The oxidation behaviour of pure magnesium in hexafluoropropylene/air atmosphere

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Abstract. The oxidation behaviour of pure magnesium in hexafluoropropylene/air atmosphere at 670-800 °C was investigated by TG, XRD, SEM and EDS. Results show that the oxidation rate of molten pure magnesium increased with the increase of temperature and decrease of HFP concentration. The film formed on the melt surface mainly consisted of MgF2, MgO, C.

Keywords: Magnesium, Hexafluoropropylene, Oxidation, Gas protection.

1. Introduction

Magnesium and its alloys have excellent properties and are commonly used in aerospace, biomedicine, electronic communications, and automotive industries [1-3]. However, magnesium and its alloys are very susceptible to oxidation, combustion and even explosion during the melting process [4]. SF_6 gas has a good protective effect on the smelting of magnesium alloys, but it has been banned due to its strong greenhouse effect [5]. Therefore, it is a challenge for magnesium alloy smelting researchers to find a protective gas with excellent protection effect and little impact on the ecological environment. Thermogravimetric analysis (TGA) is extensively used to determine thermal behavior and reaction kinetics [6]. In this paper, the oxidation behavior of Magnesium melt in air containing 0.05–5% HFP has been studied from 670 to 800 °C. The oxidative weight gain curve has been measured by the weight gain method. The oxidized surface of the melt has been characterized by SEM, XRD, EDS and the oxidation rules were also discussed.

2. Experiment

The materials for the study were pure Magnesium and high pure HFP gas. The chemical composition of pure Magnesium was 0.0006 wt.% Al, 0.0008 wt.% Zn, 0.0004 wt.% Mn, 0.0008 wt.% Fe, 0.0004 wt.% Si, and Mg balance. The chemical composition of HFP gas was 99.99 vol.% HFP, 0.0011 vol.% O_2 and 0.0004 vol.% H_2O. The cylindrical sample of pure Magnesium with a height of 3 mm and a diameter of 25 mm was cut from an as-cast rod. Before the experiment, the surface of the sample was ground by hand with SiC paper up to 2000 grit and then rinsed with acetone.

The oxidation experiments of molten pure Magnesium in HFP/air atmospheres were carried out in a TG measuring instrument. The instrument was composed of a vertical tube furnace with a quartz pipe (Φ44×800 mm), an electronic balance (with an accuracy of 0.1 mg) connected to a computer, and a gas supply system that can supply the gas mixture of HFP and air to the quartz pipe. The details of the experimental setup can be referred to Reference [7]. In each experiment, HFP was mixed with air purified by activated carbon at a given ratio, and then the mixed gas was led into the quartz pipe from the bottom at the flow of 300 ml/min. After about 1 h, the sample of pure Magnesium placed in a high-purity corundum crucible (Φ27×5 mm) was suspended from the bottom of the electronic balance to the hot zone of the quartz pipe by using a platinum wire, and quickly heated to a given temperature, and then held at this temperature for 2.5 h. During this time, the weight gain of the sample in air containing a given concentration of HFP over time was continuously measured and recorded by the electronic balance and the computer connected to it, respectively. Once the holding time was attained, the sample was rapidly cooled, taken out of the quartz tube, and stored in a desiccator for XRD, SEM and EDS measurements. The oxidation behavior was measured in the atmospheres of air containing 0.05–5% HFP at the temperatures from 670 °C to 800 °C for 2.5 h.

The morphology of the surface and cross section of the oxidized pure Magnesium sample was observed by a scanning electron microscope (SEM). The chemical composition of the oxidation products on the surface of

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the sample was analyzed by an energy dispersive spectrum (EDS). The phase composition of the oxidation products was identified by an X-ray diffraction (XRD) with a Cu-Kα source operated at 40 kV and 40 mA.

3. Results and Discussion

3.1 Thermogravimetric analysis

Figure 1 shows the oxidative weight gain curves of pure magnesium in HFP/air mixture at different concentrations at 730°C. As seen in Figure 1, the curve of the sample exposed to 0.05% HFP in air exhibited a rapid and almost linear increase over time. For the sample exposed to 0.1% HFP in air, the curve deviated from linearity and the weight gain was lower than that of the sample exposed to 0.05% HFP in air. For the sample exposed to 0.5% HFP in air, there was a rapid weight increase at the initial stage and later weight gain decreased gradually with time, and the weight gain was lower than that of the sample exposed to 0.1% HFP in air. As the concentration of HFP was increased to 1%, the weight gain of the sample increased slowly with time. The curve of the sample exposed to 5% HFP in air was similar to that of the sample exposed to 1% HFP in air, and the weight gain was the smallest. These results show that the oxidation rate of molten pure magnesium in HFP/air atmospheres decreased with the increase of HFP concentration.

