Oxidation characteristics of MgF$_2$ in air at high temperature

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Abstract. High temperature oxidation properties of MgF$_2$ in air were studied. The changes of phase composition, macro surface morphology, weight and elemental composition of MgF$_2$ samples with temperature were investigated by using XRD, EDS and gravimetric analyses. The results show that the oxidation reaction of MgF$_2$ converted to MgO occurred at high temperature, and the reaction was accelerated by the increase of temperature and the presence of impurities. This result clarifies the understanding of the high temperature oxidation behavior of MgF$_2$ in air, and provides a theoretical basis for the reasonable application of MgF$_2$ in optical coating materials, electronic ceramic materials and magnesium melt protection.

1. Introduction

MgF$_2$ is an excellent optical coating material. Because of its outstanding properties such as wide transparent band, low refractive index, wide energy gap, high mechanical strength and laser damage threshold, it is considered to be the first choice for the preparation of the films with high reflectivity and high damage threshold [1]. MgF$_2$ is also an important electronic ceramic material. It has been attracting extensive attention in the development of metal ceramic materials due to its good insulating performance. In addition, in the process of smelting of magnesium and its alloys, MgF$_2$, as a major component of composite protective film, plays a key role in the protection of magnesium melt against its combustion by SF$_6$ and other fluorine containing gases. The content of MgF$_2$ determines the protective effect of SF$_6$ and other fluorine containing gases for magnesium melt [2~5].

It is generally believed that MgF$_2$ is a stable ionic compound, which does not decompose under normal circumstances, and it will not be converted into other compounds. However, recent studies have found that MgF$_2$ become less stable at high temperatures when impurities participate and it has a tendency to change to MgO. In the experiment of MgF$_2$/Al composite films deposited by electron beam evaporation in vacuum, Weimer et al. [6] found that there was about 1% MgO was present in the MgF$_2$/Al composite film. They believe that the emergence of MgO may be due to the raw materials containing 2% of the impurities Na that leads to the oxidation of MgF$_2$. Xu Zhiyuan and co-workers [7] 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 ^{o}C, MgF$_2$ component in the Ag-MgF$_2$ cermet will change to MgO by oxidation. But pure MgF$_2$ in the atmosphere, even though at 1000 ^{o}C, is rarely oxidized, while Ag participates in, MgF$_2$ will be severely oxidized into MgO under this condition. Sun Daming et al. [8] 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; otherwise, MgF_2 is rarely oxidized or not oxidized at all.

However, others have also come to the other results. Liu Meiyan et al [9] studied the oxidation of MgF_2 in air by X ray diffractometer and found that with the increase of temperature above 800 ^{o}C, whether or not it is doped with other elements, MgF_2 will be converted to MgO. The higher the temperature, the greater the conversion rate. Obviously, these results are different from those of Xu Zhiyuan and Sun Daming et al.

Therefore, whether MgF_2 can be oxidized in the air at high temperatures, and whether the participation of impurities has an effect on the oxidation of MgF_2 are still controversial issues. Because of the oxidation of MgF_2 decreases the quality of MgF_2, which diminishes its practical performance badly, it is necessary to further study the high temperature oxidation behavior of MgF_2 in the air. In this paper, the oxidation properties of MgF_2 in the air at high temperatures were studied. The purpose of the paper is to clarify the conditions and rules of the oxidation reaction of MgF_2 in the air, which will provide a theoretical basis for the reasonable processing and application of MgF_2 as optical coating materials and electronic ceramic materials and for the optimization of protection conditions of fluorine-containing gases for magnesium melt.

2. Experimental

The raw materials used for the present study were high purity MgF_2 (HP MgF_2) and analytical reagent MgF_2 (AR MgF_2) powder. Their chemical composition is shown in Table 1.

