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Reaction kinetics of MgF_2 powder in air at high temperature

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ABSTRACT

The reaction kinetics of MgF_2 powder in air at 750–1050 °C was investigated by using TG, XRD, SEM and EDS techniques. The results show that the reaction of MgF_2 in air started at 800 °C and the porous MgO was formed on the surface of MgF_2. At temperatures higher than 800 °C, the rate of the reaction increased significantly with increasing temperature, producing more porous MgO product. The reaction was caused by the reaction of MgF_2 with water vapor in the air, which was controlled by the interface chemical reaction. The apparent activation energy of the reaction was measured.

1. Introduction

MgF_2 is an excellent optical coating material and an important electronic ceramic material. Due to its outstanding properties such as wide transparent band, low refractive index, wide energy gap, high mechanical strength and laser damage threshold, MgF_2 has been widely used in the preparation of various optical coatings with high reflectivity and high damage threshold. And because of its good insulation properties, MgF_2 has attracted much attention in the development of metal ceramic material [1]. In addition, in the process of processing of magnesium and its alloys, as the main component of the protective film formed on the surface of magnesium and its alloy melt, MgF_2 plays a key role in the protection of the melt from burning by SF_6 and other fluorine-containing gases. The content of MgF_2 in the protective film determines the protective effect of SF_6 and other fluorine-containing gases for magnesium and its alloy melt [2–5].

It has been considered that MgF_2 is a stable ionic compound, which does not decompose and will not be converted into other compounds under ordinary conditions. Nevertheless, some studies [6–9] have found that MgF_2 becomes less stable, and it has a tendency to change to MgO at high temperature in air due to chemical reaction, especially when impurities participate. Because of the reaction reduces the quality of MgF_2 and seriously weakens its practical performance, it is necessary to further study the high temperature reaction behavior of MgF_2 in air in order to prevent the reaction. However, so far the research on the reaction behavior is limited. Although our previous research [10]. has given some evidences about the influence of temperature on the reaction behavior, the high temperature reaction mechanism and kinetics of MgF_2 in air are still unclear, which are of great significance for understanding the high temperature reaction behavior of MgF_2 in air.

In the present study, the reaction kinetics curve of MgF_2 powder at high temperature in air was measured by the thermogravimetric method. The phase composition, elemental composition and surface morphology of MgF_2 sample after reaction in air at different temperatures were characterized by the X ray diffraction (XRD), energy dispersive spectrometer (EDS) and scanning electron microscopy (SEM), respectively. The thermodynamic analysis of the reaction process was carried out, and a reaction kinetic model was developed based on the thermodynamic analysis and the experimental results. The objective of this paper is to obtain a deeper understanding of the high temperature reaction behavior of MgF_2 in air, and provide a theoretical basis for the reasonable application of MgF_2 as coating materials, electronic ceramic materials and film materials for magnesium melt protection.

2. Experimental

The material used for the present study was high purity MgF_2 powder. Its chemical composition 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+}, $0.001 H_2O$ and balance MgF_2. The average particle size of the powder was about 60 μm. X-ray diffraction analysis showed that all the characteristic peaks correspond to those of MgF_2, and no other compound could be detected (see Fig. 2).

The reaction kinetic experiments were carried out on a PerkinElmer Pyris Diamond TG/DTA instrument under air atmosphere within a temperature range of 750 ~ 1050 °C. In the test, approximately 0.01 g (accurate to 0.0001 g) of MgF_2 powder sample was weighed by using an electronic balance and put into a Φ4.8mm × 3.8 mm alumina crucible. Then the sample and crucible were moved into the TG/DTA instrument, heated to the required temperature at a rate of 10 °C min^{-1}, and kept

