The oxidation properties of MgF$_2$ particles in hydrofluorocarbon/air atmosphere at high temperatures

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Abstract. The high temperature oxidation properties of magnesium fluoride powders in the atmosphere of air containing hydrofluorocarbon (HFC-134a) were characterized by EDS, SEM, XRD, and gravimetric analyses. The results showed that the oxidation property of magnesium fluoride powder was related to the concentration of HFC-134a, temperature and reaction time. With the concentration of HFC-134a decreasing, the temperature rising and the reaction time prolonging, the extent of magnesium fluoride oxidation increased. This result is great significance for further study of the protective theory of fluorine-containing gases on Mg and its alloys.

1. Introduction

As one of the lightest structural metals, Mg alloys are used in the automotive and aerospace industries. However, their applications are still limited due to oxidation and combustion during processing [1]. In order to prevent the oxidizing and burning, sulfur hexafluoride (SF$_6$) is generally used as a protection gas during the processing of Mg alloys. In recent years, SF$_6$ has been forbidden owing to its strong greenhouse effect [2]. Therefore, it is urgent and necessary to look for possibilities to replace the SF$_6$ during the processing. Hydrofluorocarbon (CF$_3$CH$_2$F, HFC-134a) has been recently introduced to protect the melting process of Mg alloys [3]. Further studies show that when Mg alloys are smelted and processed by HFC-134a/air protection, a composite protective film of MgF$_2$ and MgO is formed on the surface of the melt. MgF$_2$ is the key component in the membrane, which is of great importance for melt protection, and its content could reflect the protection influence of the compound gas [4].

In generally, MgF$_2$ is stable and would not decompose under normal circumstances. However, some studies have confirmed the fact that MgF$_2$ can be transformed into MgO in air at high temperatures [5-8]. Then, will this oxidation reaction occur in HFC-134a/air atmosphere at high temperature? If so, what factors will affect the reaction process? So far, these problems are still unknown, and related research has not been reported. Therefore, the oxidation properties of MgF$_2$ in the high temperature atmosphere of HFC-134a/air at were researched. In order to provide theoretical elements for further research of protective mechanism of fluorine-containing gases on magnesium and its alloys.

2. Experiments

In this study the feed stocks were high purity of MgF$_2$ particles and its chemical composition (wt%) is 0.002 SO$_4^{2-}$, 0.001 Pb, 0.002 Si, 0.002 Ca, 0.001 Fe, 0.001 Na, 0.001 H$_2$O and balance MgF$_2$. The
gases used in this study were the mixture of hydrofluorocarbon (HFC-134a>99.9%, water<0.001%) and air.

The oxidation of MgF₂ powders was studied by means of a high-temperature test method. The tests were conducted in a tubular furnace in an HFC-134a/air atmosphere. The experimental apparatus includes air generating pump, a Φ 50 mm×1000 mm quartz tube in a tubular furnace with temperature control device. In this work, air and HFC-134a were mixed in the setted proportion and then continuously fed into the quartz tube at 300 mL/min. After purging the tube inside was using the compound gas for 1 h, about 2.5 g of MgF₂ sample, which had sieved a 200 mesh screen sieve, was positioned in the crucible, and then heated to the desired temperament at a rate of 8 ~ 10 °C/min and hold in the atmosphere for a certain time. And then, the sample was refrigerated to room temperature, and deposited in a desiccator for the, energy dispersive spectrometer and scanning electron microscope analyses.

The phase composition of the oxidized MgF₂ specimens was tested by a Rigaku Ultima IV X-ray diffractometer with Cu-Kα source operated at 40 kV and 40 mA. The morphology and elemental composition of the oxidized MgF₂ examples were investigated by Quanta FEG 250 FESEM and EDAX Genesis APEX EDS respectively.

