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Oxidation behavior of molten magnesium in air/HFC-134a atmospheres

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Abstract The oxidation behavior of molten magnesium in the atmosphere of air containing HFC-134a has been investigated in the temperature range of 660–760 °C. The oxidation rates and kinetics have been measured by the weight gain method and oxidation products have been characterized by XRD, SEM, EDS, XPS and AES. The results show that the oxidation kinetics is complex which cannot be described by simple equations. The rate of oxidation of molten magnesium in air/HFC-134a covering gas mixtures varies with the concentration of HFC-134a and molten temperature. Increasing the concentration of HFC-134a and decreasing the temperature can slow down the oxidation rate of molten magnesium. The film formed +on the surface of molten magnesium is mainly composed of MgF_2, MgO and C. MgF_2 is predominant product at the top layer and decreased gradually with the depth while MgO and C remain almost constant with relatively low content. The mechanisms of the oxidation of molten magnesium in air containing HFC-134a have also been discussed based on the experimental results.

Introduction

The excellent properties such as high specific strength, high specific rigidity and low density make magnesium alloys suitable candidates for many applications in the aerospace and automotive industries. Liquid magnesium oxidizes rapidly and burns in the air, however, it is thus necessary to protect the melt from oxidation and burning in the process of melting and processing of magnesium alloys. There are many measures to suppress the serious oxidation and burning of molten magnesium. Among the methods, sulphur hexafluoride (SF_6) has proved to be a successful inhibitor for its non-toxic, non-corrosive and good melt protection property [1], which has been widely used by the magnesium industry. In recently, SF_6 has been recognized as a very potential greenhouse gas and is becoming increasingly expensive, and thus there is a strong drive for the magnesium industry to look for substitute for SF_6 in magnesium melting process [2, 3]. Hydrofluorocarbon gas 1,1,1,2-tetrafluoroethane (HFC-134a) has been recently developed for magnesium melt protection [4]. Its global warming potential is 18 times lower than SF_6 and its atmospheric lifetime is only 0.46% of SF_6. This gas is only about one-third the cost of SF_6 and is readily available worldwide. HFC-134a has been shown to be an effective replacement for SF_6 and to have some unique properties resulting in more possible applications for magnesium melts protection than SF_6. However, the oxidation behavior of molten magnesium under air/HFC-134a gas atmosphere has little reported until now.

In the present study, the oxidation behavior of molten magnesium in the atmosphere of air containing HFC-134a has been investigated from 660 to 760 °C. The oxidation rates and kinetics have been measured by the weight gain method and oxidation products have been characterized by XRD, SEM, EDS, XPS and AES.

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Experimental procedure

The material used for oxidation tests was commercial pure magnesium. Its chemical composition in weight percent is 0.0029% Al, 0.01% Zn, 0.0025% Mn, 0.0001% Ni, 0.0008% Fe, 0.0004% Cu, 0.0046% Si, less than 0.0001% each of Sn, Pb and Mg balance. The samples, cylinders of 3 mm height and 50 mm diameter, were sectioned from the central part of the as-cast ingot. Before each experiment, they were manually polished with grade 320 SiC paper and rinsed with acetone.

The experimental set-up of static oxidation, shown schematically in Fig. 1, consisted of a recording electronic balance, a resistance furnace with sealing cover, a magnesia crucible that was hung in the resistance furnace with platinum silk connecting with the electronic balance 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 $CaCl_2$ 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 gain of the oxidized sample was measured in a certain interval by an electronic balance with an accuracy of 0.1 mg as soon as the desired temperature was reached.

The static oxidation was performed in the atmosphere of air containing different concentration of HFC-134a under different temperatures from 660 to 760 °C for different times.

