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The characterization of surface films formed on molten magnesium and AZ91D alloy in air/1,1,1,2-tetrafluoroethane atmospheres

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ABSTRACT

During the melting and casting of magnesium and its alloys, it must be taken appropriate protective measures to prevent the melt from oxidizing and burning, because magnesium is a very active and readily ignitable element. In this paper, the morphologies and compositions of the surface films formed on magnesium and AZ91D alloy in air/1,1,1,2-tetrafluoroethane gas mixture at different conditions were investigated and analyzed by means of SEM, XRD and XPS. The experimental results showed that the morphologies and compositions of the surface films formed on molten magnesium and AZ91D alloy were different under the atmosphere of air containing different contents of 1,1,1,2-tetrafluoroethane. When the concentration of 1,1,1,2-tetrafluoroethane was less than 0.1 vol.%, the surface films were mainly composed of MgO, and MgF_2 for magnesium, and MgO, Mg_3N_2, AlN and $MgAl_2O_4$ for AZ91D alloy, which presented very coarse and incompact surfaces. When the concentration of 1,1,1,2-tetrafluoroethane was more than 1 vol.%, the surface film on molten magnesium was not uniform, which was mainly composed of MgF_2. The surface formed on molten AZ91D alloy was relatively smooth and compact, which was mainly composed of MgF_2 and C.

1. Introduction

Magnesium and its alloys are the lightest structure metal materials, having extensive applications in automobile, communication, electron and aerospace industries because of its excellent properties, such as low density, high specific strength and stiffness, good electromagnetic shieiding and castability, etc. [1,2]. However, magnesium is a very active element, having a high affinity with oxygen and high vapor pressure at high temperature. Magnesium and its alloys readily oxidize and burning at high temperature in the process of melting and casting. It is therefore necessary to take appropriate measures to prevent the melt from oxidizing and burning. Many methods have been investigated and applied to reduce or inhibit the oxidizing and burning of molten magnesium and its alloys in air, such as flux covering protection, gas protection without flux [3,4] and ignition-proof by alloying [5,6]. Among these methods, sulfur hexafluoride (SF_6) is currently considered as an effective protective gas and extensively used to prevent magnesium and its alloys from oxidizing and burning during melting and casting processes. Because SF_6 can form a thin, coherent and stable film on its surface which can effectively reduce or inhibit the melt further contacting with oxygen in the atmosphere [3,4]. But in the process of SF_6 gas being used, there is a lot of SF_6 gas leftover and decomposition products being released in environment, which will result in serious greenhouse effect and environment pollution [7,8]. With increasing environmental concerns in recent years, the use of SF_6 gas in industries is strict restricted or forbidden in many countries of the world. It is an urgent subject to develop or look for alternative gases which are low environmental impact and low toxicity to replace or reduce the use of SF_6 for the melt protection in the melting and casting of magnesium and its alloys.

1,1,1,2-Tetrafluoroethane (CF_3CH_2F, HFC-134a) has been suggested as the protective gas for magnesium and its alloys melt by the Cooperative Research Center for Cast Metals Manufacturing in Australia [9]. The global warming potential of HFC-134a is 18 times lower than that of SF_6, and its atmospheric lifetime is only 0.46% of SF_6. Ha and Kim [10] investigated the melt protection properties of inhibitors (SF_6, HFC-134a and SO_2)/air cover gas mixtures for different magnesium alloys. The results indicated that HFC-134a and SF_6 showed better protection properties than SO_2. HFC-134a provided fluorine easier than SF_6 due to its relatively low thermal stability at magnesium melting temperature. The surface film formed in HFC-134a/air cover gas mixtures containing more magnesium fluoride than that formed in SF_6/air cover gas mixtures, which could provide excellent melt protection for magnesium alloys. Chen et al. [11] have researched the oxidation behavior of molten magnesium in the atmospheres of air/HFC-134a. However, the morphologies and compositions of the surface films formed on magnesium and its alloys in the atmospheres are not clear. In order to reveal the

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Table 1
Chemical compositions of magnesium and AZ91D alloy used in the experiments, in wt%.

	Al	Zn	Mn	Si	Cu	Fe	Ni	Mg
Mg	0.0029	0.01	0.0025	0.0046	0.0004	0.0008	0.0001	Bal.
AZ91D	9.06	0.70	0.30	0.025	0.0017	0.0037	0.0007	Bal.

protection mechanism of HFC-134a gas and provide a more effective protection for magnesium and its alloys, the characteristics of morphologies and compositions of the surface films formed on magnesium and its alloys melts under the atmospheres are necessary to be studied.

