Thermal Stability and Soft Magnetic Properties of Co-Fe-M-B (M=Nb, Zr) Amorphous Alloys with Large Supercooled Liquid Region

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A ferromagnetic amorphous phase with a large supercooled liquid region prior to crystallization and good soft magnetic properties was formed in melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) alloys. The glass transition temperature (T_g) increases monotonously with increasing Zr content. The crystallization temperature (T_x) also increases by the dissolution of Zr up to 2% and then decreases with further increasing Zr content. The increases is more significant for T_x , resulting in a maximum $\Delta T_x (= T_x - T_g)$ of 98 K at 2% Zr. The Co-based amorphous alloys exhibit good soft magnetic properties, i.e., saturation magnetization of 0.41 T–0.42 T, low saturated magnetostriction of 2.4×10^{-6} – 2.9×10^{-6} , low coercivity of 1.2–2.0 A/m, and high permeability of 29000–33000 at 1 kHz over the whole Zr content range. In addition, the cylindrical $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ glassy alloy with a diameter of 1.0 mm was prepared by the copper mold casting method. With increasing the cylindrical diameter up to 1.5 mm, the structure changes to coexistent amorphous, $\text{Co}_{21}\text{Nb}_2\text{B}_6$, Co_3ZrB_2 and Co_2B phases. It is noticed that the maximum thickness for glass formation is about 6 times larger than that for Co-based amorphous alloys reported up to date. The success of forming Co-based bulk amorphous alloys with high stability of supercooled liquid and good soft magnetic properties is encouraging further development of bulk amorphous soft magnetic materials.

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1. Introduction

Since the synthesis of a ferromagnetic Fe-P-C amorphous alloy in 1967, it has been found that some ferromagnetic Fe- and Co-based amorphous alloys exhibit good soft magnetic properties.^{1,2)} However, the glass-forming ability of the Fe- and Co-based amorphous alloys is not always high and hence their formation has required higher cooling rates than about 10^5 K/s. Therefore the resulting sample thickness by the ordinary melt spinning method has been limited to be less than about 50 μm for Fe-Si-B and Co-Si-B systems.^{3,4)}

Recently, great effort has been devoted to the production of bulk amorphous alloys. As a result of great effort, Mg-,⁵⁾ Lanthanide (Ln)-,⁶⁾ Zr-,^{7,8)} Pd-Cu-⁹⁾ based amorphous alloys with a large supercooled liquid region above 60 K prior to crystallization have been found for the last decade. Among these amorphous alloys, the largest critical sample thickness reaches about 72 mm and the critical cooling rate is as low as 0.1 K/s.¹⁰⁾ The search for an amorphous alloy with large supercooled liquid region prior to crystallization is important because the extension of the supercooled liquid region implies high resistance against crystallization. The use of such an alloy component enables us to produce a bulk amorphous alloy by the casting process with low cooling rates.¹¹⁾

More recently, ferromagnetic Fe-based amorphous alloys with a large supercooled liquid region above 60 K before crystallization and good soft magnetic properties have been synthesized in Fe-(Al, Ga)-(P, C, B, Si, Ge)^{12–14)} and Fe-(Co, Ni)-(Zr, Nb, Ta, Mo, W)-B systems.^{15–17)} The critical thickness of Fe-based amorphous alloys reaches 3 mm for Fe-(Al, Ga)-(P, C, B, Si, Ge)¹⁴⁾ and 5 mm for Fe-(Co, Ni)-(Zr, Nb, Ta, Mo, W)-B¹⁷⁾ system by the copper mold casting method. Subsequently, ferromagnetic Co-based amorphous alloys with a large supercooled liquid region above 50 K were found in Co-Al-Ga-(Fe, Cr, V)-P-B-C-Si¹⁸⁾ and Co-

Fe-(Zr, Nb, Ta, W)-B with 20 at% B systems.^{19,20)} However, little is known about the production of Co-based bulk amorphous alloys and their magnetic properties. This paper is intended to present the thermal stability and magnetic properties of Co-Fe-M-B (M=Nb, Zr) amorphous alloys containing 30 at% B in melt-spun ribbon and cast cylindrical forms.

