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Effect of Nb addition on the glass-forming ability, mechanical and soft-magnetic properties in $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ bulk glassy alloys

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ABSTRACT

The effect of Nb addition on the glass-forming ability (GFA), mechanical and soft-magnetic properties in $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ alloys system was investigated. In addition to the increase of glass-forming ability, the increase of Nb content was found to be effective for the improvement of mechanical and soft-magnetic properties. By copper mold casting, Co-based bulk glassy alloys with diameters up to 4 mm were formed in $(Co_{0.942}Fe_{0.058})_{67}Nb_5B_{22.4}Si_{5.6}$ glassy alloy. The bulk glassy alloys exhibit a superhigh fracture strength of 2980–3600 MPa and Young's modulus of 121–166 GPa. The bulk glassy alloys also exhibit excellent soft-magnetic properties, i.e., high saturation magnetization of 0.6 T, low coercive force within 0.2–0.5 A/m, high permeability of 47165 at 1 KHz and zero magnetostriction.

1. Introduction

Since the good soft-magnetic properties in Fe-metalloid amorphous alloys system were found in 1974 [1–3], the worldwide interest in soft-magnetic amorphous alloys has been sustained to a great degree by the clear benefits seen in their practical applications, However, the shape and dimension of the Fe- and Co-based amorphous magnetic alloys had been limited to thin ribbon form with thicknesses below almost 30 μm because of the necessity of a high cooling rate of almost 10^6 K/s for the formation of an amorphous phase [4]. Since the first finding of glass transition before crystallization in Fe-based amorphous alloys as well as successful synthesis of Fe–Al–Ga–P–C–B bulk glassy alloys (BGAs) [5,6], a variety of BGAs have been synthesized for the purpose of applications as soft-magnetic materials [7,8]. Now, the development of Fe- and Co-based BGAs with high glass-forming ability (GFA) has become a very hot research topic not only because of the soft-magnetic properties but also of the high fracture strength (σ_f) [9–18]. Co-based amorphous alloys with zero magnetostriction are formed with approximately 5% and 95% relative Fe and Co contents, respectively. Recently, we synthesized the Co-based glassy alloys with glass transition and supercooled liquid region in Co–Fe–Nb–B–Si systems with good soft-magnetic properties [19]. Also, we investigated the effect of B to Si concentration ration on the GFA of $(Co_{0.705}Fe_{0.045}B_{0.25-x}Si_x)_{96}Nb_4$ alloys, found that the increase in B to Si concentration ratio is effective in improving the GFA, and successfully synthesized $(Co_{0.705}Fe_{0.045}B_{0.2}Si_{0.05})_{96}Nb_4$ BGAs with diameters in the range up to 2 mm exhibiting zero saturation magnetostrction (λ_s) [20]. In this study, to further increase the GFA of the Co-based BGAs, we increased the B and Si contents and investigated the effect of Nb addition on the thermal stability of the supercooled liquid and the cooling behavior of the alloys. As a result, Co-based BGAs $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ with diameters in the range up to 4 mm were synthesized. In addition, this glassy alloy system exhibited superhigh σ_f of 2980–3600 MPa, high saturation magnetization (I_s) of 0.26–0.60 T, extremely low coercive force (H_c) of 0.2–0.5 A/m, high effective permeability (μ_e) of 2.13–4.72 × 10^4.

