Effect of Al Content on the Stability of MgF₂ Powder in Air at High Temperatures

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Abstract. The effect of Al on the stability of MgF₂ powder at 600–1000 °C in air has been investigated by XRD, EDS and SEM. It is found that the thermal stability of MgF₂ is strongly influenced by both Al content and temperature. With the increase of Al content and temperature, MgF₂ was gradually oxidized to MgO, that is, the thermal stability of MgF₂ was gradually lowered. The reason that the addition of Al causes the thermal stability of MgF₂ to decrease may be related to the oxidation of Al and the formation of MgAl₂O₄ at high temperatures.

1. Introduction
As an excellent optical coating material, MgF₂ is the preferred choice for preparing the film with high reflectivity and high damage threshold due to its wide transparent band, low refractive index, wide energy gap, high mechanical strength and laser damage threshold [1]. MgF₂ is also an important electronic ceramic material, which has attracted widespread attention in the development of metal-ceramic materials because of its good insulating performance. Besides, during processing of Mg and its alloys, MgF₂, as a main component of the composite protective film formed on the surface of Mg and its alloy melt, plays a crucial role in the protection of the melt against burning by SF₆ and other fluorine-containing gases, and its content determines the protective effect of SF₆ and other fluorine-containing gases for the melt [2~5].

MgF₂ is considered to be a stable compound, which generally does not decompose or change to other compounds in air. However, some studies have found that MgF₂ becomes less stable at high temperatures and it has a tendency to convert to MgO. Liu et al [6] examined the stability of MgF₂ in air by X-ray diffractometer and found that MgF₂ would be changed to MgO with the temperature above 800 °C, and the conversion rate increased with increasing temperature. Chen et al [7] researched the oxidation of MgF₂ in air and found that the reaction of MgF₂ converted to MgO could occur at high temperatures, and the reaction was accelerated by the increase of temperature and the presence of impurities. In the study of preparing MgF₂/Al composite films by electron beam evaporation deposition, Weimer et al [8] found that about 1% MgO was present in the MgF₂/Al composite film. They believed that the presence of MgO may be due to the 2% Na impurity contained in the raw material, which leads to the oxidation of MgF₂ at high temperature. Xu and co-workers [9] investigated the preparation process of a 30% Ag-MgF₂ cermet material. It was found that MgF₂ component in the 30%Ag-MgF₂ cermet material would turn into MgO in high oxygen partial pressure atmosphere at the temperature of over 600 °C. But pure MgF₂ was rarely oxidized in the atmosphere even though at 1000 °C, while Ag participated in, MgF₂ would be severely oxidized into MgO under this condition. Sun et al [10] investigated the oxidation behavior of MgF₂ in Ag-MgF₂ cermets. They also found that when Ag...
participated in, MgF₂ could be oxidized to MgO at high temperature and high oxygen partial pressure atmosphere or air; otherwise, MgF₂ was rarely oxidized or not oxidized at all under the condition. Obviously, these results are different from those of Liu et al.

Thus it can be seen that whether the participation of impurities has an effect on the oxidation of MgF₂ remains a debate issue. Since the conversion of MgF₂ to MgO reduces the quality of MgF₂ and seriously damages its practical performance, it is necessary to further study the effect of impurities on the stability of MgF₂ in the air. In this paper, the oxidation properties of MgF₂ powder with different Al contents in air at high temperatures were investigated. The purpose of the paper is to clarify the effect impurities on the stability of MgF₂ in air, which will provide a theoretical basis for the reasonable processing and application of MgF₂ as optical coating materials and electronic ceramic materials and for the optimization of protection conditions of fluorine-containing gases for Mg and its alloy melt.

2. Experimental procedure

The raw materials used for the present study were high purity MgF₂ and high purity Al powders. The chemical composition of MgF₂ powder (wt.%) is 99.99 MgF₂, 0.001 Na, 0.001 Fe, 0.002 Si, 0.002 Ca, 0.001 Pb, 0.002 SO₄²⁻ and 0.001 H₂O. The chemical composition of Al powder (wt.%) is 99.8 Al, 0.08 Fe, 0.06 Si, 0.01Cu, 0.05 H₂O.

The MgF₂ powders with a particle size of 72 μm and Al powders with a particle size of 45 μm were mixed in the R-1002 rotary evaporator with the weight ratios of Al to MgF₂ of 0%, 1%, 5%, 10%, 20%, 30% and 40%, respectively. The mixed MgF₂ and Al powder was placed in a stainless steel mold with a diameter of 20 mm and pressed at a pressure of 100 MPa for 15 min, then a disk sample with the size of 20mm×2mm was obtained.

The experiment was conducted in an SK-G05123K tube furnace and the experimental procedure was as follows: The disk sample was first placed in an alumina crucible and then moved into a quartz glass tube in the tube furnace. Next, the sample was heated to the desired temperature at the rate of 8 °C/min and held for 2 h. After the time was reached, the oxidized sample was cooled and taken out for X-ray diffractometer (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analyses. XRD analysis of the oxidized sample was carried out on a Rigaku Ultima IV X-ray diffractometer with a Cu-Kα source operated at 40 kV and 40 mA. The scanning speed was 4°/min, the step width was 0.02°, and the diffraction angle was 20° to 80°. The elemental composition and morphology of the oxidized sample were investigated by an EDAX Genesis APEX EDS and Quanta FEG 250 FESEM.