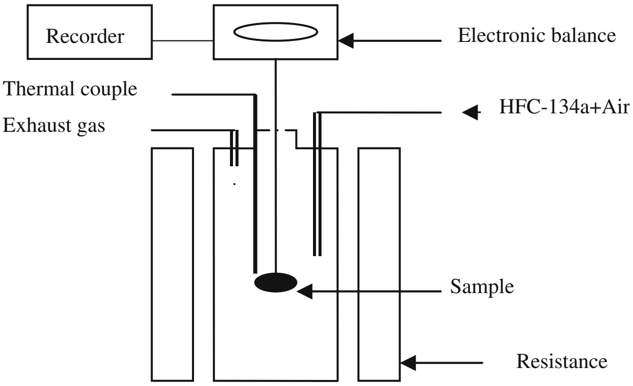


Fig. 1 Schematic diagram of apparatus used in oxidation test

After the static oxidation, the oxidized surface films were examined by scanning electron microscope (SEM) with energy dispersive spectrum (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The distribution of some elements across the oxides and substrate interface in oxidized layer was examined using Auger electron spectroscopy (AES) with argon ion beam sputtering.

Results and discussion

The analysis of oxidation kinetics

Figure 2 shows the curves of weight gain versus time for molten magnesium under air containing different concentration HFC-134a at 660, 720 and 760 °C, respectively. As seen in Fig. 2a, at 660 °C, the sample exposed to the atmosphere of air containing 0.001%HFC-134a oxidized more rapidly than others, which indicated that the covering gas did not provide protection to magnesium melt at the HFC-134a concentration of 0.001%. For samples tested under the atmospheres of air containing 0.01% and 0.1%HFC-134a, the weight increase were lower than that of the sample under 0.001%HFC-134a, which indicated that under this condition the covering gas had a certain protection for magnesium melt, but its effect were not very good. For the samples under the atmosphere containing 1%, 3% or 5%HFC-134a, there were rapid weight increase at the initial stage and later weight gain held approximately constant, which showed that the covering gas provided a effective protection to magnesium melt at the concentration of HFC-134a over 1%. When the temperature increased to 720 °C (Fig. 2b), the curve for the sample exposed air containing 0.01%HFC-134a experienced a rapid weight gain at the initial stage of oxidation, and a approximately linear increase for later, which indicated that the covering gas could not provide an effective protection to magnesium melt under this condition. The trend of the mass gain versus time curves of molten magnesium under the atmospheres of air containing 0.001, 0.1, 1, 3 and 5%HFC-134a was similar to that at 660 °C. It can be seen from Fig. 2c, as the temperature increased further up to 760 °C, the curves of the weight gain versus time for molten magnesium under the atmospheres of air containing 0.001, 0.1, 1, 3 and 5%HFC-134a were similar to that of at 660 °C. However, the sample exposed air containing 0.01%HFC-134a experienced a rapid weight gain in the initial stage and then continued to increase its weight at a relatively lower rate, which indicated that the cover gas mixture