2. Experimental Procedure

Multicomponent $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) alloys ingots were prepared by arc melting pure Co, Fe, Nb and Zr metals and pure crystalline B in an argon atmosphere. From the master alloy ingots, ribbons with a cross section of about $1.0 \times 0.02 \text{ mm}^2$ and cylinders with diameters up to 1.5 mm and a length of 40 mm were prepared by single-roller melt-spinning and copper-mold casting methods, respectively, in an argon atmosphere. The amorphous structure was examined by X-ray-diffractometry (XRD) with Cu-K α radiation, optical microscopy (OM) and transmission electron microspectroscopy (TEM). The thermal stability associated with glass transition and crystallization was examined at a heating rate of 0.67 K/s by differential scanning calorimetry. Magnetization at room temperature was measured in a maximum applied field of 1500 kA/m with a vibrating sample magnetometer (VSM). Coercive force was measured with a I-H loop tracer. Permeability was evaluated at 1 kHz with an impedance analyzer. Saturated magnetostriction was measured under a field of 240 kA/m by a three-terminal capacitance method.

3. Results

3.1 Thermal stability and crystallization behavior of melt-spun Co-Fe-Nb-Zr-B amorphous alloys

Figure 1 shows X-ray diffraction patterns of the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) alloys

Fig. 1 X-ray diffraction patterns of $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) melt-spun ribbons.

Fig. 2 DSC curves of $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) melt-spun amorphous ribbons.

at room temperature. Broad diffraction peaks are seen at diffraction angles (2θ) of 44 and 78 degrees. No diffraction peak corresponding to a crystalline phase is seen for all the alloys. The X-ray diffraction data clearly indicate that these alloys are composed of an amorphous phase without any crystallinity. Figure 2 shows the DSC curves of the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) al-

Fig. 3 Change in the glass transition temperature (T_g), crystallization temperature (T_x) and supercooled liquid region ($\Delta T_x = T_x - T_g$) as a function of Zr content for the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) amorphous alloys.

loys. The distinct glass transition, followed by a large supercooled liquid region is recognized in the temperature range prior to crystallization. Two exothermic peaks correspond to the crystallization have been observed for the 0% Zr alloy. It was reported that the double crystallization process (amorphous $\rightarrow$ amorphous + $\text{Co}_{21}\text{Nb}_2\text{B}_6 \rightarrow \text{Co}_{21}\text{Nb}_2\text{B}_6 + \text{Co}_2\text{B}$) has been observed for Co-Fe-Nb-B amorphous alloy.²¹⁾ Further increasing in Zr element, crystallization behavior occurred to single stage. Based on the DSC data, the glass transition temperature (T_g), the crystallization temperature (T_x), and the temperature interval of supercooled liquid region ($\Delta T_x = T_x - T_g$) were plotted as a function of Zr content in Fig. 3. The T_g is 895 K for the 0% Zr alloy, increases by the dissolution of Zr, and shows a maximum value of 917 K for the 8% Zr alloy. The T_x also increases by the dissolution of Zr up to 2% and then decreases with further increasing Zr content. The increase is more significant for T_x than for T_g , leading to an increase in ΔT_x from 81 K for the 0% Zr alloy to 98 K for the 2% Zr alloy. The DSC data indicate that the substitution of Nb by 2% Zr in the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_8\text{B}_{30}$ alloy is effective for the stabilization of the supercooled liquid.