2. Experimental

Co-based alloy ingots with composition of $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3–6 at.%) were prepared by arc melting the mixtures of each pure Fe (99.99 mass%), Co (99.9 mass%), Nb (99.99 mass%), B (99.99 mass%), Si (99.99 mass%) in an argon atmosphere. The alloy compositions represent nominal atomic percentages. Alloy rods with diameters up to 5 mm were produced by the copper mold casting method. Glassy structure was examined by X-ray diffraction with Co 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 temperature (T_l) and melting (T_m) was measured by cooling the molten alloy samples with DSC. To reduce the influence of undercooling, DSC measurements were performed at a very low cooling rate of 0.067 K/s. Mechanical properties of Young's modulus(E), σ_f were measured by compression testing with an Instron

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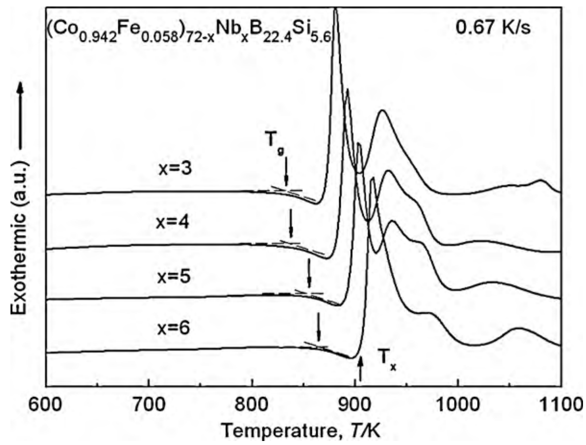

Fig. 1. DSC curves of melt-spun $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3, 4, 5, 6) glassy alloy ribbons.

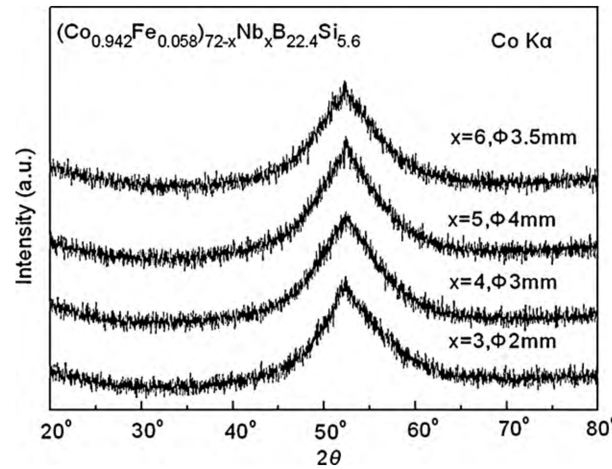

Fig. 3. XRD patterns of the cast $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3, 4, 5, 6) alloy rods with diameters of 2, 3, 4, and 3.5 mm, respectively.

testing machine. The gauge dimension was 2 mm in diameter and 4 mm in length and the strain rate was $5 \times 10^{-4}\,s^{-1}$. Magnetic properties of I_s, H_c, and 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. As the magnetic properties are affected with the sample sizes, so that to clarify the intrinsic soft-magnetic properties of this Co-based glassy alloy system, ribbon samples with the same size as mentioned above were used for measurement. 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.

3. Results and discussion

Fig. 1 shows the DSC curves of melt-spun $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3, 4, 5, 6) glassy alloy ribbons. It is seen that all of the alloys exhibit distinct glass transition, followed by a supercooled liquid region, and then crystallization. Although T_g and T_x increase gradually from 829 to 871 K and from 873 to 917 K, respectively, ΔT_x maintains a nearly constant value of about 46 K. In addition, with the increase of Nb content, the second exothermic peak gradually decreases. When the Nb contents increase to 6%, crystallization of the Co-based glassy alloys occurs through a mostly single exothermic reaction. We have also examined the composition dependence of the reduced glass transition temperature (T_g/T_l). As shown in Fig. 2, the T_l decreases from 1405 to 1326 K with an increase of Nb content from 3% to 5%, resulting in the increase of T_g/T_l from 0.589 to 0.642. This result indicates that higher glass-forming ability may be obtained by increasing Nb contents. However, when Nb contents increase to 6%, as can be seen in Fig. 2, the T_l increases to 1363, and the T_g/T_l decreases to 0.632 accordingly, glass-forming ability also begins to decrease with it.