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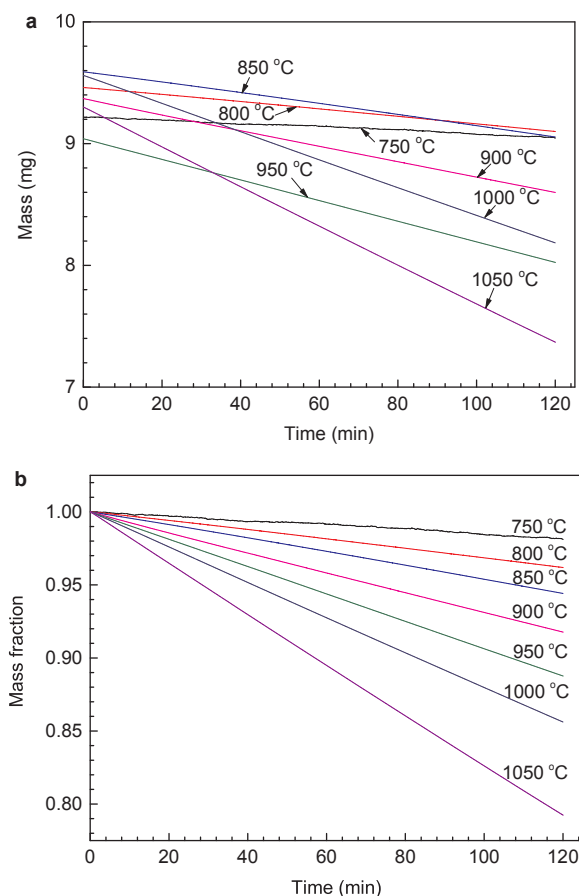* Corresponding author.
  E-mail address: hk7115@yahoo.com (H. Chen).

Fig. 1. Thermogravimetric curves of MgF_2 samples at different temperatures in air. (a) Mass versus time curves, (b) Mass fraction versus time curves.

Fig. 2. XRD patterns of MgF_2 samples before and after exposed to air at different temperatures for 2 h.

for 2 h at the temperature. During this period, the mass change of the sample was continuously recorded by a computer attached to the TG/DTA device at intervals of 0.5 s. When the holding time was reached, the test was terminated, and the sample was cooled down to room temperature, taken out and stored in a dryer for the XRD, SEM and EDS analyses. The selected reaction temperatures were 750, 800, 850, 900, 950, 1000 and 1050 °C, respectively.

The phase composition of the product of MgF_2 reaction was studied by a Rigaku Ultima IV X-ray diffractometer with a Cu-Kα source operated at 40 kV and 40 mA. The surface morphology and elemental composition of the reaction product were investigated by using a Quanta FEG 250 field emission scanning electron microscope equipped with an EDAX Genesis APEX energy dispersive spectrometer system.

3. Results

3.1. Isothermal thermogravimetric analysis

Fig. 1 shows the thermogravimetric curves of MgF_2 samples in air at 750, 800, 850, 900, 950, 1000 and 1050 °C. Here the original mass versus time curves and the mass fraction versus time curves are given together. As can be seen, at 750 °C, the mass of MgF_2 sample had no obvious change with the increase of time, which means that MgF_2 almost did not react in air at the temperature. However, at 800 °C, the mass of the sample had an obvious reduction with the prolonging of time. From 800 °C to 1050 °C, the mass of MgF_2 sample decreased linearly with time at each temperature, and the mass loss rate increased gradually with the increase of temperature. Since the molar mass of MgF_2, 62.3 g mol^{-1}, is larger than that of its reaction product MgO, 40.3 g mol^{-1}, the reduction in the mass of MgF_2 sample means that
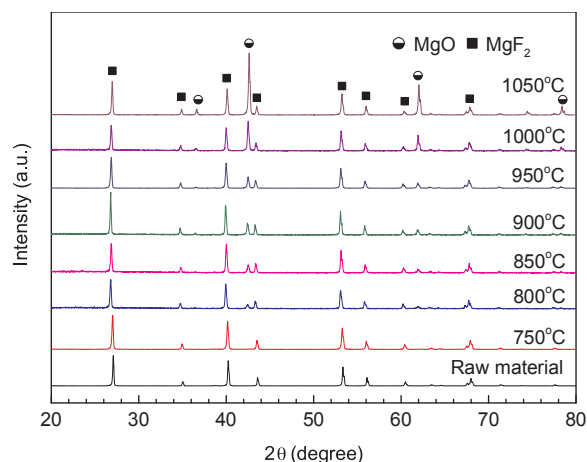
MgF_2 underwent a chemical reaction. Therefore, these results indicate that the obvious reaction of MgF_2 in air started at 800 °C and the rate of the reaction increased gradually with the further increase of temperature.