In the present study, the morphologies and compositions of the surface films formed on molten magnesium and AZ91D alloy in HFC-134a/air atmospheres at different conditions have been investigated and compared, and the effect of alloying elements on the oxidation behavior of molten magnesium have been discussed.

2. Experimental

The materials used for the experiment were pure magnesium and AZ91D alloy, whose compositions in weight percent are listed in Table 1. The samples with 3 mm thickness and 20 mm in diameter were cut from the central part of the as-cast ingot. Before each experiment, the samples were polished with grade 320 SiC paper, washed with acetone and dried in room temperature to ensure its surface smoothness and cleanness.

The samples were put in a magnesia crucible to heat and melt in resistance furnace. The furnace is sealed and immit the air/HFC-134a gas mixture. When the samples were melt at certain temperatures and the protection of air containing different content of HFC-134a for different times, the melts were cooled under the atmosphere to room temperature to analyze the morphologies and compositions of the oxidized surface layers formed on samples by SEM, XPS and XRD.

3. Results

3.1. The morphology analysis of surface oxidation layer

Fig. 1 shows the morphologies of some typical surface films formed on molten magnesium and AZ91D alloy under different con-

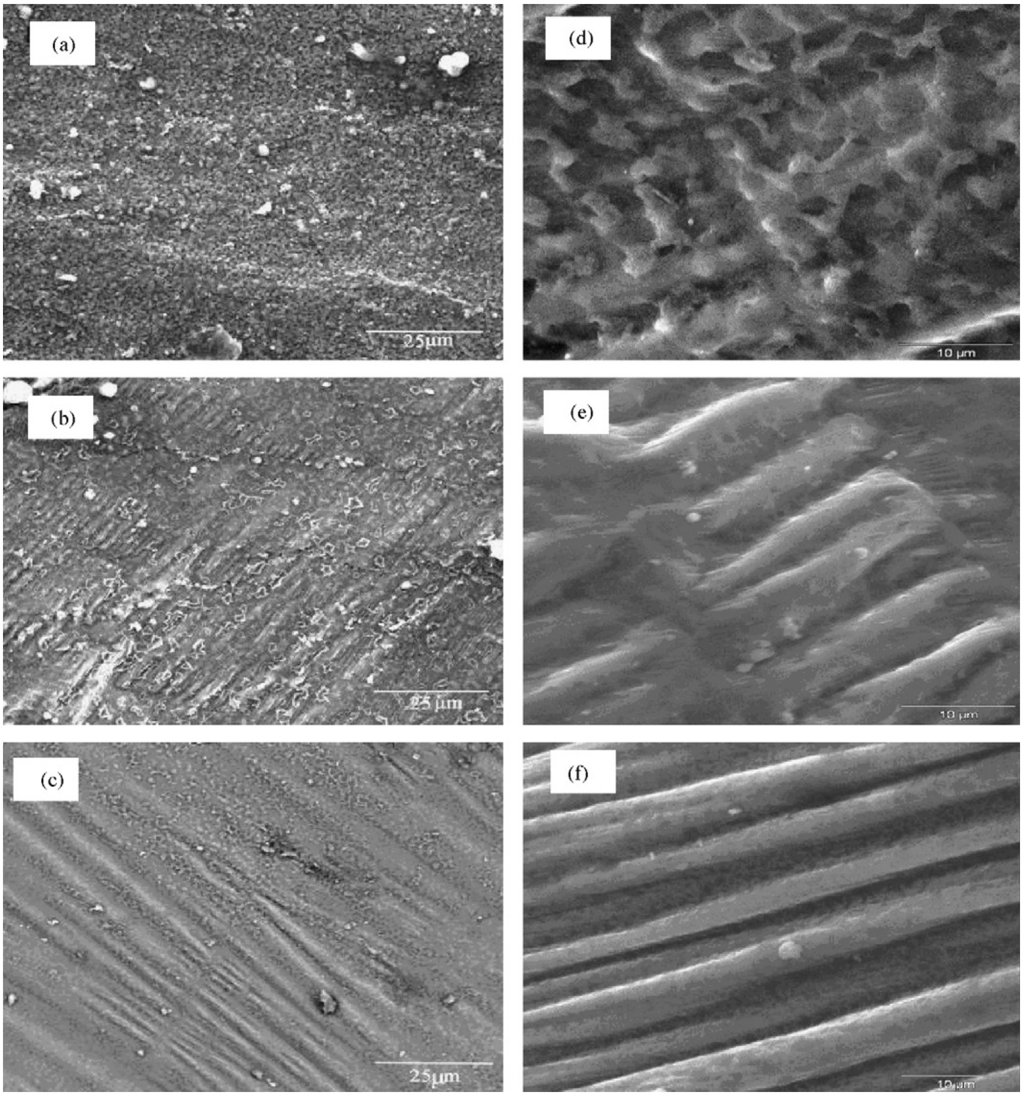

Fig. 1. The morphologies of surface film formed on molten magnesium and AZ91D alloy after exposure in different concentration of HFC-134a at 700 °C for 10 min: (a) 0.25%, (b) 0.5% and (c) 0.75% for magnesium; (d) 0.25%, (e) 0.5% and (f) 0.75% for AZ91D alloy.

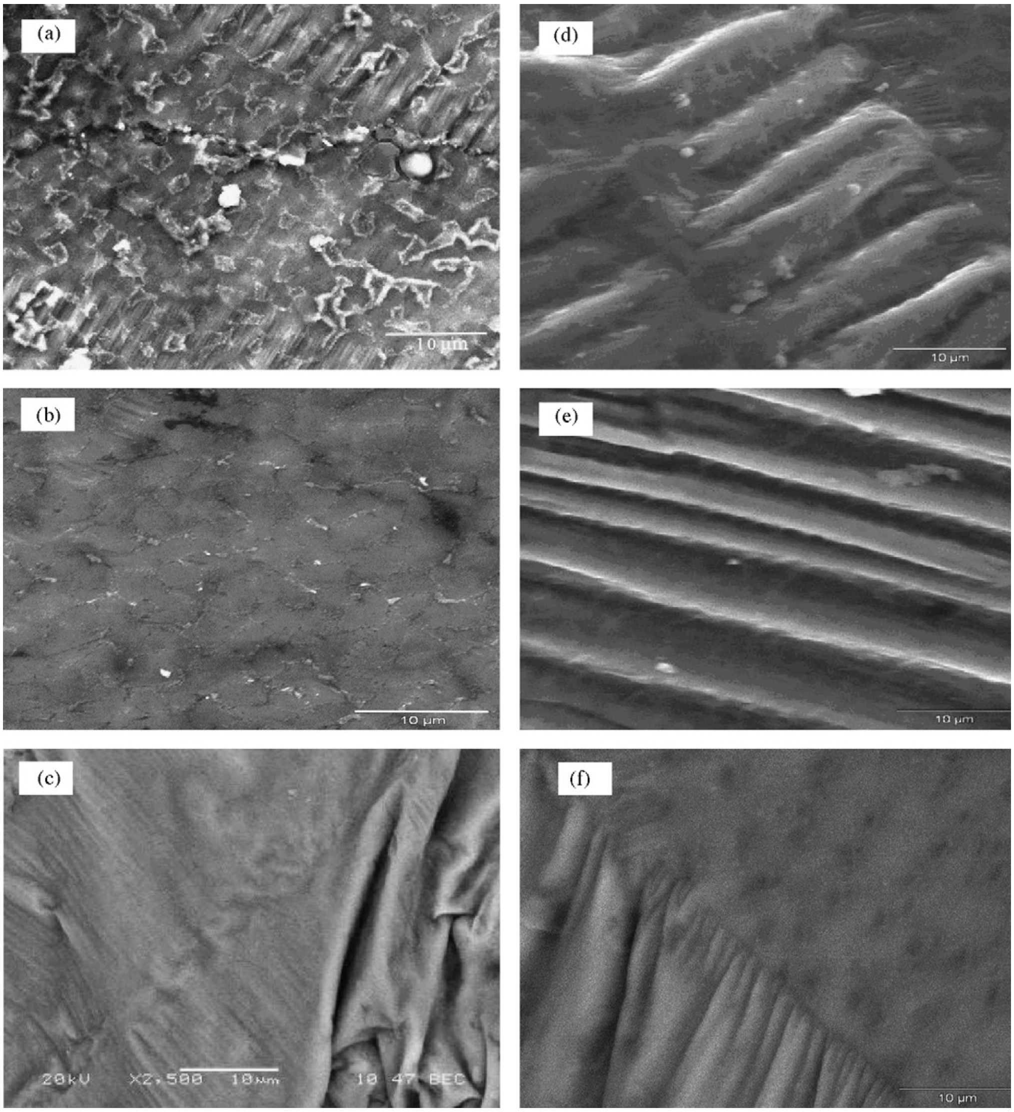

Fig. 2. SEM micrographs of the surface films under the atmosphere of air containing 0.5% HFC-134a at 700 °C formed on magnesium for (a) 10 min, (b) 30 min and (c) 60 min; formed on AZ91D alloy for (d) 10 min, (e) 30 min, (f) 60 min.

