



Reaction behavior of MgF_2 powder in hexafluoropropylene/air atmospheres at high temperatures

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ABSTRACT

The protection of fluorine-containing gases for magnesium melt is based on a dense composite film containing MgF_2 on the melt surface. However, the stability of MgF_2 is still a problem. In this paper, the reaction behavior of MgF_2 powder in the atmosphere of air containing hexafluoropropylene (HFP) at 750–1000 °C was investigated. The results showed that the reaction was related to the concentration of HFP and temperature. In the atmosphere of air containing high concentration of HFP or at lower temperatures, MgF_2 almost did not react. In the atmosphere of air containing low concentration of HFP or at higher temperatures, MgF_2 underwent a reaction to convert to MgO . The kinetics of the reaction followed a linear or quasi-linear rate law in most cases, while it followed a mixed linear-parabolic rate law in air containing 0.05%, 0.01% and 0.005% HFP at 1000 °C and 0.01% HFP at 950 °C. The apparent activation energy was calculated to be 80.54 kJ mol⁻¹. These results help to better understand the protective mechanism of fluorine-containing gases on magnesium melt.

1. Introduction

The oxidation of liquid metals in air is an important problem in melting and casting operations. This is especially true for molten magnesium because it has extreme affinity for oxygen and high vapor pressure, which causes molten magnesium to oxidize rapidly and burn in air during its handling. To address this issue, the melting and casting process of magnesium is usually protected by the use of protective gases over the melt. Among the various cover gases, sulfur hexafluoride (SF_6) is considered to be a successful cover gas for its non-toxic, non-corrosive and good melt protection property, which has been widely used by the magnesium industry [1]. However, due to its extremely high greenhouse effect (the global warming potential is 23,900 [2]), the use of SF_6 is no longer acceptable environmentally and the researchers in magnesium industry are trying to find a suitable alternative to SF_6 [2–4]. Until now, although much research has been done on the protection of fluorine-containing gases for magnesium melts, the environment-friendly fluorine-containing gas that can replace SF_6 is still a problem that has not been solved. This is mainly due to the fact that the protection mechanism of fluorine-containing gases for magnesium melt has not been fully elucidated.

Previous studies have found that the protection of fluorine-containing gases for magnesium melt is based on a dense composite film containing MgF_2 and MgO on the melt surface, in which MgF_2 plays a

key role and its content determines the protectiveness of fluorine-containing gases for magnesium melt [5–8]. More importantly, the MgF_2 in the film is thought to be very stable at high temperatures due to the high electro-negativity of the F element, which means it does not decompose and will not transform into other compounds under the condition. However, some studies have found that MgF_2 has a tendency to convert to MgO in air at high temperatures. In the experiment of MgF_2/Al composite films deposited by electron beam evaporation in vacuum, Weimer et al. [9] found that there was about 1% MgO was present in the MgF_2/Al composite film. Xu and co-workers [10] researched the preparation process of a 30% Ag- MgF_2 cermet material. It was found that when the 30% Ag- MgF_2 cermet material was prepared in high oxygen partial pressure at temperature higher than 600 °C, MgF_2 component in the Ag- MgF_2 cermet will change to MgO by oxidation. Sun et al. [11] investigated the oxidation behavior of MgF_2 in Ag- MgF_2 cermets. They also found that when there is Ag participation, MgF_2 at high temperature and high oxygen partial pressure atmosphere (such as air) can be oxidized to produce MgO . Liu et al. [12] studied the oxidation of MgF_2 in air by X-ray diffractometer and found that with the increase of temperature above 800 °C, whether or not it is doped with other elements, MgF_2 will be converted to MgO . The higher the temperature is, the greater the conversion rate will be. Our recent research has also found this phenomenon [13,14]. This means that MgF_2 is actually unstable in the air at high temperatures, so in a mixed gas of

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fluorine-containing gas and air, whether the conversion reaction of MgF_2 to MgO can occur at high temperatures? If it happens, what law does it follow? These questions are not known yet, which are of great significance for better understanding of the protection mechanism of fluorine-containing gases for magnesium melt.

In the present work, hexafluoropropylene (HFP, C_3F_6) was used as a fluorine-containing gas that is a possible substitute for SF_6 , which has much lower global warming potential (its global warming potential is close to 1 [15]) than SF_6 and can provide effective protection for magnesium melt when it was mixed with either air or CO_2 [15,16], the reaction behavior of MgF_2 powder in HFP/air atmospheres at high temperatures was investigated by using thermo-gravimetric (TG), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersion spectrum (EDS) techniques and the effect of HFP concentration and temperature on the reaction behavior was especially discussed. Based on this, the reaction kinetics was also investigated. The purpose of the study is not only to better understand the protection mechanisms of HFP gas for magnesium melt, but also to provide a theoretical basis for the control and optimization of HFP gas for magnesium melt protection.

2. Experimental

The materials used in the study were high purity MgF_2 powder and high purity HFP gas. The chemical composition of MgF_2 powder in weight percent (wt%) is 0.001 Na, 0.001 Fe, 0.002 Si, 0.002 Ca, 0.001 Pb, 0.002 SO_4^{2-} and 0.001 H_2O . X-ray diffraction analysis (Fig. 1a) showed that all the characteristic peaks corresponded to those of MgF_2 and no other compounds were detected. The average particle size of the powder is around 60 μm and the microstructure is shown in Fig. 1b. The chemical composition of HFP gas in volume percent (vol%) is 99.99 C_3F_6 , 0.0001 HCl and 0.001 H_2O .

The reaction experiments of MgF_2 in HFP/air atmospheres at high temperatures were performed in a vertical tube furnace with an electronic balance and a gas system that provides gas mixtures of HFP and air to the tube furnace. The experimental set-up is shown schematically in Fig. 2. In the test, HFP and air, which was purified through a column of activated carbon, were mixed in the certain proportion and introduced into a quartz pipe ($\Phi 44 \times 800 \text{ mm}$) from the bottom of the furnace at the flow rate of 300 ml/min. After the quartz pipe was flushed with the mixed gas for 1 h, approximately 1.0 g (accurate to 0.0001 g) of MgF_2 powder sample, which was homogeneously placed in a high-purity alumina crucible ($\Phi 16 \times 18 \text{ mm}$) with the powder bed depth of 3.8 mm, was hung into the hot zone of the quartz pipe from the bottom of the electronic balance with a platinum wire, heated to a given temperature as quickly as possible, and then kept for a certain amount of time at the temperature. During this period, the weight

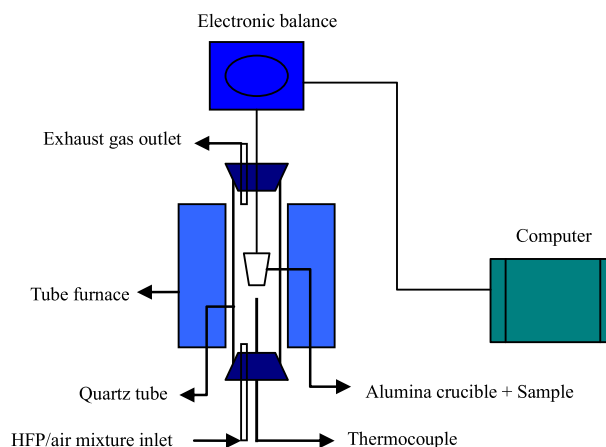


Fig. 2. Schematic diagram of apparatus used in the reaction test.

change of the sample in the atmosphere of air containing a certain concentration of HFP with time was continuously recorded by a computer that was connected to the electronic balance with an accuracy of 0.1 mg. When the holding time was reached, the sample was cooled down quickly and removed from the quartz tube for XRD, XPS, SEM and EDS analysis.