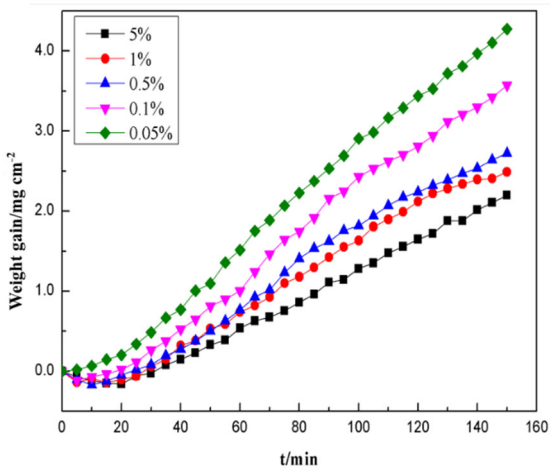

Figure 1. Oxidative weight gain curves of pure magnesium in HFP/air mixture at different concentrations at 730°C.

Figure 2 shows the oxidative gain curves of pure magnesium at different temperatures in 0.5% HFP/air mixture. As seen in Figure 2, at 670 °C, the sample slowly gained weight over time, whereas at 700 °C the weight gain of the sample increased significantly with time after 40 minutes. When the temperature reached to 730 °C, the weight gain of the sample was greater than that at 700 °C. As the temperature increased to 760 °C, the weight gain of the sample was significantly greater than that of 730 °C. The sample exposed to 800 °C experienced a rapid weight gain in the initial stage and then continued to increase its weight at a relatively lower rate with time, and the weight gain was the largest. These results show that the oxidation rate of molten pure magnesium in 0.1% HFP/air atmosphere increased with the increase of temperature.

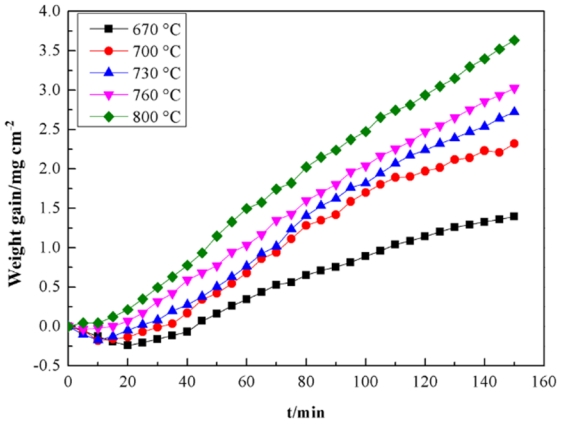

Figure 2. Oxidative gain curves of pure magnesium at different temperatures in 0.5% HFP/air mixture

3.2 SEM and EDS Analysis of Surface Film

Figure 3 shows the SEM topography of magnesium melt in different concentrations of HFP/air mixture at 730 °C. HFP concentration reduced from 5% to 0.05% in the process of surface film was flat, continuous and had a few small holes, the different light and dark places in the membrane were caused by uneven surface height, Figure 3 (a) 5% HFP film surface had some white particles, Figure 3 (b)-(e) different HFP concentration membrane morphology also appeared. Table 1 was the distribution results of EDS surface scanning elements of the surface film under the corresponding HFP concentration, the film was mainly composed of Mg, F, O and C elements, with the decrease of HFP concentration, the content of F element in the surface film decreased, the content of O and C elements increased, the F/O mass ratio decreased, and the oxidation showed an increasing trend, but the content of F element was much greater than that of O element, so oxidation was only a relative degree of increase. From the surface film section of Figure 3 (f)-(j), it can be seen that with the decrease of HFP concentration, the thickness and compactness of the film were decreased. It can be seen that with the decrease of HFP concentration at 730 °C, the white particles on the film surface increased, the content of F element decreased, the content of O and C elements increased, the mass ratio of F/O decreased, and the oxidation trend increased.