3.2. Reaction product analysis

3.2.1. XRD analysis

Fig. 2 shows the X-ray diffraction analysis results of MgF_2 samples after exposed to air at different temperatures for 2 h. It can be seen that only MgF_2 was present in the sample exposed to 750 °C. From 800 °C to 1050 °C, in addition to MgF_2, MgO was also present in all reacted samples. Moreover, with the increase of temperature, the content of MgO increased gradually and the content of MgF_2 decreased gradually. These results indicate that the reaction of MgF_2 in air occurred at 800 °C and the degree of the reaction increased with the further increase in temperature. These results are consistent with the results of the thermogravimetric analysis above.

3.2.2. SEM analysis

The surface morphology observed by SEM for MgF_2 sample after exposed to air at 750–1050 °C is shown in Fig. 3. It can be seen that the surface microstructure of MgF_2 sample varied considerably with the temperature. After exposure to 750 °C, the surface of the sample was dense and smooth, and only a very small amount of white particles, which was MgO determined by EDS, appeared on the surface (Fig. 3a). After exposure to 800 °C, however, the microstructure of the sample looked different from that at 750 °C. The surface was covered by the large MgO particles and there were a large number of holes between the particles, and the surface became coarse and loose (Fig. 3b). At the temperatures of 850 °C and above, with the temperature increasing, the surface of the reacted sample became coarser and MgO particles became larger, and there were still a large number of holes with different sizes on the surface (Fig. 3c ~ g). This result indicates that the reaction product of MgO was porous and loose. The porosity of the MgO produced by the reaction can also be seen in the process of high temperature oxidation of magnesium [11], this is because the reaction mechanism of MgF_2 is likely to be somewhat similar to that of magnesium.