The reaction tests were carried out in the atmospheres of air containing different concentrations of HFP at different temperatures for a certain amount of time. The selected concentrations of HFP were 0.005%, 0.01%, 0.05%, 0.1%, 0.5% and 1%, respectively, reaction temperatures were 750, 800, 850, 900, 950 and 1000 $^{\circ}\text{C}$, respectively, and the reaction time was 2 h for all samples.

XRD analysis of the reacted MgF_2 samples was carried out on a Rigaku Ultima IV X-ray diffractometer with a $\text{Cu-K}\alpha$ source operated at 40 kV and 40 mA. The scanning speed is $4^{\circ}/\text{min}$, the step width is 0.02° , and the diffraction angle is 20° to 80° . The surface morphology and elemental composition of the reacted MgF_2 samples were examined by using a Quanta FEG 250 field emission SEM and an attached EDAX Genesis APEX EDS system operated at 20 kV, respectively. The chemical state of the reacted MgF_2 sample was determined by a ThermoFisher K-Alpha XPS using Al $\text{K}\alpha$ radiation. The binding energies were calibrated by taking carbon C1s peak (284.6 eV) as reference. The measurement accuracy for the electron binding energy was about 0.2 eV.

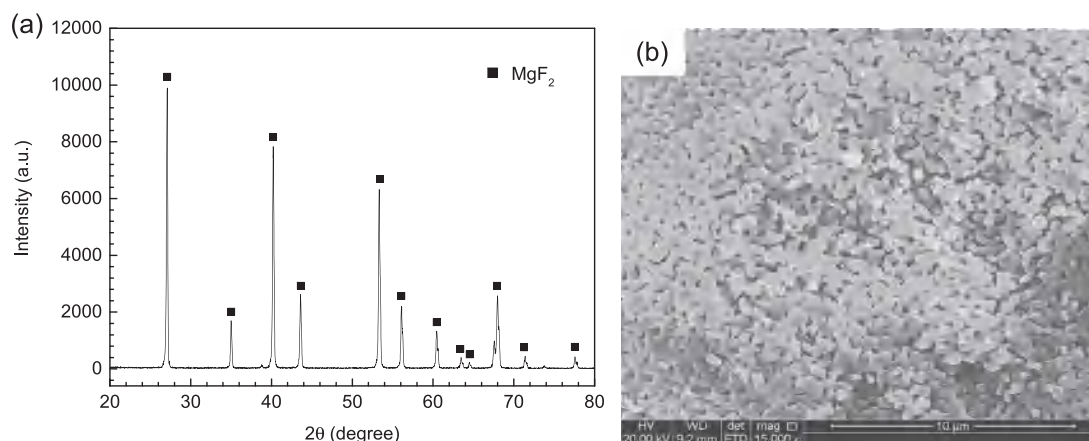


Fig. 1. XRD pattern (a) and SEM micrograph (b) of MgF_2 powder.

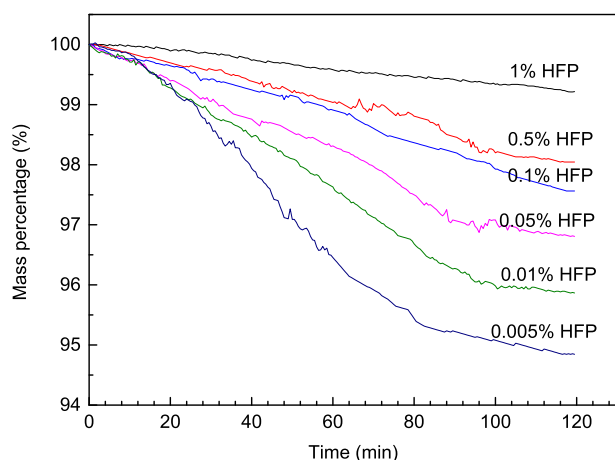


Fig. 3. TG curves of MgF_2 samples in the atmospheres of air containing different concentrations of HFP at 1000 °C.

3. Results

3.1. Thermo-gravimetric analysis

Fig. 3 shows the thermo-gravimetric (TG) curves recorded for MgF_2 samples in the atmospheres of air containing 1%, 0.5%, 0.1%, 0.05%, 0.01% and 0.005% HFP at 1000 °C. It can be seen that with the decrease of HFP concentration, the total mass of MgF_2 samples was gradually reduced and the mass versus time curves exhibited different behaviors. In the atmosphere of air containing 1% HFP, the mass of the sample decreased slightly with the increase of time. However, in the atmosphere of air containing 0.5%–0.005% HFP, the mass of the sample decreased significantly with the time at each HFP concentration. For the samples exposed to the atmospheres containing 0.5% and 0.1% HFP, the mass decreased approximately linearly with time. For the samples exposed to the atmospheres containing 0.05% and 0.005% HFP, the mass decreased rapidly in the first about 85–101 min, followed by a slow decrease with time. Since MgF_2 does not decompose and evaporate within 1000 °C [17], the reduction in the mass of MgF_2 sample means that MgF_2 underwent a chemical reaction. Therefore, these results indicate that the obvious reaction of MgF_2 started at the HFP concentration of 0.5% and the rate of the reaction increased gradually with the further decrease of HFP concentration.

Fig. 4 shows the TG curves recorded for MgF_2 samples in the atmospheres of air containing 0.01% and 0.005% HFP at the temperature of 750–1000 °C. As can be seen, with increasing temperature in the two atmospheres, the total mass of MgF_2 samples was gradually reduced. At 750 °C, the mass of MgF_2 sample did not change significantly with time.

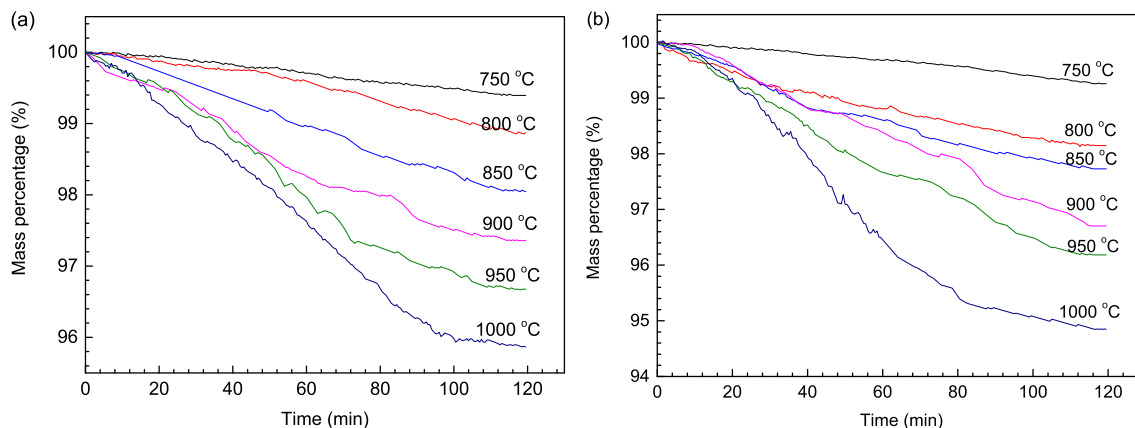


Fig. 4. TG curves of MgF_2 samples in the atmospheres of air containing (a) 0.01% and (b) 0.005% HFP at different temperatures.

