Glass-Forming Ability and Mechanical Properties of Sm-Doped Fe–Cr–Mo–C–B Glassy Alloys

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Glass-forming ability and mechanical properties of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$ alloy were systematically studied in terms of the effect of substitution of rare-earth element Sm for the metalloid element B from 0 to 6 at%. It was found that the thermal stability and glass-forming ability of studied alloys were greatly enhanced by the replacement of B with Sm. With merely 1 at% Sm addition, the supercooled liquid region was extended from 66 to 88 K, and the diameter of the cast rod with fully glassy state increased from 1.5 to 4 mm. When the Sm content is in the range of 2 to 4 at%, the critical diameter for glass formation further increased up to 5 mm. The mechanical properties were also greatly improved by the Sm additions. The Young's modulus and compressive strength increase respectively from 140 GPa and 2400 MPa for the $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10}$ alloy to 189 GPa and 3400 MPa for the $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ alloy. However, no improvement in plasticity was observed in the Sm-added glassy alloys. Similar to the Sm-free glassy alloys, the Sm-doped glassy alloys deformed inhomogeneously and failed in a brittle manner. The mechanism for the improved GFA by the addition of Sm is discussed.

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1. Introduction

Since an amorphous structure was first obtained in the Au–Si system in the end of 1950's,¹⁾ the physics of glass-forming ability (GFA) has been one of the most important topics in the investigations of metallic glass.^{2–6)} Several theoretical and empirical criterions for easy glass formation have been established. They include Turnbull's 'deep eutectic' rule,²⁾ Egami's atomic size rule,³⁾ Nagel's electronic density rule⁴⁾ and Whang's thermodynamic rule (T_0 concept),⁵⁾ as well as Inoue's component rule.⁶⁾ Especially, guided by Inoue's component rule, numerous bulk form metallic glasses with large sizes in all three-dimensions (generally named as bulk metallic glasses (BMGs)), have been found.^{7–11)}

Recently, unusual glass-forming behavior has been noted in some poor glass formers with small addition of certain alloying elements. For example, the GFA was strongly enhanced by adding a small amount of rare-earth element, such as Er or Y, to Fe-based alloys,^{12–14)} or by adding Si to Cu- and Ti-based alloys.^{15–17)} These phenomena could not be simply interpreted by the criterions mentioned above. It is suggested that the remarkable enhancement in GFA originates mainly from two important effects. The first is the intrinsic role of the minor alloying elements in destabilizing the competing crystalline phase and stabilizing the liquid phase.^{6,13,14,18)} The second is that the alloying elements, such as Y and Er, may also act as an oxygen scavenger, which leads to the suppression of heterogeneous nucleation and, consequently, improves the GFA.^{12,19,20)} Though the details of the intrinsic role of the minor alloying elements in the glass former is still unclear, the fact that rare-earth elements can work as oxygen scavengers have been well known for a long time. That fluxing treatment improves the manufacturability for some Fe-based alloys^{21,22)} supports the second postulate and indicates that oxygen can be minimized or neutralized through alloying.

Sm (Samarium) is a rare-earth element and has a stronger affinity for the oxygen than most transition metals. It is thus reasonably expected that Sm may act as an oxygen scavenger and help to suppress heterogeneous nucleations, and consequently improve the GFA of Fe-based alloys. On the other hand, Sm is of relatively large atomic size, which is favor to improve the GFA.²³⁾ Fe–Cr–Mo–C–B alloys are known as glass formers and a fully glass structure rod with 2.5 mm in diameter can be produced at $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10}$ (all alloy compositions in this paper are in atomic percent).²⁴⁾ In this study, we have selected $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10}$ as the base alloy to study the effect of Sm addition on GFA. Because the Fe-based glassy alloys generally exhibit brittle fracture due to the existence of metalloid elements,²⁵⁾ therefore, for the purpose of simultaneously improving the GFA and modifying the mechanical properties, we introduce Sm through substitution of Sm for B in the base alloy.

