Air Oxidation of an Fe₄₈Cr₁₅C₁₅Mo₁₄B₆Er₂ Bulk Metallic Glass at 600–725°C

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The oxidation behavior of an Fe₄₈Cr₁₅C₁₅Mo₁₄B₆Er₂ bulk metallic glass (Fe-BMG) was studied over the temperature range of 600–725°C in dry air. The oxidation kinetics of the glassy alloy followed a two-stage parabolic rate law at $T \leq 650^\circ\text{C}$, while the single-stage linear rate was observed at higher temperatures ($T \geq 675^\circ\text{C}$). The oxidation rates of the Fe-BMG at $T \leq 625^\circ\text{C}$ were much lower than those of the commercial 304 stainless steel (304 SS), revealing the excellent oxidation resistance of the amorphous alloy. A continuous, thin layer of chromium oxide (Cr₂O₃) containing some iron was formed at $T \leq 650^\circ\text{C}$, while typical hump iron oxides intermixed with minor amounts of Cr₂O₃ and MoO₂ were observed at $T \geq 675^\circ\text{C}$. In addition, a substrate phase transformation from the amorphous structure to Fe-Cr and FeCrMo crystalline phases was detected after the oxidation. Very likely, the formation of the non-protective Fe₃O₄ and MoO₂ breaks the scale integrity and allows the rapid cation/anion transportation, resulting in the fast linear-kinetics behavior of the Fe-BMG at $T \geq 675^\circ\text{C}$.

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1. Introduction

Bulk metallic glasses (BMGs) based on Ln and Mg,^{1,2)} Zr and Ti,³⁾ Cu⁴⁾ by copper mold casting have been extensively developed during the past two decades to meet the needs for practical applications.^{5,6)} Most of these studies concentrated on the processing and mechanical properties of the BMGs, and were conducted mainly on non-ferrous systems. Ternary- or multi-component BMGs based on Fe-(Al, Ga)-(P, C, B, Si) systems were first proposed in 1995.⁷⁾ These Fe-based BMGs exhibited an excellent combination of mechanical and magnetic properties, as compared to those of the conventional steels.^{8–12)} Very recently, it was reported that a new Fe₄₁Cr₁₅C₁₅Mo₁₄Co₇B₆Y₂ BMG exhibits high fracture strength of 3500 MPa and Vickers hardness of 1,253 Kg/mm⁻².¹³⁾ Yet, little work has been done on the oxidation of the Fe-base BMGs except for a previous study on the oxidation of the Fe₇₂B₂₂Y₆ BMG.¹⁴⁾ It was found that the formation of B₂O₃ on the surface of the Fe₇₂B₂₂Y₆ BMG was responsible for the reduced oxidation rates, as compared to those of the crystalline counterpart.

It is known that commercial stainless steels always contain certain amounts of chromium, nickel, and molybdenum to meet the needs for their multi-purposed applications. It is hoped that the developed amorphous steels can possess the same composition but have superior mechanical properties, as compared to commercial steels. In addition, to use the amorphous steels for structural materials at elevated temperatures, an understanding of their oxidation properties is certainly essential. Thus, it is of interest to study the oxidation behavior of Fe₄₈Cr₁₅C₁₅Mo₁₄B₆Er₂ BMG in dry air, in particular, the role of alloying elements on the scale formation and the phase transformation after the oxidation.

2. Experimental

The Fe₄₈Cr₁₅C₁₅Mo₁₄B₆Er₂ BMG (Fe-BMG; hereafter in

atomic percent (at.%) unless otherwise stated) was prepared by an injection-casting technique, as described elsewhere.¹¹⁾ Average composition of the as-cast Fe-BMG at four different locations analyzed by the X-ray wavelength-dispersive spectroscopy (WDS) is 51.6% Fe, 15.3% Cr, 10.8% C, 13.3% Mo, 6.0% B, and 3.0% Er. The Fe-BMG samples were sheared into a rectangular shape (3 × 3 × 0.5 mm), ground and polished with 0.3-μm diamond paste, cleaned with acetone, and immediately dried before the tests.