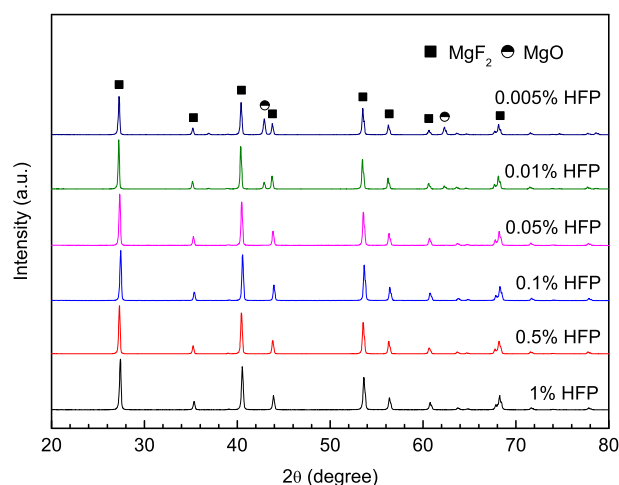


Fig. 5. XRD patterns of MgF_2 samples after exposure to air containing different concentrations of HFP at 1000 °C.

While at 800 °C, the mass had an obvious reduction with the extension of time. From 850 °C and 900 °C, the mass decreased approximately linearly with time. At 950 °C, the mass of the sample versus time curves was different in the two atmospheres. In the atmosphere of air containing 0.005% HFP, the mass decreased approximately linearly with time, but in the atmosphere of air containing 0.01% HFP, the mass decreased quickly in the first about 73 min and then decreased slowly with time. At 1000 °C, the mass decreased quickly in the first about 85–101 min and then decreased slowly with time. These results indicate that temperature had an important effect on the reaction of MgF_2 in HFP/air atmospheres and the rate of the reaction increased gradually with increasing temperature. Comparing Figs. 4a and b, it can be seen that the mass loss of the sample in 0.005% HFP/air atmosphere was greater than that in 0.01% HFP/air atmosphere at the same temperature, which also reflects the important effect of the concentration of HFP on the reaction.

3.2. Characterization of the reacted samples

3.2.1. XRD analysis

Fig. 5 shows the XRD patterns of MgF_2 samples after exposed to air containing 1%, 0.5%, 0.1%, 0.05%, 0.01% and 0.005% HFP at 1000 °C. As seen in the Figure, only the diffraction peaks of MgF_2 were detected in the samples exposed to the atmospheres with the HFP concentrations of 0.05%, 0.1%, 0.5% and 1%. For the samples exposed to air containing 0.005% and 0.01% HFP, in addition to the diffraction peaks of MgF_2 , the diffraction peak of MgO appeared and the content of MgO in

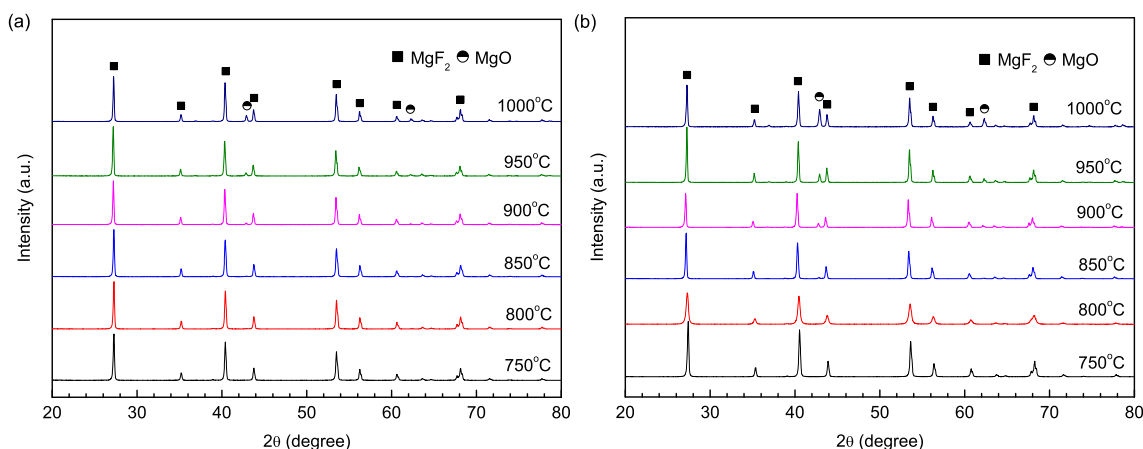


Fig. 6. XRD patterns of MgF_2 samples after exposure to air containing (a) 0.01% and (b) 0.005% HFP at different temperatures.

the sample exposed to 0.005% HFP/air atmosphere was higher than that of MgO in the sample exposed to 0.01% HFP/air atmosphere. These results indicate that MgF_2 underwent a reaction to convert to MgO in the atmosphere with low concentration of HFP. The lower the concentration of HFP was, the higher the degree of the reaction would be. It should be noted that the XRD results of the samples in atmospheres containing 0.005%, 0.01% and 1% HFP are consistent with the corresponding kinetic results. However, the XRD results of the samples in atmospheres containing 0.05%, 0.1% and 0.5% HFP do not agree with the corresponding kinetic results, which indicate that MgO should exist. In fact, MgO did exist in this case, which can be confirmed by the following EDS results. The reason for the difference may be that the content of MgO in this case was below the detection limit of XRD, which resulted in XRD failing to detect its existence.

Fig. 6 shows the XRD patterns of MgF_2 samples after exposed to air containing 0.01% and 0.005% HFP at the temperature of 750–1000 °C. It can be seen that in air containing 0.01% HFP, only the diffraction peaks of MgF_2 appeared in the samples exposed to 750–850 °C. With the temperature increasing from 850 °C up, MgO peaks also appeared and the intensity of MgO peak increased with the increase of temperature. In air containing 0.005% HFP, only the diffraction peaks of MgF_2 were detected in the samples exposed to 750–800 °C. At temperatures above 850 °C, MgO peaks also appeared and the intensity of MgO peak increased with the increase of temperature. These results indicate that MgF_2 underwent a reaction to convert to MgO at higher temperatures and the extent of the reaction increased with temperature. It can also be seen that the peak intensity of MgO in the atmosphere with 0.005% HFP was greater than that in the atmosphere with 0.01% HFP at the same temperature, which indicates that the reaction degree of MgF_2 in the former atmosphere was greater than that in the latter atmosphere. However, MgO was not detected in the samples exposed to 800 °C and 850 °C by XRD. In fact, MgO indeed existed in this case. The reason is the same as above.

3.2.2. XPS analysis

The MgF_2 sample after exposure to air containing 0.01% HFP at 1000 °C was also analyzed by XPS and the results are shown in Fig. 7. As shown in Fig. 7a, the MgF_2 sample exposed to air containing 0.01% HFP at 1000 °C contained Mg, F, O and C elements. Since the XRD and subsequent EDS analyses did not detect the presence of C or its compounds, the C element may be the impurity introduced in the XPS analysis. According to Mg 1s spectrum (Fig. 7b), Mg was present in two chemical states. The lower binding energy peak at 1304.17 eV was assigned to MgO and the higher binding energy peak at 1305.74 eV was attributed to MgF_2 . Fig. 7c showed that F was present in a single chemical state at binding energy peak of 686.09 eV, which was associated with MgF_2 . Two component peaks were evident in the O 1s spectrum

(Fig. 7d). The binding energy peak at 530.24 eV was attributed to MgO , the binding energy peak at 532.03 eV was assigned to CO_2 , which could result from the adsorption of CO_2 in the air on the surface of MgF_2 sample during its preparation for XPS analysis.