Table 1. Chemical composition of HP MgF_2 and AR MgF_2 (wt%)

| Specimen	Na	Fe	Si	Pb	Ca	SO_4^{2+}	H_2O	MgF_2
HP MgF_2	0.001	0.001	0.002	<0.001	0.002	0.002	0.001	99.99
AR MgF_2	0.05	0.3	0.2	0.05	0.3	0.6	1.0	97.5

The oxidation tests of MgF_2 in the air were carried out in a SX2-10-12 box-type resistance furnace. Approximately 1g (accurate to 0.0001g) of MgF_2 powder, which was ground to 200 meshes in an agate mortar before the test, was weighed by using an electronic balance and put into a 50mm$\times$28mm$\times$10mm alumina crucible. Then the sample and crucible were moved together into the resistance furnace, heated to the set temperature at a rate of 5-7 ^{o}C/min, and held at the temperature for 2h. After that, the sample was cooled down to room temperature, weighed and stored in a dryer for the X ray diffraction (XRD) analysis, macroscopic morphology and energy dispersive spectrometer (EDS) analyses. The selected oxidation temperatures were 600, 700, 750, 800, 850, 900 and 1000 ^{o}C, respectively.

XRD analysis of the oxidized MgF_2 samples was carried out on a Rigaku Ultima IV X-ray diffractometer with a Cu-Kα source operated at 40kV and 40mA. The scanning speed is 4°/min, the step width is 0.02^o, and the diffraction angle is 20° to 80°. 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.
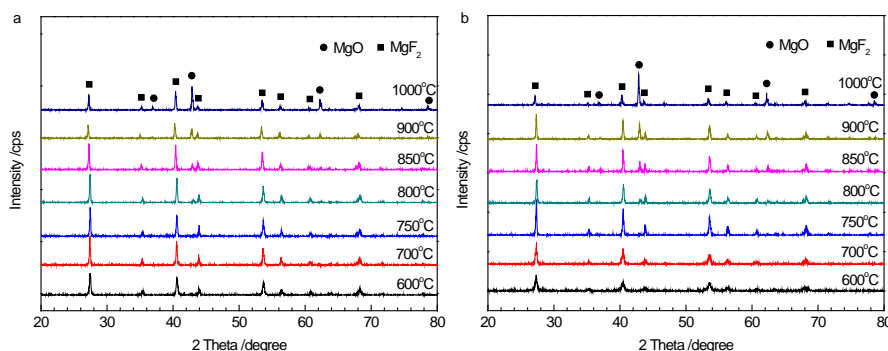
3. Results

3.1. XRD analysis

The X-ray diffraction analysis results of HP MgF_2 samples after oxidation at different temperatures in the air for 2h are shown in figure 1. It can be seen that there was obvious MgO appeared in HP MgF_2 at 800 ^{o}C. From 800 ^{o}C to 1000 ^{o}C, with the increase of temperature, the content of MgO increased gradually and MgF_2 content decreased gradually. This result shows that MgF_2 was oxidized and converted to MgO at high temperature in the air, and the degree of the oxidation gradually increased with the increase of temperature. These results are consistent with those of Liu Yanmei et al [9], but different from those of Xu Zhiyuan and Sun Daming et al [6~8].
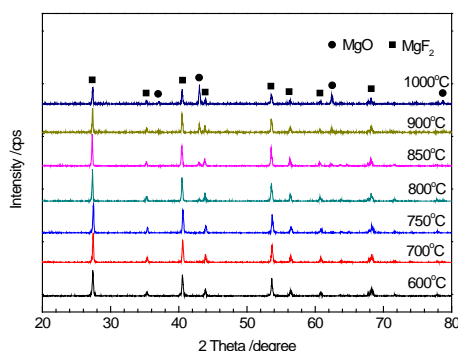
Figure 1. XRD results of HP MgF_2 samples after
oxidized at different temperatures for 2h.