In order to clarify the reason for the change in the crystallization behavior, the X-ray diffraction patterns of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) alloys heated for 1.8 ks at the temperatures of $T_x(T_{x1}) + 50$ K are shown in Fig. 4. The X-ray diffraction pattern was identified as $\text{Co}_{21}\text{Nb}_2\text{B}_6 + \text{Co}_2\text{B}$ for the Zr 0% alloy and $\text{Co}_3\text{ZrB}_2 + \text{Co}_{21}\text{Nb}_2\text{B}_6 + \text{Co}_2\text{B}$ phases for the 2% Zr and the 4% Zr alloys. No appropriate diffraction peaks of Fe-containing compounds without Co are observed for the 0, 2 and 4% Zr alloys. It is therefore considered that the Fe element is dissolved into the Co sites in $\text{Co}_{21}\text{Nb}_2\text{B}_6$, Co_2B and Co_3ZrB_2 phases for the 0 to 4% Zr alloys. With further increasing Zr content, αFe and FeB phases precipitated in the 6% Zr and the

Fig. 4 X-ray diffraction patterns of the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) amorphous alloys annealed at $T_x(T_{x1}) + 50$ K for 1.8 ks.

8% Zr alloys, together with $\text{Co}_{21}\text{Nb}_2\text{B}_6$, Co_3ZrB_2 and Co_2B phases.

3.2 Magnetic properties of melt-spun Co-Fe-Nb-Zr-B amorphous alloys

Figure 5 shows the hysteresis I-H loops of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) amorphous alloys subjected to annealing for 600 s at the temperature of $T_g - 50$ K. No distinct compositional dependence in I_s and H_c is seen. That is, the I_s lies from 0.41 T at 0% Zr to 0.42 T at 8% Zr and the H_c is in the range of 1.2 to 2.0 A/m. Figure 6 shows the changes in the saturated magnetostriction (λ_s) and effective permeability (μ_e) at 1 kHz with the Zr content for the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ amorphous alloys, together with the data of I_s and H_c . The λ_s is in range of 2.4×10^{-6} – 2.9×10^{-6} over the whole Zr content range. The small λ_s values are nearly the same as those for the Co-Fe-Zr-M- 20% B (M=Nb, Ta, W) amorphous alloys with ΔT_x above 40 K.¹⁹⁾ The maximum μ_e has high values of 33000 at 8% Zr to 32000 at 2% Zr. Table 1 summarizes the thermal stability and magnetic properties of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_8\text{B}_{30}$ and $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ amorphous alloys, together with the data of the other glassy alloys including commercial Co-Fe-Ni-Mo-Si-B amorphous alloy.²²⁾ The features of the present Co-Fe-Nb-Zr- 30% B amorphous alloys are summarized as follows: (1) high thermal stability as is evident from the higher T_x and the larger ΔT_x exceeding 80 K; (2) lower H_c as compared with Co-Al-(Fe, Cr, V)-Ga-P-B-C-Si and Co-Fe-Zr-Ta- 20% B amorphous alloys; (3) higher μ_e exceeding 30000 at 1 kHz as compared with the Co-Fe-Zr-Ta- 20% B and METGLAS 2705M (Co-Fe-Mo-B-Si amorphous alloy);

Fig. 5 Hysteresis I-H loops of the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) amorphous alloys subjected to annealing for 600 s below 50 K at T_g .

Fig. 6 Changes in the saturation magnetization (I_s), saturated magnetostriction (λ_s), coercive force (H_c) and permeability at 1 kHz (μ_e) as a function of Zr content for the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_x\text{B}_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) amorphous alloys.

(4) low λ_s comparable to the Co-Fe-Zr-Ta- 20% B amorphous alloy.

It is thus characterized that the present alloys have higher

Table 1 Thermal stability and magnetic properties of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{B}_{30}$ and $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ amorphous alloys. The data of the other Co-based amorphous alloys containing 20 at% B and commercial Co-based amorphous alloys are also shown for comparison.