3.2.3. EDS analysis

The EDS analysis results of the elemental composition of MgF_2 samples after exposed to air at different temperatures for 2 h are listed in Table 1. According to Table 1, all the reacted samples contained only O, F and Mg elements. The content of oxygen element in the sample after exposure to 750 °C was very low. From 800 °C onwards, with the
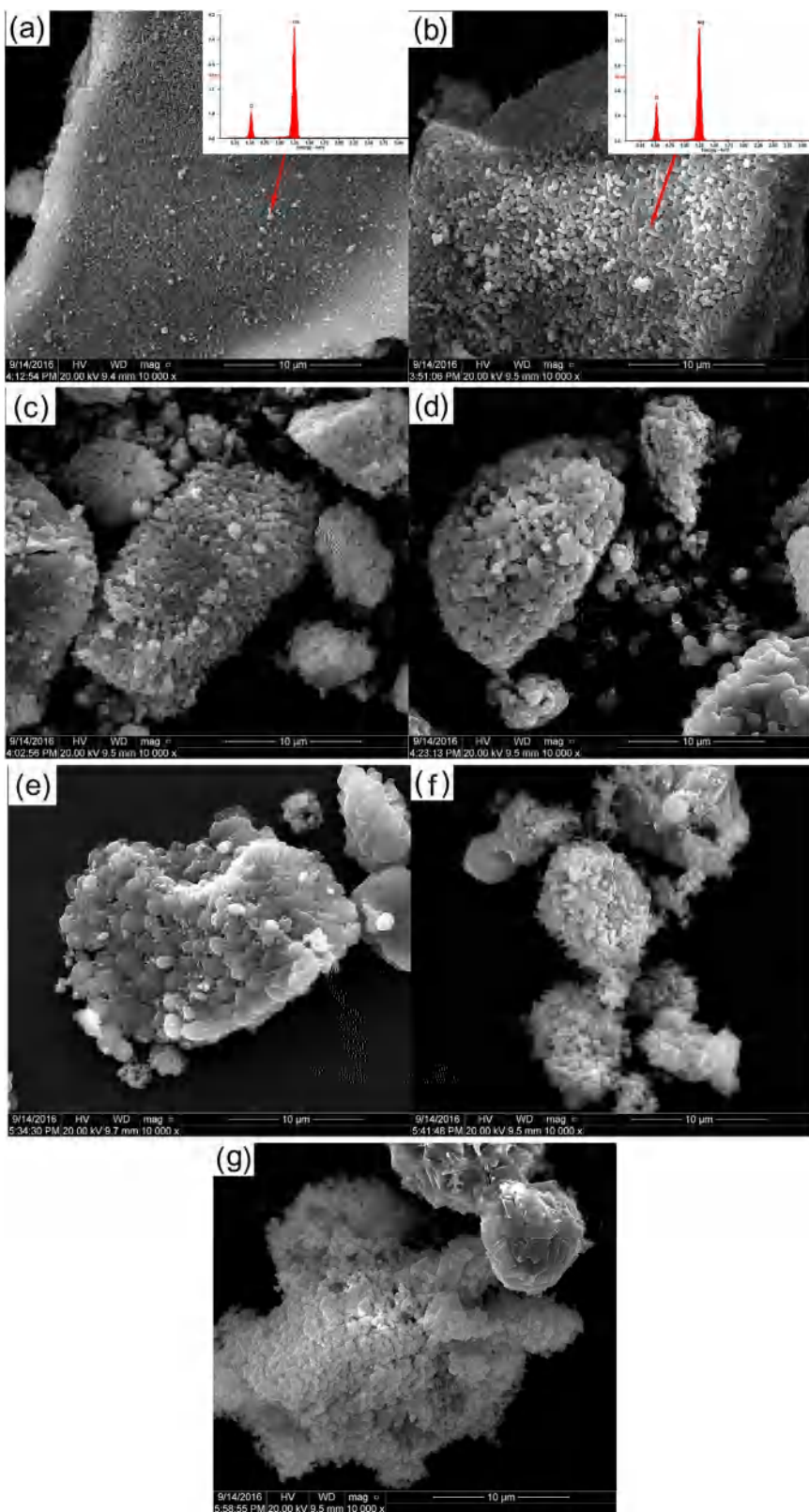
Fig. 3. SEM photos of MgF$_2$ samples exposed to air at (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C, (f) 1000 °C and (g) 1050 °C for 2 h.

increase of temperature, the content of oxygen element in the reacted samples increased obviously and the content of fluorine element decreased distinctly. These results indicate that MgF$_2$ had a very weak reaction at 750 °C. At the temperature higher than 800 °C, MgF$_2$ underwent significant reaction, and the degree of the reaction increased gradually with the increase of temperature. These results confirm the results of XRD analysis above and are consistent with the results of SEM analysis above.

Table 1
Elemental composition of MgF_2 samples exposed to air at different temperatures for 2 h determined by EDS (wt.%).

Element	750 °C	800 °C	850 °C	900 °C	950 °C	1000 °C	1050 °C
O	1.03	3.66	5.37	7.46	10.83	15.09	21.17
F	57.50	52.91	50.26	46.85	40.75	34.49	24.52
Mg	41.47	43.43	44.37	45.69	48.42	50.42	54.31

4. Discussion

4.1. Thermodynamics analysis

When MgF_2 was exposed to air at high temperature, it may react with oxygen and water vapor in the air as follows

$$MgF_2 (s) + 1/2O_2 (g) = MgO (s) + F_2 (g) \tag{1}$$

$$MgF_2 (s) + H_2O (g) = MgO (s) + 2HF (g) \tag{2}$$
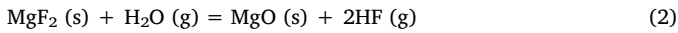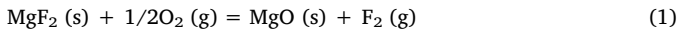
Under practical conditions, the changes of Gibbs free energy of reactions Eqs. (1) and (2), ΔG_1 and ΔG_2, can be calculated as follows

$$\Delta G_1 = \Delta G_1^o + RT\ln\left(\frac{a_{MgO} \quad p_{F_2}}{a_{MgF_2} \quad (p_{O_2})^{1/2}}\right) \tag{3}$$

$$\Delta G_2 = \Delta G_2^o + RT \ln\left(\frac{a_{MgO} \quad p_{HF}^2}{a_{MgF_2} \quad p_{H_2O}}\right) \tag{4}$$