centration of HFC-134a at 700 °C for 10 min. It can be seen from Fig. 1 that comparing with the surface films formed on molten magnesium and AZ91D alloy, the surface films on AZ91D alloy presented slipperier and more symmetrical than the films on magnesium at the same conditions. In the atmosphere of air containing 0.25 vol.% HFC-134a, the surface films were all rough and uneven, and appeared some white granules of MgO which were identified by EDS (Fig. 1a and d). With increasing the concentration of HFC-134a in cover gas mixtures, the surface films appeared some zonal goffers and grooves which could result from the disturbing of gas current or the shrinking of the molten solidification, and the white granules of MgO reduced or disappeared. The surface films became gradually relatively slippery and compact. When the concentration of HFC-134a in cover gas mixtures increased to 0.75 vol.%, the surface films became relatively smooth and compact (Fig. 1 c and f). The experimental results indicated that the protection properties for molten magnesium and AZ91D alloy increased with the proportion of HFC-134a in cover gas increase, and the property of oxidation resistant of AZ91D alloy was better than that of magnesium under the same condition.

Fig. 2 shows the SEM micrographs of the surface films formed on molten magnesium and AZ91D alloy in the atmosphere of air/0.5 vol.% HFC-134a at 700 °C for different times. For magnesium, the surface layer formed in 10 min presented some cracks and grains which were coarse and discontinuous (Fig. 2a). The surface layer formed in 30 min became relatively smooth and compact, but there were similar grain boundary of magnesium (Fig. 2b). This indicated that the film was relatively intact but very thin. The surface layer formed in 60 min became smooth and compact besides the surface rumples (Fig. 2c). For AZ91D alloy, the surface films formed in different times all presented smooth and uniform except some rumples (Fig. 2d–f). The experimental results indicated that under the same temperature and atmosphere, the surface films became smooth and compact with increasing the time prolonging.

The above results indicated that the morphologies of the surface films gradually became smooth and compact, and the oxidation resistant properties of the films gradually increased with increasing the concentration of HFC-134a in cover gas or the time. Because the chemical compositions of magnesium and AZ91D alloy are different, the alloying elements of AZ91D alloy could change the properties and composition of its surface films. The oxidation resistant property of AZ91D alloy was better than that of magnesium at the same condition.

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

HFC-134a Concentration (%)	Phase in the films formed on Mg	Phase in the films formed on AZ91D
5	MgF_2, Mg	MgF_2, Mg, C
3	MgF_2, Mg	MgF_2, Mg, C
1	MgF_2, Mg	MgF_2, Mg, C
0.1	MgF_2, MgO, Mg	MgO, Mg_3N_2, AlN, MgF_2
0.01	MgO, MgF_2, C, Mg	MgO, Mg_3N_2, AlN, $MgAl_2O_4$
0.001	MgO, Mg_3N_2	MgO, Mg_3N_2, AlN, $MgAl_2O_4$

3.2. *The analysis of phase composition of the surface film*

In order to determine the phase compositions of the surface films formed on molten magnesium and AZ91D alloy, the magnesium or AZ91D alloy were heated to 760 °C under the protection of air containing different concentration HFC-134a for 2.5 h to obtain the surface films. The XRD analysis results of the surface films formed on magnesium and AZ91D alloy were shown in Table 2. It can be seen from Table 2 that Mg phase appeared in majority XRD analysis results, which resulted from the substrates of magnesium and AZ91D alloy. The other phase compositions except Mg phase depended on the concentration of HFC-134a in air and the alloy component. When the HFC-134a concentration was equal to or more than 1 vol.%, MgF_2 phase appeared in the films formed on magnesium surface, while the films formed on AZ91D alloy surface presented C phase and MgF_2 phase. Based on the properties of magnesium, there must be reaction between Mg and O_2 at high temperature and the reaction product MgO must exist in the surface film. 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 in the surface films was fewer which went beyond the analysis range of XRD. When the HFC-134a concentration decreased to 0.1 vol.%, the films on magnesium surface consisted of MgF_2, MgO, and the films on AZ91D alloy surface consisted of MgO, Mg_3N_2, AlN, MgF_2. As the HFC-134a concentration decreased further to 0.01 vol.% or below, the films on magnesium surface were mainly composed of MgO and small amount of MgF_2, C and Mg_3N_2, and the films on AZ91D alloy surface were mainly composed of MgO and small amount of Mg_3N_2, AlN and $MgAl_2O_4$.

