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Glass-forming ability and soft magnetic properties of $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ bulk glassy alloys

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ABSTRACT

The glass-forming ability (GFA) and soft-magnetic properties of $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ ($x = 0$–1.5) bulk glassy alloys was investigated. The DSC curves show that the $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ bulk glassy alloys have a wide supercooled liquid region (ΔT_x) of about 60 K, and high reduced glass transition temperature (T_g/T_l) lies in the range from 0.628 to 0.649. By copper mold casting method, the bulk glassy alloys with diameters up to 4.5 mm can be formed. In addition to high GFA, the Co-based bulk glassy alloys also exhibit good soft-magnetic properties, i.e., saturation magnetization of 0.58–0.61 T, low coercive force of 0.83–1.46 A/m, and high permeability of $(1.79$–$2.2) \times 10^4$ at 1 kHz under a field of 1 A/m. These Co-based bulk glassy alloys are promising for future applications as a new structural and functional material.

1. Introduction

Beginning in 1988, systematic studies of glass formation in a variety of multi-component alloys were carried out, and bulk glassy alloys (BGAs) in Mg- and lanthanide (Ln)-based systems were firstly synthesized by copper mold casting [1,2]. From then on, a large number of BGAs have been developed and some glassy alloys have been used as practical materials [3]. For ferromagnetic BGAs, Fe–(Al, Ga)–metalloid system was synthesized for the first time in 1995 [4]. Subsequently, a variety of Fe- and Co-based ferromagnetic BGA systems have been synthesized [5–9]. Among them, Co-based BGAs are drawing increasing attention due to their superior mechanical and soft magnetic properties [10,11]. It has been reported that $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{72}B_{19.2}Si_{4.8}Nb_4$ alloy has a wide supercooled liquid region of 45 K and can be formed to cylindrical glassy alloy rods with diameter of 2.5 mm by copper mold casting method, which indicates that the alloy has relatively high glass-forming ability (GFA) [12]. However, compared with Zr- [13], Pd- [14], Y- [15], Mg- [16], La- [17] based BGAs, the critical diameter of Co-based BGAs is smaller, which limits the extensive practical applications. As Nb content and B to Si concentration ratio are effective for increasing GFA [11,18,19], we optimized the alloy compositions by modifying the B to Si concentration ratio as well as increasing Nb content. As a result, the glassy alloy rod with maximum diameter of 4.5 mm was successfully formed by copper mold casting method. This paper reports the GFA and magnetic properties of the $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ alloy system.

2. Experimental procedure

Multi-component (Co, Fe, Ni)–B–Si–Nb alloy ingots with compositions of $(Co_{0.6}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ ($x = 0$–1.5) were prepared by arc melting the mixtures of pure Co, Fe, Ni and Nb metals, and pure B and Si crystals in an argon atmosphere. The alloy compositions represent nominal percentages. Cylindrical alloy rods with different diameters of 1–5 mm were produced by copper mold casting method. Glassy alloy ribbons were produced by the melt spinning method. The structures of as-quenched samples were identified by X-ray diffraction (XRD) with Cu Kα radiation. Thermal stability associated with glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T_x = T_x - T_g$) was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus (T_l) temperatures were measured by cooling the molten alloy samples with DSC at a cooling rate of 0.067 K/s. Magnetic properties of saturation magnetization (I_s), coercive force (H_c) and effective permeability (μ_e) at 1 kHz were measured with a vibrating sample magnetometer under an applied field of 400 kA/m, a B–H loop tracer under a field of 800 A/m, and an impedance analyzer under a field of 1 A/m, respectively. All of the samples for magnetic property measurements were annealed for 300 s at the temperature of $T_g - 50$ K for improving soft-magnetic properties through structural relaxation.

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Table 1
Maximum diameter, thermal stability, and magnetic properties of cast $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0, 0.5, 0.7, 1, 1.5) glassy alloy rods.