	T_g (K)	T_x (K)	ΔT_x (K)	I_s (T)	H_c (Am^{-1})	λ_s (10^{-6})	μ_e (at 1 kHz)
$\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$	717	768	51	0.27	4.5	—	5800
$\text{Co}_{67}\text{V}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$	722	769	47	0.29	5.8	—	4600
$\text{Co}_{56}\text{Fe}_{16}\text{Zr}_8\text{B}_{20}$	840	879	39	0.77	8.0	8.0	17100
$\text{Co}_{63}\text{Fe}_7\text{Zr}_6\text{Ta}_4\text{B}_{20}$	858	895	37	0.54	1.7	3.4	23000
$\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{B}_{30}$	895	976	81	0.41	2.0	2.4	29300
$\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$	903	1001	98	0.41	1.2	2.6	32000
Co-Fe-Ni-Mo-B-Si METGLAS 2705M	—	793	—	0.7	0.4	<1	30000

thermal stability, higher μ_e and lower λ_s as compared with the Co-based amorphous alloys with a large supercooled liquid region reported up to date.

3.3 Thermal stability and magnetic properties of Co-based bulk amorphous alloys

Figure 7 shows the outer morphology and surface appearance of the cast $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 and 1.5 mm. These samples have a smooth surface and metallic luster. To examine a cross sectional morphology and solidification structure of the cast cylinders, optical micrographs of both samples are shown in Figs. 8(a) to (d). As shown in Figs. 8(a) and (b), no appreciable contrast revealing the precipitation of a crystalline phases is observed in the cross sectional structure of the 1.0 mm sample. The featureless contrast indicates that the cast cylinder consists

Fig. 7 Shape and outer morphology of the cast $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 mm and 1.5 mm.

(a) ϕ 1.0 mm

(c) ϕ 1.5 mm

(b) ϕ 1.0 mm

(d) ϕ 1.5 mm

Fig. 8 Transverse cross sectional structures of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 mm and 1.5 mm. (a) central region, ϕ 1.0 mm, (b) new surface region, ϕ 1.0 mm, (c) central region, ϕ 1.5 mm, (d) new surface region, ϕ 1.5 mm.

of an amorphous phase. In the 1.5 mm sample, the featureless contrast due to the formation of an amorphous phase is observed in the outer region within 200 μm from the outer surface. However columnar precipitates with a particle size of 5–10 μm are observed in the central cross section having a lower cooling rate in comparison with the outer surface region, as shown in Figs. 8(c) and (d). The formation of amorphous phase is also confirmed by means of X-ray diffraction. As shown in Fig. 9, no diffraction peak corresponding to a crystalline phase is seen for the 1 mm sample. On the other hand, as indexed in Fig. 9, the structure consists of coexistent amorphous, $\text{Co}_{21}\text{Nb}_2\text{B}_6$, Co_3ZrB_2 and Co_2B phases for the ϕ 1.5 mm sample.

Figure 10 shows the DSC curves of the cast amorphous $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 and 1.5 mm. The data of the melt-spun amorphous ribbon with a thickness of 20 μm are also shown for comparison. As shown Fig. 10, the T_g , T_x and heat of crystallization (ΔH_x) are 903 K, 1001 K and 7.39 kJ/mol respectively, for the ϕ 1.0 mm sample, which approximately agree with those for melt-spun amorphous ribbon. However, the T_g and T_x of the ϕ 1.5 mm sample are 903 K and 995 K, respectively, indicating a slight decrease in T_x . Moreover, the ΔH_x of the ϕ 1.5 mm sample is 2.46 kJ/mol which is about one third of that of melt-spun amorphous ribbon. The peak temperature and single-stage crystallization mode of the ϕ 1.5 mm sample agree with those for the other samples. The slight decrease in T_x seems to result from an easy growth reaction of the crystalline phase at the interphase between the pre-existing crystalline and amorphous phases. Substantially, it is said that the cast sample has a large supercooled liquid region of 98 K, which is the same as that for the melt-spun ribbon amorphous alloy.

