Oxidation behaviour of molten magnesium and AZ91D magnesium alloy in 1,1,1,2-tetrafluoroethane/air atmospheres

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1. Introduction

Magnesium alloys are the lowest density of structure metal materials, having been paid much attention to its applications for automobile, communication, electron, aerospace and other industries because of its excellent properties [1]. However, magnesium is a very active element, and it has extremely high affinity with oxygen and high vapor pressure. The oxidation film on its surface is loose and porous which do not prevent magnesium and its alloys from oxidation. Magnesium and its alloys appear badly oxidizing or even burning at high temperature. It is therefore necessary to take measures to prevent the melt from oxidizing and burning in the process of melting and casting operations. Many methods have been investigated to reduce or inhibit the oxidation of molten magnesium and its alloy in air, such as flux covering, gas protection and alloying element addition. Among them, the protection method of SF6 gas mixture is currently considered to be the most effective technique for the melt, because SF6 gas mixture can form a thin, coherent and stable film on the melt surface of magnesium and its alloys [2]. But, many researches indicate [3,4] that SF6 gas has serious greenhouse effect. With the increasing cost of SF6 and concern over the contribution of SF6 to the greenhouse, SF6 has been restricted or forbidden to use in some countries in recent years. It is an urgent subject to develop new alternatives with both low environmental impact and low toxicity.

1,1,2-Tetrafluoroethane (CF3CH2F, HFC-134a) has been recently developed for magnesium melt protection by the Cooperative Research Center for Cast Metals Manufacturing in Australia [5]. Because the global warming potential of HFC-134a is 8 times lower than SF6 and its atmospheric lifetime is only 0.46% of SF6. The researches of Ricketts and Cashion [5,6] have reported that HFC-134a can provide excellent protection for molten magnesium and is the candidate for the replacement of SF6. The thermal stability of HFC-134a is inferior to that of SF6 at high temperature, so HFC-134a can give up its fluorine more readily to protect the melt compared with SF6 [7]. Chen et al. [8] have investigated the oxidation behaviour in the atmospheres of air containing HFC-134a. However, the effect of alloying elements on the oxidation behaviour of magnesium and the composition of oxidation films formed in the atmospheres are not clear. In order to provide more effective protection for magnesium alloys, the oxidation characteristics of magnesium alloys under the atmospheres are necessary to be studied.

In the present study, the oxidation behaviour of magnesium and AZ91D alloy in HFC-134a/air atmospheres at 760 °C has been investigated and discussed based on its oxidation rates, morphologies and compositions of the surface films formed.

2. Experimental

The materials used for oxidation tests were pure magnesium, AZ91D alloy and HFC-134a gas. The chemical composition of pure magnesium and AZ91D magnesium alloy in weight percent are listed in Table 1. The composition of HFC-134a gas in weight percent is HFC-134a ≥ 99.8%, HCl < 0.0001%, H2O ≤ 0.001%. The samples with 3 mm thick and 20 mm in diameter were cut from the
central part of the as-cast ingot. Before each experiment, they were ground with grade 320 SiC paper, washed with acetone and dried in room temperature, in order to obtain a relatively flat and clean surface which is in favor of the analysis for morphology of the surface film formed.

The experimental set-up of static oxidation is shown in Fig. 1, which consisted of a recording electronic balance, a resistance furnace with sealing cover, magnesia crucible which was hung into the resistance furnace connecting with the electronic balance using platinum silk and a gas system which provides gas mixtures of air and HFC-134a to the hot chamber. Before experiment, the crucible was heated to 800 °C until constant weight was achieved, and then put it into a desiccator to room temperature. The air and HFC-134a, which were dried and purified through columns of CaCl₂ and silica-gel desiccant, were mixed in the required proportion in a gas pot and then continuously fed into the hot chamber at 500 ml/min. After purging inside the chamber using gas mixture for at least 1 h, the sample was placed in the crucible that had been hung in the chamber, and then heated to the desired experimental temperature at a rate of 100 °C/min and hold the temperature constant. The weight gains of the oxidized samples were measured in a certain interval by an electronic balance with an accuracy of 0.1 mg.

Thermogravimetry measurements were used to study the oxidation kinetics. The weight gains of the oxidized samples were measured in an electronic balance with an accuracy of 0.1 mg in the atmosphere of air containing different concentrations of HFC-134a at 760 °C for different times.

After the oxidation, the oxidized surface layers were examined by SEM, XPS and XRD. The distribution of some elements across the oxide and substrate interface in oxidized specimens was examined by AES with argon ion beam sputtering.