3.2.3. EDS analysis

The EDS analysis results of the elemental composition of MgF_2 samples after exposure to air containing different concentrations of HFP at 1000 °C are shown in Table 1. The results of EDS analysis of the samples after exposure to air containing 0.01% and 0.005% HFP at different temperatures for 2 h are shown in Tables 2 and 3, respectively. It can be seen from Table 1 that oxygen element was not detected by EDS for the sample in air containing 1% HFP, which indicates that MgF_2 almost did not react in this case or reacted very weakly, causing the content of oxygen element to be too low for EDS to be detected. With the decrease of HFP concentration from 0.5% to 0.005%, the content of oxygen element gradually increased, which suggests that the reaction of transformation of MgF_2 into MgO obviously occurred in air with HFP concentration below 1% and the degree of reaction increased with decreasing the concentration of HFP. From Tables 2 and 3, it can be seen that at 750 °C, oxygen element was not detected by EDS. As the temperature increased from 800 °C to 1000 °C, the content of oxygen element gradually increased. These results indicate that the reaction of MgF_2 into MgO obviously occurred at 800 °C and with further increase in temperature the reaction gradually accelerated. Since the oxygen content of the sample in 0.005% HFP atmosphere was higher than that of the sample in 0.01% HFP atmosphere at the same temperature, the reaction degree of MgF_2 in the atmosphere with 0.005% HFP was greater than that in the atmosphere with 0.01% HFP at the same temperature. These results are in accordance with the results of TG analysis above.

3.2.4. SEM analysis

The surface morphologies observed by SEM for MgF_2 samples after exposure to air containing 1%, 0.5%, 0.1%, 0.05%, 0.01% and 0.005% HFP at 1000 °C are shown in Fig. 8. Comparing Fig. 8a with Fig. 1b, it can be seen that the microstructure of the sample in air containing 1% HFP is similar to that of the original powder, which consisted of irregularly sized grains with mainly columnar shape. However, in the atmosphere containing 0.5% HFP, a small amount of white granules, which were identified as MgO by EDS, appeared on the surface of the sample and the grains were obviously enlarged. With the decrease of HFP concentration from 0.1% to 0.005%, white granules increased, the grains became larger. These results suggest that in air with the HFP concentration below 0.5%, the reaction of converting MgF_2 to MgO occurred and the extent of the reaction increased with further decrease of the HFP concentration. The reason why the grain size in the

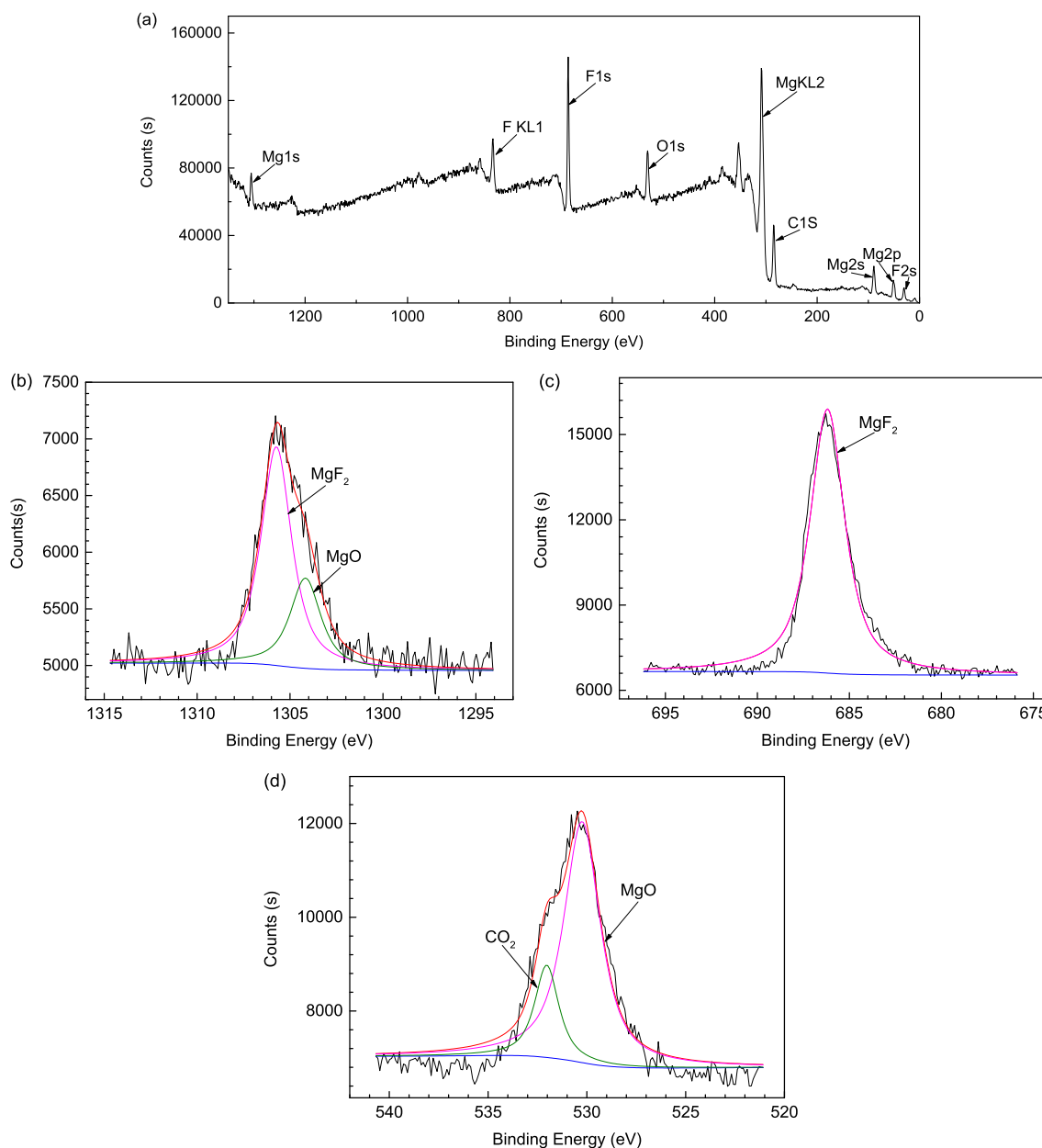


Fig. 7. XPS spectra of MgF_2 sample after exposure to air containing 0.01% HFP at 1000 °C: (a) whole survey, (b) Mg1s, (c) F1s and (d) O1s.

Table 1

Elemental composition of MgF_2 samples after exposure to air containing different concentrations of HFP at 1000 °C determined by EDS (wt%).

HFP concentration (%)	Mg	O	F
1	45.9	–	54.1
0.5	45.9	0.3	53.8
0.1	42.4	0.7	56.9
0.05	42.7	1.2	56.1
0.01	47.7	6.9	45.4
0.005	44.6	8.1	47.3

Table 2

Elemental composition of MgF_2 samples after exposure to air containing 0.01% HFP at different temperatures determined by EDS (wt%).

Temperature (°C)	Mg	O	F
750	42.5	–	57.5
800	41.0	0.9	58.1
850	41.1	1.3	57.6
900	43.5	2.6	53.9
950	42.0	4.0	54.0
1000	47.7	6.9	45.4

atmosphere containing 1% HFP was so different from the others is still unclear, which needs further research.

The surface morphologies observed by SEM for MgF_2 samples after exposure to air containing 0.01% and 0.005% HFP at different temperatures are shown in Figs. 9 and 10, respectively. As can be seen, the microstructure evolution with temperature was quite similar in both atmospheres. At 750 °C, the microstructure of the sample is similar to

that of the original powder. At 800 °C, there were a small amount of white granules appeared on the surface of the sample. With the temperature increasing from 800 to 1000 °C, white granules increased and the grain on the surface became larger. These results indicate that the reaction of converting MgF_2 to MgO gradually accelerated with the increase of temperature.

Table 3
Elemental composition of MgF₂ samples after exposure to air containing 0.005% HFP at different temperatures determined by EDS (wt%).