The hysteresis I-H loops of the bulk amorphous $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 and 1.5 mm are shown in Fig. 11, where the data of the 1.0 mm

sample crystallized by annealing at 1051 K for 1.8 ks and the as-spun amorphous ribbon are also presented for comparison. The I-H loop was measured by VSM because the conventional I-H loop tracer could not be used for the cylindrical bulk amorphous alloy. The cast sample has a saturation magnetization (I_s) of 0.41 T and a coercivity (H_c) of 78 A/m. One can't see any distinct difference in the hysteresis I-H loops

Fig. 10 DSC curves of cast $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 mm and 1.5 mm. The data of the melt-spun amorphous ribbon are also shown for comparison.

Fig. 9 X-ray diffraction patterns taken from the transverse cross section of cast $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 mm and 1.5 mm.

Fig. 11 Hysteresis I-H loops of cast $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ cylinders with diameters of 1.0 and 1.5 mm. The cast cylinder sample of 1.0 mm in diameters annealed for 1.8 ks at 1051 K and melt-spun amorphous ribbon are also shown for comparison.

between the $\phi 1.0$ mm sample and the melt-spun ribbon. The I_s and H_c of the crystallized $\phi 1.0$ mm sample are 0.66 T and 3.2 kA/m, respectively, which are higher than those of the as-cast amorphous sample, because of the precipitation of the ferromagnetic crystalline phases. The coercivity of the crystallized sample is about 40 times as large as that of the as-cast bulk amorphous sample. With increasing sample diameter up to 1.5 mm, I_s and H_c increase to 0.44 T and 170 A/m, respectively. This change is also due to the precipitation of the ferromagnetic phase.

From these results, it is concluded that the critical sample thickness for glass formation by copper mold casting lies in the range between 1.0 mm and 1.5 mm for the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ alloy. It is noticed that the critical sample thickness is about 6 times larger than that for Co-based amorphous alloys reported up to date.⁴⁾ The $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ amorphous alloy has the combination of high-glass forming ability and good soft magnetic properties.

4. Discussion

As is described above, the substitution of Nb by 2% Zr cause the significant extension of the supercooled liquid region before crystallization by an increase in T_x exceeding the degree of the increase in T_g (see Fig. 2). The largest ΔT_x of 98 K at 2% Zr is larger by about 40 K than those for the Co–Al–(Fe, Cr, V)–Ga–P–B–C–Si and the Co–Fe–(Zr, Nb, Ta, W)–20% B glassy alloys. The significant increase of ΔT_x allows us to expect the formation of bulk amorphous alloys with diameters of several millimeters by the copper mold casting process. Consequently, it is of interest to discuss the reason for the significant extension of supercooled liquid region prior to crystallization. It has recently been pointed out that all alloys having the high stability of supercooled liquid against crystallization satisfy the three empirical rules for achievement of large glass forming ability,¹¹⁾ i.e., (1) the multicomponent system consisting of more than three elements, (2) the different atomic size ratios more than 12% among the main constituent elements, and (3) the negative heats mixing among their elements. The atomic radius changes in the order of $\text{Zr} > \text{Nb} \gg \text{Co} > \text{Fe} \gg \text{B}$ ²³⁾ and the predicted heat of mixing has negative values of 37–60 kJ/mol for equiatomic Co–Zr, Fe–Zr, 23–37 kJ/mol for Co–Nb, Fe–Nb pairs, 34–38 kJ/mol for Co–B, Fe–B pairs, and 79–102 kJ/mol for Zr–B, Nb–B pairs.²⁴⁾ The Co–Fe–Nb–Zr–B system also satisfies the three empirical rules. Moreover, it is noticed that the crystallized phases of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ and the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_2\text{Zr}_6\text{B}_{30}$ alloys shown in Fig. 4 were including the Co–Zr–B and the Co–Nb–B ternary compounds, respectively. This result indicates a small amount of substitution by Nb or Zr in the $\text{Co}_{40}\text{Fe}_{22}\text{M}_8\text{B}_{30}$ (M=Nb, Zr) amorphous alloys affects the stabilization of the supercooled liquid state. As a result, the significant increase in the supercooled liquid region was observed for the 2% Zr-containing alloy. With further increasing Zr content, the supercooled liquid region decreases from 98 K to 42 K. The precipitation of αFe and FeB phases implies that the crystallization becomes easy for the 6 and 8% Zr alloys, because their crystallization temperatures and ΔT_x decrease rapidly.

