxidation of MgF₂. The results can provide a theoretical basis for the study of the protection mechanism of SF₆ gas on magnesium and its alloy melt.

1. Introduction

Magnesium and its alloy are being widely used in the automotive industry, aerospace industry, 3C products and other fields due to their excellent properties such as low density and high specific strength. However, magnesium is a very active element. It has extremely high affinity for oxygen and high vapor pressure, which causes molten magnesium to rapidly oxidize in air. Therefore, it is necessary to take measures to prevent the melt from oxidizing or burning in the process of melting and casting operations. Many methods have been investigated to inhibit the oxidation of molten magnesium and its alloy in air. Among them, the protection method of SF₆ gas is considered to be the most effective method [1]. The protection of SF₆ gas for magnesium and its alloy melt is based on a dense MgF₂ and MgO composite protective film on the surface of the melt. MgF₂, as a major component of the film, plays a key role in the protection of magnesium melt against its combustion by SF₆ and other fluorine-containing gases [2-4].

It is generally believed that MgF₂ is a stable compound under normal circumstances. However, some studies have found that MgF₂ become less stable at high temperatures in air and it has a tendency to change to MgO [5, 6]. In a previous study, we also found this phenomenon [7,8]. In SF₆/air atmosphere, whether MgF₂ will oxidize at high temperatures and what rule it follows if the oxidation occurs, these problems are unclear. In view of the important role of MgF₂ in the protection of magnesium melt by SF₆, it is necessary to study the high temperature oxidation behavior of MgF₂ in the atmosphere. In this work, the oxidation characteristics of MgF₂ particles in SF₆/air atmosphere at high temperatures were studied. The effects of the concentration of SF₆, temperature, and reaction time on the oxidation characteristics were investigated. The purpose of this paper is to elucidate the

conditions and laws of oxidation reaction of MgF_2 in SF_6 /air atmosphere, which will provide a theoretical basis for the optimization of protection conditions of SF_6 gas for magnesium melt.

2. Experimental

The main raw materials used in the tests were high purity MgF_2 powder and SF_6 gas. The composition of MgF_2 powder (wt%) is MgF_2 99.99, Na 0.001, Fe 0.001, Si 0.002, Ca 0.002, SO_4^{2+} 0.002, H_2O 0.001, Pb less than 0.001. The composition of SF_6 gas (wt%) is $\text{SF}_6 \geq 99.999$, $\text{H}_2\text{O} \leq 0.0001$.

The oxidation of MgF_2 powder was studied by means of a high-temperature test method. The tests were carried out in a SK-G05123K tube furnace in the SF_6 /air atmosphere. The apparatus includes a SF_6 and air supply device, a $\Phi 110 \times 420$ mm tube furnace and a $\Phi 50 \times 1000$ mm silica-glass tube with an alumina crucible. In experiment, air and SF_6 were mixed in the required proportion and then continuously fed into the silica-glass tube at 200 ml/min. After purging inside the silica-glass tube using the gas mixture for at least 1 h, MgF_2 sample was placed in the crucible, and then heated to the desired temperament at a rate of $8^\circ\text{C}/\text{min}$ and hold for a certain time. After that, the sample was cooled down to room temperature, and stored in a dryer for the X ray diffraction (XRD) analysis and energy dispersive spectrometer (EDS) analyses.

XRD analysis of the oxidized MgF_2 samples was carried out on a Rigaku Ultima IV X-ray diffractometer with a Cu-K α source operated at 40 kV and 40 mA. The elemental composition of the oxidized MgF_2 samples was investigated by an EDAX Genesis APEX energy dispersive spectroscopy assembled in Quanta FEG 250 field emission scanning electron microscope.