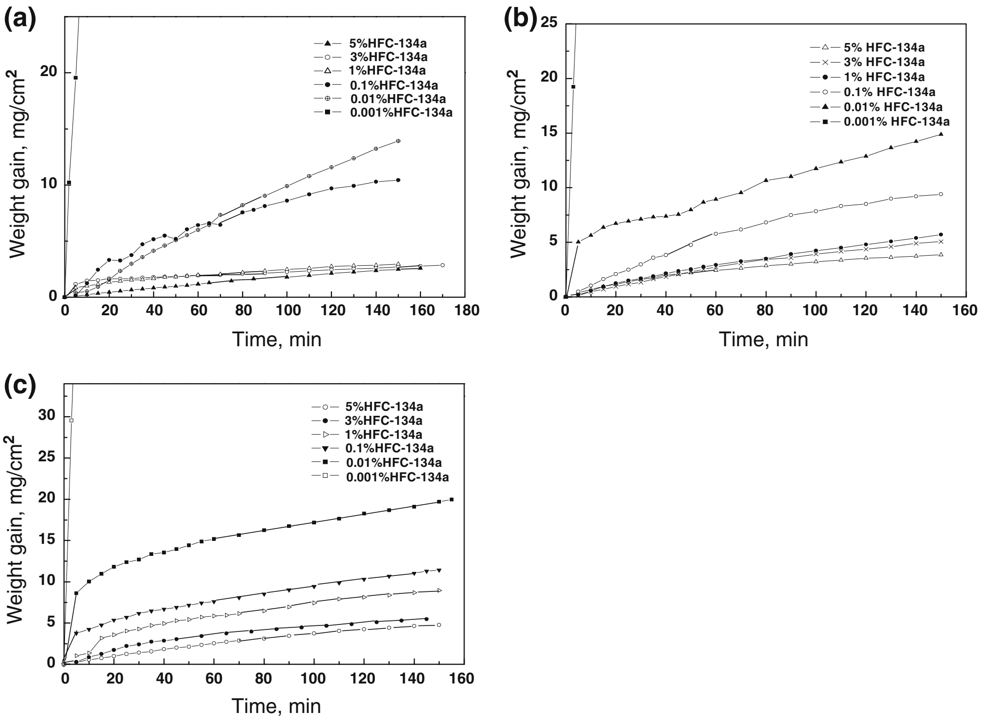


Fig. 2 The curves of weight gain versus time for molten Mg in the atmospheres of air containing different concentration of HFC-134a at (**a**) 660 °C, (**b**) 760 °C and (**c**) 760 °C

exhibited a poor protection to magnesium melt at the HFC-134a concentration of 0.01%.

The analysis of surface film morphology

Some typical surface film morphologies of the samples in the atmospheres of air containing different concentration of HFC-134a at different temperatures for 2.5 h are shown in Fig. 3. The element composition of the surface films measured by EDS is listed in Table 1. The surface morphology of the sample changed with the concentration of HFC-134a in air and the temperature. At a temperature of 660 °C, a dense and compact protective oxide layer could be seen at the surfaces of the samples oxidized in air containing 0.1%HFC-134a and 1%HFC-134a, although the surfaces were relatively rough (Fig. 3a, b). Except a few oxide nodules on the surface of the sample after exposure to air containing 0.1%HFC-134a, there was no significant difference in the surface morphology between the two samples. This indicates that the concentration of HFC-134a in air has a little effect on the surface morphology of the sample at lower temperature. When the temperature rose up to 760 °C, the surface of the sample oxidized in air containing 0.1%HFC-134a was rough and contained numerous white oxide nodules. However, the number of oxide nodules obviously decreased on the surface of the sample oxidized in air containing 1%HFC-134a and the surface got compact, although some grooves and folds appeared on the surface (Fig. 3c, d). This indicates that the concentration of HFC-134a in air has an important influence on the surface morphology of the sample at higher temperature. Increasing the concentration of HFC-134a in air will increase the compactness of the surface film, which result in more effective protection for molten magnesium.

Table 1 indicates that there are F, Mg, O and C elements in the surface film. The concentration of F element in the film is higher than that of other elements and increases with increasing the HFC-134a concentration in the cover gas and temperature.

The analysis of surface film phase composition

The typical XRD patterns of the surface films formed in containing 0.001% and 3%HFC-134a are shown in Fig. 4. The results of other XRD patterns for the surface films formed in containing different HFC-134a concentrations are given in Table 2. It can be seen from Fig. 4 and Table 2 that the oxidation products are different under different concentration of HFC-134a at different temperatures. After exposure to air containing 0.001%HFC-134a, the surface of the sample mainly consisted of MgO and small amount of Mg_3N_2 (Fig. 4a, b). With the increasing of HFC-134a concentration in covering gas, the content of MgF_2 increased gradually, and MgO and Mg_3N_2 reduced until disappearing when