Finally we discuss the glass forming ability of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ alloy. A number of glassy alloys with a supercooled liquid region beyond 90 K have maximum thickness diameters of about 8–10 mm.¹⁰⁾ Considering the empirical relation of ΔT_x , a more large scale bulk amorphous may be obtained for this alloy. There is clear tendency for glass forming ability which enhances with increasing the reduced glass transition temperature (T_g/T_m).¹¹⁾ Here, T_m represents the melting temperature. The T_m of the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ alloy is 1585 K, and the resulting T_g/T_m is estimated as 0.57. The T_g/T_m value is slightly lower than those (0.60 to 0.72) for the other glassy alloy.¹¹⁾ The T_m is also higher than those for the other glassy alloys. In the use of the copper mold casting method, it seems that the inconsistency for the maximum sample thickness with the empirical relation is due to the high T_m value as compared with the Mg-, Ln-, Zr-, and Pd–Cu-based amorphous alloys.

5. Summary

With the aim of developing a new ferromagnetic Co-based amorphous alloy, we investigated the compositional dependence of T_g , T_x , ΔT_x , crystallization behavior and soft magnetic properties for the $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_xB_{30}$ ($x = 0, 2, 4, 6$, and 8 at%) amorphous alloys. Using a $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ alloy with ΔT_x of 98 K, we examined the formation of bulk glassy alloy in a cylindrical form by the copper mold casting method and the thermal stability and magnetic properties of the resulting bulk glassy alloys. The results obtained are summarized as follows;

(1) The glass transition and subsequent supercooled liquid region were observed in the temperature range before crystallization for all the alloys. The maximum ΔT_x was 98 K for the 2% Zr alloy.

(2) The crystallization phases are Co_2B , $\text{Co}_{21}\text{Nb}_2\text{B}_6$ and/or Co_3ZrB_2 phases for the alloys containing less than 4% Zr, and αFe , FeB, Co_2B , $\text{Co}_{21}\text{Nb}_2\text{B}_6$ and/or Co_3ZrB_2 phases for the alloys containing more than 6% Zr.

(3) The I_s , λ_s , H_c , and μ_e at 1 kHz are 0.41 T–0.42 T, 2.4×10^{-6} – 2.9×10^{-6} , 1.2–2.0 A/m, and 29000–33000 over the whole Zr content range for the melt-spun $\text{Co}_{40}\text{Fe}_{22}\text{Nb}_{8-x}\text{Zr}_xB_{30}$ amorphous alloys.

(4) The cast bulk glassy alloys with a length of 40 mm were produced in the diameter range up to 1.0 mm. The T_g , T_x , and ΔH_x of the $\phi 1.0$ mm glassy alloy are 903 K, 1000 K and 7.39 kJ/mol, respectively, which are in agreement with those for melt-spun amorphous ribbon. The critical diameter is about 6 times larger than that for Co-based amorphous alloys reported up to date.

(5) The bulk glassy alloy of $\phi 1$ mm in diameter has good soft magnetic properties of 0.41 T for I_s and 78 A/m for H_c . The magnetic properties are nearly the same as those for the melt-spun amorphous ribbon. The success of forming Co-based bulk amorphous alloys with high stability of supercooled liquid and good soft magnetic properties promotes further development of bulk amorphous soft magnetic materials.

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