### 3. Experimental results

#### 3.1. Oxidation Kinetics

Fig. 2 shows the curves of weight gain to time for molten magnesium and AZ91D alloy in the atmosphere of air containing different concentrations of HFC-134a at 760 °C. From Fig. 2a, it is found that with the concentration of HFC-134a increase, the weight gain curves of molten magnesium exhibited different behaviours and the oxidation rate decreased gradually. In the atmosphere of air containing 0.001% HFC-134a, the weight gain curve of molten magnesium increased more rapidly than others and presented linear raise. When the concentration of HFC-134a increased to 0.01%, the weight gain curve moved up rapidly at the initial stage of oxidation and almost linearly increased with time after about 20 minutes. When the concentration of HFC-134a increased from 0.1% to 5%, the weight gain curves were similar to each other, approximately followed parabolic law, and its oxidation rates decreased gradually. It can be seen from Fig. 2b that with the concentration of HFC-134a increase, the curve variation of oxidation weight gain for molten AZ91D alloy were different from that for molten magnesium. In the atmosphere of air containing 0.001%, 0.01%, and 0.1% HFC-134a, the weight gain curves of molten AZ91D alloy moved up linearly. This indicated that the oxidation rate of molten AZ91D alloy was higher than that of molten magnesium under the conditions. In the atmosphere of air containing 1%, 3%, and 5% HFC-134a, the weight gain curves obeyed parabolic law and the oxidation rate of molten AZ91D alloy was lower than that of molten magnesium. The difference in oxidation rates between molten magnesium and AZ91D alloy may be related to the alloying elements.

#### 3.2. Surface oxidation layer morphology

Fig. 3 shows some typical surface film morphologies of molten magnesium and AZ91D alloy after exposure in different concentrations of HFC-134a at 760 °C for 2.5 h. It can be seen from Fig. 3a and c that the surface film formed on molten magnesium in the atmosphere of the air containing 0.1% HFC-134a presented numerous small and relative symmetrical distribution oxide nodules on the surface film of magnesium. This indicated that under this condition, the covering gas had a certain protection for magnesium melt, but its protective effect was not very good. For the surface layer on AZ91D alloy, it was covered by a large number of cluster oxidation reaction products (Fig. 3c). This indicated that in the atmosphere of air containing 0.1% HFC-134a, the oxidation resistance of AZ91D alloy was not as good as magnesium. Compared Fig. 3b with d, the surface film formed on molten magnesium in the atmosphere of air containing 1% HFC-134a was not uniform, and some grooves and folds appeared on its surface. However, the surface formed on molten AZ91D alloy was relatively smooth and compact. The results showed that AZ91D alloy had better oxidation resistance than magnesium under the atmosphere of air containing 1% HFC-134a.

#### 3.3. Oxidation products

XRD measurements were performed to determine the phase composition of the surface films formed on magnesium and AZ91D alloy and the results are shown in Table 2. It can be seen from Table 2 that Mg phase appeared in all XRD analysis results, which resulted from the substrates of magnesium and AZ91D alloy. The other phase composition except Mg phase depended on the concentration of HFC-134a in air and the alloy composition. When the HFC-134a concentration was equal to or more than 1%, MgF₂ phase appeared in the films formed on magnesium surface, while the films formed on AZ91D alloy surface presented C phase besides MgF₂ phase. Based on the properties of magnesium, there must be

### Table 1

Chemical compositions of magnesium and AZ91D alloy used in the experiments, in wt%.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.0029</td>
<td>0.01</td>
<td>0.0025</td>
<td>0.0046</td>
<td>0.0004</td>
<td>0.0008</td>
<td>0.0001</td>
<td>Balance</td>
</tr>
<tr>
<td>AZ91D</td>
<td>9.06</td>
<td>0.70</td>
<td>0.30</td>
<td>0.025</td>
<td>0.0017</td>
<td>0.0037</td>
<td>0.0007</td>
<td>Balance</td>
</tr>
</tbody>
</table>
the reaction between Mg and O₂ and the production MgO should exist in the surface film in this case. However, MgO was not detected by X-ray diffraction analysis on the surface films of magnesium and AZ91D alloy. The reason might be that the content of MgO was fewer in the surface film which went beyond the analysis range of XRD. When the HFC-134a concentration decreased to 0.1%, the films on magnesium surface were consisted of MgF₂, MgO, Mg, C, and Mg₃N₂, AlN, MgF₂. As the HFC-134a concentration decreased further to 0.01% and below, the films on magnesium surface were mainly composed of MgO and small amount of MgF₂, C, and Mg₃N₂, and the films on AZ91D alloy surface were mainly composed of MgO and small amount of Mg₂N₂, AlN, MgF₂ and MgAl₂O₄.