Where ΔG_1^o and ΔG_2^o are the standard Gibbs free energy of reactions Eqs. (1) and (2) (J mol^{-1}), which can be calculated by using the thermodynamic data taken from Ref. [12]. R is the molar gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K). a_{MgO} and a_{MgF_2} are the activities of MgO and MgF_2, respectively, which are assumed to be unity in these calculations. p_{F_2}, p_{O_2}, p_{HF} and p_{H_2O} are the partial pressures of fluorine, oxygen, HF and water vapor in the air, respectively, which are assumed to be 5.0×10^{-6} Pa, 0.21×10^5 Pa, 3.0×10^{-2} Pa and 30 Pa, respectively, under the present experimental conditions. By substituting the values of the above parameters into Eqs. (3) and (4), the changes of Gibbs free energies of the reactions Eqs. (1) and (2) in the temperature range of 750–1050 °C were calculated and the results are shown in Table 2. It can be seen from Table 2 that the values of Gibbs free energy for the reaction Eq. (1) are positive at 750–1050 °C, which indicates that the reaction cannot occur in the temperature range from thermodynamic viewpoint. The values of Gibbs free energy for the reaction Eq. (2) are negative from 800 °C to 1050 °C, which indicates that the reaction can take place in the temperature range. Therefore, it can be concluded that the change of MgF_2 to MgO in air at high temperature is mainly caused by the reaction of MgF_2 with water vapor. The reaction of MgF_2 with water vapor was also observed in the experiments of some researchers [13], which confirm the results of thermodynamic analysis. It should be noted that other factors, such as the presence of a small amount of impurities in MgF_2, can also influence the reaction of MgF_2 in air at high temperature. This question will be explored in future research.

Table 2
Gibbs free energies of reactions (1) and (2) at different temperatures calculated by Eqs. (3) and (4) (The standard Gibbs free energy data of the reactions were taken from Ref. [12[]]).

Temperature (°C)	ΔG_1(J mol^{-1})	ΔG_2(J mol^{-1})
750	335377	564
800	321371	−10125
850	307365	−20813
900	293359	−31501
950	279353	−42189
1000	265347	−52877
1050	251341	−63565

4.2. MgF_2 reaction process

From the results of the above thermodynamic analysis and XRD, SEM and EDS analysis, it can be seen that when MgF_2 was exposed to air at elevated temperature, it has reacted, and the total reaction can be expressed as Eq. (2). The overall reaction process involves three different intermediate processes and the reaction rate limiting step may be one of the following steps.

(1) Diffusion of the gaseous reactant H_2O in the bulk gas phase through MgO product layer to the MgF_2/MgO interface.
(2) Chemical reaction between MgF_2 and H_2O at the MgF_2/MgO interface.
(3) Diffusion of gaseous reaction product HF through the MgO product layer to the external surface of the product layer.

In the experiments, we found that the MgO formed by the reaction was porous, and the change in mass of MgF_2 samples versus time was linear. Therefore, it can be considered that the diffusion of H_2O vapor and HF was a fast step, the effect of the steps Eqs. (1) and (3) on the rate of the reaction can be negligible, and the overall reaction rate was mainly limited by steps Eq. (2), that is, the interface chemical reaction was the rate-controlling step of the whole reaction process.

4.3. MgF_2 reaction kinetic model

The reaction process of MgF_2 in air proceeds first with the chemical reaction between MgF_2 and H_2O vapor in the air to form a thin layer of MgO at the outer surface of MgF_2. This stage proceeds very quickly. As the product layer of MgO is porous, once a thin MgO film is formed, the H_2O vapor in the air will pass through the porous MgO layer to react with MgF_2 further and the HF produced by the reaction will escape from the layer. In the whole reaction process, the chemical reaction between MgF_2 and H_2O at the MgF_2/MgO interface is the rate-controlling step.