Temperature (°C)	Mg	O	F
750	43.2	–	56.8
800	42.4	1.2	56.4
850	42.3	2.9	54.8
900	42.7	3.3	54.0
950	44.7	6.0	49.3
1000	44.6	8.1	47.3

4. Discussion

4.1. Thermodynamic analysis

From the results obtained in the present study, it is found that the

reaction behavior of MgF₂ powder in HFP/air atmospheres at high temperatures depended on the concentration of HFP in the gas mixtures and temperature. In the atmosphere of air containing high concentration of HFP or at lower temperatures, MgF₂ almost did not react. In the atmosphere of air containing low concentration of HFP or at higher temperatures, MgF₂ reacted and was converted to MgO. Increasing the concentration of HFP and decreasing temperature reduced the rate of the reaction. These results could be understood based on following thermodynamic analysis.

When MgF₂ is exposed to the atmosphere of air containing HFP at high temperatures, the following reactions may occur:

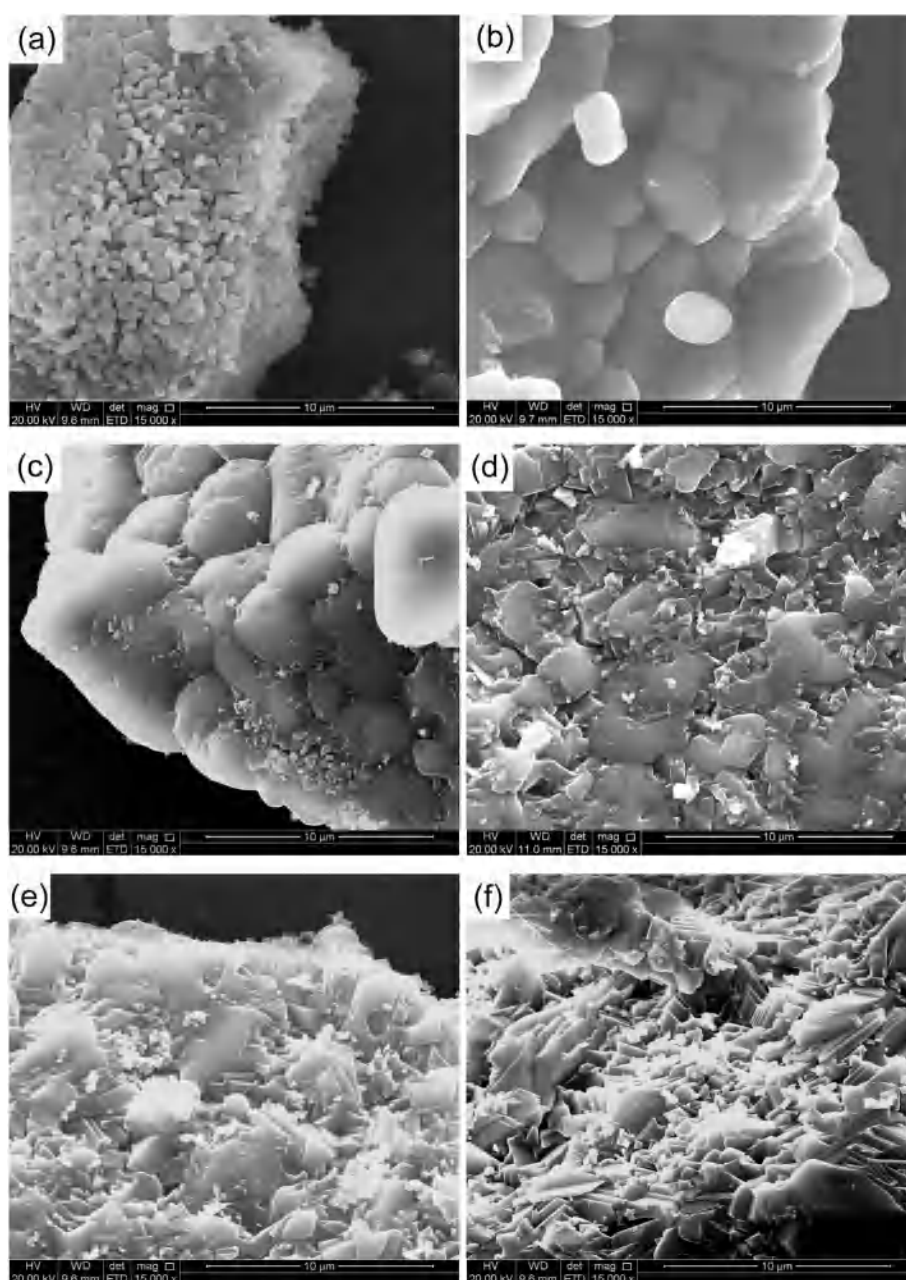
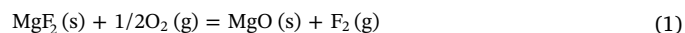


Fig. 8. SEM micrographs of MgF₂ samples after exposure to air containing (a) 1%, (b) 0.5%, (c) 0.1%, (d) 0.05%, (e) 0.01% and (f) 0.005% HFP at 1000 °C.

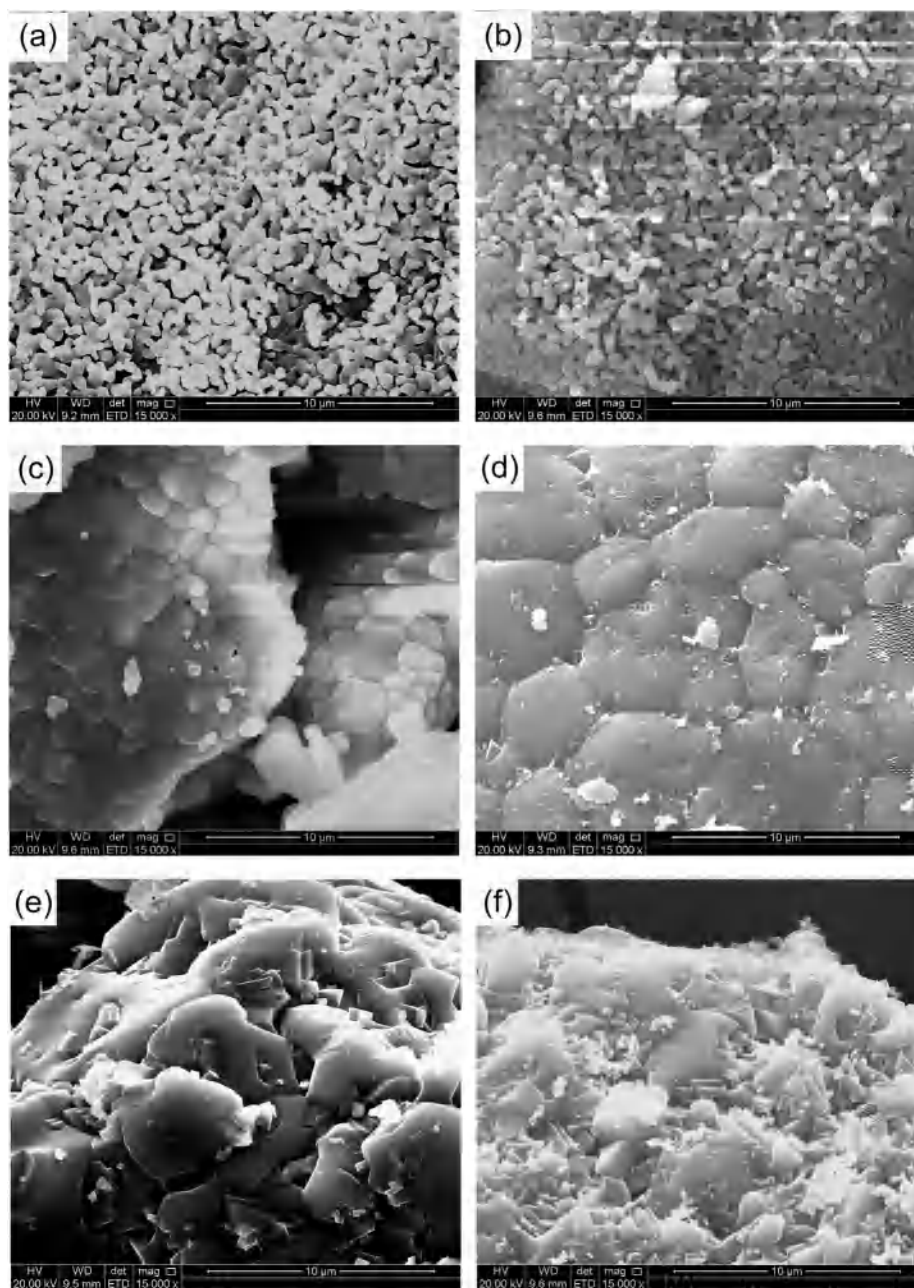
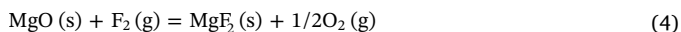


Fig. 9. SEM micrographs of MgF₂ sample after exposure to air containing 0.01% HFP air at (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C and (f) 1000 °C.