The thermal stability of the Fe-BMG samples was examined by the differential scanning calorimetry (DSC) at a heating rate of 10°C/min. Oxidation tests were performed by means of the thermogravimetric analyzer (TGA) in dry air (> 99.999 vol% pure). For each experiment, the net flow rate of air was kept constant at 40 cm³/min., and the heating and cooling rates of the TGA furnace were set at 10°C/min. The characterization of the Fe-BMG alloy and oxide-scales was performed using the x-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with X-ray energy-dispersive spectrometry (EDS), electron probe microanalyzer (EPMA) equipped with WDS, and transmission electron microscopy (TEM) equipped with EDS and selected-area diffraction (SAD), as described previously.¹⁴⁾

3. Results and Discussion

3.1 Alloy constitutions and thermal stability

XRD spectra of the as-cast Fe-BMG are shown in Fig. 1, revealing a typical wide-broadening peak, which indicates the amorphous structure. The DSC curves of the Fe-BMG shown in Fig. 2 reveal that the glass transition temperature (T_g) and the crystallization temperature (T_x) are around 565.6 and 619.1°C, respectively. Thus, the supercooled liquid region ($\Delta T_x = T_x - T_g$) of the Fe-BMG is about 54°C, and the oxidation temperature of interest is set over the range of 550–725°C to cover from the amorphous to crystalline states.

3.2 Oxidation kinetics

The oxidation-kinetics curves of the Fe-BMG over the

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Fig. 1 XRD analyses of the Fe₄₈Cr₁₅C₁₅Mo₁₄B₆Er₂ BMG.

Fig. 2 DSC curve obtained in a heating rate at of 10°C/min.

temperature range of 600–725°C are shown separately in Fig. 3(a) and 3(b). The oxidation kinetics followed a two-stage parabolic-rate law at $T \leq 650^\circ\text{C}$. For example, the oxidation-rate constants (k_p values) at 625°C during the initial period of 6 h was around $7.4 \times 10^{-15} \text{ g}^2/\text{cm}^4/\text{s}$, and then decreased down to $7.7 \times 10^{-16} \text{ g}^2/\text{cm}^4/\text{s}$ at the steady-state stage (6 to 24 h). The mass gain of the Fe-BMG at 600°C was very small, only $4.14 \times 10^{-7} \text{ g}/\text{cm}^2$ after a 24-h exposure. Attempts to oxidize two BMG samples at 550°C for 36 h were not successful because the overall mass-gain data was negligible and beyond the TGA detection limits. This implies that nearly no oxidation occurred for the Fe-BMG at temperatures below T_g . Nevertheless, the observed parabolic-kinetics at 600–650°C indicates that solid-state diffusion is the rate-controlling step. The oxidation-rate constants (k_p values) of the Fe-BMG at the steady-state stage are tabulated in Table 1. For comparative purposes, the k_p values of the commercial 304 stainless steel (304 SS) obtained in the same atmosphere are also shown in Table 1. According to the table, the k_p values of the Fe-BMG at 600°C and 625°C are lower than those of 304 SS, while the reverse condition is obtained at 650°C, indicating that the amorphous alloy exhibited the excellent oxidation resistance at $T \leq 625^\circ\text{C}$.

On the other hand, the single-stage linear kinetics obtained

Fig. 3 Oxidation kinetics of the Fe-base BMG at (a) 600–650°C and (b) 675–725°C.

Table 1 Steady-state oxidation rate constants ($\text{g}^2/\text{cm}^4/\text{s}$) of Fe-base BMG and alloys.

	600°C	625°C	650°C
Fe-base BMG	1.27×10^{-18}	7.74×10^{-16}	8.68×10^{-14}
304 SS	5.75×10^{-15}	6.52×10^{-15}	7.38×10^{-15}

over the temperature range of 675–725°C are most likely genuine since double runs at each temperature showed very similar trend. The linear-rate constants (k_l values) of the Fe-BMG increased with the temperature, being around 1.73×10^{-9} , 2.55×10^{-9} , and $7.12 \times 10^{-9} \text{ g}/\text{cm}^2/\text{s}$ at 675, 700, and 725°C, respectively. The observed linear kinetics indicates that the gas-metal interface-reaction is the rate-determining step for the oxidation of the Fe-BMG at higher temperatures. The discrepancy of the oxidation kinetics obtained at $T \leq 650^\circ\text{C}$ and at $T \geq 675^\circ\text{C}$ is due presumably to the formation of various scales, as discussed later.