It is well known that magnesium has an extremely high chemical affinity with oxygen. MgO would exist in the surface layers of magnesium and its alloys under the atmosphere of air/HFC-134a. In order to confirm the presence of MgO and other minor phases, the surface films formed on magnesium and AZ91D alloy in air/1 vol.% HFC-134a at 760 °C were also examined by XPS and the results are shown in Figs. 3 and 4, respectively. It was observed from Fig. 3a 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 Mg2s spectrum (Fig. 3b), Mg presented in two chemical states. The lower binding energy peak at 90.93 ± 0.2 eV was assigned to MgO [12] and the higher binding energy peak at 93.94 ± 0.2 eV was attributed to MgF_2. Three component peaks were evident in the C1s core level spectrum of the same surface film (Fig. 3c). 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 $O{=}C–O^-$ [13]. $C–O^-$ and $O{=}C–O^-$ could be negligible due to their very low content in the film.

XPS spectra of the surface film formed on molten AZ91D alloy showed that the primary signals came from F, Mg, C, O and Al (Fig. 4a). The N, Si and Na peaks might be contaminants introduced in the process of preparation and analysis of the sample. From Fig. 4b, it can be seen that Mg presented in three chemical states. The binding energy peak at 51.29 ± 0.2 eV was MgF_2, 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

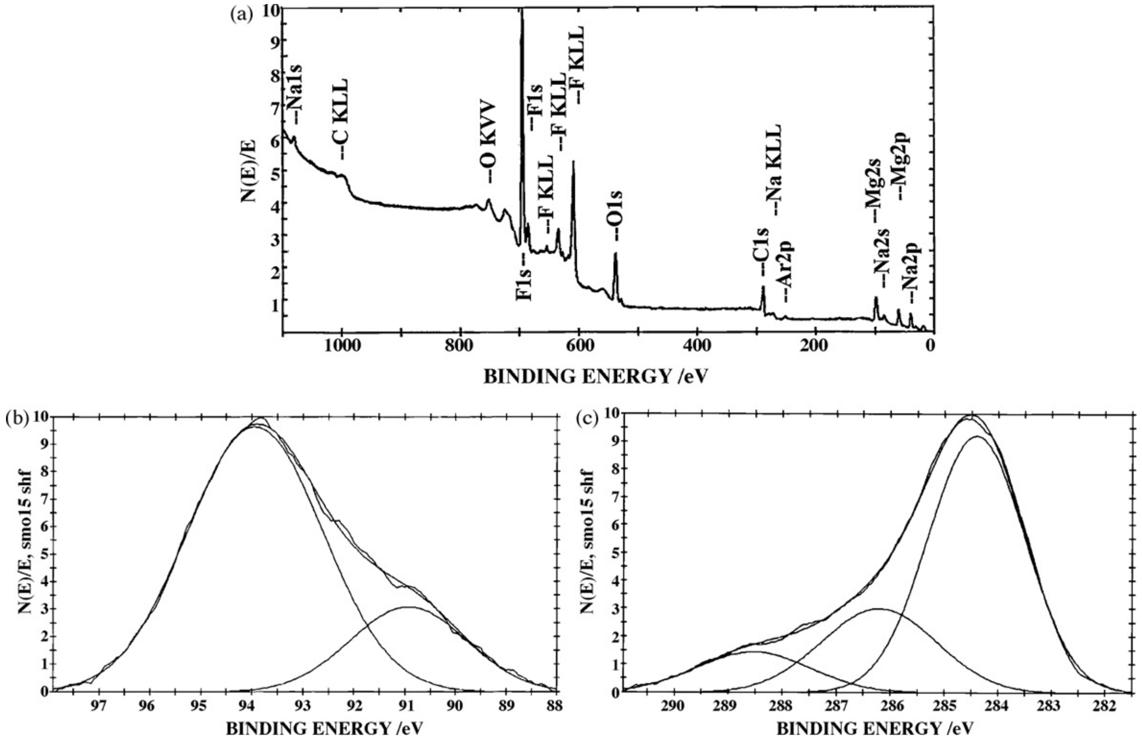

Fig. 3. XPS spectra of the surface film formed on magnesium in air containing 1% HFC-134a at 760 °C for 2.5 h (after 30 min sputtering with Ar^+ ion): (a) the whole survey spectra, (b) Mg2s, (c) C1s.