Under the present experimental conditions, the changes of Gibbs free energy of reactions (1) and (2), ΔG_1 and ΔG_2 , can be calculated by the following formulas:

$$\Delta G_1 = \Delta G_1^\circ + RT \ln \left(\frac{a_{\text{MgO}} p_{\text{F}_2}}{a_{\text{MgF}_2} p_{\text{O}_2}^{1/2}} \right) \quad (5)$$

$$\Delta G_2 = \Delta G_2^\circ + RT \ln \left(\frac{a_{\text{MgO}} p_{\text{HF}}^2}{a_{\text{MgF}_2} p_{\text{H}_2\text{O}}} \right) \quad (6)$$

where ΔG_1° and ΔG_2° are the standard Gibbs free energy changes of reactions (1) and (2) (J mol^{-1}), respectively, which can be calculated by using the thermodynamic data taken from Ref. [18]. R is the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K). a_{MgO} and a_{MgF_2} are the activities of MgO and MgF₂, respectively, which are

assumed to be unity in these calculations. p_{F_2} , p_{O_2} , p_{HF} and $p_{\text{H}_2\text{O}}$ are the partial pressures of F₂, O₂, HF and H₂O vapor in the atmosphere (Pa), respectively. In this experiment, the partial pressure of F₂ was in the range of 3.0×10^3 to 15 Pa, O₂ was 2.04×10^4 to 2.1×10^4 Pa, HF was 3.0×10^{-2} Pa, and H₂O was 25 Pa. By substituting the values of the above parameters into Eqs. (5) and (6), the changes of Gibbs free energy of the reactions (1) and (2) at different HFP concentration in the temperature range of 750–1000 °C were calculated and the results are shown in Fig. 11. From Fig. 11, it can be seen that the Gibbs free energy changes of reaction (1) at 750–1000 °C are positive, which indicates that reaction (1) cannot occur in this temperature range. The Gibbs free energy changes of reaction (2) are negative at 800–1000 °C, which indicates that reaction (2) can occur in the temperature range. Therefore, it can be concluded that the conversion of MgF₂ to MgO in the HFP/air atmospheres at high temperatures can take place and this conversion is mainly caused by the reaction of MgF₂ with H₂O vapor. This result can also be found in the study of oxidation of MgF₂ in air at high

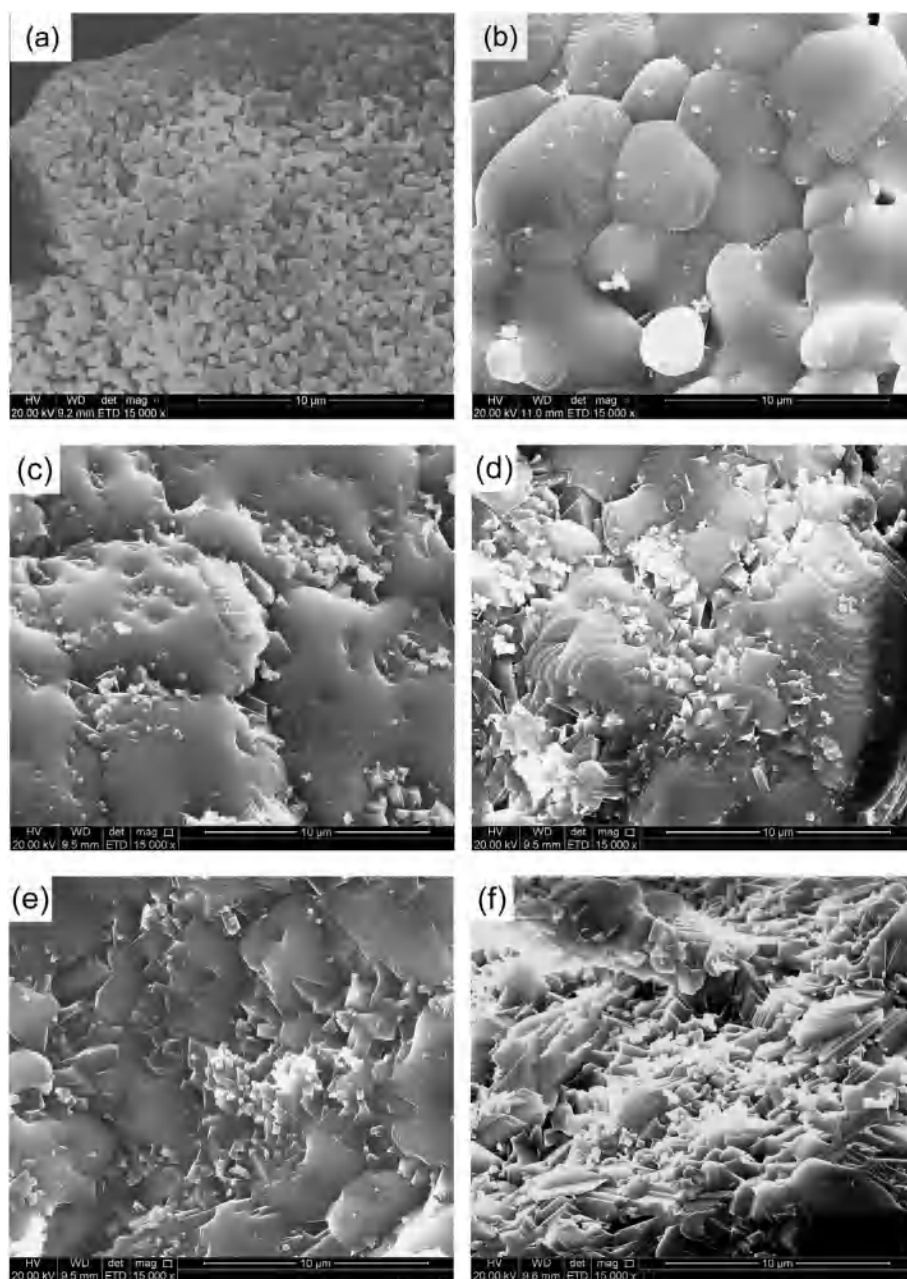


Fig. 10. SEM micrographs of MgF_2 samples after exposure to air containing 0.005% HFP air at (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C and (f) 1000 °C.

temperatures in the literature [20], and its experimental results confirmed that MgF_2 can react with H_2O vapor to form MgO at high temperature.

Since reaction (4) is the reverse reaction of reaction (1), the Gibbs free energy change of reaction (4) is negative, which indicates that reaction (4) can take place, that is, the resulting MgO will react with F_2 to form MgF_2 again. In fact, due to the high activity of F_2 , it can react with MgO [21]. HFP decomposes at 700 °C [22], therefore the reaction of (4) between MgO and F_2 may occur in the temperature range of concern.