2. Experimental Procedure

Alloy ingots with nominal compositions of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$ ($x = 0\text{--}6$ at%) were prepared by arc melting the mixtures of pure Fe (99.9 mass%), Cr (99.9 mass%), Mo (99.9 mass%), C (99.9 mass%), and Sm (99.9 mass%), as well as pre-alloyed $\text{Fe}_{79.5}\text{B}_{20.5}$ (99.5 mass%) ingots in an argon atmosphere. From the obtained alloy ingots, ribbons of ~ 0.02 mm thick and 1 mm wide were produced by a single-roller melt spinner. Bulk rod samples of about 40 mm long and up to 5 mm diameter were prepared by copper mold casting. The purity of argon gas was 99.99%.

The structures of the rapidly solidified ribbon and rod specimens were examined by X-ray diffraction (XRD) using Cu $K\alpha$ radiation and optical microscopy (OM). The thermal stability associated with glass transition, supercooled liquid and crystallization for the glassy alloys was investigated by differential scanning calorimetry (DSC) at a heating rate of 0.33 K/s. The compressive strength was evaluated by uniaxial compression test using specimens cut from the 3 mm

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Fig. 1 DSC curves of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$ ($x = 0, 1, 2, 4, 6$) melt-spun ribbons.

diameter rods. Compression tests were carried out on a SANS CMT5504 testing machine at an initial strain rate of $2.4 \times 10^{-4} \text{ s}^{-1}$ in ambient atmosphere. Fracture surface was examined by scanning electron microscopy (SEM).

3. Results

3.1 Glass forming behavior of Sm-doped Fe–Cr–Mo–C–B–Sm alloys

Melt-spun alloy ribbons were fabricated for the Sm-doped alloys $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$ ($x = 0, 1, 2, 4, 6$ at%). XRD analysis revealed that all these ribbon samples consisted of a single glass phase. DSC analyses also confirmed their glassy nature. Figure 1 shows the DSC curves of these glassy alloy ribbons. All the samples exhibit an apparent glass transition, followed by the appearance of a supercooled liquid region and then crystallization. The glass transition temperature (T_g), onset temperature of crystallization (T_x) and supercooled liquid region ($\Delta T_x = T_x - T_g$) as a function of Sm content for the $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$ glassy alloys derived from the DSC curves are shown in Fig. 2. The T_x increases with an increase in Sm content from 0 to 1 at% and then decreases slightly with further Sm addition, while the T_g does not change distinctly. At 1 at% Sm, T_x has the highest value of 955 K, which results in the highest ΔT_x value of 88 K. When the Sm content is more than 2 at%, T_g , T_x and ΔT_x decrease apparently. At the same time, the shape of the DSC curves change greatly, suggesting the crystallization behavior is changed by the Sm additions.

Rod samples with different diameters were fabricated to evaluate the GFA of these Sm-added alloys by determining their critical diameters ($D_{\max}$) for glass formation. As a typical example, Fig. 3 shows the XRD patterns of the cast rods with various diameters of the $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ alloy; the data of the melt-spun alloy ribbon was also included. These XRD patterns show a broad hump, and with no evidence of crystalline phases, indicating that the melt-spun ribbon and cast rods with diameters of 3 and 5 mm consist of mostly amorphous structure. However, some sharp

Fig. 2 Changes in T_g , T_x and ΔT_x with Sm content for the bulk glassy $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$.

Fig. 3 XRD patterns of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ cast rods with different diameters.

diffraction peaks superimposed on the main hump and the background were observed for the 7 mm rod, suggesting partial crystallization. The crystalline phases were identified to be $\text{Mo}_5\text{Cr}_6\text{Fe}_{18}$, $\text{Fe}_{17}\text{Sm}_2$ and Fe_{23}C_6 . Therefore, it is believed that the critical diameter for the Sm-added $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ alloy is between 5 and 7 mm.