3. Results and discussion

3.1. Effects of SF_6 concentration on MgF_2 oxidation

Figure 1 presents the XRD analysis results of MgF_2 samples oxidized in the atmospheres of air containing different concentrations of SF_6 for 2 h at 1000°C . It can be seen that in the atmospheres of air containing 1% SF_6 or 0.5% SF_6 , only the MgF_2 peak was detected. As the concentration of SF_6 was reduced to 0.1%, one new peak attributed to MgO occurred. When the concentration of SF_6 decreased from 0.05% to 0.01%, another MgO peak appeared outside the peak of SF_6 concentration of 0.1%. The results indicate that with the decrease of SF_6 concentration, the oxidation degree of MgF_2 increased.

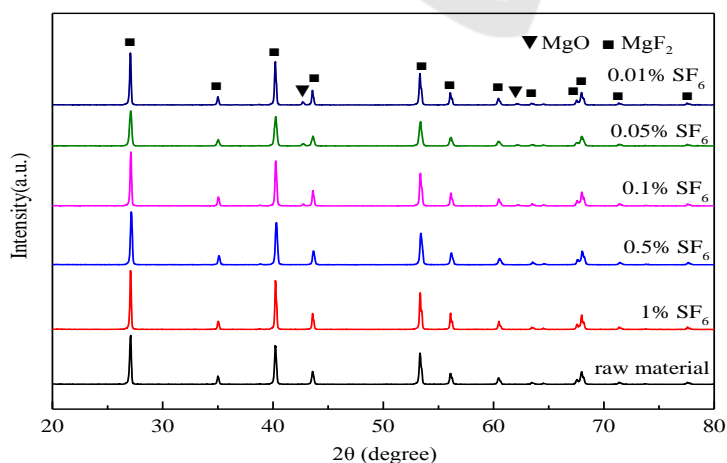


Figure 1. XRD analysis results of MgF_2 samples oxidized in air containing different concentrations of SF_6 at 1000°C for 2 h.

The samples were also analyzed by EDS and the results are shown in Table 1. We can see from the table that with the decrease of SF₆ concentration, the content of F element decreased and the content of O element increased, which indicates that the oxidation degree of MgF₂ increased with the decrease of SF₆ concentration. In addition, EDS detected a small amount of O element at SF₆ concentrations of 0.5% and 1%, indicating that the sample contained a small amount of MgO, but XRD did not detect the presence of MgO. The reason might be that the content of MgO was lower than the detection limit of XRD.

The reason for the increase in the oxidation degree of MgF₂ with decreasing SF₆ concentration is as follows. In the mixed gas with high concentration of SF₆, SF₆ will decompose to form more reactive species like F₂ at high temperature. The resulting F₂ may react with MgO produced by the oxidation reaction to form MgF₂, which makes MgO actually not produced. In the mixed gas with low SF₆ concentration, since the content of SF₆ in the mixed gas is very small, as is the case where MgF₂ is exposed to high temperature air, MgF₂ would change into MgO by oxidation reaction [8]. Therefore, MgF₂ will undergo oxidation reaction in the mixed gas with low concentration of SF₆.

Table 1. EDS analysis results of MgF₂ samples oxidized in air containing different concentrations of SF₆ at 1000 °C for 2 h (at%)

SF ₆ concentration/%	F	Mg	O
1	62.42	36.44	0.84
0.5	62.70	36.16	1.05
0.1	61.40	36.15	2.45
0.05	60.60	36.18	3.22
0.01	59.83	36.54	3.63

3.2. Effects of temperature on MgF₂ oxidation

Figure 2 presents the XRD analysis results of MgF₂ samples after oxidation at different temperatures in 0.01% SF₆/air atmosphere for 2 h. As can be seen, when the temperature was 850 °C, a very weak MgO peak appeared. As the temperature increased from 900 °C to 1000 °C, another one MgO peak appeared besides the one at 850 °C. The results indicate that MgF₂ was oxidized and converted to MgO at high temperature in the atmosphere, and the oxidation degree increased with the increase of temperature. Table 2 shows the EDS results of MgF₂ samples after oxidation at the above condition. The EDS results showed that as the temperature rose from 850 °C to 1000 °C, the content of F element decreased, while the O element content increased. That is to say that the degree of oxidation of MgF₂ increased with the increase of temperature. These results are consistent with the results of XRD analysis above.

