

# Oxidation of MgF<sub>2</sub> Particles in Hexafluoropropylene/Air Atmosphere at High Temperatures

H K Chen, Y Y Jie and L Chang

Baoji University of Arts and Science, Baoji 721013, PR China

Corresponding author and e-mail: H K Chen, hk7115@yahoo.com

**Abstract.** High temperature oxidation properties of MgF<sub>2</sub> in hexafluoropropylene (HFP)/air atmosphere were investigated by using XRD, EDS and gravimetric analyses. The results show that HFP concentration, temperature, gas flow and reaction time have important effects on the oxidation properties. The degree of the oxidation reaction of MgF<sub>2</sub> converted to MgO was increased with the decrease of the concentration of HFP, the rise of temperature, the increase of gas flow and the extension of reaction time. These results can provide a theoretical basis for the study on the mechanism of the protection of magnesium and its alloy melt by fluorine-containing gas.

## 1. Introduction

As a lightweight structural material, magnesium alloy has many advantages, such as specific strength, high specific stiffness, good casting, cutting performance, good shock absorption and shock absorption ability, good electromagnetic shielding capability, and easy recycling [1-2]. Therefore, magnesium alloy has a wide range of applications in aerospace industry, automobile industry and 3C products, and it is known as "green structural material" in twenty-first century [3-4]. However, magnesium is a highly active and thermodynamically unstable element. In the smelting process of magnesium alloys, molten magnesium is prone to severe oxidation or even combustion, which seriously affects the quality of alloy castings, and even leads to the casting scrap. So the protection of the melting magnesium alloy has been a hot topic in scientific research.

At present, there are three kinds of main protection methods for magnesium alloy melt in the process of melting magnesium alloy, namely, solvent protection method, alloy element protection method and gas protection method [5-10]. Among them, SF<sub>6</sub> gas protection method is a widely used protection method for its safety, non-toxic, and little influence on the properties of magnesium alloy. But due to the serious greenhouse effect of SF<sub>6</sub>, which is one of the six gases that the Kyoto Protocol prohibits emissions [11], this method can no longer be used. Therefore, there is an urgent need to find protective gases that can replace SF<sub>6</sub>.

Hexafluoropropylene (HFP), also known as perfluoropropene, is a colorless and tasteless gas. The formula is C<sub>3</sub>F<sub>6</sub>. It has a very low greenhouse effect (ODP=0, GWP=2), does not burn in the air, and is almost harmless to the human body [12-13]. Recent studies have found that HFP can be used as a protective gas instead of SF<sub>6</sub>, and it has the advantages of environmental protection and economic benefits [12].

Further studies have shown that when magnesium and its alloys were smelted and processed under the protection of the mixture of HFP and air, the melt surface will form a composite protective film of MgF<sub>2</sub> and MgO. MgF<sub>2</sub> as the main component of the protective film played a key role in the protection



of the melt, and its content determines the protection effect of the mixture gas on magnesium melt [14].

It is generally believed  $MgF_2$  is stable compound. Under normal circumstances,  $MgF_2$  does not decompose and will not be converted into other compound. However, some studies have found that  $MgF_2$  in air at high temperature can be transformed into  $MgO$ , whether or not doped with other elements [15-18].

Will the oxidation of  $MgF_2$  occur in a mixture of HFP and air at high temperatures? If it occurs, what are the characteristics of the oxidation reaction? So far, research on the subject has not been reported. Considering that the important role of  $MgF_2$  in the protection of magnesium melt with fluorine-containing gas, in this paper, the oxidation characteristics of  $MgF_2$  in HFP/air atmosphere were investigated. The purpose was to provide theoretical basis for the study of the protection mechanism of fluorine gas to magnesium and its alloy melt.

## 2. Experimental

The raw material used for the present study was high purity  $MgF_2$  powder. The chemical composition (wt%) is 0.001 Na, 0.001 Fe, 0.002 Si, 0.002 Ca, 0.001 Pb, 0.002  $SO_4^{2+}$ , 0.001  $H_2O$  and balance  $MgF_2$ . The gas used for the experiment was the mixture of hexafluoropropylene (HFP > 99.9%, oxygen < 20  $ml/m^3$ , water < 10  $ml/m^3$ ) and air.