Table 2
XRD results of surface films formed on magnesium and AZ91D alloy in air containing different concentration of HFC-134a at 760 °C.

<table>
<thead>
<tr>
<th>HFC-134a concentration (%)</th>
<th>Phase in the films formed on Mg</th>
<th>Phase in the films formed on AZ91D</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>MgF₂, Mg</td>
<td>MgF₂, Mg, C</td>
</tr>
<tr>
<td>3</td>
<td>MgF₂, Mg</td>
<td>MgF₂, Mg, C</td>
</tr>
<tr>
<td>1</td>
<td>MgF₂, Mg</td>
<td>MgF₂, Mg, C</td>
</tr>
<tr>
<td>0.1</td>
<td>MgO, MgF₂, Mg, Mg₃N₂</td>
<td>MgO, MgF₂, Mg, Mg₃N₂, AlN, MgF₂</td>
</tr>
<tr>
<td>0.01</td>
<td>MgO, MgF₂, C, Mg₃N₂</td>
<td>MgO, MgF₂, Mg₃N₂, AlN, MgAl₂O₄</td>
</tr>
<tr>
<td>0.001</td>
<td>MgO, Mg₃N₂</td>
<td>MgO, Mg₃N₂, AlN, MgAl₂O₄</td>
</tr>
</tbody>
</table>

Fig. 2. The curves of oxidation weight gain to time for (a) magnesium and (b) AZ91D alloy in the atmosphere of air containing different concentration of HFC-134a at 760 °C.

Fig. 3. Surface film morphologies of magnesium after oxidation in the atmosphere of air containing (a) 0.1% HFC-134a, (b) 1% HFC-134a and AZ91D alloy in (c) 0.1% HFC-134a, (d) 1% HFC-134a at 760 °C.
Since magnesium has an extremely high affinity for oxygen, MgO will exist in the surface of the substrate. In order to determine the presence of MgO and other minor phase in the surface film formed on magnesium and AZ91D alloy in air containing 1% HFC-134a at 760 °C, the films were also examined by XPS and the results are shown in Figs. 4 and 5, respectively. From Fig. 4a, it was observed that there were F, Mg, C, and O elements in the surface film formed on molten magnesium. Na and Ar elements might be the contaminants introduced in the process of preparation and analysis of the sample. According to Mg 2s spectrum (Fig. 4b), Mg was present in two chemical states. The lower binding energy peak at 90.93 ± 0.2 eV was assigned to MgO [9] and the higher binding energy peak at 93.94 ± 0.2 eV was attributed to MgF2. Three component peaks were evident in the C 1s core level spectrum of the same surface film (Fig. 4c). The binding energy peak at 284.41 ± 0.2 eV was attributed to simple substance of carbon, the binding energy peak at 286.21 ± 0.2 eV was due to C–O and the binding energy peak at 288.54 ± 0.2 eV was attributed to O=C–O [10]. C–O and O=C–O could be negligible due to their very low content in the film.

XPS survey spectra of the surface film formed on molten AZ91D alloy showed that the dominant signals came from F, Mg, C, O, and Al, and the N, Si, and Na peaks might be contaminants introduced in the process of preparation and analysis of the sample (Fig. 5a). From Fig. 5b, it can be seen that Mg was present in three chemical states. The binding energy peak at 51.29 ± 0.2 eV was MgF2, the binding energy peak at 50.70 ± 0.2 eV was Mg(OH)2, and the binding energy peak at 49.63 ± 0.2 eV was MgO. Since the intensity of the peak at 51.29 ± 0.2 eV was greater than that of the peaks at 50.70 ± 0.2 eV and 49.70 ± 0.2 eV, it could be concluded that the content of MgF2 in the surface film was higher than that of MgO and Mg(OH)2, and the amount of Mg(OH)2 was very fewer. From Fig. 5c, it can be seen that F presented in two chemical states. The binding energy peak at 683.17 ± 0.2 eV was AlF3, and the content of MgF2 was much greater than that of AlF3 in the film. In Fig. 5d, the binding energy peak at 76.00 ± 0.2 eV was the peak of Al2p3/2 in AlF3 and the binding energy peak at 73.50 ± 0.2 eV was the peak of Al2p3/2 in Al2O3. Here the content of AlF3 was much greater than that of Al2O3. Fig. 4e showed that C was present in three chemical states. The lower binding energy peak at 284.51 ± 0.2 eV was attributed to simple substance of carbon and the peaks at 286.85 ± 0.2 eV and 288.01 ± 0.2 eV which resulted from CO and CO2. CO and CO2 may come from the adsorption of CO and CO2 in covering gas on the surface of MgF2 and MgO film. CO and CO2 could be negligible due to their very low content in the film.