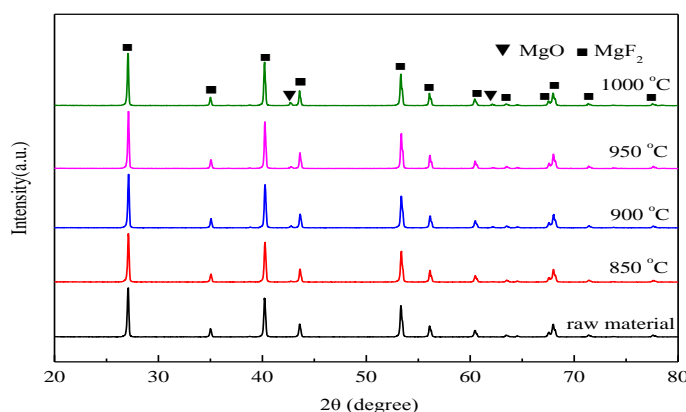


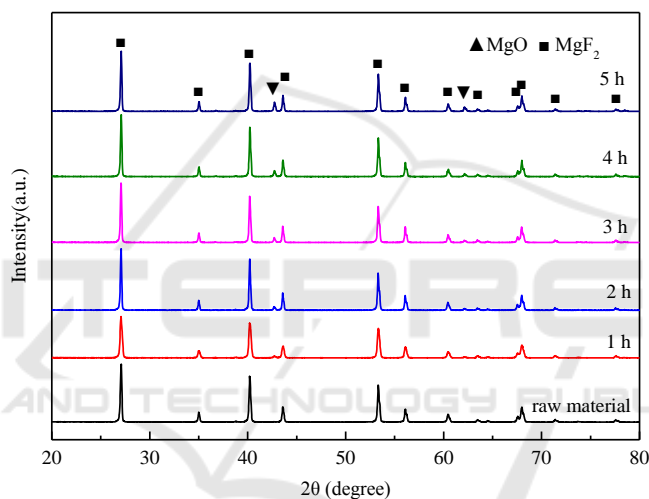
Figure 2. XRD results of MgF₂ samples oxidized in 0.01% SF₆/air mixture at different temperatures for 2 h.

Table 2. EDS results of MgF₂ samples oxidized in 0.01% SF₆/air mixture at different temperatures for 2 h (at%)

Reaction temperature/°C	F	Mg	O
850	61.76	36.28	1.96
900	61.43	36.38	2.19
950	61.16	36.48	2.36
1000	59.83	36.54	3.63

3.3. Effects of reaction time on MgF₂ oxidation

Figure 3 shows the XRD analysis results of MgF₂ samples oxidized in 0.01% SF₆/air atmosphere at 1000 °C for different reaction times. It can be seen that the oxidation degree of MgF₂ increased with the increase of reaction time. When the reaction time was 1 h, two weak MgO peaks appeared. As the reaction time increased from 1 h to 5 h, the content of MgO increased and MgF₂ content decreased. Table 3 shows the EDS analysis results of MgF₂ samples oxidized under the above conditions. The EDS results indicated that the tendency of MgF₂ oxidation to MgO increased with the reaction time.

**Figure 3.** XRD results of MgF₂ samples oxidized in 0.01% SF₆/air atmosphere at 1000 °C for different reaction times.**Table 3.** EDS results of MgF₂ samples oxidized in 0.01% SF₆/air mixture at 1000 °C for different times (at%)

Reaction time/h	F	Mg	O
1	61.51	36.39	2.09
2	59.83	36.54	3.63
3	55.14	40.98	5.03
4	57.00	38.19	7.42
5	55.73	38.11	9.30

3.4. Effects of gas flow and particle size on MgF₂ oxidation

The XRD results of MgF₂ samples oxidized in 0.01% SF₆/air mixed gas at 1000 °C at different gas flows and particle sizes for 2 h are shown in Figure 4. According to Figure 4, as the flow of mixed gas and the particle size of the sample increased, the intensity of MgO peak was almost unchanged. Table 4 shows the results of EDS analysis of MgF₂ samples oxidized under the same conditions. It

can be seen that oxygen content was almost unchanged, which means that the effect of particle size and gas flow on the oxidation of MgF₂ are also very small. The reason may be that the flow of gas was too high. In addition, it can be seen from the MgO peak in the XRD results by using the Scherrer equation that MgO is a small particle.