In order to investigate the influence of impurities on the oxidation process of MgF_2, HP MgF_2 and AR MgF_2 samples were put into the resistance furnace together and oxidation experiments on them was carried out. Figure 2 shows the results of X ray diffraction analysis of the samples after oxidized at different temperature for 2h. As can be seen, in this case, HP MgF_2 and AR MgF_2 also began to produce MgO at 800 ^oC. From 800 ^oC onwards, as the temperature increased, MgO content increased gradually and MgF_2 content decreased gradually. Up to 1000 ^oC, the main phase of AR MgF_2 has become MgO. In addition, it can be seen that at the same temperature, the content of MgO in AR MgF_2 was greater than that of MgO in HP MgF_2. These results indicate that not only the increase of temperature accelerates the process of oxidation reaction of MgF_2, but also the presence of impurities accelerates the oxidation process of MgF_2. The results confirm the conclusion of Weimer et al [6], Xu Zhiyuan and Sun Daming et al [7,8] that the impurities accelerate the oxidation of MgF_2, but the results are inconsistent with those of Liu Yanmei et al [9].
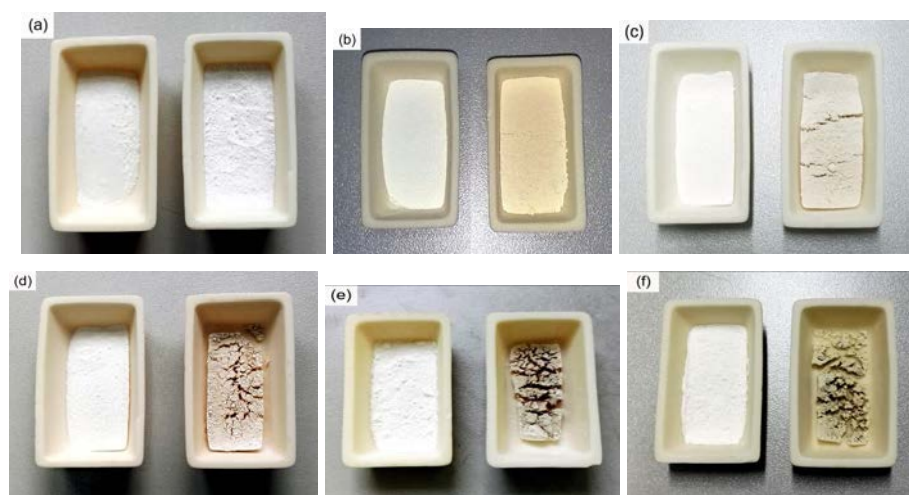

Figure 2. XRD results of MgF_2 samples after simultaneously oxidized at different
temperatures for 2h: (a) HP MgF_2; (b) AR MgF_2.

Compared with figure 1 and figure 2 (a), we can see that at the same temperature, the content of MgO produced by the individual oxidation of HP MgF_2 is less than that produced by HP MgF_2 that was simultaneously oxidized with AR MgF_2. This result indicates that the rate of individual oxidation of HP MgF_2 is less than that of HP MgF_2 that was simultaneously oxidized with AR MgF_2 at the same temperature. The reason for this result may be that the high temperature evaporation or decomposition products of impurities in AR MgF_2 promoted the process of MgF_2 oxidation. The problem needs to be further studied, but the result can also confirm that the participation of impurities can accelerate the oxidation reaction of MgF_2.

3.2. Macroscopic morphology

Figure 3 shows the macro-morphology photos of HP MgF_2 and AR MgF_2 samples after oxidation at the same time at different temperatures in the air for 2h. As is seen from figure 3, the macro-morphology of HP MgF_2 samples showed no significant difference with the increase of temperature, while the macro-morphology of AR MgF_2 samples changed significantly with the increase of temperature. At 750 ^oC, the color of AR MgF_2 sample has been turned from white to pale red. As the temperature increased to 800 ^oC, there were cracks appeared in the sample. From 800 ^oC onwards, with the increase of temperature, the cracks gradually increased and was accompanied by obvious shrinkage. Combined with the results of XRD analysis, it can be considered that the macro-morphology changes of HP MgF_2 and AR MgF_2 samples are mainly caused by the oxidation of MgF_2. Therefore, from the macro-morphology changes in the samples, it can be seen that the oxidation rate of AR MgF_2 was higher than that of HP MgF_2, and the rate increased with the increase of the temperature. These results also show that the participation of impurities and the increase of temperature accelerate the rate of MgF_2 oxidation.

Figure 3. Macro surface morphologies of MgF_2 samples after simultaneously oxidized at different temperatures in the air for 2h: (a) before oxidation; (b) 750 ^oC; (c) 800 ^oC; (d) 850 ^oC; (e) 900 ^oC; (f) 1000 ^oC (The left is HP MgF_2 and the right is AR MgF_2 in each figure).