The high temperature oxidation experiment was carried out in a SK-G05123K atmosphere tube furnace. The experimental apparatus includes gas supply equipment, a tube furnace of  $\Phi$  110 mm $\times$ 420 mm, a corundum tube of  $\Phi$  50 mm $\times$ 1000 mm, and temperature control device. Before the experiment, in order to remove the possible impurities and some pollutants in the corundum pipe, the corundum tube was kept at 1000 degrees for a period of time. During the experiment, approximately 1 g (accurate to 0.0001 g) of  $MgF_2$  powder sample, which was ground with an agate mortar and passed through a 200 mesh screen sieve, was placed in a 50 $\times$ 28 $\times$ 10 mm alumina crucible. Then, the sample and the crucible were placed together into the central heating zone of the tube furnace, and the mixed gas of HFP/air was passed into the corundum tube at the flow rate of 300  $ml\ min^{-1}$  for a period of time in order to achieve the desired concentration of mixed gas in the corundum tube. Next, the tube furnace was heated to the desired temperature at a rate of 8  $^\circ C/min$  and kept a certain period of time. After that, the sample was cooled down to room temperature, taken out, weighed and stored in a dryer for X-ray diffraction (XRD) and energy dispersive spectrometer (EDS) analysis.

The phase composition of the oxidized  $MgF_2$  sample was tested by a Rigaku Ultima IV X-ray diffractometer with a Cu-K $\alpha$  source operated at 40 kV and 40 mA. The scanning speed is 4 $^\circ/min$ , the step width is 0.02 $^\circ$ , and the diffraction angle is 20 $^\circ$  to 80 $^\circ$ . 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 HFP concentration on $MgF_2$ oxidation

Figure 1 shows the XRD analysis results of  $MgF_2$  samples after oxidation in the atmosphere of air with different concentrations of HFP at 1000  $^\circ C$  for 2 h. It can be seen that with the decrease of the concentration of HFP, the intensity of  $MgO$  peaks increased. In the atmospheres containing 1%, 0.5%, 0.1%, and 0.05% HFP, only the peaks of  $MgF_2$  were present, and no  $MgO$  peaks appeared. In the atmospheres containing 0.01% and 0.005% HFP, in addition to the peaks of  $MgF_2$ ,  $MgO$  peaks appeared, and the intensity of  $MgO$  peaks increased with decreasing the concentration of HFP. This suggests that at 1000  $^\circ C$ ,  $MgF_2$  did not oxidize in the air with high concentration of HFP, but  $MgF_2$  oxidized in the air with low concentration of HFP and the oxidation degree of  $MgF_2$  increased with the decrease of HFP concentration.

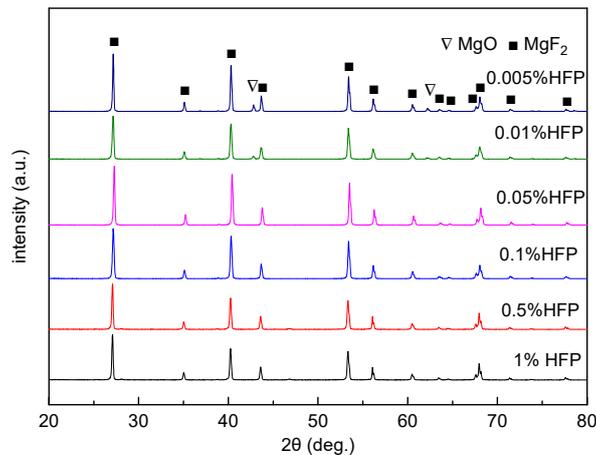


Figure 1. XRD analysis results of  $\text{MgF}_2$  samples after oxidation in the atmosphere of air with different concentrations of HFP at  $1000\text{ }^\circ\text{C}$  for 2h.

The EDS analysis results of  $\text{MgF}_2$  samples after oxidation in the atmosphere of air containing different concentrations of HFP at  $1000\text{ }^\circ\text{C}$  for 2 h are shown in Table 1. According to Table 1, at HFP concentrations of 1%, 0.5%, 0.1% and 0.05%, the content of O element was low and it had little change with the concentration of HFP. At HFP concentrations of 0.01% and 0.005%, the content of O element was markedly elevated and increased with the decrease of HFP concentration. These results indicate that  $\text{MgF}_2$  underwent a weak oxidation in 1%, 0.5%, 0.1% and 0.05%, with the decrease of HFP concentration, the oxidation degree of  $\text{MgF}_2$  increased. The EDS result in the atmospheres of 1%, 0.5%, 0.1% and 0.05% HFP is not very consistent with the result of the XRD in the same atmospheres. The reason may be that the content of magnesia is lower than the detection limit of XRD.