Based on the results obtained from DSC measurements, it is considered that this Co-based glassy alloy system may exhibit high GFA. Then, we tried to form cylindrical glassy rods with different diameters up to 5 mm. The glassy alloy rods were produced at all alloy compositions in this system. The critical diameter for the formation of a glassy single phase was 2 mm at x = 3, 3 mm at x = 4, 4 mm at x = 5, and 3.5 mm at x = 6. Fig. 3 shows XRD patterns of those cast alloy rods. Only broad peaks without a crystalline peak can be seen for all of these bulk samples, indicating the formation of a glassy phase in the diameter range up to 4 mm. The DSC examination results also denote the formation of a glassy phase. As one of the DSC examination results, Fig. 4 shows DSC curves of the $(Co_{0.942}Fe_{0.058})_{67}Nb_5B_{22.4}Si_{5.6}$ glassy alloy rods with diameters of 2, 4 mm, respectively, together with the data for the melt-spun glassy alloy ribbon. It is seen that the bulk alloys exhibit a distinct glass transition at 851 K, followed by a supercooled liquid region of 46 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 the Co-based glassy alloy rods with diameters in the range up to 4 mm.

Table 1 summarizes the maximum diameter, thermal stability, and mechanical and magnetic properties of the $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3, 4, 5, and 6) glassy alloy

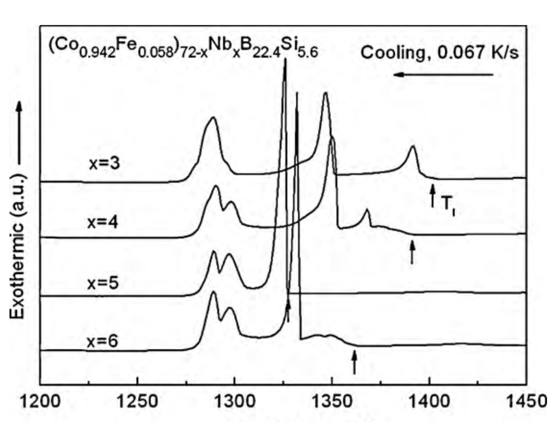

Fig. 2. DSC curves of $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3, 4, 5, 6) alloys.

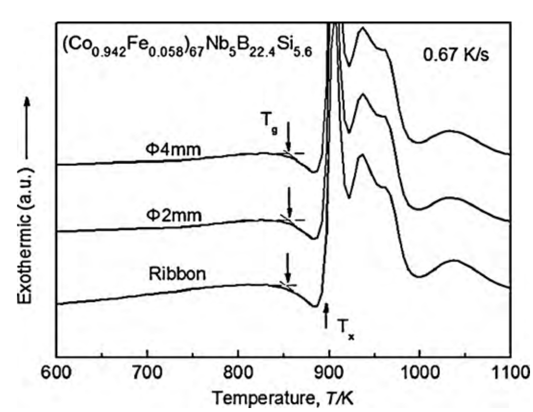

Fig. 4. DSC curves of the $(Co_{0.942}Fe_{0.058})_{67}Nb_5B_{22.4}Si_{5.6}$ glassy alloy rods with diameters of 2, 4 mm, together with the data for the melt-spun glassy alloy ribbon for comparison.

Table 1
Maximum diameter, thermal stability, mechanical and magnetic properties of cast $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ (x = 3, 4, 5, and 6) glassy alloy rods.