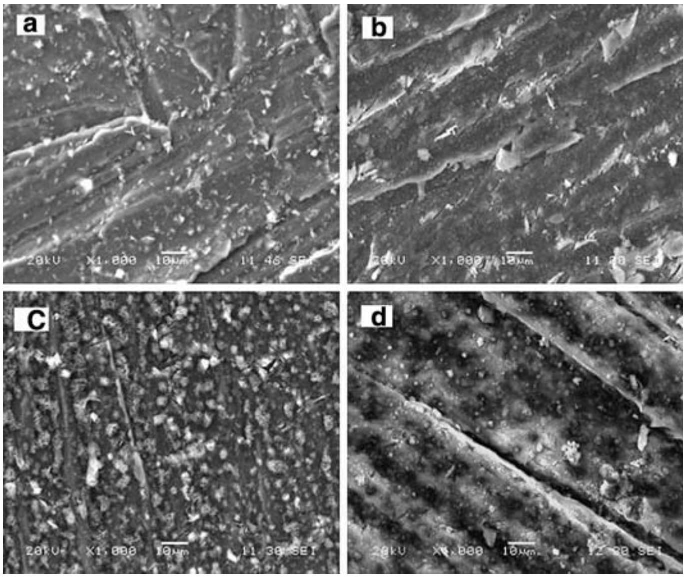


Fig. 3 The SEM photographs of Surface films for the samples after oxidation in air containing different concentration of HFC-134a for 2.5 h, (**a**) 0.1%HFC-134a, 660 °C; (**b**) 1%HFC-134a, 660 °C; (**c**) 0.1%HFC-134a, 760 °C and (**d**) 1%HFC-134a, 760 °C

the concentration of HFC-134a was more than 1% for MgO and 0.01% for Mg_3N_2. The surface oxidized in air containing HFC-134a concentration over 1% contained only the characteristic patterns of MgF_2 and the peaks of MgO, Mg_3N_2 and C were not detected (Fig. 4c, d and Table 2). The surface oxidized in air containing 0.01%HFC-134a mainly consisted of MgO, MgF_2 and C. The oxidation products on the surface of the sample exposed to the atmosphere of air containing 0.1%HFC-134a changed with the temperature. At 660 and 720 °C, the products were MgF_2, MgO and C, whereas the products were only MgF_2, MgO at 760 °C. The presence of Mg peaks in all patterns was due to the X-ray radiation penetrating the thin film into the substrate metal.

To determine the presence of MgO and C in the film formed in air containing 1%HFC-134a at 760 °C, the films were also examined by XPS. The results are showed in Figs. 5 and 6. It can be seen that the outermost layer of the sample contained F, Mg, O and C elements. Ar and Na elements may be contaminants introduced in the process of preparation and analysis of the sample (Fig. 5a). After 30 min sputtering with Ar^+, elements F, Mg, O and C were still present (Fig. 5b). This is in agreement with the above results of EDS analysis. The intensity of F1s peak increased, however, the intensities of O1s peak and C1s peak decreased noticeable compared with as received. This indicates that the concentration of each element is not uniform from the outer surface of the film to the interface of the film and metal magnesium.

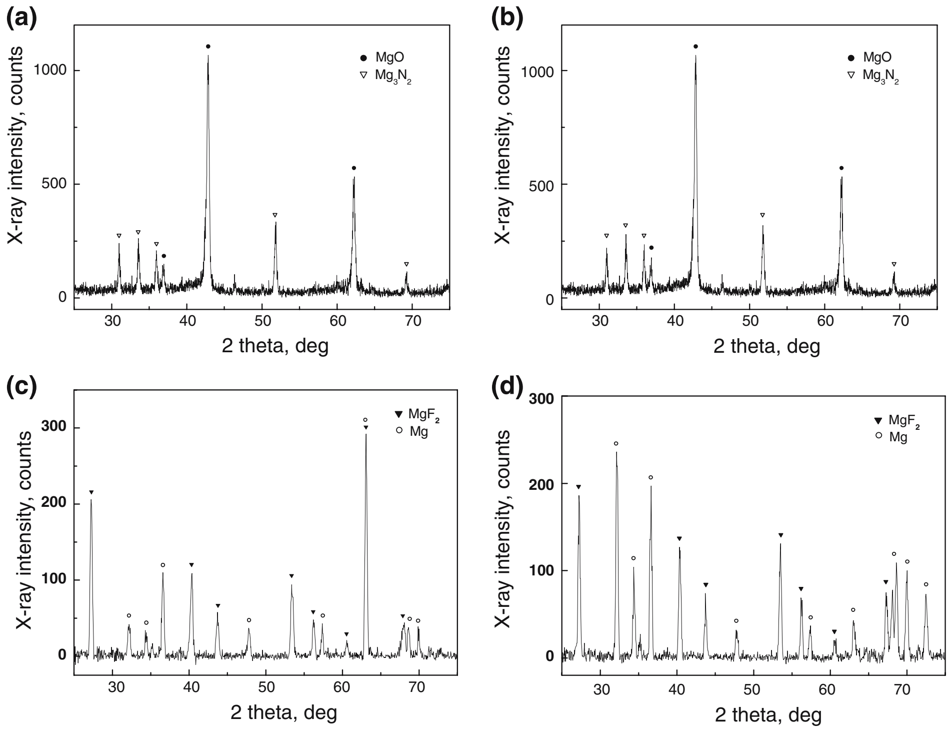
Table 1 The analysis results by EDS for elements in the surface films formed on samples after exposure to air containing 0.1% and 1%HFC-134a at 660 and 760 °C for 2.5 h (at%)