3.3. Weight loss

Figure 4 shows the weight loss of HP MgF_2 and AR MgF_2 samples after individual and simultaneous oxidation in the air at different temperatures for 2h. As shown in figure 4, from 800 ^oC onwards, the weight loss rate of HP MgF_2 and AR MgF_2, whether they were oxidized individually or simultaneously, showed a significant increase with the increasing of temperature. The weight loss rate of AR MgF_2 was the highest, the weight loss rate of HP MgF_2 that was simultaneously oxidized with AR MgF_2 was in the middle, and the weight loss rate of HP MgF_2 that was individually oxidized was the least. Since MgF_2 does not decompose and evaporate at atmospheric pressure within 1000 ^oC [10], and the oxidation process of MgF_2 into MgO will result in weight loss (the molar mass of MgF_2 is 62.3g/mol^{-1}, MgO is 40.3g/mol^{-1}, and theoretically the weight loss rate of 1mol MgF_2 completely oxidized and converted to MgO is 35.31%), it can be considered that the weight loss of MgF_2 samples means the occurrence of MgF_2 oxidation, and the greater the weight loss rate, the greater the degree of the oxidation. Therefore, from the weight changes of MgF_2 samples, we can see that the oxidation reaction of MgF_2 converted to MgO occurred in the air at high temperature, and the increase of temperature and the addition of impurities accelerated the rate of the reaction. In addition, it can be seen from figure 4 that the weight loss rate of AR MgF_2 after oxidation at 1000 ^oC is close to the theoretical value, which shows that the majority of AR MgF_2 has changed to MgO at the temperature.
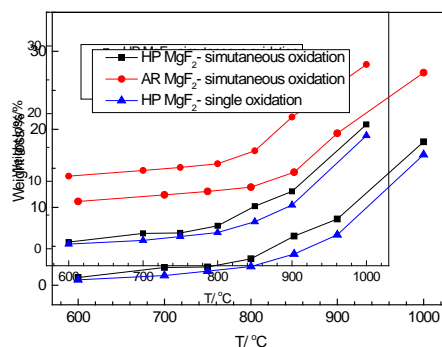
Figure 4. Weight loss of MgF_2 samples after oxidation
in the air at different temperatures for 2h.

3.4. EDS analysis

The EDS analysis results of the elemental composition of HP MgF_2 and AR MgF_2 samples after individual or simultaneous oxidation in the air at different temperatures for 2h are shown in table 2. According to table 2, from 800 $^{\circ}$C onwards, the content of O element in HP MgF_2 and AR MgF_2, whether they were oxidized individually or simultaneously, was significantly increased with the increase of temperature. The increase of O element content in AR MgF_2 with the temperature was the highest, the increase in HP MgF_2 that was simultaneously oxidized with AR MgF_2 was in the middle, and the increase in HP MgF_2 that was individually oxidized was the least. This shows that from 800 $^{\circ}$C onwards, HP MgF_2 and AR MgF_2 had an obvious oxidation and the degree of oxidation was increased with the temperature. The oxidation rate of AR MgF_2 was higher than that of HP MgF_2 oxidized simultaneously with AR MgF_2, and the oxidation rate of HP MgF_2 oxidized individually was the least. The results also indicate that MgF_2 in the air at high temperatures does undergo the oxidation reaction of conversion to MgO, and the presence of impurities accelerates the oxidation reaction of MgF_2. These results are consistent with the results of XRD analysis above.

Table 2. Elemental composition of MgF_2 samples after oxidizing at different temperatures for 2h
(wt%)

Sample	Element	600 $^{\circ}$C	700 $^{\circ}$C	750 $^{\circ}$C	800 $^{\circ}$C	850 $^{\circ}$C	900 $^{\circ}$C	1000 $^{\circ}$C
HP MgF_2	O	1.15	1.40	1.53	2.31	3.98	6.86	16.84
(Single	F	56.75	56.12	55.96	54.85	51.90	47.67	29.68
oxidation)	Mg	42.10	42.48	42.51	42.84	44.12	45.47	53.48
HP MgF_2	O	1.19	1.51	1.69	2.74	4.28	9.58	18.79
(Simultaneous	F	48.37	48.78	50.36	50.02	48.06	41.04	22.50
oxidation)	Mg	50.44	49.71	47.95	47.24	47.66	49.38	58.71
AR MgF_2	O	1.79	2.62	2.98	4.88	7.55	19.34	28.43
(Simultaneous	F	50.80	50.93	50.43	48.28	45.64	25.88	6.29
oxidation)	Mg	47.41	46.45	46.59	46.84	46.81	54.78	65.28