Therefore, the reaction rate, r, in the case of chemical reaction control can be expressed as

$$r = \frac{dx}{dt} \tag{5}$$

where t is the reaction time (min), x is the reacted fraction of the sample at time t.

Since the interface chemical reaction is the rate-controlling step for the reaction of MgF_2 with H_2O vapor and the influence of diffusion on the reaction rate can be negligible, according to Eq. (2), the kinetic equation of the reaction can be expressed as follows

$$\frac{dx}{dt} = k_o(1 - x)^n P_{H_2O} \tag{6}$$

where k_o is the rate constant for this reaction (Pa^{-1} min^{-1}), which is a function of temperature; P_{H_2O} is the water vapor partial pressure of the bulk gas phase (Pa); n is the reaction order. Since the partial pressure of water vapor in air was kept constant during the reaction, the reaction rate was independent of water vapor partial pressure. Since the mass loss of MgF_2 sample was proportional to time at each temperature, according to the theory of gas-solid reaction kinetics, the reaction of MgF_2 with H_2O vapor was in accordance with the kinetic characteristics of zero order reaction and n is taken as zero. If the reaction was diffusion-controlled, the reaction kinetics would have been semi-parabolic [14]. Define the apparent rate constant as

$$k = k_o P_{H_2O}$$

Thus, Eq. (6) will become

$$\frac{dx}{dt} = k \tag{7}$$ At constant temperature, integrating the above equation with the initial condition of $x = 0$ when $t = 0$, one can obtain

$$x = kt \tag{8}$$

The above equation (8) describes the relation between the reacted fraction x and reaction time t at a certain temperature, which follows a linear law.

4.4. The application of the model

4.4.1. Estimation of reaction rate constant

The reacted fraction x of MgF_2 at time t can be calculated in terms of the following equation

$$x = \frac{\Delta m}{\Delta m_{max}} \tag{9}$$

where Δm is the lost mass of MgF_2 sample after time t and Δm_{max} is the theoretical maximum lost mass of MgF_2 sample after it is completely reacted. According to Eq. (1), if MgF_2 powders were completely reacted, Δm_{max} is calculated to be $0.3531 m_o$, where m_o is the initial mass of MgF_2 sample (mg). Using Eq. (9), the reacted fraction x of MgF_2 at different times for different temperatures was calculated with the experimental data shown in Fig. 1, and the plots of the reacted fraction versus time at different temperatures are presented in Fig. 4. It can be seen that the reaction fraction at a certain temperature increased linearly with time. The linear relationships obtained at all temperatures further support the assessment of chemical reaction control of the MgF_2 reaction process. The apparent rate constants of the reaction at different temperatures were then determined by using the model (Eq. [8]) to fit the experimental data of the reacted fraction versus time shown in Fig. 4, and the results are given in Table 3. As shown in Table 3, the apparent rate constant increased with increasing temperature.

4.4.2. The effect of temperature and activation energy

The reaction behavior of MgF_2 follows Arrhenius's law, that is, the apparent rate constant k increases exponentially with temperature

$$k = A_o \exp(-\frac{E}{RT}) \tag{10}$$

where A_o is a temperature-independent constant (min^{-1}), E is the apparent activation energy of the reaction (kJ mol^{-1}), R is the molar gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K). Taking a logarithm on both sides, Eq. (10) can be written as follows