Alloy	D_{max} (mm)	Thermal stability				Magnetic properties		
		T_g (K)	ΔT_x (K)	T_l (K)	T_g/T_l	I_s (T)	H_c (A/m)	μ_e (1 kHz)
$(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22}Si_6Nb_5$	3.5	855	59	1343	0.636	0.58	1.22	18600
$(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22.5}Si_{5.5}Nb_5$	4	853	60	1327	0.642	0.59	1.18	20300
$(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22.7}Si_{5.3}Nb_5$	4.5	853	62	1314	0.649	0.61	0.83	22000
$(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{23}Si_5Nb_5$	4	853	62	1345	0.634	0.60	1.42	18200
$(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{23.5}Si_{4.5}Nb_5$	3.5	851	63	1354	0.628	0.60	1.46	17900

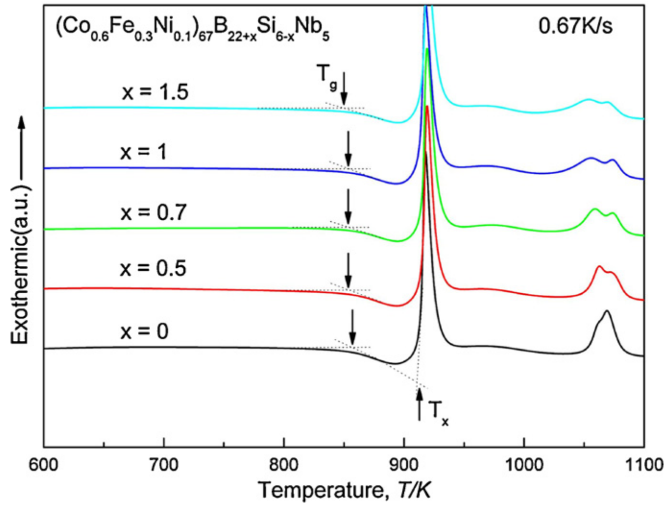

Fig. 1. DSC curves of melt-spun $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0, 0.5, 0.7, 1, and 1.5) glassy alloy ribbons.

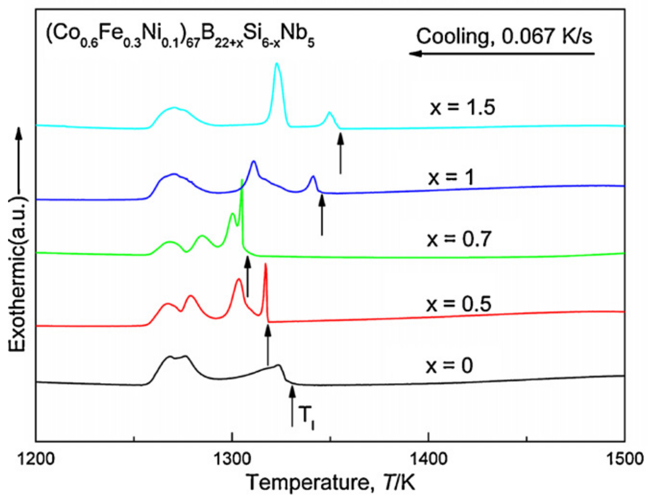

Fig. 2. DSC curves of $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0, 0.5, 0.7, 1, and 1.5) alloys.