3.3 Microstructure and Phase Constitution of Scales

A cross-sectional back-scattered-electron-image (BEI) micrograph of the scale formed on the Fe-BMG at 600°C for 40 h is shown in Fig. 4(a). The scale thickness is very thin and barely visible on the top of the substrate, which is in good agreement with the observed slow-kinetics, as indicated above. Another cross-sectional BEI micrograph and XRD analyses of the scale and the substrate formed on the Fe-BMG at 625°C for 24 h are depicted in Fig. 4(b), (c), revealing a uniform, flat scale-surface. The scale-layer was around 0.1 μm thick and remained good adherent to the

Fig. 4 Cross-section BEI micrographs of the BMG alloy oxidized at (a) 600°C for 40 h, (b) 625°C for 24 h, (c) 650°C for 24 h, and the corresponding XRD of (b).

substrate. XRD analyses revealed that the scale consisted of an exclusive layer of Cr_2O_3 (although EDS confirmed small amounts of Fe present), which intermixed with two crystalline Fe-Cr and σ -FeCrMo phases. The presence of two crystalline phases may be due to the thin-scale nature, so that X-ray may penetrate down to the non-oxidized substrate. The observed crystalline phases also indicated the occurrence of the phase transformation for the amorphous substrate. Furthermore, the scales formed on the Fe-BMG after the oxidation at 650°C for 24 h (Fig. 4(d)) are similar to those at 625°C except that the thickness of the Cr_2O_3 layer is slightly thicker ($\sim 1 \mu\text{m}$) and some discontinuous iron-oxide islands grew on the top of the scale surface.

Unlike the formation of the uniform scales at $T \leq 650^\circ\text{C}$, typical hump scales started to form on the Fe-BMG after the oxidation at 675°C for 24 h, as shown in Fig. 5(a). At higher magnification (Fig. 5(b)), the BEI micrograph and corresponding EPMA analyses revealed a complicated scale-nature. It should be pointed out that the hump-scale is not

compact and contained numerous pores near the dark areas. The composition of the outermost scale (shown in Fig. 5(b) as pt. 1) analyzed by EPMA contained mostly O (64.23%), some Fe (28.31%), low Cr (4.71%), and minor amounts of other alloying elements, which is corresponding to the formation of iron oxides dissolved with Cr_2O_3 . On the other hand, the composition of the dark areas near pores (shown in Fig. 5(b) as pt. 2) has mostly O (61.96%), high amounts of Mo (13.57%) and Fe (14.96%), low Cr (4.65%) and minor amounts of other alloying elements, which may be close to a mixture of iron oxides, MoO_2 , Cr_2O_3 , or ternary oxides. However, although not shown here, XRD analyses failed to identify MoO_2 throughout the hump scale. In addition, the composition of the innermost scale (shown in Fig. 5(b) as pt. 3) contained mostly O (59.69%), high Cr (17.85%), some Fe (13.80%) and Mo (6.74%) and minor amounts of other alloying elements, corresponding to the formation of significant amounts of Cr_2O_3 , dissolved with some iron oxides. It should be pointed out that the iron oxides present in the

	Fe	Cr	Mo	B	Er	C	O
1	28.31	4.71	1.72	0.11	0.90	0.02	64.23
2	14.96	4.65	13.57	0.18	0.92	3.76	61.96
3	13.80	17.85	6.74	0.12	0.65	1.15	59.69

Fig. 5 Cross-section BEI micrographs of the BMG alloy oxidized at (a) 675°C for 24 h, (b) high magnification of (a).

current study may be close to Fe₂O₃ or Fe₃O₄. In fact, Fe₂O₃ exists in two forms; α -Fe₂O₃, a rhombohedral structure, and γ -Fe₂O₃, a cubic structure.^{15,16} Fe₃O₄ may react with oxygen to only form α -Fe₂O₃ at $T \geq 400^\circ\text{C}$ (the γ -modification is unstable). Nevertheless, the possible iron oxides existed in the scales still remain an unsolved puzzle because XRD and EPMA analyses failed to distinguish the two phases. Thus, to clarify the existence of MoO₂ and the exact phase constitution of iron oxides in the scales at $T \geq 675^\circ\text{C}$, TEM analyses (with camera length of 80 cm) of the cross-sectional scales were prepared, and the results inserted with the SAD patterns are shown in Fig. 6. A typical cross-sectional TEM image, as shown in Fig. 6(a), revealed that the scales consisted of numerous oxide-particles embedded in a continuous scale-layer. The particle size of oxides increased gradually from the scale/substrate interface (< 10 nm) to the scale surface (up to ~ 70 nm). SAD patterns taken from various locations of the scales reveal that a larger dark particle is exclusive Fe₃O₄ (Fig. 6(b)) while the bright particles were mostly Cr₂O₃ (Fig. 6(c)). On the other hand, SAD ring-patterns of the nano-particles (~ 10 nm), as shown in Fig. 6(d), confirmed the MoO₂ phase present in the scale.