$$\ln k = \ln A_o - \frac{E}{R}\frac{1}{T} \tag{11}$$

According to Eq. (11), the apparent rate constant data presented in Table 3 are plotted as the logarithmic rate constant against the reciprocal of temperature and the linear regression was then performed. The results are shown in Fig. 5. The regression result shows that the relationship between the logarithm of the rate constants and the reciprocal of absolute temperature is as follows
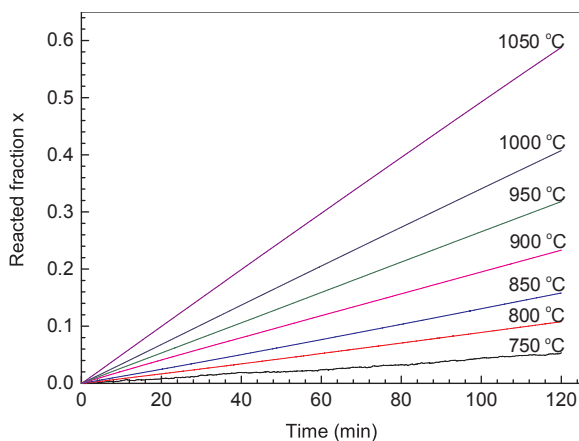

Fig. 4. Curves of the reacted fraction of MgF_2 against time at different temperatures.

Table 3
The rate constants of the reaction of MgF_2 in air at different temperatures obtained by fitting the curves of the reacted fraction of MgF_2 versus time.

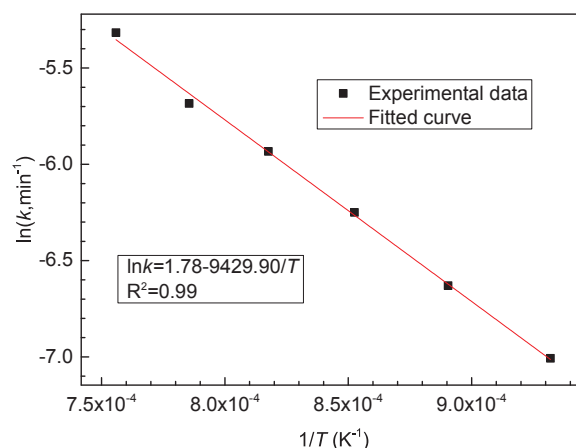| Temperature (°C)	Rate constant k (min^{-1})	Correlation coefficient R^2
750	0.00043	0.99239
800	0.00091	0.99976
850	0.00132	0.99972
900	0.00193	0.99993
950	0.00265	1
1000	0.00340	0.99997
1050	0.00491	0.99995

Fig. 5. Arrhenius plot for the reaction of MgF_2 in air.

$$\ln k = 1.78 - 9429.90\frac{1}{T} \tag{12}$$

Comparing Eqs. (10) and (11), one obtains

$$\frac{E}{R} = 9429.90, \ln A_o = 1.78$$

$$E = 9429.90R = 78.40 \text{kJ mol}^{-1}, A_o = 5.93 \text{min}^{-1}$$

That is, the apparent activation energy for the reaction-controlled reaction process was 78.40 kJ mol^{-1}. Therefore, the complete rate equation is now expressed as follows

$$x = 5.93 \exp(-\frac{9429.90}{T})t \tag{13}$$

The value of the activation energy for the reaction-controlled reaction process obtained in this study is much less than that for the reaction of Mg powder in steam at high temperature [15]. This value is close to that reported in the study of the reaction of Mg powder in steam at low temperatures [16]. The most likely reason for these differences is that the chemical property of MgF_2 is different from Mg and the reaction mechanism of MgF_2 with water is different from that of Mg with water.

5. Conclusions

High temperature reaction kinetics of MgF_2 powder in air was investigated. The results show that the reaction of MgF_2 in air started at 800 °C, forming porous MgO as the reaction product. At temperatures above 800 °C, the rate of the reaction increased significantly with increasing temperature, producing more porous MgO. The reaction of MgF_2 in air was attributed to the reaction of MgF_2 with water vapor in the air. The reaction kinetics is greatly influenced by temperature. The interface chemical reaction was the rate-controlling step in the whole reaction process, and the apparent activation energy for the reaction was 78.40 kJ mol^{-1}. These results are helpful for further understanding of the high temperature reaction behavior of MgF_2 in air, and can provide a theoretical basis for the reasonable application of MgF_2 in

coating materials, electronic ceramic materials and in magnesium melt protection.

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