Based on the above XPS analysis results, it can be concluded that MgO existed in the surface films formed on magnesium and AZ91D alloy in the air containing 1% HFC-134a at 760 °C, and C existed in the surface films formed on magnesium. In addition, the surface film on AZ91D alloy also contained small amount of AlF3 and Mg(OH)2. Because the amount of this compounds were much less than that of MgF2, these compounds were not detected in the XRD analysis results of the films formed on magnesium and AZ91D alloy surfaces in the atmosphere of air containing 1% or more HFC-134a at 760 °C.

4. Discussion

The results of isothermal oxidation of molten magnesium and AZ91 alloy in the atmospheres of the air containing HFC-134a in the present study show that the oxidation behaviour between molten magnesium and AZ91 alloy was different, and the difference varied with the concentration of HFC-134a in air. The results can be explained by following reasons.

In the atmospheres of the air containing high concentration of HFC-134a, molten magnesium may react with O2 and HFC-134a...
or F₂ which is the decomposition product of HFC-13a. The reactions may be as follows:

\[
\text{Mg(l) + 1/2O}_2(g) \rightarrow \text{MgO(s)} \quad \Delta G^0_1 = -612955 + 128.08T
\]

\[
\text{Mg(l) + CF}_3\text{CH}_2\text{F(g) + 2O}_2(g) \rightarrow \text{MgF}_2(s) + 2\text{HF(g) + 2CO}_2(g)
\quad \Delta G^0_2 = -1577662 - 60.45T
\]

\[
\text{Mg(l) + F}_2(g) \rightarrow \text{MgF}_2(s) \quad \Delta G^0_3 = -1120000 + 171.2T
\]

Based on the Gibbs free energies (\(\Delta G^0_i\)) of the above reactions, the reaction trend of magnesium with HFC-134a or F₂ is greater than that of magnesium with O₂. So the surface films formed on molten magnesium mainly consisted of MgF₂. Due to the large amounts of oxygen in the gas mixture, the surface film also contained small amount of MgO. This was confirmed by the results of XRD and XPS. Since the compactness coefficient of MgF₂ (1.32) is greater than that of MgO (0.81), the composite film of MgF₂ and MgO was compact, which effectively blocked the outward evaporation of magnesium and the inward diffusion of oxygen through the surface film, and provided effective protection for molten magnesium. In this case, the oxidation kinetics curves of magnesium obeyed parabola law and the oxidation rate was lower. For molten AZ91D alloy, in addition to the reaction between Mg and O₂, HFC-134a or F₂, alloying elements Al, Zn, and Mn might react with oxygen and HFC-134a or F₂:

\[
\text{Al(l) + 3/2F}_2(g) \rightarrow \text{AlF}_3(s) \quad \Delta G^0_4 = -1507750 + 257.90T
\]

\[
\text{Al(l) + 3/4O}_2(g) \rightarrow 1/2\text{Al}_2\text{O}_3(s) \quad \Delta G^0_5 = -841450 + 161.62T
\]

\[
\text{Zn(l) + F}_2(g) \rightarrow \text{ZnF}_2(s) \quad \Delta G^0_6 = -768600 + 174.72T
\]

\[
\text{Zn(l) + 1/2O}_2(g) \rightarrow \text{ZnO(s)} \quad \Delta G^0_7 = -348360 + 103.28T
\]

\[
\text{Mn(l) + 1/2O}_2(g) \rightarrow \text{MnO}_2(s) \quad \Delta G^0_8 = -380491 + 135.30T
\]

\[
\text{Mn(l) + O}_2(g) \rightarrow \text{MnO}_2(s) \quad \Delta G^0_9 = -531830 + 188.78T
\]

For reaction (4), the change of its standard free energy is more negative than that of the reactions (6)–(9) and the content of Zn and Mn in AZ91D alloy is relative less, so the reaction (4) could

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**Fig. 5.** The XPS survey spectra of the surface film formed on AZ91 in air containing 1% HFC-134a at 760 °C for 2.5 h (after 30 min sputtering with Ar⁺ ion), (a) the whole survey spectra, (b) Mg 2p, (c) F 1s, (d) Al 2p, and (e) C 1s.
take place but the reaction (6)–(9) did not occur. As a result, the surface films on molten AZ91D alloy in the air containing high concentration of HFC-134a were mainly composed of MgF2 with small amount of MgO and AlF3. Similar to the case with molten magnesium, the oxidation kinetics curves of molten AZ91D alloy obeyed parabola law too. However, because the surface film on molten AZ91D alloy contained small amount of AlF3 and higher content of C compared with the film formed on molten magnesium, the oxidation rate of AZ91D alloy in the atmospheres of the air containing high concentration of HFC-134a was lower than that of magnesium in the same atmospheres.