3. Results and discussion

3.1. Influences of HFC-134a concentration on MgF₂ oxidation

Figure 1 presented the X-ray diffraction spectrum of MgF₂ specimens after oxidation in the compound gas of atmosphere with diverse concentrations of HFC-134a at 1000 °C for 2 hours. There was no obvious MgO transformed in the mixture gases containing 1 % and 0.5 % HFP-134a. In air with HFC-134a concentration under 0.1% the peaks of MgO appeared, also their intensities increased as the concentration of HFP-134a went down. It indicates that at 1000 °C, MgF₂ was not oxidized in air with relative high concentration of HFC-134a. While in air with relative low concentration of HFC-134a, MgF₂ was oxidized, and with the concentration of HFC-134a decreasing, the oxidation degree increased gradually.

Figure 1. XRD spectra of MgF₂ samples oxidized in diverse concentrations of HFC-134a at 1000 °C for 2 hours.

The morphologies were scanned by scanning electron microscope for MgF₂ samples after exposure to air containing concentrations of 1% ~ 0.01% HFC-134a at 1000 °C were shown in Figure 2. There in air containing 1% and 0.5% HFC-134a, MgF₂ particles were larger. There were a small amount of white granules on the samples surfaces in the atmosphere containing 0.1% HFC-134a, which were identified as MgO by energy dispersive spectrometer spot scanning. With the reduction of HFC-134a gas concentration from 0.1% to 0.01%, white granules increased. These results suggest that in air with
HFC-134a concentration below 0.1%, the reaction of converting MgF₂ to MgO occurred and the extent of the reaction increased with the decrease of the HFC-134a concentration.

![Figure 2. SEM photos of oxidized MgF₂ samples in different concentrations of HFC-134a/air atmosphere at 1000 °C for 2 hours. (a) 1%, (b) 0.5%, (c) 0.1%, (d) 0.05%, (e) 0.01%](image)

Table 1 lists the EDS data results of oxidized MgF₂ samples in the atmosphere of air containing diverse concentrations of HFC-134a at 1000 °C for 2 hours. It clearly shows that when the concentration of HFC was 1% and 0.5%, the content of oxygen element was low and did little variation. As HFC-134a concentration fell to 0.1%, 0.05% and 0.01 %, the content of oxygen element was obviously improved and elevated with the reduction of HFC-134a concentration. This demonstrates that MgF₂ underwent a weak oxidation in the atmospheres of air containing 1 % and 0.5 % HFC-134a. With the decrease of HFC-134a concentration, the oxidation extent of MgF₂ elevated.

| HFC-134a concentration (%) | Mg  | O   | F    |
|---------------------------|-----|-----|------|
| 1                         | 20.10 | 1.83 | 78.07 |
| 0.5                       | 25.27 | 2.17 | 72.56 |
| 0.1                       | 31.35 | 12.39 | 56.26 |
| 0.05                      | 50.78 | 29.08 | 20.14 |
| 0.01                      | 52.38 | 42.59 | 5.04  |

The weight loss of oxidized MgF₂ samples in different concentrations of HFC-134a/air atmosphere at 1000 °C for 2 hours is shown Figure 3. As shown in Figure 3, with the reduction of the

![Figure 3. The weight loss of oxidized MgF₂ samples in atmosphere with diverse concentrations of HFC-134a/air at 1000 °C for 2 hours](image)
concentration of HFC-134a, the weight loss of oxidized MgF$_2$ sample increased. Because of MgF$_2$ does not decompose and evaporate within 1000 °C, and the oxidation process of MgF$_2$ into MgO will result in weight loss (the molar mass of MgF$_2$ is 62.3 g mol$^{-1}$, MgO is 40.3 g mol$^{-1}$). Therefore, the weight loss of oxidized MgF$_2$ samples improved with the decrease of the concentration of HFC-134a. The outcome is corresponding with the outcome of energy dispersive spectrometer analysis above.