The critical diameters of the studied alloys were summarized in Table 1. The reported critical diameter for the Sm-free alloy is 2.5 mm, but in the present study only 1.5 mm was obtained. The presumable reason is the difference in the experimental conditions. Nevertheless, the Sm-added alloys have larger critical diameters compared to the Sm-free alloy. When the Sm content is in the range of 2 to 4 at%, the critical diameter reaches ~ 5 mm. Figure 4(a) illustrates the surface morphology of the cast $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ glassy alloy rods with diameters of 3 and 5 mm. These rods display a smooth surface and metal luster. The optical micrograph of

Table 1 Alloy compositions and thermal properties. ($D_{\max}$: maximum casting diameter)

Alloy composition (at%)	T_g (K)	T_x (K)	$\Delta T_x = T_x - T_g$	$D_{\max}$ (mm)
$\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_0$	870	936	66	1.5
$\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_9\text{Sm}_1$	867	955	88	4
$\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$	875	950	75	5
$\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_6\text{Sm}_4$	836	895	59	5
$\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_4\text{Sm}_6$	846	901	55	4

(a)

(b)

Fig. 4 (a) Outlook of cast glassy rods with diameters of 3 and 5 mm, and (b) optical morphology of cross section of 5 mm rod.

the transverse cross-section [Fig. 4(b)] of 5 mm rods does not show any contrast from crystalline phases.

Figure 5 shows the DSC curves of the 5 mm $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ glassy alloy rod, together with the data of the melt-spun alloy ribbon. It is seen that the bulk alloys exhibit distinct glass transition at 875 K, followed by a large supercooled liquid region of 75 K and then crystallization at 950 K. Furthermore, there is no appreciable difference in T_g and T_x between the cast rod and melt-spun ribbon. The heat of crystallization (ΔH_x) for the first exothermic peak is evaluated to be -3.6 kJ/mol for the 5 mm rod and

Fig. 5 DSC curves of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ melt-spun ribbon and glassy alloy rod with diameter of 5 mm. Fig. 6 Compressive stress-strain curve of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ amorphous alloy cylinder with diameter of 3 mm. The insert is a SEM image showing typical fracture morphology of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ glassy alloy.

-3.7 kJ/mol for the melt-spun ribbon. Here, it is worth pointing out that the Sm contents of the largest $D_{\max}$ value (5 mm at 2 at%Sm) and the widest supercooled liquid region (88 K at 1 at%Sm) are not the same.

3.2 Mechanical properties

Mechanical properties of the 3 mm $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10-x}\text{Sm}_x$ glassy rods were measured by uni-axial compression test. Figure 6 shows the compressive stress-strain curve of the bulk glassy $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_8\text{Sm}_2$ alloy. This Sm-added alloy is subjected to elastic deformation and then fracture. The compressive strength, Young's modulus, and elastic strain are 3400 MPa, 189 GPa, and 2.01%, respectively. (The corresponding data for the Sm-free alloy ($\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{15}\text{B}_{10}$) are 2400 MPa, 140 GPa, and 1.70%, respectively). It is evident that the Sm-containing alloys have higher compressive strength than the base alloy. It should be pointed out that the compression samples crushed into small

Table 2 Enthalpies of mixing calculated by Miedema's model^{27,28)} and atomic-size ratio between Sm and the existing components.

Element	Radius (nm)	$\Delta H_{(\text{Sm})}^{\text{mix}}$ (kJ/mol)	$R_{\text{Sm}}/R_{\text{A}}$	$ R_{\text{A}} - R_{\text{Sm}} /R_{\text{Sm}}$
C	0.077	-72	2.338	0.572
B	0.097	-64	1.856	0.461
Cr	0.128	16	1.406	0.289
Fe	0.128	-1	1.406	0.289
Mo	0.140	35	1.286	0.222
Sm	0.180	—	1.0	—

fragments after compression test. A small amount of shear bands are seen on the side surfaces, suggesting the specimen undergoes highly localized shear deformation. A typical SEM image of fracture surface is inserted in Fig. 6. Except little amount of stages caused by rapid crack development, no typical vein-pattern is seen, suggesting a brittle failure of the Sm-added glassy alloys.