In the atmospheres of the air containing low concentration of HFC-134a, although the reaction trend between Mg and HFC-134a or F2 was greater than the reaction trend between Mg and O2, the reaction probability between Mg and HFC-134a or F2 was less than that of Mg and O2 because of the lower content of HFC-134a in the mixture gas. The reaction products between Mg and HFC-134a or F2 were less than that of Mg and O2. So the surface films on molten magnesium mainly consisted of MgO. Due to the porous and loose structure of MgO, it could not act as a barrier to prevent the further oxidation of magnesium, which resulted in the weight gain curve of molten magnesium increasing linearly. For molten AZ91D alloy, in addition to the reaction between Mg and O2, alloying elements Al, Zn, and Mn could react with O2 to produce Al2O3, ZnO, and MnO. Al as a main alloying element for AZ91D alloy, its reaction activity with O2 was greater than that of Zn and Mn, so the content of Al2O3 was more than that of ZnO and MnO. The amphoteric Al2O3 could directly react with the alkaline MgO to form MgAl2O4. Therefore, the surface films formed on molten AZ91D alloy were mainly composed of MgO and MgAl2O4. It is accepted that the growth of a continuous surface film depends on the outward diffusion of cation, and the easiest mode for the diffusion of cation is the transfer of cation vacancy. In this study, MgAl2O4 could be seen as a composite of Al2O3 dissolving completely in MgO in the solid state. According to Wayner–Hauffe “value law” [11], when the high value cation Al3+ dissolves in the cation conductor MgO in the solid state, the concentration of Mg2+ ions vacancy increases, which results in the oxidation of magnesium speeding up. So, the oxidation rate of AZ91D alloy was higher than that of magnesium in the atmospheres of air containing low concentration of HFC-134a. The analysis result was consistent with the result of Leontis and Rhines [12]. Leontis found that if the addition of Al to magnesium is over 1%, the oxidation rate of magnesium in the atmospheres of air was lower than 0.1%, the oxidation kinetics curve of molten magnesium followed parabola law, but the oxidation kinetics curve of molten AZ91D alloy obeyed linear law. When the concentration of HFC-134a in air was lower than 0.1%, the oxidation kinetics curve of molten magnesium and AZ91D magnesium alloy basically obeyed linear law, but the oxidation rate of AZ91D magnesium alloy was greater than that of magnesium. The difference in the oxidation rates of molten magnesium and AZ91D alloy might be related to the alloying element Al. The results indicated that the mixture gas of air containing HFC-134a can provide an effective protection for molten magnesium and its alloys under an appropriate concentration of HFC-134a. HFC-134a gas would replace SF6 as a protective gas to be applied to the production process of magnesium and its alloys in the future.

Since the changes in standard free energy for reaction (10) and (11) are not highly negative, the reaction rates of the reaction (10) and (11) is relatively slow, which lead to small amount of Mg3N2 and AlN existing in the surface film. The effects of Mg3N2 and AlN on the oxidation behaviour of molten AZ91D alloy could be negligible.

5. Conclusions

The oxidation behaviour of molten magnesium and AZ91D magnesium alloy in the atmospheres of HFC-134a/air was different. When the concentration of HFC-134a in air was higher than 1%, the oxidation kinetics curve of magnesium and AZ91D magnesium alloy obeyed parabola law, and the oxidation rate of AZ91D magnesium alloy was less than that of magnesium. When the concentration of HFC-134a in air was in the range of 0.1–1%, the oxidation kinetics curve of molten magnesium followed parabola law, but the oxidation kinetics curve of molten AZ91D alloy obeyed linear law. When the concentration of HFC-134a in air was lower than 0.1%, the oxidation kinetics curve of molten magnesium and AZ91D magnesium alloy basically obeyed linear law, but the oxidation rate of AZ91D magnesium alloy was greater than that of magnesium. The difference in the oxidation rates of molten magnesium and AZ91D alloy might be related to the alloying element Al. The results indicated that the mixture gas of air containing HFC-134a can provide an effective protection for molten magnesium and its alloys under an appropriate concentration of HFC-134a. HFC-134a gas would replace SF6 as a protective gas to be applied to the manufacture process of magnesium and its alloys in the future.

References