3.2. Influences of temperature on MgF$_2$ oxidation

Figure 4a presents the XRD analysis results of oxidized MgF$_2$ samples at diverse temperatures in air containing 0.01% HFC-134a for 2 hours. At temperatures of 600 and 700 °C, there is only MgF$_2$ peak and no MgO peak in the spectrum. At 800 – 1000 °C, the MgO peak appeared, and as the temperature increased, the height of MgO peak increased stage by stage. The XRD analysis results of MgF$_2$ samples after oxidation at different temperatures in air containing 0.1% HFC-134a for 2 h has been shown in Figure 4b. It can be seen that when the temperature was 600–850 °C, there was only the peaks of MgF$_2$ in the spectra and no MgO peak. Between 900 and 1000 °C, the MgO peaks appeared, and the intensity of MgO peak increased gradually with the increase of temperature. This result is similar to that of MgF$_2$ in the mixing atmosphere of 0.01% HFC-134a/air. It is indicated that temperature is also an important factor affecting the oxidation behaviour of MgF$_2$ in HFC-134a/air atmosphere, and the oxidation degree of MgF$_2$ increases with the increase of temperature.

The EDS analysis results of MgF$_2$ samples after oxidation at different temperatures in air containing 0.01% HFP for 2 h have been shown in Table 2. According to Table 2, at 800 and 850 °C, O element content was very low and it increased slightly with increasing temperature. At 900, 950 and 1000 °C, the content of O element increased obviously with the increase of temperature. These results are consistent with the results of XRD analysis above.

Table 2. Elemental composition of oxidized MgF$_2$ samples at different temperatures in air containing 0.01% HFP for 2 h (wt%)

| Temperature (°C) | Mg    | O     | F     |
|-----------------|-------|-------|-------|
| 600             | 27.69 | 0.75  | 71.56 |
| 700             | 27.24 | 1.12  | 71.64 |
| 800             | 33.78 | 11.49 | 54.73 |
| 850             | 31.99 | 13.89 | 54.12 |
| 900             | 33.20 | 14.47 | 52.34 |
| 950             | 37.50 | 16.58 | 45.92 |
Figure 5 shows the weight loss of MgF$_2$ samples after oxidation in the air at different temperatures for 2h. As shown in Figure 5, the weight loss of MgF$_2$ samples increased with the increase of temperature. This further indicates that the temperature has a considerable influence on the high temperature oxidation character of MgF$_2$ in HFC-134a/air atmosphere.

![Figure 5. Weight loss of MgF$_2$ samples exposed to 0.1% HFC-134a/air at different temperatures for 2h](image)

3.3. Influences of reaction time on MgF$_2$ oxidation

The XRD analysis results of oxidized MgF$_2$ samples at diverse times in air containing 0.1% HFC-134a at 1000 °C was showed by Figure 6. There was no MgO peaks at 1 h, while from 2 h to 5 h, the height of MgO peaks was slightly increased. This indicates that as the reaction time increased from 1 h to 5 h, the content of MgO increased and MgF$_2$ content decreased.

![Figure 6. XRD results of oxidized MgF$_2$ samples at diverse times in air containing 0.1%HFC-134a at 1000 °C.](image)

Table 3 presents EDS analysis results of oxidized MgF$_2$ samples at diverse times in air containing 0.1% HFC-134a at 1000 °C. According to the form, when the reaction time was 1 h, the content of oxygen element was small. As the reaction time increased from 2 hours to 5 hours, the content of oxygen element distinctly increased, which was matching with the corresponding XRD analysis results.

Table 3. Elemental composition of oxidized MgF$_2$ samples at diverse times in air containing 0.1% HFC-134a at 1000 °C (wt%)

| Time(h) | Mg    | O     | F     |
|---------|-------|-------|-------|
| 1       | 29.16 | 0.43  | 70.41 |
| 2       | 31.35 | 12.39 | 56.26 |
4. Conclusions
The oxidation of MgF$_2$ particles in HFC-134a/air atmosphere at high temperatures was studied. It was found that the oxidation of MgF$_2$ in the atmosphere was mainly related to the concentration of HFC-134a, temperature and reaction time. With the decrease of HFC-134a concentration, the increase of temperature and the prolongation of reaction time, the degree of oxidation of MgF$_2$ increased. The results can provide a theoretical basis for the study of the protection mechanism of HFC-134a gas on magnesium and its alloy melt.

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