The topography and cross-sectional BEI micrographs as

well as XRD spectra of the Fe-BMG oxidized at 700°C for 24 h are shown in Fig. 7, revealing that the typical hump-scales were present and the outermost scale severely detached after cooling. XRD analyses revealed a mixed scale of Fe₃O₄ and Cr₂O₃ but no MoO₂. Although not shown here, a similar scaling behavior existed in the Fe-BMG after the oxidation at 725°C for 24 h, except that the size of the humps significantly increased with an increase in temperature. Apparently, the presence of hump scales of Fe₃O₄, Cr₂O₃, and MoO₂ at $T \geq 675^\circ\text{C}$ differs from that of layered scales of mostly Cr₂O₃ with dissolved Fe at $T \leq 650^\circ\text{C}$.

According to the Gibbs free energy of the formation of the possible stable oxides (Table 2),¹⁷ the free energies of Cr₂O₃ and Er₂O₃ per mole oxygen are much lower than those of Fe₃O₄ and MoO₂. One would expect that the initial selective oxidation of Cr and Er should be thermodynamically favorable, and their formation may be effective to suppress the outward diffusion of Fe and Mo. However, Er₂O₃ was absent in the scale; perhaps its amount is too low to be detected (2 $\sim$ 3% in the original alloy). Instead, the first formation of Cr₂O₃ at the initial stage of oxidation becomes thermodynamically and kinetically favorable. The fact is that the growth of Cr₂O₃ certainly removes some chromium in the

Fig. 6 (a) TEM cross-section of the scales formed on the Fe-BMG oxidized for 24 h at 675°C, (b-d) SAD of region 1, 2, and 3 of (a).

substrate, which in turn produces a local increase of the Fe and Mo activities at the metal/scale interfaces, thereby favoring the formation of both Fe_3O_4 and MoO_2 at the steady-state stage. Although both oxides were absent at lower temperatures, the kinetic prediction for the formation of Fe_3O_4 and MoO_2 is likely genuine when the Fe-BMG oxidized at $T \geq 675^\circ\text{C}$ because a mixture of MoO_2 , Fe_3O_4 , and Cr_2O_3 scales was observed in the dark areas around the pores. Very likely, the nucleation and growth of Fe_3O_4 and MoO_2 at $T \leq 650^\circ\text{C}$ is so slow that no evidence of their formation could be obtained by XRD or TEM during a 24-h exposure time.

In a review of the literature,¹⁶⁾ the initial oxidation of Fe-Cr-Mo alloys preferentially form a protective scale of chromium and iron oxides, while MoO_2 is formed by inward diffusion of oxygen at the later steady-state stage. Under high partial pressures of oxygen (such as in the current study), a further oxidation of MoO_2 to form the molten $\text{MoO}_{3(g)}$ is probably occurring. In fact, the MoO_2 - MoO_3 mixture could be characterized as a low eutectic reaction at 778°C .¹⁶⁾ Although the oxidation temperature in this study is lower than the eutectic point, it is very likely that the minor evaporation of MoO_3 in the scales has occurred, and this phenomenon could deteriorate the scale integrity, thereby resulting in a fast, catastrophic linear kinetics at $T \geq 675^\circ\text{C}$. Based on JCPDS data, the theoretical densities and molar

volumes (V_m) of some oxides are tabulated in Table 3. According to the table, the growth of MoO_2 from the Cr_2O_3 scale causes a 31.9% reduction of the molar volume, so that a residual tensile stress may be generated in the two-oxide boundary, which in turn results in the initial cracks in the scales. Once the cracks propagate through the scales, the scale integrity is broken and the substrate is exposed to air, thereby leading to a catastrophic linear-kinetics. However, the growth of Fe_3O_4 from the Cr_2O_3 may produce a reverse situation which causes a 37.2% increase of the molar volume, and results in a residual compressive stress. The compressive stress may be beneficial to cease the crack propagation through the scale, but the formation of Fe_3O_4 further indicates the Cr_2O_3 scale is not so protective to suppress the outward diffusion of iron during the steady-state stage. Thus, the formation of Fe_3O_4 and MoO_2 in the scales is responsible for the fast, linear oxidation kinetics of the Fe-BMG at $T \geq 675^\circ\text{C}$.