Table 1. Elemental composition of  $\text{MgF}_2$  samples after oxidation in different concentrations of HFP/air atmosphere at  $1000\text{ }^\circ\text{C}$  for 2 h (wt %)

HFP concentration (%)	Mg	O	F
1	41.98	0.86	57.36
0.5	41.76	0.92	57.32
0.1	42.45	0.99	56.55
0.05	42.45	1.48	56.07
0.01	43.21	4.20	52.59
0.005	43.50	6.74	49.76

The weight loss of  $\text{MgF}_2$  sample after oxidation in different concentrations of HFP/air atmosphere at  $1000\text{ }^\circ\text{C}$  for 2 h is shown Figure 2. As shown in Figure 2, with the decrease of the concentration of HFP, the weight loss rate of  $\text{MgF}_2$  sample increased. Since  $\text{MgF}_2$  does not decompose and evaporate at atmospheric pressure within  $1000\text{ }^\circ\text{C}$ , and the oxidation process of  $\text{MgF}_2$  into  $\text{MgO}$  will result in weight loss (the molar mass of  $\text{MgF}_2$  is  $62.3\text{g mol}^{-1}$ ,  $\text{MgO}$  is  $40.3\text{g mol}^{-1}$ ). Therefore, the weight loss rate of  $\text{MgF}_2$  samples increased with the decrease of the concentration of HFP means that the oxidation degree of  $\text{MgF}_2$  increased with the decrease of HFP concentration. The result is consistent with the result of EDS analysis above.

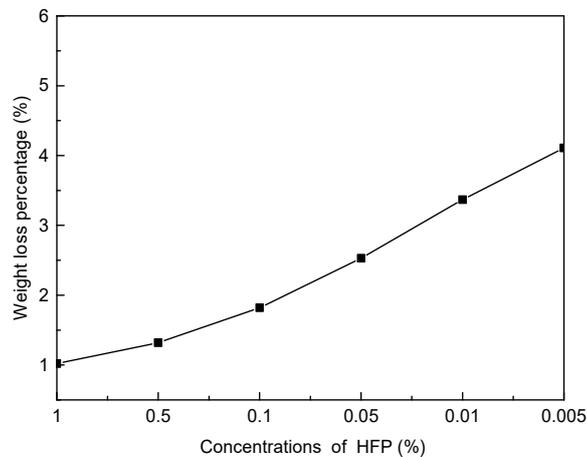


Figure 2. Weight loss of MgF<sub>2</sub> sample after oxidation in different concentrations of HFP/air atmosphere at 1000 °C for 2 h.

### 3.2. Effects of temperature on MgF<sub>2</sub> oxidation

Figure 3a shows the XRD analysis results of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing 0.01% HFP for 2 h. It can be seen that at temperatures of 800 °C and 850 °C, the spectra has only MgF<sub>2</sub> peaks and no MgO peaks. At 900, 950 and 1000 °C, with the increase of temperature, the MgO peak appeared, and the intensity of MgO peak increased gradually. Figure 3b shows the XRD analysis results of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing 0.005% HFP for 2 h. It can be seen that when the temperature was 800 °C, there was only the peak of MgF<sub>2</sub> in the spectra and no MgO peak. At 850, 900, 950 and 1000 °C, the MgO peak appeared, and the intensity of the MgO peak increased gradually with the increase of temperature. This result is similar to that of MgF<sub>2</sub> in the mixing atmosphere of 0.01% HFP/air. It is indicated that temperature is also an important factor affecting the oxidation behavior of MgF<sub>2</sub> in HFP/air atmosphere, and the oxidation degree of MgF<sub>2</sub> increases with the increase of temperature.