The results show that the reaction rate of MgF_2 to MgO depends on the HFP concentration. In the atmosphere of air containing high concentration of HFP, from the viewpoint of thermodynamics, MgF_2 may first react with H_2O vapor at high temperatures to produce MgO . The resulting MgO may then continue to react with F_2 to form MgF_2 . Since the Gibbs free energy change of reaction (4) is more negative than that of reaction (2), the reaction trend between MgO and F_2 was much

greater than that between MgF_2 and H_2O , which leads to the possibility that the resulting MgO will be almost completely transformed into MgF_2 again. Therefore, the overall result is that the amount of MgF_2 has hardly change in this case, which means that MgF_2 almost does not react in the atmospheres of air containing high concentration of HFP.

In the atmospheres of air containing low concentration of HFP, according to the above analysis, MgF_2 may first react with H_2O vapor and produce MgO , and then the resulting MgO may continue to react with F_2 to regenerate MgF_2 . However, because of the low content of HFP in the mixture gas, although the reaction trend between MgO and F_2 is greater than that between MgF_2 and H_2O , the reaction rate of MgO and F_2 is less than that of MgF_2 and H_2O . Therefore, the MgO produced by the reaction of MgF_2 and H_2O cannot all be converted to MgF_2 by the reaction of MgO and F_2 , which results in the presence of MgO in this case. That is, MgF_2 undergoes a reaction to convert to MgO in the atmospheres of air containing low concentration of HFP. Comparing the reaction results of MgF_2 in air containing low concentration of HFP

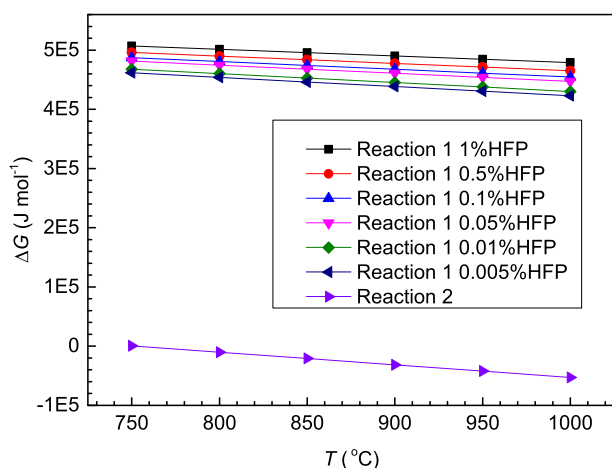


Fig. 11. Gibbs free energies of reactions (1) and (2) at different HFP concentrations and temperatures calculated by Eqs. (5) and (6). (The standard Gibbs free energy data of the reactions were taken from Ref. [18, 19].)

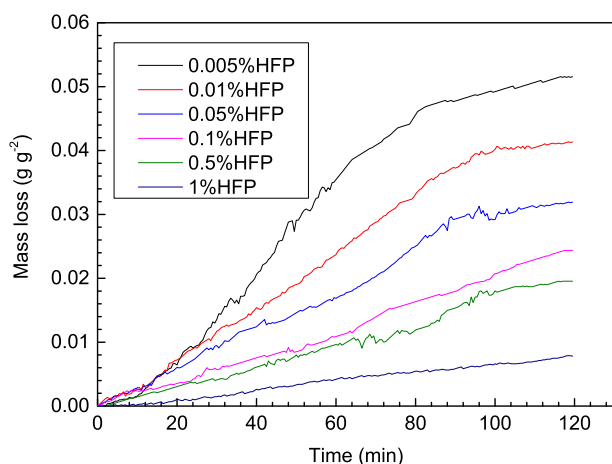


Fig. 12. Curves of mass loss vs. time for MgF₂ samples in the atmospheres of air containing different concentrations of HFP at 1000 °C.

with that of MgF₂ in air [14], we can see that at the same temperature the reaction degree of MgF₂ in the atmospheres of air containing low concentration of HFP is less than that of MgF₂ in air, which suggests that the above analysis is reasonable.

In addition, it can also be seen from Fig. 11 that as the reaction

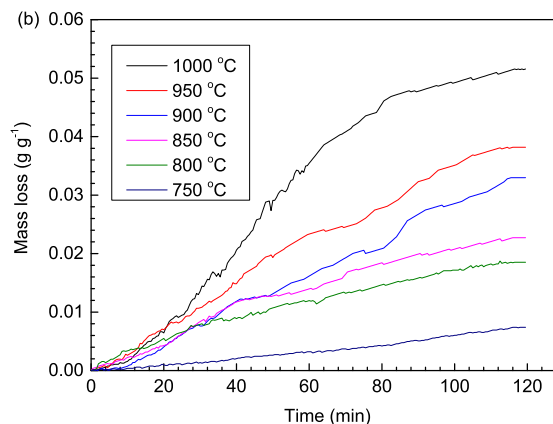
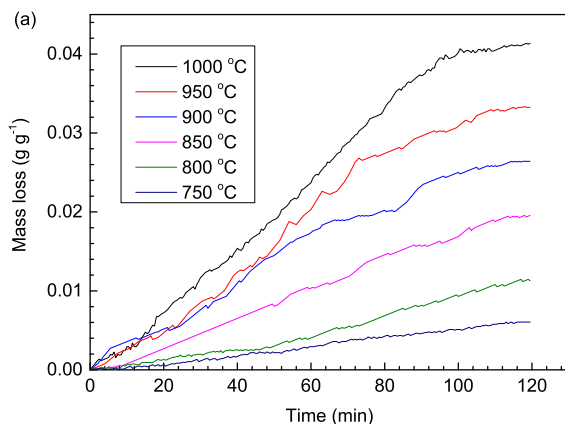


Fig. 13. Curves of mass loss vs. time for MgF₂ samples in the atmospheres of air containing (a) 0.01% and (b) 0.005% HFP at different temperatures.

Table 4

The rate constants of MgF₂ reaction at different temperatures and HFP concentrations obtained by fitting the data in Figs. 12 and 13 according to eqs. (7) and (8).

HFP concentration (%)	Temperature (°C)	Rate constant (min ⁻¹)	Correlation coefficient R ²		
1	1000	$k = 0.000069$	0.991		
		$k = 0.00018$	0.987		
		$k = 0.00021$	0.993		
		$k = 0.00031$ (0–96 min)	0.996		
		$k_p = 0.00001$ (96–120 min)	0.905		
		$k = 0.00043$ (0–101 min)	0.997		
		$k_p = 0.000063$ (101–120 min)	0.951		
		$k = 0.00064$ (0–85 min)	0.991		
		$k_p = 0.000013$ (85–120 min)	0.991		
		0.01	750	$k = 0.000055$	0.993
$k = 0.00010$	0.974				
$k = 0.00018$	0.996				
$k = 0.00023$	0.978				
$k = 0.00036$ (0–73 min)	0.985				
$k_p = 0.00016$ (73–120 min)	0.979				
$k = 0.00043$ (0–101 min)	0.997				
$k_p = 0.000063$ (101–120 min)	0.951				
0.005	750			$k = 0.000063$	0.988
				$k = 0.00015$	0.979
		$k = 0.00020$	0.969		
		$k = 0.00030$	0.996		
		$k = 0.00034$	0.990		
		$k = 0.00064$ (0–85 min)	0.991		
		$k_p = 0.000013$ (85–120 min)	0.991		
		0.005	1000	$k = 0.000063$	0.988
				$k = 0.00015$	0.979
				$k = 0.00020$	0.969
$k = 0.00030$	0.996				
$k = 0.00034$	0.990				
$k = 0.00064$ (0–85 min)	0.991				
$k_p = 0.000013$ (85–120 min)	0.991				

temperature increases, the Gibbs free energy change of reaction (2) becomes more negative, indicating that the reaction tendency of reaction (2) is increased with temperature. This explains the reason why the reaction rate of MgF₂ to MgO increased with temperature at the same HFP concentration from the viewpoint of thermodynamics.