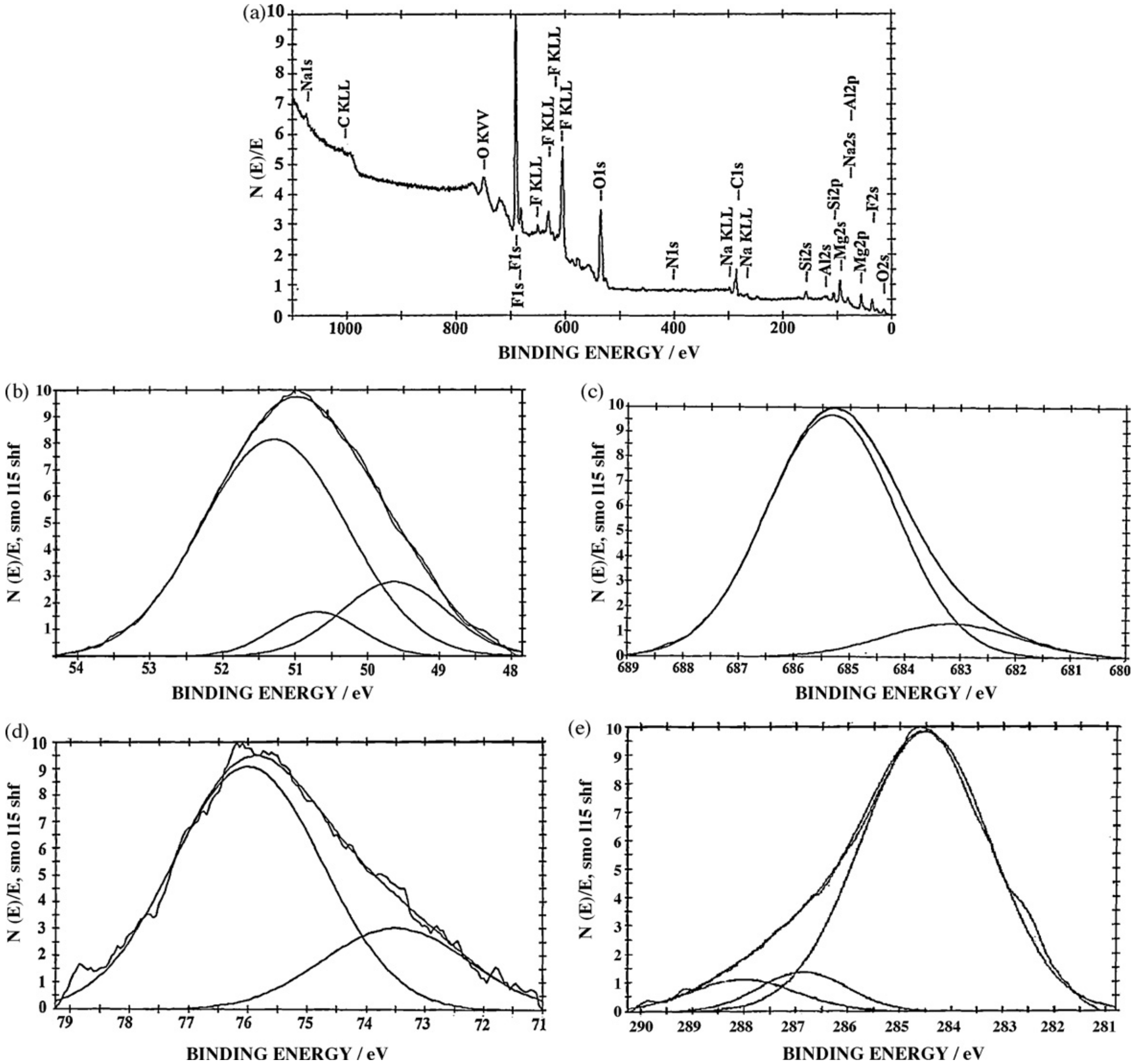

Fig. 4. XPS spectra of the surface film formed on AZ91D magnesium alloy in air containing 1% HFC-134a at 760 °C for 2.5 h (after 30 min sputtering with Ar+ ion): (a) the whole survey spectra, (b) Mg2p, (c) F1 s, (d) Al2p and (e) C1s.