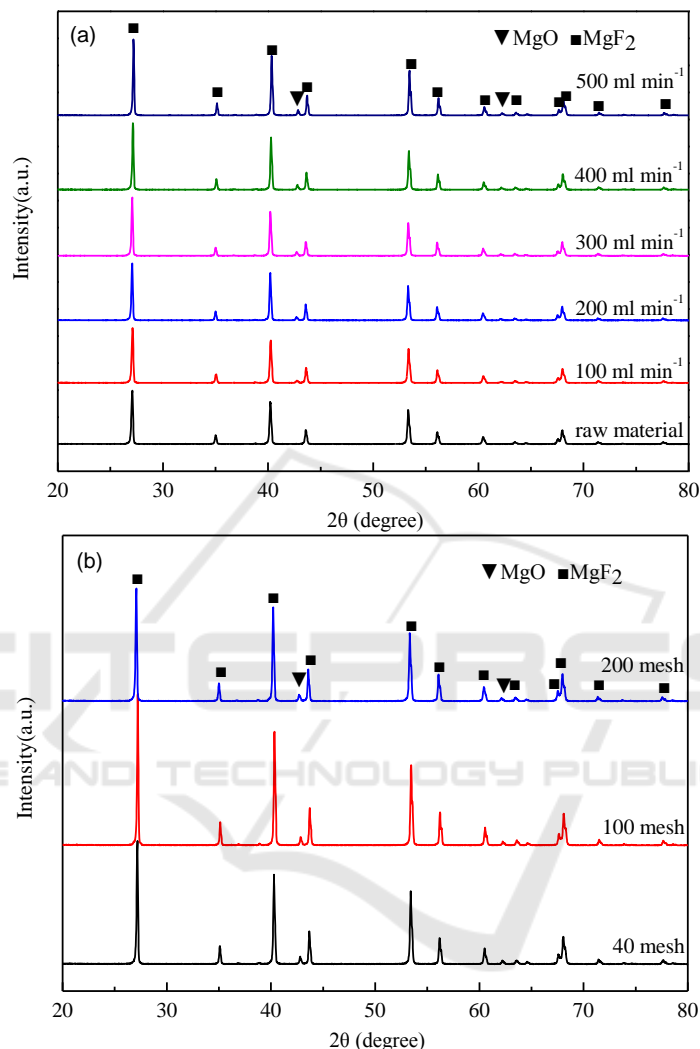


Figure 4. XRD results of MgF₂ samples oxidized in 0.01% SF₆/air mixed gas at 1000 °C for 2 h (a) different flows, (b) different particle sizes.

Table 4. EDS results of MgF₂ samples oxidized at 1000 °C in 0.01% SF₆/air atmosphere for 2 h at different gas flows and particle sizes (at%)

Gas flow/ml min ⁻¹	Sieve/mesh	F	Mg	O
100		59.24	37.02	3.73
200		59.83	36.54	3.63
300	200	56.77	39.46	3.77
400		59.24	37.02	3.76
500		59.18	36.97	3.86
200	40	60.16	36.64	3.67
	100	60.21	36.56	3.73

4. Conclusions

The oxidation of MgF_2 particles in SF_6 /air atmosphere at high temperatures was studied. It was found that the oxidation of MgF_2 in the atmosphere was mainly related to the concentration of SF_6 , temperature and reaction time. With the decrease of SF_6 concentration, the increase of temperature and the prolongation of reaction time, the degree of oxidation of MgF_2 increased. The particle size of MgF_2 and the mixed gas flow had little effect on the high temperature oxidation of MgF_2 . The results can provide a theoretical basis for the study of the protection mechanism of SF_6 gas on magnesium and its alloy melt.

Acknowledgments

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