4. Discussion

The present results strongly suggest that the GFA of Fe–Cr–Mo–C–B alloys is greatly enhanced by minor alloying with Sm. As mentioned in the introduction section, the remarkable enhancement in GFA originates from the intrinsic role of the minor alloying elements, *i.e.* destabilizing the competing crystalline phase, stabilizing the liquid phase, and the extrinsic role of acting as oxygen scavengers.

The detailed mechanism about the intrinsic role of the minor Sm addition is unclear. It has been suggested that the significantly different atomic size and large negative heats of mixing favor glass formation.^{3,6,26)} The heat of mixing calculated based on Miedema's model^{27,28)} and atomic radii of the components are summarized in Table 2. Sm has the largest atomic radius of 0.18 nm among all the constituent elements,²⁹⁾ and has a large atomic size ratio with the other constituent elements. This causes large atomic mismatch, which may result in a large spectrum of atomic sizes that favors dense random atomic packing.²³⁾ On the other hand, Sm has a large negative heat of mixing with C (−72 kJ/mol) and B (−64 kJ/mol), but a relatively large positive heat of mixing with Cr (16 kJ/mol) and Mo (35 kJ/mol).^{27,28)} Clearly, the thermodynamic data do not satisfy the Inoue's criterion very well. But we could not rule out the possibility that some new atomic pairs among Sm, C and B are formed in supercooled liquid, which destabilize the competing crystalline phase and stabilize the liquid phase, and consequently, improve the GFA.

As for the oxygen scavenger effect of Sm, it is noted that Sm has a stronger affinity for the oxygen than other elements in this alloy system. The heat of forming Sm oxide is −1822.6 kJ/mol, which is far higher than that of forming other oxide (Fe₂O₃, −823.4 kJ/mol; MoO₃, −745.2 kJ/mol; Cr₂O₃, −1134.7 kJ/mol).³⁰⁾ The reaction between Sm and oxygen is thermodynamically favorable, which can alleviate the harmful effect of oxygen impurities and enhance the GFA. Similar results were reported by Liu *et al.*¹⁹⁾ and Zhang *et al.*²⁰⁾

Finally, it should be pointed out that the replacement of B with Sm in Fe–Cr–Mo–C–B–Sm alloys greatly improve their compressive strength, but does not improve their deformation behavior, though the content of metalloid B was lowered. The understanding for the mechanism of increasing strength by Sm addition is the further research work.

5. Conclusions

The effect of a small addition of Sm on the glass-forming ability and mechanical properties of bulk glassy Fe₄₃Cr₁₆Mo₁₆C₁₅B_{10x}Sm_x ($x = 0\text{--}6$ at%) alloys was studied. It was found that the thermal stability and glass-forming ability of Fe–Cr–Mo–C–B alloys were greatly enhanced by the minor alloying with Sm. With merely 1 at%Sm addition, the supercooled liquid region has been extended from 66 K for Fe₄₃Cr₁₆Mo₁₆C₁₅B₁₀ alloy to 88 K for Fe₄₃Cr₁₆Mo₁₆–C₁₅B₉Sm₁ alloy, and the cast rod with fully glassy structure increased from 1.5 mm to 4 mm in diameter. When the Sm content is in the range of 2 to 4 at%, the critical diameter for glass formation further increased to 5 mm. The possible reasons for the enhancement of GFA by the minor addition of Sm are the intrinsic effect of Sm that facilitate the formation of more stable supercooled liquid and the extrinsic effect of Sm that act as an oxygen scavenger.

The mechanical properties were also greatly improved by the Sm additions. The Young's modulus and compressive strength increase respectively from 140 GPa and 2400 MPa for Fe₄₃Cr₁₆Mo₁₆C₁₅B₁₀ alloy to 189 GPa and 3400 MPa for Fe₄₃Cr₁₆Mo₁₆C₁₅B₈Sm₂ alloy. But no improvement in deformation behavior was observed in the Sm-added glassy alloys. Similar to the Sm-free glassy alloys, the Sm-added glassy alloys deformed inhomogeneously and fractured brittly.

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