Element	Air + 0.1%HFC-134a		Air + 1%HFC-134a	
	660 °C	760 °C	660 °C	760 °C
F	50.46	53.51	63.09	68.01
Mg	37.05	25.32	31.87	28.02
O	9.60	12.10	3.54	2.95
C	2.89	9.07	1.17	1.02

It can be seen from Fig. 6 that there are two main component peaks in the Mg2s core level spectrum of surface film formed in air containing 1%HFC-134a at 760 °C (Fig. 6a). The lower binding energy peak at 90.93 ± 0.2 eV is assigned to MgO [5]. The higher binding energy peak at 93.94 ± 0.2 eV is attributed to MgF_2. The content of MgF_2 is greater than that of MgO. The presence of MgO also can be confirmed by O1s peak at binding energy of 531.02 ± 0.2 eV, which is attributed to MgO oxygen atom (O^{2-}) [6]. Three component peaks are evident in the C1s core level spectrum of the same surface film (Fig. 6b). The lower binding energy peak at 284.41 ± 0.2 eV is attributed to simple substance of carbon. The peak at 286.21 ± 0.2 eV is due to $C–O^-$ and the higher binding energy peak at 288.54 ± 0.2 eV is attributed to $O=C–O^-$ [7]. $C–O^-$ and $O=C–O^-$ could result from CO or CO_2 adsorbed in the MgO or MgF_2 scale layer. $C–O^-$ and $O=C–O^-$ can be negligible due to their very low content in the film.

Based on the XRD and XPS results, it is understood that MgO and C do exist on the surface film formed in air containing 1%HFC-134a at 760 °C. The reason for the absence of MgO and C peaks in X-ray diffraction

Fig. 4 X-ray diffraction patterns of the surface films after exposure to air containing 0.001% and 3%HFC-134a for 2.5 h, (**a**) 0.001%, 660 °C; (**b**) 0.001%, 760 °C; (**c**) 3%, 660 °C and (**d**) 3%, 760 °C



patterns of the surface film may be that MgO and C were amorphous or the amount of MgO and C were too small to produce a sufficient X-ray signal. Therefore, the surface film of molten magnesium formed in air/HFC-134a mixture gas was mainly composed of MgF_2, MgO and C. However, the relative content of each component in the surface film varied with the concentration of HFC-134a in mixture gases and temperature.

Table 2 XRD results of surface films formed on samples in air containing different concentration of HFC-134a at 660–760 °C

Oxidized temperature (°C)	HFC-134a Concentration (%)	Phase
660	5	MgF_2, Mg
660	1	MgF_2, Mg
660	0.1	MgF_2, MgO, C, Mg
660	0.01	MgO, MgF_2, C, Mg
720	5	MgF_2, Mg
720	3	MgF_2, Mg
720	1	MgF2, Mg
720	0.1	MgF_2, MgO, C, Mg
720	0.01	MgO, MgF_2, C, Mg
720	0.001	MgO, Mg_3N_2
760	5	MgF_2, Mg
760	1	MgF_2, Mg
760	0.1	MgF_2, MgO, Mg
760	0.01	MgO, MgF_2, C, Mg