3. Results and discussion

Fig. 1 shows the DSC curves of the $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0–1.5) glassy alloys produced by melt spinning. It is seen that all of the alloys exhibit distinct glass transition, followed by a large ΔT_x of over 60 K, and then crystallization. With decreasing Si content of x = 0 to x = 1.5, the T_g slightly decreases from 855 K to 851 K, but it is noticed that the T_x is over 910 K, which indicates that this kind of ferromagnetic bulk metallic glassy alloys could be used at high temperature. By XRD measurement, it is confirmed that the primary precipitation phase of this glassy alloy system is a $(Co, Fe)_{23}B_6$ metastable phase, which is consistent with the former results obtained from Co-based BGAs [19,20]. The primary precipitation of the $Fe_{23}C_6$-type phase having a complex fcc structure with a large lattice parameter of 1.12 nm including 96 atoms [21], the complex structure of the precipitation with 96 atoms will make crystallization difficult, leading to the high stability of the supercooled liquid against crystallization [22]. The cooling behaviors of the $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0–1.5) glassy alloys were also investigated. First, as shown in Fig. 2, with increasing x from 0 to 0.7, T_l decreases from 1343 to 1314 K, and increases to 1354 K again as x = 1.5, which means that increase of the B to Si concentration ratio to x = 0.7 is effective in decreasing T_l of the alloy system. As a result, the reduced glass transition temperatures (T_g/T_l) of these glassy alloys lie in a high value range of 0.628–0.649. Second, the alloy with x = 0, 1 and 1.5 exhibits nearly three exothermic peaks and four peaks for the alloy of x = 0.5 and 0.7. The high value of T_g/T_l reflects a low nucleating rate in the undercooled liquid, and a low critical cooling rate for glass formation. The alloy of x = 0.7 exhibits the highest T_g/T_l of 0.649, implying this alloy may exhibits high GFA, compared with the other alloys in this alloy system.

Based on the results obtained from the heating and cooling curves of DSC measurements, it is expected that this Co-based glassy alloy system exhibits high GFA. Then, we tried to form cylindrical glassy rods with different diameters up to 5 mm by cooper mold casting method. The critical diameters of glassy alloy rods were 3.5 mm, 4 mm, 4.5 mm, 4 mm and 3.5 mm for the alloys with B to Si concentration ratio of x = 0, 0.5, 0.7, 1, and 1.5, respectively. Fig. 3 shows the outer surface and morphology of the cast glassy alloy rods with diameters of 3.5 mm, 4 mm and 4.5 mm. Their as-cast surfaces all appear smooth and lustrous. No apparent volume reductions can be recognized on their surfaces, indicating that there was no drastic crystallization during the formation of these samples. Fig. 4 shows XRD patterns of those cast alloy rods. Only broad peaks without a crystalline peak can be seen for all of these rods,

Fig. 3. Outer surface and morphology of the cast glassy alloy rods with critical diameters of 3.5 mm, 4 mm and 4.5 mm.

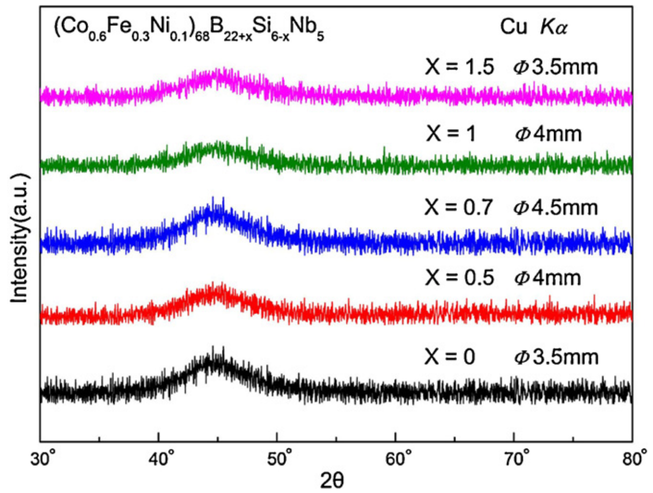

Fig. 4. XRD patterns of the cast $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0, 0.5, 0.7, 1, and 1.5) alloy rods with critical diameters of 3.5, 4, 4.5, 4, and 3.5 mm, respectively.

indicating the formation of a glassy phase in the diameter range up to 4.5 mm. The DSC examination results also denote the formation of a glassy phase. As an example, Fig. 5 shows DSC curves of the cast $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22.7}Si_{5.3}Nb_5$ alloy rods with diameters of 3 mm, 4 mm and 4.5 mm prepared by copper mold casting method, together with the data of the melt-spun glassy alloy ribbon for comparison. It is seen that the bulk alloys exhibit a distinct glass transition at 853 K, followed by a supercooled liquid region of 62 K. No appreciable difference in T_g, T_x, ΔT_x, or crystallization process was observed between the melt-spun ribbon and rod samples. The XRD and DSC measurement results indicate clearly the formation of Co-based glassy alloy rods with diameters up to 4.5 mm.