4.2. Reaction process

Based on the results of the above thermodynamic analysis and TG, XRD, XPS, EDS and SEM analysis, it can be seen that when MgF₂ was exposed to HFP/air atmospheres at elevated temperature, it underwent two different processes depending on the concentration of HFP and temperature. In the atmosphere of air containing high concentration of HFP or at lower temperatures, MgF₂ first reacted with H₂O vapor to

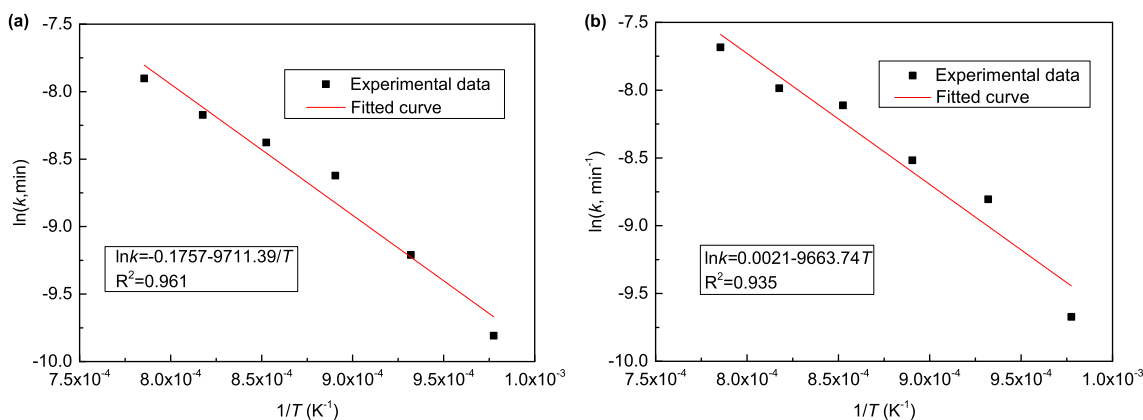


Fig. 14. Arrhenius plot of $\ln k$ vs. $1/T$ for the reaction of MgF_2 in (a) 0.01% and (b) 0.005% HFP.

produce MgO , and then the resulting MgO continued to react with F_2 and was converted to MgF_2 . In this process, MgF_2 almost did not react. In the atmospheres of air containing low concentration of HFP or at higher temperatures, MgF_2 reacted with H_2O vapor and produced MgO . In the process, MgF_2 underwent a reaction of being converted into MgO . The detailed reaction process of MgF_2 and H_2O vapor can be found in the literature [14].

4.3. Reaction kinetics

The plots of mass loss against time for MgF_2 samples in the atmospheres of air containing different concentrations of HFP at 1000 °C are displayed in Fig. 12 and those for MgF_2 samples in the atmospheres of air containing 0.01% and 0.005% HFP at different temperatures are displayed in Fig. 13. Since the molar mass of MgF_2 is 62.3 g mol^{-1} and MgO is 40.3 g mol^{-1} , theoretically the calculated mass loss should be 0.35 if MgF_2 is completely converted to MgO . However, in the present experiment, it can be seen from Figs. 12 and 13 that the maximum mass loss of the sample was approximately 0.052, which indicates that the reaction extent of MgF_2 was not high in the HFP/air atmospheres.

The reaction kinetics for MgF_2 samples in the HFP/air atmospheres can be represented by the following equations:

$$\frac{\Delta m}{m_o} = kt + c \quad (7)$$

$$\left(\frac{\Delta m}{m_o}\right)^2 = k_p t + c' \quad (8)$$

where $\Delta m/m_o$ is the mass loss (g g^{-1}), k and k_p are the linear and parabolic rate constants, respectively (min^{-1}), t is the reaction time (min), c and c' are the integration constants that define the onset of linear and parabolic kinetics. By fitting the $\Delta m/m_o$ in Figs. 12 and 13 against reaction time according to Eqs. (7) and (8), the values of k and k_p at different reaction temperatures and HFP concentrations were determined and the results are listed in Table 4. It is found from Table 4 that at 1000 °C, the reaction of MgF_2 powder followed a linear rate law in the atmospheres of air containing 0.1%–1% HFP, while in the atmospheres of air containing 0.05%–0.005% HFP, the reaction obeyed a mixed linear-parabolic rate law. It can also be seen from Table 4 that the reaction of MgF_2 powder in the atmospheres of air containing 0.01% and 0.005% HFP showed similar kinetic laws at 750–900 °C and 1000 °C. At 750–900 °C, the reaction followed a linear or quasi-linear rate law, and at 1000 °C, the reaction followed a mixed linear-parabolic rate law. At 950 °C, however, the reaction kinetics behaved differently in both atmospheres. In the atmosphere of air containing 0.01% HFP, the reaction exhibited mixed linear-parabolic rate kinetics, while in the atmosphere of air containing 0.005% HFP, the reaction followed linear rate kinetics. Normally, the gas-solid reaction phenomena are

investigated for one gaseous reactant and they could show linear and parabolic behaviors that correspond to surface reaction rate limited and diffusion limited processes, respectively. But for two reactant species, H_2O and HFP, the reaction behavior could be more complicated. It may be considered that in the atmospheres of air containing 0.01%–1% HFP at 1000 °C, 0.01% HFP at 750–900 °C and 0.005% HFP at 750–950 °C, the reaction process of MgF_2 powder were limited by surface reactions. While under the remaining conditions, the reaction process may be limited not only by surface reactions but also by other factors. According to the SEM photographs, in these cases, the reaction product MgO did not completely cover the surface of the sample, so diffusion may not be the main factor. This requires further research.

In addition, Table 4 also shows that the rate constant of the reaction increased with the decrease of HFP concentration and the increase of temperature.

The effect of temperature on the rate constant can be evaluated by the Arrhenius equation:

$$k = k_o \exp(-E_a/RT) \quad (9)$$

where k_o is the pre-exponential factor, R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the reaction temperature (K). By plotting the logarithm of the rate constant, $\ln k$, against the reciprocal of the reaction temperature, as shown in Fig. 14, the apparent activation energy (E_a) for the reaction of MgF_2 was calculated to be $80.74 \text{ kJ mol}^{-1}$ in 0.01% HFP/air and $80.34 \text{ kJ mol}^{-1}$ in 0.005% HFP/air. Considering the experimental error, the activation energies for the reaction in 0.01% and 0.005% HFP/air atmospheres may be consistent. Therefore, the average value was taken as the apparent activation energy of the reaction, which was $80.54 \text{ kJ mol}^{-1}$. The value obtained in this study is close to that reported in the study of the reaction of MgF_2 powder in air ($78.40 \text{ kJ mol}^{-1}$ [14]).

5. Conclusions

The concentration of HFP had an important influence on the reaction of MgF_2 in HFP/air atmospheres at high temperatures. In the atmosphere of air containing high concentration of HFP, MgF_2 almost did not react. With the decrease of HFP concentration in the atmosphere, the reaction of converting MgF_2 to MgO occurred and the rate of the reaction increased gradually. Temperature also had an important effect on the reaction. With the increase of temperature, the rate of the reaction increased gradually at a certain concentration of HFP. In most cases, the kinetics followed a linear or quasi-linear rate law, while in air containing 0.05%, 0.01% and 0.005% HFP at 1000 °C and 0.01% HFP at 950 °C, the kinetics followed a mixed linear-parabolic rate law. The apparent activation energy was calculated to be $80.54 \text{ kJ mol}^{-1}$. These results are useful for further understanding the protection mechanisms of HFP gas for magnesium melt, and can provide a theoretical basis for

the control and optimization of HFP gas for magnesium melt protection.

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