The analysis of cross section for the film

Figure 7 shows some typical cross-sectional images of the samples oxidized in air containing 0.1% and 1%HFC-134a at 720 and 760 °C for 2.5 h. It was observed that there was a thin oxide layer on the metal base. The thickness of the oxide layer, which can reveal the protective effect of the covering gas mixture, was different after oxidation under different conditions. The film formed in air containing 0.1%HFC-134a at 720 °C was continuous and compact. No pore was found within the film and the film exhibited good adhesion with the substrate metal. But the surface of the film was not very smooth. The thickness of the film was estimated to be about 3–4 μm (Fig. 7a). As the concentration of HFC-134a was increased to 1%, the film became uniform and relatively smooth. The thickness of the film decreased as compared with that of Fig. 7a, which indicated that the film got more compact (Fig. 7b). The film formed in air containing 1%HFC-134a at 760 °C had a similar thickness and compactness as compared with that of Fig. 7b. However, the adhesion was not very good due to a crack between the film and the substrate metal.

To reveal the internal structure of the film, the entire surface film of the sample oxidized in air containing 1%HFC-134a at 720 °C was analyzed by depth profiling, using ion-beam etching in conjunction with AES and the result was shown in Fig. 8. It can be seen

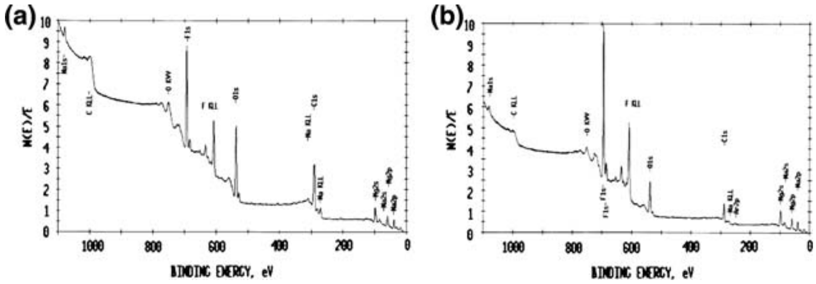


Fig. 5 XPS survey spectra of surface film formed in air containing 1%HFC-134a at 760 °C for 2.5 h (**a**) as received, (**b**) after 30 min sputtering with Ar^+ ion

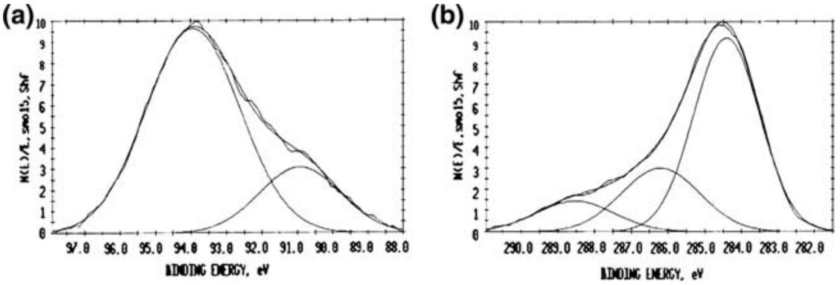


Fig. 6 (**a**) Mg_2s and (**b**) C1s XPS spectra of surface film formed in air containing 1%HFC-134a at 760 °C for 2.5 h

that the fluorine content, amounting to about 55 at% at the surface, decreased gradually towards the substrate; whereas the magnesium concentration increased gradually. The concentration of oxygen and carbon held constant within about 5–15%. This indicated that the surface film was made up of MgF_2, MgO and C. The content of MgF_2 was greater than that of MgO and C, which is consistent with the results of XPS analysis. Within the film, MgF_2 was unevenly distributed along the direction of depth, and the content of MgF_2 in outer layer was greater that that in the inner layer.