Table 1 summarizes the maximum diameter, thermal stability, and magnetic properties of the $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ (x = 0–1.5) glassy alloy rods. In addition to high GFA, this Co-based BGA system also exhibits excellent soft-magnetic properties as well, i.e., moderate saturation magnetization of 0.61 T, low coercive force of 0.83–1.46 A/m and high permeability of (1.79–2.2) × 10^4 at 1 kHz under a field of 1 A/m.

Finally, we discuss why $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ glassy alloys exhibit a high GFA and good soft magnetic properties. First, It has been pointed out that alloys should satisfy the three empirical requirements for achieving of a high GFA, i.e., (1) the multicomponent system consisting of more than three elements, (2) the different atomic size ratios above about 12% among the main constituent elements, and (3) the negative heats of mixing among their elements [3]. In this study, the atomic radii of Co, Fe, Ni, Nb, Si and B are 0.125, 0.124, 0.124, 0.143, 0.117 and 0.09 nm, respectively [23]. The atomic size ratios are 1.14 for Nb/Co, 1.15 for Nb/(Fe, Ni) and 1.22–1.59 for Nb/(Si, B). The mixing enthalpies are −25 kJ/mol for the Nb–Co pair, −30 kJ/mol for the Nb–Ni, −39 kJ/mol for the Nb–(B, Si), −9 kJ/mol for the (Co, Ni)–B, −21 kJ/mol for Co–Si, and −23 kJ/mol for Ni–Si [24]. It is clear that these Co-based glassy alloys satisfy the three empirical requirements for BMG formation resulting in the high GFA. Second, in this glassy alloy system, only B atom holds a small atomic radius. It has been pointed out that the large (L) and small (S) atoms may form a strong L–S percolating network or reinforced “backbone” in the amorphous structure [25]. Therefore, it is considered that the bonding nature of the networklike structure increases with an increase of B content, resulting in the enhancement of the stability of the undercooled liquid, which further suppresses crystallization. On the other hand, the increase of the B to Si concentration ratio effectively causes the alloy composition to approach the eutectic point as shown in Fig. 2, resulting in the increase of T_g/T_l. The good soft magnetic properties of the present alloy are presumably due to a higher degree of structural homogeneity resulting from its high GFA [26].

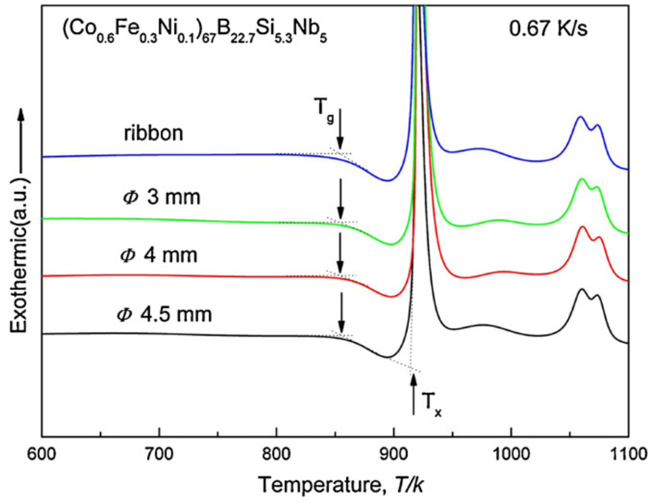

Fig. 5. DSC curves of the cast $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22.7}Si_{5.3}Nb_5$ alloy rods with diameters of 3 mm, 4 mm and 4.5 mm. The data for the melt-spun glassy alloy ribbon is also shown for comparison.

4. Conclusion

In conclusion, the bulk glassy alloy system $(Co_{0.6}Fe_{0.3}Ni_{0.1})_{67}B_{22+x}Si_{6-x}Nb_5$ with high glass-forming ability and good soft magnetic properties were synthesized. This Co-based ferromagnetic bulk glassy alloy system with excellent combination properties is promising for future applications as new structural and functional materials.

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