at 50.70 ± 0.2 eV and 49.70 ± 0.2 eV, it could be deduced that the content of MgF_2 in the film was higher than that of MgO and $Mg(OH)_2$, and the amount of $Mg(OH)_2$ was very small. From Fig. 4c, it can be seen that F presented in two chemical states. The binding energy peak at 685.33 ± 0.2 eV was MgF_2, the binding energy peak at 683.17 ± 0.2 eV was AlF_3, and the content of MgF_2 was much greater than that of AlF_3 in the film. In Fig. 4d, the binding energy peak at 76.00 ± 0.2 eV was the peak of $Al2p_{3/2}$ in AlF_3 and the binding energy peak at 73.50 ± 0.2 eV was the peak of $Al2p_{3/2}$ in Al_2O_3. Here the content of AlF_3 was much greater than that of Al_2O_3. 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 resulted from CO and CO_2. CO and CO_2 might come from the adsorption of CO and CO_2 in covering gas on the surface of MgF_2 and MgO film. CO and CO_2 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 atmosphere of air containing 1 vol.% 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 AlF_3 and $Mg(OH)_2$. Because the amount of this compounds were much less than that of MgF_2, these products were not detected in the XRD analysis results of the films formed on magnesium and AZ91D alloy surfaces in the atmosphere of air/1 vol.% or more HFC-134a at 760 °C.

4. Discussion

The above experimental results indicated that the morphologies and compositions of the surface films formed on magnesium and AZ91 alloy melt under the atmosphere of air/HFC-134a cover gas mixtures were different, which depended on the concentration of HFC-134a in cover gas mixtures and the matrix component. The results could be understood based on following analysis.

When the concentration of HFC-134a was higher, the cover gas mixtures were mainly composed of O_2, HFC-134a, HF and F_2. Here HF and F_2 are the decomposition products of HFC-13a at high temperature, which have been identified by analysis of FTIR, gas chromatography (GC) and gas chromatography-mass spectrograph (GC-MS) to the gas at high temperature. The following reactions might happen on the surface of molten magnesium:

$$Mg(l) + 1/2O_2(g) \rightarrow MgO(s) \qquad \Delta G_1^0 = -612{,}955 + 128.08T \tag{1}$$

$$Mg(l) + CF_3CH_2F(g) + 2O_2(g) \rightarrow MgF_2(s) + 2HF(g) + 2CO_2(g) \qquad \Delta G_2^0 = -1{,}577,662 - 60.45T \tag{2}$$

$$\mathrm{Mg(l) + HF(g) \rightarrow MgF_2(s) + 1/2H_2(g)} \quad \Delta G_3^0 = -571{,}060 + 178.14T \qquad (3)$$

$$\mathrm{Mg(l) + F_2(g) \rightarrow MgF_2(s)} \quad \Delta G_4^0 = -1{,}120{,}000 + 171.2T \qquad (4)$$

Based on the Gibbs free energies (ΔG^0, J) of the above reactions, the reaction trend between magnesium and HFC-134a or F_2 (reaction (2) or (4)) is greater than the reaction trend between magnesium and O_2. So the surface films formed on molten magnesium mainly consisted of MgF_2. This was confirmed by the analysis results of XRD and XPS. Since the compact coefficient of MgF_2 (1.32) is greater than that of MgO (0.81), the composite film of MgF_2 and MgO formed was compact which could effectively inhibit and reduce the outward evaporation of magnesium and the inward diffusion of oxygen through the surface film, and provide effective protection for molten magnesium.

For molten AZ91D alloy, in addition to the reactions between Mg and O_2, HFC-134a or F_2, alloying elements Al, Zn and Mn might react with oxygen and HFC-134a or F_2:

$$\mathrm{Al(l) + 3/2F_2(g) \rightarrow AlF_3(s)} \quad \Delta G_5^0 = -1{,}507{,}750 + 257.90T \qquad (5)$$

$$\mathrm{Al(l) + 3/4O_2(g) \rightarrow 1/2Al_2O_3(s)} \quad \Delta G_6^0 = -841{,}450 + 161.62T \qquad (6)$$

$$\mathrm{Zn(l) + F_2(g) \rightarrow ZnF_2(s)} \quad \Delta G_7^0 = -768{,}600 + 174.72T \qquad (7)$$

$$\mathrm{Zn(l) + 1/2O_2(g) \rightarrow ZnO(s)} \quad \Delta G_8^0 = -348{,}360 + 103.28T \qquad (8)$$

$$\mathrm{Mn(l) + F_2(g) \rightarrow MnF_2(s)} \quad \Delta G_9^0 = -800{,}491 + 135.306T \qquad (9)$$

$$\mathrm{Mn(l) + O_2(g) \rightarrow MnO_2(s)} \quad \Delta G_{10}^0 = -531{,}830 + 188.78T \qquad (10)$$