Magnesium is easy to react with oxygen because it has a high affinity to oxygen, which results in producing MgO on the surface of magnesium. Since the structure of MgO film is loose, it can not act as a barrier to prevent the further oxidation of magnesium [8], Moreover, the formation heat of MgO is so large that some local zones are heated to a considerably high temperature [9], which speeds up the oxidation reaction and even results in burning. When the molten magnesium was exposed to the protective atmospheres of air containing HFC-134a, the cover gas reacted with the metal and formed a protective film on the melt surface where a large amount of MgF_2 existed (Table 2, Figs. 4–6). It can be concluded that the formation of MgF_2 in the oxide film is the main reason that the HFC-134a provides effective protection for molten magnesium. Since the compact coefficient of MgF_2 is 1.6, it significantly holds back the diffusion of magnesium and oxygen through the oxide film. So the oxidation resistance of the molten magnesium is improved remarkably. According to above analyses, the oxidation resistance of the molten magnesium under the air/HFC-134a cover mixture gas depends on the concentration of MgF_2 in the cover mixture gas. When the concentration of HFC-134a in the mixture gas was very low, the surface film, consisted of large amount of MgO and small amount of MgF_2, was loose, which resulted in a rapid oxidation. As the concentration of HFC-134a was increased, the amount of MgF_2 in the film increased, which made the film get compact and the oxidation rate of magnesium decrease. The carbon that occurred in the film plays an important role in the protection of molten magnesium by HFC-134a. A possible reason is that the carbon, mainly

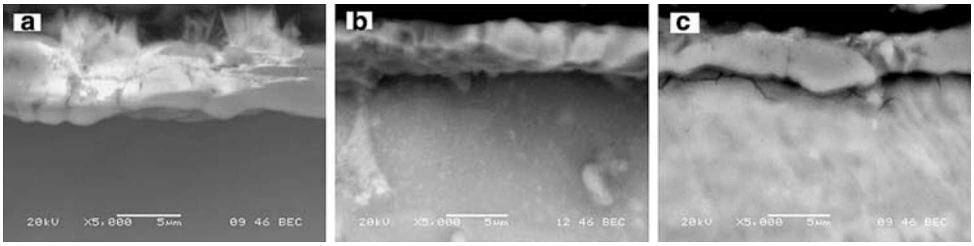


Fig. 7 Cross-sectional images of the samples after oxidation in air containing, (**a**) 0.1%HFC-134 at 720 °C; (**b**) 1%HFC-134 at 720 °C and (**c**) 1%HFC-134 at 760 °C for 2.5 h

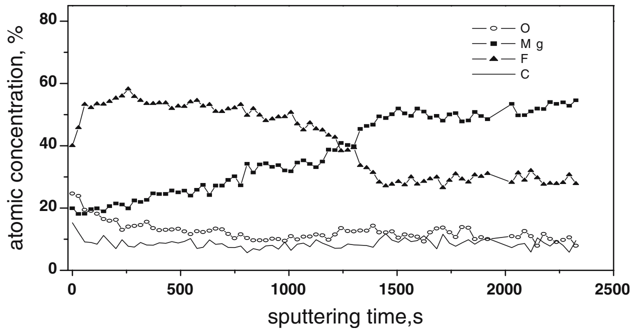


Fig. 8 AES depth profile of the oxide layer formed in 1%HFC-134a in air at 760 °C for 2.5 h

existed in the film as a simple substance, filled up the holes of MgO, which made the film more compact and decreased the diffusion rate of magnesium and oxygen through the oxide film.

The reactions between air/HFC-134a cover mixture gas and magnesium at high temperature may be as follows:

$$C_2H_2F_4(g) \rightarrow 2C(s) + 2HF(g) + F_2(g), \tag{1}$$

$$\begin{aligned} &Mg(l) + F_2(g) \rightarrow MgF_2(s), \\ &\Delta G_2^0 = -1120000 + 171.2T \end{aligned} \tag{2}$$

$$\begin{aligned} &Mg(l) + 1/2O_2(g) \rightarrow MgO(s), \\ &\Delta G_3^0 = -612955 + 128.08T \end{aligned} \tag{3}$$