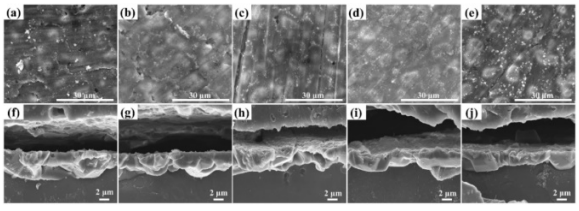

Figure 3. SEM diagram of surface film and cross-section of magnesium melt at different concentrations of HFP/air at 730 °C for 2.5 h: (a), (f) 5%; (b), (g) 1%; (c), (h) 0.5%; (d), (i) 0.1%; (e), (j) 0.05%.

Table 1 Element composition measured by EDS for the surface films formed in air containing different concentrations of HFP at 730 °C (wt.%)

elemental	Mg	F	O	C	Si	F/O
5%	48.37	50.68	0.65	0	0.3	77.97
1%	50.02	48.75	0.75	0	0.48	65.00
0.5%	50.15	47.39	0.81	1.03	0.62	58.51
0.1%	48.79	46.25	1.6	1.82	1.54	28.90
0.05%	51.6	44.13	2.03	1.16	0.78	21.89

Figure 4 shows the SEM diagram of surface film and cross-section of pure magnesium in 0.5% HFP/air for 2.5 h. As seen in Figure 4(a), there were more particles on the surface of the film at 670 ℃, but the film was relatively dense; In Figure 4(b)-(e), the particles on the film surface decreased at 700 ℃, the particles on the film surface increased when the temperature rised from 730 ℃ to 800 ℃, the roughness increased, and the melt oxidation trend accelerated. From the EDS results of the surface film in Table 2, it can be seen that the surface film mainly consists of Mg, F and O. With the increase of temperature, the contents of Mg and C elements gradually decreased, the contents of F and O elements increased, the mass ratio of F/O gradually decreased, and the oxidation rate of melt increased relatively, but the content of F element far exceeded that of O element. The surface film was mainly composed of Mg and F elements, and Si element was the impurity. It can be seen from Figure 4 (f)-(j) that the thickness of the surface film increased in turn with the increase of temperature, and the roughness of the surface film can be seen more clearly from the cross section of the surface film the degree increased.

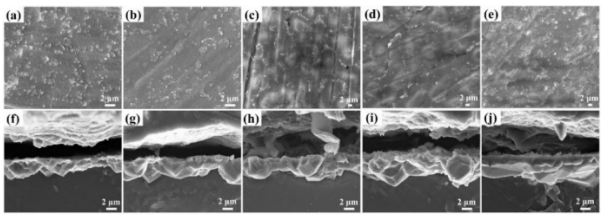

Figure 4. SEM diagram of surface film and cross-section of pure magnesium in 0.5% HFP/air for 2.5 h: (a), (f) 670 ℃; (b), (g) 700 ℃; (c), (h) 730 ℃; (d), (i) 760 ℃; (e), (j) 800 ℃.

Table 2 Element composition measured by EDS for the surface films formed in 0.1% HFP/air atmosphere at different temperatures (wt.%).

elemental	Mg	F	O	C	Si	F/O
670 ℃	56.12	40.6	0.39	2.63	0.26	104.1
700 ℃	45.03	50.89	0.7	3.13	0.25	72.7
730 ℃	50.15	47.39	0.81	1.03	0.62	58.51
760 ℃	48.8	48.13	1.32	0.8	0.95	36.46
800 ℃	47.88	48.49	1.7	0.75	1.18	28.52

3.3 XRD Analysis of Surface Film

Figure 5 shows the XRD diagram of the phase composition of the surface film in the HFP/air mixed atmosphere at different concentrations at 730 °C for 2.5 h, from which it can be seen that MgF_2 was present in the surface film of different concentrations of HFP/air mixed gas, and the peak intensity gradually decreased with the decrease of HFP concentration, the peak intensity of Mg matrix was very strong, the peak intensity of MgO was weak and with the decrease of HFP concentration, the peak intensity of MgO is slightly enhanced. The peak of the impurity $MgSiO_3$ was weak at HFP concentrations of 5% and 0.05%, and stronger at other HFP gas concentrations.