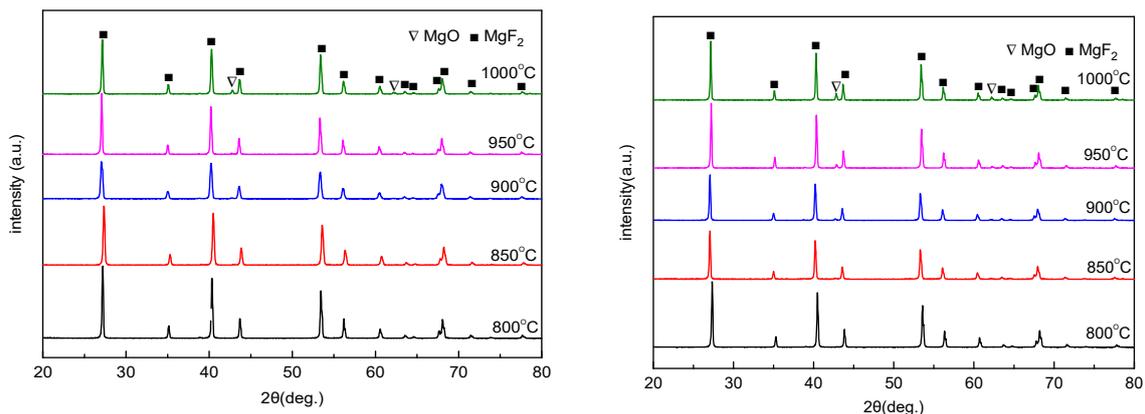


Figure 3. XRD results of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing (a) 0.01%, (b) 0.005% HFP for 2 h.

The EDS analysis results of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing 0.01% HFP for 2 h are shown in Table 2. According to Table 2, at 800 and 850 °C, O element content was very low and it increased slightly with increasing temperature. At 900, 950 and 1000 °C, the content of O element increased obviously with the increase of temperature.

Table 2. Elemental composition of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing 0.01% HFP for 2 h (wt%)

Temperature (°C)	Mg	O	F
800	42.76	0.92	56.32
850	44.19	1.04	54.77
900	42.74	2.19	55.07
950	53.10	3.34	43.56
1000	43.21	4.20	52.59

The weight loss of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing 0.01% and 0.005% HFP for 2 h is shown in Figure 4. As shown in Figure 4, in the atmospheres containing 0.01% and 0.005% HFP, the weight loss rate of MgF<sub>2</sub> samples increased with the increase of temperature. However, the weight loss rate of MgF<sub>2</sub> sample at the concentration of 0.005% HFP was higher than that at 0.01% HFP. This further indicates that the temperature has an important effect on the high temperature oxidation behavior of MgF<sub>2</sub> in HFP/air atmosphere.

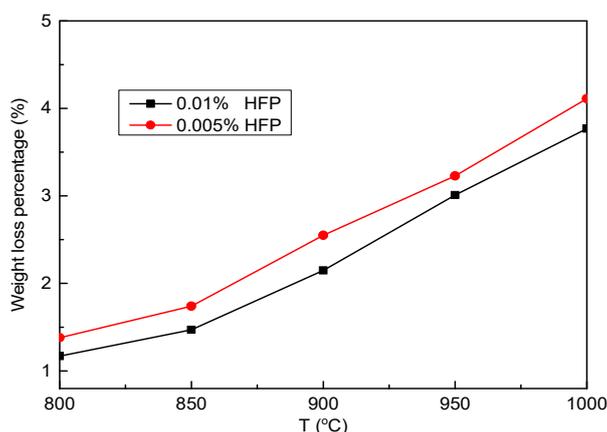


Figure 4. Weight loss of MgF<sub>2</sub> samples after oxidation at different temperatures in air containing 0.01% and 0.005% HFP for 2 h.

### 3.3. Effects of reaction time on MgF<sub>2</sub> oxidation

Figure 5a shows the XRD analysis results of MgF<sub>2</sub> samples after oxidation at different times in air containing 0.01% HFP at 1000 °C. It can be seen that the peaks of MgO appeared at the reaction time from 1 h to 5 h. The intensity of MgO peaks increased obviously from 1 h to 3 h, while the intensity was slightly increased from 3 h to 5 h. Figure 5b shows the XRD analysis results of MgF<sub>2</sub> samples after oxidation at different times in air containing 0.005% HFP at 1000 °C. It can be seen that when the reaction time increased from 1 h to 5 h, not only the MgO peak appeared, but also the intensity of MgO peak increased, and the enhancement was more obvious than that in 0.01% HFP.

The EDS analysis results of MgF<sub>2</sub> samples after oxidation at different times in air containing 0.01% HFP at 1000 °C are shown in Table 3. According to Table 3, when the reaction time increased from 1 h to 3 h, the content of O element was increased obviously, while the reaction time from 4 h to 5 h, the content of O element increased little, which was consistent with the corresponding XRD analysis results.