4. Discussion

MgF_2 and MgO are ionic compounds. Because of the electronegativity of fluorine element (3.90) is greater than that of oxygen (3.50) and the change in standard Gibbs free energy for the reaction of MgF_2 and O_2 to produce MgO and F_2 is highly positive, which is 502 kJ·mol^{-1} at 25 $^{\circ}$C, the chemical stability of MgF_2 is greater than that of MgO, and the oxidation reaction of MgF_2 converted into MgO will not occur at normal temperature and pressure in the air. Can the oxidation reaction of MgF_2 converted to MgO occur at high temperatures? There are still different views on this issue [7~9]. And there are also different views on the problem whether the participation of impurities can accelerate the reaction of MgF_2 transformation into MgO at high temperature [7~9].

Our experiments confirmed that when the temperature was higher than 800 ^{o}C, the reaction of MgF_2 transformed into MgO in the air did take place, and with the further increase in temperature, the rate of the reaction increased gradually. The impurities in MgF_2 accelerated the rate of the reaction of conversion of MgF_2 to MgO.

According to the literature [9], there is an abnormal expansion zone in MgF_2 at about 700 ^{o}C, and the two F atoms of MgF_2 have a tendency to rotate around the Mg atom with the increase of temperature. Therefore, we hypothesized that the mechanism of oxidation and conversion of MgF_2 into MgO at high temperature might be as follows: At high temperature, F^- ions in MgF_2 have very high thermal motion energy. They are easy to break away from the shackles of Mg^{2+} under the collision of O_2 molecules in the air, give electrons to Mg^{2+}, and leave in the form of F atoms. Then the F atoms combine to form F_2 molecules and escape. Since O element has a very high electronegativity (3.50) next only to F^-, when F^- ions leave, the O_2 immediately combines with the atomic Mg to produce MgO. The reason for the presence of impurities to accelerate the rate of MgF_2 oxidation may be that the impurities play an intermediary role in the process of MgF_2 oxidation. It is involved in the process of MgF_2 oxidation and there may be a coupling effect between the reaction of impurities and the reaction of MgF_2 oxidation reaction, which reduces the free energy and activation energy of MgF_2 oxidation reaction and makes the reaction rate of MgF_2 oxidation increase. The detailed mechanism needs to be further investigated.

Our experimental result that MgF_2 in air at high temperatures can be converted to MgO is in agreement with that of Liu Yanmei et al [9], but different from that of Xu Zhiyuan and Sun Daming et al [7, 8]. The reason may be that Xu Zhiyuan and Sun Daming's experiments were carried out in an open high temperature furnace, due to the presence of air convection, the temperature of O_2 contacted with MgF_2 was relatively low, which caused MgF_2 not to be oxidized or slightly oxidized. The result of our experiment that the presence of impurity in MgF_2 accelerated the oxidation reaction process of MgF_2 confirms the conclusion by Weimer, Xu Zhiyuan and Sun Da Ming that impurities accelerate the oxidation reaction of MgF_2, but the result is not consistent with that of Liu Yanmei et al. The reason may be that in the experiment of Yan Mei Liu et al, the time of MgF_2 oxidation reaction is too short (only 30 minutes) so that the role of impurities has not come into play, which causes the result that impurities have no effect on the oxidation of MgF_2.

5. Conclusions

The oxidation properties of MgF_2 in the air at 600 ^{o}C~1000 ^{o}C were studied. The results show that the oxidation reaction of MgF_2 transformation into MgO in the air actually did take place at high temperature. The rise of temperature and the impurity added to MgF_2 accelerated the reaction process of MgF_2 oxidation. These results clarified the understanding of the high temperature oxidation behavior of MgF_2 in air and provided a theoretical basis for the reasonable processing and application of MgF_2 as coating materials and electronic ceramic materials, and for optimizing the protection condition of fluorine-containing gases on magnesium melt.

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