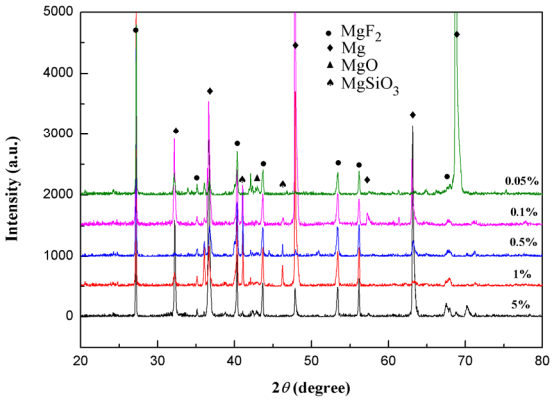

Figure 5. XRD diagram of surface film of magnesium melt at different concentrations of HFP/air at 730 °C for 2.5 h.

In order to see the changes of each substance at different temperatures under the condition of a certain concentration of HFP/air mixed gas, Figure 6 XRD analysis of the surface film in 0.5% HFP/air mixture gas, the temperature obtained from the figure was an important influencing factor of the high temperature oxidation behavior of magnesium melt, with the increase of temperature, the degree of reaction between effective protective gas HFP and magnesium melt deepens, the peak intensity of MgF_2 basically showed an enhanced trend. At lower temperature 670 °C-700 °C the impurity $MgSiO_3$ was not generated, and when the temperature continued to rise, the peak of the $MgSiO_3$ will appear, the MgO peak intensity was still weak, and a small amount of magnesium matrix peaks was also can be seen.

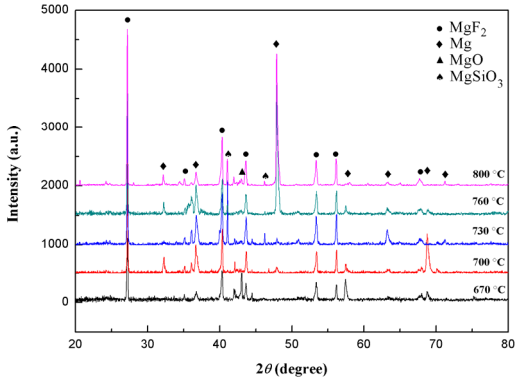

Figure 6. XRD diagram of the surface film of magnesium melt in 0.5% HFP/air mixture at different temperatures.

4. Conclusions

In the present study, the oxidation behavior of molten pure magnesium in air/HFP
mixed gases was investigated. During the smelting process of magnesium melt, the concentration and temperature of HFP in the protective gas had great influence on the oxidation behavior of magnesium melt, and the oxidation behavior of magnesium melt was concentrated with HFP the increase of degree and the decrease of melting temperature will be gradually suppressed, so that the melting protection of magnesium melt can be realized. The film formed on the melt surface mainly consisted of MgF2, MgO, C.

Acknowledgements

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References

1. W.J. Liu, F.H. Cao, B.L. Jia, L.Y. Zheng, J.Q. Zhang, C.N. Cao, X.G. Li, Corrosion behaviour of AM60 magnesium alloys containing Ce or La under thin electrolyte layers. Part 2: corrosion product and characterization, Corros. Sci. 52 (2010) 639–650.
2. X.L. Chen, Y. Zhao, L.J. Gu, B.L. Zou, Y. Wang, X.Q. Cao, Hot corrosion behaviour of plasma sprayed YSZ/LaMgAl11O19 composite coatings in molten sulfate-vanadate salt, Corros. Sci. 53 (2011) 2335-2343.
3. F. Czerwinski: ‘Controlling the ignition and flammability of magnesium for aerospace applications’, Corros. Sci., 86(2014), 1– 16.
4. C. M. Yuan, L. F. Yu, C. Li. Thermal analysis of magnesium reactions with nitrogen/oxygen gas mixtures. Journal of Hazardous Materials. 260(2013) 707-714.
5. H. Jiang, H. Chen, J. Huang, X. Mu, Y. Jiang, Y. Jie. Protection of magnesium melt by hexafluoropropylene/air atmosphere. IOP Conf. Series: Mater. Sci. Eng. 711 (2020) 012028.
6. S. Niu, K. Han, F. Zhou, C. Lu. Thermogravimetric analysis of the decomposition characteristics of two kinds of calcium based organic compounds. Powder Technol. 209(2011)46-52.
7. H. Chen, Y. Jie, L. Chang, X. Chen, Reaction behavior of MgF2 powder in hexafluoropropylene/air atmospheres at high temperatures, Solid State Ionics 340 (2019) 115016.