HFC-134a is easy to decompose at high temperature [10], the products of which mainly contain HF, F_2 and C [11]. From thermodynamic point of view, Mg will react with F_2 and O_2 under the protective atmosphere of air/HFC-134a in the temperature of 650–760 °C because ΔG_2^0 and ΔG_3^0 are negative. Since ΔG_2^0 is more negative than ΔG_3^0, MgF_2 will form on the molten magnesium prior to MgO. However, because large amounts of oxygen are present in the protective atmosphere, and no complicated dissociation process is necessary for the oxidation to take place, magnesium will react with oxygen first to form MgO at the surface of molten magnesium in the early stages of reactions [12]. As the reactions proceeded, the relative concentration of F_2, a decomposed product of HFC-134a, gradually increased at molten surface. F_2 gas is denser than air, so the surface of magnesium molten was covered by a gas enriched with the gas resulting from HFC-134a decomposition, which led to the formation of large amounts of MgF_2. This is confirmed by the result of the Auger depth profile (Fig. 8). Furthermore, since HFC-134a is less stable thermally than SF6, the amount of MgF_2 in the surface film formed in cover gas mixtures containing HFC-134a was greater than that formed in SF_6/air mixtures, which is consistent with Cashion' result [13]. According to reaction (1), the decomposition of HFC-134a gas might produce C. The C might partly fall on the scale surface. When the concentration of HFC-134a in gas mixture was low, the amount of C coming from the decomposition was fewer and the C depositing on the scale surface was little. For example, the surface film formed under the atmosphere containing 0.001%HFC-134a, the C was not detected by XRD analysis (Fig. 4a, b). With increasing the concentration of HFC-134a in mixture gas, the amount of C resulting from the decomposition increased and there was some C depositing on the scale surface, which might be confirmed by the XRD analysis results for the surface film formed in air containing 0.01% and 0.1%HFC-134a (Table 2). As the HFC-134a concentration was increased further, the surface films formed under the atmospheres contained large amount of MgF_2 and the content of the C depositing on the surface of molten magnesium was relatively less comparing with the content of MgF_2 on the surface. So the C could not be detected by XRD on the surface film formed in air containing high concentration of HFC-134a (Table 2, Fig. 4c, d).

Based on the above analysis, the explanation to the processes of the oxidation of molten magnesium in air containing HFC-134a atmospheres can be rationalized as follows: when molten magnesium was exposed to a cover gas mixture containing HFC-134a and oxygen, Mg rapidly reacted with oxygen to form a thin film of MgO on the melt surface. Due to the porous and loose structure of MgO, Mg vapour that evaporated from the molten magnesium surface [14] would transfer outwards through the voids and reacted with F_2 to form MgF_2 within the film. Once a dense composite film of MgF_2 and MgO was formed, the film would grow via the diffusion of ions. It was reported that the outward diffusion rate of magnesium ions were much faster than that of the inward diffusion of oxygen and fluorine ions [8, 15], so the growth of the outer layer was controlled by the outward diffusion of Mg^{2+} through the film [16]. Since the reaction (2) was easier to carry out than reaction (3) as well as the surface of magnesium molten was covered by a gas enriched with the gas resulting from HFC-134a decomposition, MgF_2 formed prior to MgO in the outer layer. Large amounts of MgF_2 present in the film made the film dense and compact. As the film was a very good barrier for further oxidation and had a good chemical stability, it formed on the surface of molten magnesium would result in the magnesium having excellent oxidation resistance at high temperature.

Conclusions

The rate of oxidation of molten magnesium in air/HFC-134a cover gas mixtures was affected by the concentration of HFC-134a in the mixture gases as well as the temperature. To achieve effective protection for molten magnesium, the HFC-134a concentration should be above 0.1% in the temperature of 660–760 °C. When the temperature is above 760 °C, the concentration of HFC-134a should be increased.

The surface film formed in air/HFC-134a cover gas mixtures mainly consisted of MgF_2, MgO and C. The content of MgF_2 in the film increased with increasing the HFC-134a concentration in the cover gas and temperature.

MgF_2 was predominant at the top layer and decreased gradually with depth while MgO and C held constant with small amounts.

MgF_2 in this film is believed to play a key role in effective protection for molten magnesium.

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