4. Conclusions

- (1) The oxidation kinetics of the glassy alloy generally followed a two-stage parabolic rate law at $T \leq 650^\circ\text{C}$, while the single-stage linear rate was observed at higher temperatures ($T \geq 675^\circ\text{C}$).
- (2) A continuous, thin layer of Cr_2O_3 dissolved in some iron

Fig. 7 Surface morphology of scale formed on $\text{Fe}_{48}\text{Cr}_{15}\text{C}_{15}\text{Mo}_{14}\text{B}_6\text{Er}_2$ BMG oxidized (a) at 700°C for 24 h; (b) cross-section BEI micrographs, and (c) corresponding XRD spectra of the sample.

Table 2 The Gibbs free energies of formation (ΔG_f°) for possible oxides.

	Fe_3O_4	Cr_2O_3	MoO_2	Er_2O_3
600°C	−413.59	−1362.57	−214.01	−1095.01
650°C	−406.13	−1343.60	−210.88	−1071.18
700°C	−398.90	−1324.63	−201.39	−1057.56

Table 3 Theoretical density (D_x) and calculated molar volumes (V_m) of some oxides.

Compounds	JCPDS No.	D_x (g/cm ³)	V_m (cm ³ /mol)
Fe_3O_4	26-1136	5.81	39.86
Cr_2O_3	38-1479	5.23	29.06
MoO_2	32.0671	6.46	19.80

was formed at $T \leq 650^\circ\text{C}$, while typical hump Fe_3O_4 intermixed with some Cr_2O_3 and MoO_2 were observed at $T \geq 675^\circ\text{C}$.

(3) The linear oxidation-kinetics of Fe-base BMG oxidized at $T \geq 675^\circ\text{C}$ is due to the formation of a mixture of Fe_3O_4 , Cr_2O_3 , and MoO_2 .

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REFERENCES

- 1) A. Inoue, K. Ohtera, K. Kita and T. Masumoto: Jpn. J. Appl. Phys. **27** (1988) L2248.

- 2) A. Inoue, T. Zhang and T. Masumoto: Mater Trans. JIM **30** (1989) 965.
- 3) T. Zhang and A. Inoue: Mater Trans. JIM **39** (1998) 1001.
- 4) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: Acta. Mater **49** (2001) 2645.
- 5) A. Inoue: Acta. Mater **48** (2000) 279.
- 6) A. Inoue: Mater Sci. Eng. A **304–306** (2001) 1.
- 7) A. Inoue, Y. Shinohara and J. S. Gook: Mater Trans. JIM **36** (1995) 1427.
- 8) T. D. Shen and R. B. Schwarz: Appl. Phys. Lett. **75** (1999) 49.
- 9) Z. P. Lu, C. T. Liu and W. D. Porter: Appl. Phys. Lett. **83** (2003) 2581.
- 10) Z. P. Lu, C. T. Liu, J. R. Thompson and W. D. Porter: Phys. Rev. Lett. **92** (2004) 245503.
- 11) V. Ponnambalam, S. J. Poon and G. J. Shiflet: J. Mater Res. **19** (2004) 1320.
- 12) A. Inoue, B. L. Shen and C. T. Chang: Acta. Mater **52** (2004) 4093.
- 13) J. Shen, Q. Chen, J. Sun, H. Fan and G. Wang: Appl. Phys. Lett. **86** (2005) 151907.
- 14) H. H. Hsieh, W. Kai, R. T. Huang, M. X. Pan and T. G. Nieh: Intermetallics **12** (2004) 1089.
- 15) N. Birk and G. H. Meier: *Introduction to high temperature oxidation of metals*, London (Edward Arnold; 1983).
- 16) P. Kofstad: *High temperature corrosion*, London (Elsevier; 1988).
- 17) I. Barin: *Thermochemical Data for Pure Substances*, (VCH Verlagsgesellschaft mbH, D-6940, Weinheim, Germany; 1989).