3. Results and discussion

Figure 1 shows the XRD patterns of 1%Al+MgF₂ samples after exposure to air at 600 °C–1000 °C for 2 h. It can be seen that at 600 °C and 700 °C, only the peaks of MgF₂ appeared, which indicates that MgF₂ was stable at the temperature and no reaction occurred. However, as the temperature reached 800 °C, in addition to the peaks of MgF₂, the peak of MgO appeared, which indicates that MgF₂ became unstable and the reaction of conversion of MgF₂ to MgO occurred at this temperature. With the further increase of temperature, the content of MgF₂ decreased rapidly, and the content of MgO increased sharply.
Figure 1. XRD patterns of MgF₂ sample containing 1% Al exposed to air at 600 °C–1000 °C.

Figure 2. XRD patterns of MgF₂ samples with different contents of Al exposed to air at 1000 °C.

Figure 2 shows the XRD patterns of MgF₂ samples with different contents of Al after exposure to air at 1000 °C for 2 h. As can be seen, after exposure to air at 1000 °C for 2 h, the sample containing 1% Al was mainly composed of MgO and a small amount of MgF₂. For the sample containing 5% Al, a small amount of MgAl₂O₄ appeared, in addition to MgO and MgF₂. With the further increase of Al content in the sample, the content of MgO increased first and then decreased, the content of MgF₂ decreased slowly, and the content of MgAl₂O₄ increased gradually.

Figure 3 shows the SEM images of MgF₂ sample containing 1% Al after exposure to air at 600 °C–1000 °C for 2 h. As shown in Figure 3, the effect of temperature on the surface morphology of the samples is not very significant. As the temperature increased, the surface became rough and white particles increased.
Figure 3. SEM images of MgF$_2$ sample containing 1% Al exposed to air at different temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C and (e) 1000 °C.

Figure 4 shows the SEM images of MgF$_2$ sample with different contents of Al after exposure to air at 1000 °C for 2 h. It can be observed that as the Al content increased, the surface of the sample became more and more rough, white particles increased and tended to become larger.
Figure 4. SEM images of MgF$_2$ sample with different contents of Al exposed to air at 1000 °C: (a) 0% Al, (b) 1% Al, (c) 5% Al, (d) 10% Al, (e) 20% Al, (f) 30% Al and (g) 40% Al.

The EDS analysis results of MgF$_2$ samples containing 1% Al after exposure to air at 600 °C–1000 °C for 2 h are listed in Table 1. According to Table 1, at 600 and 700 °C, the content of fluorine and oxygen did not change very much in the sample, and the oxygen content was small. As temperature increased from 800 to 1000 °C, the oxygen content decreased and the fluorine content increased. At 1000 °C, the oxygen content reached a maximum and the fluorine content reached a minimum. This result indicates that MgF$_2$ sample containing 1% Al undergoes significant oxidation at 800 °C. As the temperature increased further, the oxidation process intensified. At 1000 °C, MgF$_2$ was almost completely oxidized.

| Temperature [°C] | O   | F    | Mg   | Al   |
|------------------|-----|------|------|------|
| 600              | 1.92| 53.97| 41.90| 2.21 |
| 700              | 1.18| 54.91| 43.34| 0.57 |
| 800              | 9.34| 43.46| 46.44| 2.75 |
| 900              | 28.89| 9.23 | 60.88| 1.00 |
| 1000             | 30.99| 0.87 | 67.56| 0.58 |

The EDS analysis results of MgF$_2$ samples with different contents of Al after exposure to air at 1000 °C for 2 h are shown in Table 2. It can be found that the content of fluorine was very small. As the aluminum content increased, the contents of fluorine and oxygen were generally reduced and the content of aluminum was increased.
Table 2. EDS results of MgF₂ samples with different contents of Al exposed to air at 1000 °C [wt.%]

| Al [wt.%] | O  | F  | Mg  | Al  |
|-----------|----|----|-----|-----|
| 0         | 43.12 | 2.59 | 54.29 | -   |
| 1         | 30.99 | 0.87 | 67.56 | 0.58 |
| 5         | 32.15 | 1.68 | 65.56 | 0.61 |
| 10        | 34.58 | 1.60 | 55.82 | 8.00 |
| 20        | 31.24 | 0.53 | 51.46 | 16.76 |
| 30        | 30.65 | 0.95 | 47.17 | 21.23 |
| 40        | 30.35 | 1.43 | 36.52 | 31.70 |

The potential reactions that might occur in the MgF₂ + Al system in air are:

\[
\begin{align*}
&MgF_2(s) + \frac{1}{2}O_2(g) = MgO(s) + F_2(g) \quad \text{(1)} \\
&MgF_2(s) + H_2O (g) = MgO(s) + 2HF(g) \quad \text{(2)} \\
&2Al (l) + \frac{3}{2}O_2(g) = Al_2O_3(s) \quad \text{(3)} \\
&MgO(s) + Al_2O_3(s) = MgAl_2O_4(s) \quad \text{(4)}
\end{align*}
\]

According to literature 11, thermodynamically, reaction (1) is not favorable \((\Delta G > 0)\), other reactions are favorable \((\Delta G < 0)\) in the temperature range of interest, and reaction (3) has the lowest \(\Delta G\) value. Therefore, the mechanism of Al promoting the oxidation of MgF₂ at high temperatures may be as follows: Al can react with O₂ to produce Al₂O₃, the resulting Al₂O₃ then can react with MgO to form MgAl₂O₄, which consumes MgO and breaks the balance of reaction (2), thereby accelerating the reaction of MgF₂. It is clear that the formation of Al₂O₃ is the main reason for Al to accelerate the oxidation of MgF₂ in this study.

4. Conclusions

The effect of Al on the stability of MgF₂ was related to its content and temperature. With the increase of Al content and temperature, the thermal stability of MgF₂ was gradually lowered. The effect of Al on the thermal stability was linked to the oxidation of Al in the system, which produced Al₂O₃ and promoted the formation of MgAl₂O₄, resulting in the acceleration of the oxidation reaction of MgF₂.

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