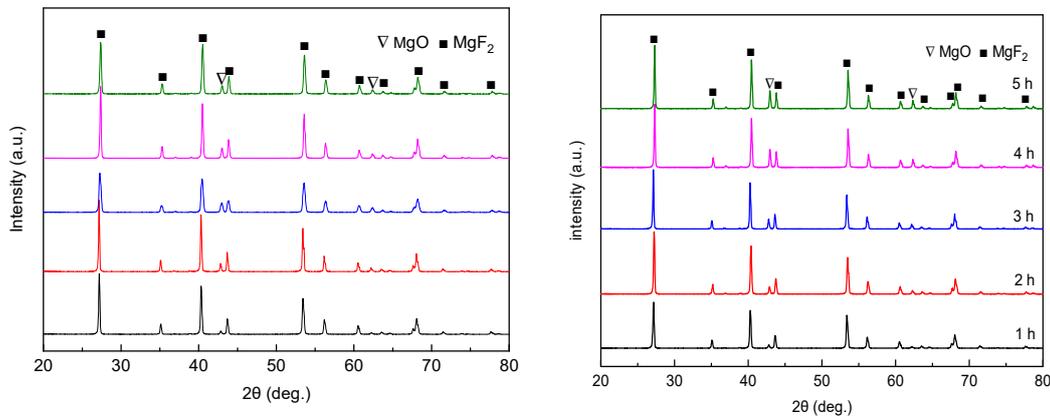


Figure 5. XRD results of MgF<sub>2</sub> samples after oxidation at different times in air containing (a) 0.01%, (b) 0.005% HFP at 1000 °C.

Table 3 Elemental composition of MgF<sub>2</sub> samples after oxidation at different times in air containing 0.01% HFP at 1000 °C (wt%)

Time (h)	Mg	O	F
1	50.28	3.36	46.05
2	43.21	4.20	52.59
3	43.07	4.58	52.35
4	42.86	5.15	51.98
5	44.10	5.84	50.06

The weight loss of MgF<sub>2</sub> samples after oxidation at different times in air containing 0.01% HFP at 1000 °C is shown in Figure 6. As shown in Figure 6, at the HFP concentration of 0.01% and 0.005%, the weight loss rate of MgF<sub>2</sub> sample increased with the increase of reaction time, this also shows that the reaction time has an effect on the high temperature oxidation behavior of MgF<sub>2</sub> in HFP/air atmosphere.

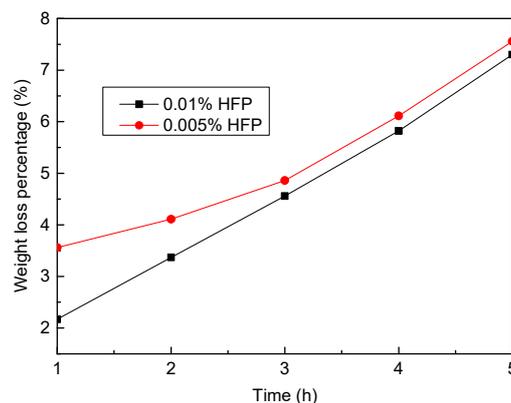


Figure 6. Weight loss of MgF<sub>2</sub> samples after oxidation at different times in air containing 0.01% and 0.005% HFP at 1000 °C.

#### 4. Conclusions

The high temperature oxidation characteristics of MgF<sub>2</sub> in HFP/air atmospheres were studied by analyzing the results of weight loss, XRD and EDS. The results showed that in the atmospheres of air containing 1%, 0.5%, 0.1% and 0.05% HFP, MgF<sub>2</sub> undergo weak oxidation. However, in the atmospheres of air containing 0.01% and 0.005% HFP, MgF<sub>2</sub> was obviously oxidized, and with the decrease of the concentration of HFP, the oxidation characteristics become more obvious. From 800 °C to 1000 °C, the higher the temperature was, the higher the oxidation degree of MgF<sub>2</sub> would be. When the reaction time was extended from 1 h to 5 h, the degree of MgF<sub>2</sub> oxidation was increased. These results indicate that HFP concentration, temperature and reaction time are important factors affecting the oxidation of MgF<sub>2</sub>. The results can provide theoretical basis for the study of the protection mechanism of fluorine-containing gas to magnesium and its alloy melt.

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