Alloy (at.%)	ϕ (mm)	T_g (K)	ΔT_x (K)	ΔT_m (K)	T_l (K)	T_g/T_l	E (GPa)	σ_f (MPa)	I_s (T)	H_c (A/m)	μ_c (1 KHz)
$(CO_{0.942}Fe_{0.058})_{69}Nb_3B_{22.4}Si_{5.6}$	2	829	44	1297	1405	0.589	121	2980	0.60	0.4	21335
$(Co_{0.942}Fe_{0.058})_{68}Nb_4B_{22.4}Si_{5.6}$	3	838	45	1300	1393	0.602	141	3140	0.52	0.3	31342
$(Co_{0.942}Fe_{0.058})_{67}Nb_5B_{22.4}Si_{5.6}$	4	851	46	1305	1326	0.642	166	3600	0.43	0.2	47165
$(Co_{0.942}Fe_{0.058})_{66}Nb_6B_{22.4}Si_{5.6}$	3.5	862	46	1301	1363	0.632	143	1360	0.26	0.5	16375

rods. The mechanical properties of E, σ_f are in the range from 121 to 166 GPa, and 2980 to 3600 MPa, respectively. Except for superhigh σ_f, this BGA system also exhibits excellent soft-magnetic properties, i.e., high I_s of 0.26–0.60 T, extremely low H_c of 0.2–0.5 A/m, high μ_e of $(1.64–4.72) \times 10^4$. The λ_s was also investigated, but it exhibited almost no distinguishable change and a nearly zero value. It is therefore concluded that this near-zero magnetostriction $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ ferromagnetic BGA system simultaneously possesses high GFA, high I_s, low H_c, and high μ_e.

Here, we discuss the reason why the Co-based glassy alloys simultaneously possess high GFA, superhigh σ_f, and excellent soft-magnetic properties. First, the essential structural feature in $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ ferromagnetic BGA system is the distorted dense random network of trigonal prisms connected with each other through glue atoms of Nb, leading to the high stability of supercooled liquid against crystallization. Second, the primary precipitation of the $Fe_{23}C_6$-type phase has a complex face-centered-cubic (fcc) structure with a large lattice parameter of 1.12 nm including 96 atoms from the networklike structure [21], which requires long-range atomic rearrangements of constituent elements, also leading to the high stability of the supercooled liquid against crystallization. Lastly, the enthalpy of mixing is −25 kJ/mol for the Nb–Co pair, −16 kJ/mol for the Nb–Fe pair, −39 kJ/mol for the Nb–B pair, −39 kJ/mol for the Nb–Si pair, −9 kJ/mol for the Co–B pair, −21 kJ/mol for the Co–Si pair, −11 kJ/mol for the Fe–B pair, and −18 kJ/mol for the Fe–Si pair [22]. It can be seen that there are larger mixing enthalpies with negative values in the atomic pairs between Nb and Co or Fe, respectively, and the mixing enthalpies with negative values of the B–Nb and Si–Nb atomic pairs are as large as 39 kJ/mol. Therefore, it can be considered that the high glass-forming ability and superhigh fracture strength of the present bulk glassy alloy system result from the addition of Nb, as well as the increase of B and Si contents. In addition, as the Nb content increases, the crystallization of the Co-based glassy alloys occurs through a mostly single exothermic reaction accompanying the increase of T_g/T_l. It can be also seen in Fig. 2 that the temperature interval between exothermic peaks decreases with increasing Nb content from 3% to 5%, implying that the composition of the alloy with Nb content 5% is close to that of eutectic alloy. These synergistic effects enable us to prepare bulk glassy alloy rods with diameters up to 4 mm. However, the temperature interval increases again when the Nb content attain to 6%, which implies that this composition of the alloy deviates from that of eutectic alloy. As a result, the GFA of the Co-based glassy alloy with Nb content 6% declines and the critical diameters reduces from 4 mm when Nb content 5% to 3.5 mm. On the other hand, the excellent soft-magnetic properties of $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ glassy alloys can be attributed to a high degree of amorphicity and structural homogeneity proceeding from the high GFA.

4. Summary

In conclusion, a BGA system $(Co_{0.942}Fe_{0.058})_{72-x}Nb_xB_{22.4}Si_{5.6}$ with high GFA, superhigh strength, and excellent soft-magnetic properties was synthesized. This Co-based ferromagnetic glassy alloy system is promising for the future applications as functional materials.

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