For reaction (5), the change of its standard free energy is more negative than that of the reactions (6)–(10) and the content of Zn and Mn in AZ91D alloy is relatively fewer, so the reaction probability of Al with F_2 (reaction (5)) is greater than that of Zn, Mn with F_2 and O_2 (reactions (6)–(10)). As a result, the surface films on molten AZ91D alloy in the air containing high concentration of HFC-134a were mainly composed of MgF_2 with small amount of MgO and AlF_3. The content of MgO or AlF_3 is far less than the content of MgF_2 in the surface films, so the MgO or AlF_3 was not detected by XRD because of its content fewer.

In the atmospheres of the air containing low concentration of HFC-134a, although the reaction trend between Mg and HFC-134a or F_2 was greater than the reaction trend between Mg and O_2, the reaction probability between Mg and HFC-134a or F_2 was less than that of Mg and O_2 because of the lower content of HFC-134a in the gas mixtures. The reaction products between Mg and HFC-134a or F_2 were less than that of Mg and O_2. So the surface films on molten magnesium mainly consisted of MgO. For molten AZ91D alloy, in addition to the reaction between Mg and O_2, alloying elements Al, Zn and Mn could react with O_2 to produce Al_2O_3, ZnO and MnO_2. The reaction probability of Al with O_2 was greater than that of Zn and Mn with O_2 because of the high content of Al in Z91D alloy, so the content of Al_2O_3 was more than that of ZnO and MnO_2. The amphoteric Al_2O_3 could directly react with the alkaline MgO to form $MgAl_2O_4$ at high temperature. Therefore, the surface films formed on molten AZ91D alloy were mainly composed of MgO and $MgAl_2O_4$. It is known that the forming 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 the surface film, $MgAl_2O_4$ could be seen as a solid solution which Al_2O_3 dissolved completely in MgO. According to Wayner-Hauffe "value law" [14], when the high value cation Al^{3+} dissolves in the cation conductor MgO in the solid state, the concentration of Mg^{2+} ions vacancy increases, which results in the oxidation of magnesium speeding up. With the reactions between Mg, Al and O_2 continuation, the concentration of O_2 decreased and the content of N_2 increased in the contiguous area of the film. This resulted in the reaction of N_2 with Mg to form Mg_3N_2, and the reaction of N_2 with Al to form AlN:

$$\mathrm{Mg(l) + N_2(g) \rightarrow Mg_3N_2(s)} \quad \Delta G_{11}^0 = -487{,}050 + 232.03T \qquad (11)$$

$$\mathrm{Al(l) + 1/2N_2(g) \rightarrow AlN(s)} \quad \Delta G_{12}^0 = -327{,}100 + 115.52T \qquad (12)$$

Since the changes of standard free energy for reactions (11) and (12) are not highly negative, the reaction rates of the reactions (11) and (12) might be relatively slow, which lead to small amount of Mg_3N_2 and AlN existing in the surface film. The effects of Mg_3N_2 and AlN on the oxidation behavior of molten AZ91D alloy could be negligible.

5. Conclusions

The morphologies and compositions of the surface films formed on molten magnesium and AZ91D magnesium alloy in the atmospheres of air/HFC-134a were different. When the concentration of HFC-134a was less than 0.1 vol.%, the surface films were mainly composed of MgO and MgF_2 for magnesium, and MgO, Mg_3N_2, AlN and $MgAl_2O_4$ for AZ91D alloy, which presented very coarse and incompact surfaces. When the concentration of HFC-134a was more than 1 vol.%, the surface films were mainly composed of MgF_2 for magnesium, and MgF_2 and C for AZ91D alloy. The morphologies of the surface films gradually became relative smooth and compact, and the oxidation resistant properties of the films gradually increased with increasing the concentration of HFC-134a in cover gas or the time. The research results indicated that the gas mixtures of air containing HFC-134a have protective effect for molten magnesium and its alloys under an appropriate concentration of HFC-134a. HFC-134a gas would replace SF_6 as a protective gas to be applied to the manufacture process of magnesium and its alloys in the future.

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