Preparation and Magnetic Properties of Co-based Bulk Glassy Alloys

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This paper deals with the formation and soft magnetic properties of Co(Fe)-M-B (M = transition Metals) glassy alloys in thin sheet and bulk ring forms prepared by single role melt spinning and copper mold casting methods. This multicomponent system was found to exhibit a distinct glass transition and a wide supercooled liquid region (ΔT_x) exceeding 70 K before crystallization. The high thermal stability of the supercooled liquid has enabled us to produce the bulk glassy alloys. The Co-Fe-Ta-B alloy samples with a ring form of $\phi 7 \text{ mm} \times \phi 3 \text{ mm} \times t 1 \text{ mm}$ consist of a single glassy phase. These bulk amorphous samples exhibit excellent soft magnetic properties, which are nearly the same as those of the corresponding melt-spun glassy thin sheets: the coercivity (H_c) and saturation magnetic flux density (B_s) are 0.25 A/m and 0.49 T, respectively. These good soft magnetic properties suggest structural homogeneity resulting from its high glass-forming ability. The excellent soft magnetic properties are useful for industrial application.

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1. Introduction

It is known that Co-based amorphous alloys are core and sensor materials for inductive applications. Since the shape of amorphous alloys has been limited to sheet, wire, and film because of their low glass-forming ability, their applicable fields have been restricted for the last two decades. For instance, it is difficult to laminate such thin amorphous sheets to make transformers and/or inductors. Recently, a number of bulk glassy alloys have been formed in multicomponent Mg-,¹⁾ Ln-,²⁾ Zr-³⁾ and Zr-Ti-based⁴⁾ (Ln = lanthanoid metal) alloy systems, which have a wide supercooled liquid region (ΔT_x) more than 60 K below crystallization temperature. The appearance of the wide ΔT_x implies a high resistance against crystallization. These bulk glassy alloys satisfy the following empirical rules for achievement of high glass-forming ability; *i.e.*, multicomponents with significantly different atomic size ratios higher than approximately 12% and negative heats of mixing.⁵⁾ Based on these rules, we have searched for new Fe and Co-based glassy alloys revealing a glass transition phenomenon and a wide supercooled liquid region before crystallization. Indeed we have found that glassy alloys with wide ΔT_x exceeding 60 K are formed in multicomponent Fe-Al-Ga-P-C-B-(Si),⁶⁾ Fe(Co,Ni)-M-B⁷⁾ and Co(Fe)-M-B⁸⁾ (M = transition metals) systems. These Fe and Co-based glassy alloys also exhibit good soft magnetic properties: an excellent soft magnetic bulk glassy alloy with a ring shape of $\phi 10 \text{ mm} \times \phi 6 \text{ mm} \times t 1 \text{ mm}$ was developed in Fe-Al-Ga-P-C-B-(Si)⁹⁾ system. However, no bulk glassy alloys with good soft magnetic properties had been obtained in Co-based glassy alloys. We have further investigated the relation between glass-forming ability and soft magnetic properties. This paper is intended to present the structure, thermal stability of supercooled liquid region and soft magnetic properties for Co(Fe)-Ta-B glassy alloys in thin sheet and bulk ring forms prepared by single role melt spinning and copper mold casting methods.

2. Experimental Procedure

Multicomponent Co-Fe-Ta-B alloy master ingots were prepared by arc melting mixtures of pure Co, Fe and M metals and pure B crystal in an argon atmosphere. The alloy compositions represent the nominal atomic percentage of the mixture. Rapidly solidified ribbons with a cross section of $0.02 \times 1 \text{ mm}^2$ were prepared by melt-spinning method. Bulk ring shape samples with an outer diameter of 7 mm, an inner diameter of 3 mm and a thickness of 1 mm were prepared by the copper mold casting method.

The glassy structure was examined by X-ray diffraction, optical and scanning electron microscopy (OM and SEM). Thermal stability associated with glass transition temperature (T_g), crystallization temperature (T_x) and $\Delta T_x (= T_x - T_g)$ was examined at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). The melting temperature (T_m) was measured by cooling the molten alloy samples at a cooling rate of 0.08 K/s by DSC. Magnetic properties, saturation magnetic flux density (B_s) under an applied field of 1500 A/m, coercive force (H_c) and maximum permeability ($\mu_{\max}$), were measured with a D.C. B-H curve tracer. The effective permeability (μ_e) was measured with an impedance analyzer at the frequency of 1 kHz. The saturated magnetostriction (λ_s) was also measured by a capacitance method. These magnetic properties were measured at room temperature.

3. Results and Discussion

Since Co-based amorphous alloys have the non-magnetostorictive and the excellent soft magnetic properties, they are important for application to magnetic induction. Through our systematic works on Co-M-B (M = transition metals) alloys, we have found such a Co-based glassy alloy in the vicinity of $\text{Co}_{63}\text{Ta}_{5.5}\text{B}_{31.5}$ ternary eutectic composition.¹⁰⁾ However, its magnetization is rather small because of high B content exceeding 30%, whereas the ΔT_x is about 30 K. Therefore, we have examined the effect of replacement of Co by Fe in the $\text{Co}_{63}\text{Ta}_{5.5}\text{B}_{31.5}$.

It has been confirmed in the X-ray diffraction patterns that

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Fig. 1 DSC curves of the glassy $\text{Co}_{63-X}\text{Fe}_X\text{Ta}_{5.5}\text{B}_{31.5}$ alloys.

the melt-spun $\text{Co}_{63-X}\text{Fe}_X\text{Ta}_{5.5}\text{B}_{31.5}$ alloy ribbons are composed of a glassy phase without any crystallinity over the whole composition range up to 63 at%Fe.

Figure 1 shows the DSC curves of the $\text{Co}_{63-X}\text{Fe}_X\text{Ta}_{5.5}\text{B}_{31.5}$ glassy alloys. All the glassy alloys exhibit the glass transition and supercooled liquid region. The ΔT_x increases with increasing Fe content, reaches a maximum value of 72 K and then decreases gradually with further increasing Fe content. It is noticed that a wide ΔT_x exceeding 70 K is obtained at 20 at%Fe.

Figure 2 shows B_s , H_c , μ_e at 1 kHz and λ_s as a function of Fe content for the $\text{Co}_{63-X}\text{Fe}_X\text{Ta}_{5.5}\text{B}_{31.5}$ glassy alloys in as-quenched and annealed states for 300 s at 870 K. The magnetic properties of as-quenched and annealed state samples change in a same tendency with Fe content. It is seen that the replacement by more than 10 at% Fe causes gradual increases in B_s and λ_s and a significant decrease in μ_e . On the other hand, the H_c slowly decreases in the range up to 20 at%Fe and then gradually increases in the higher Fe content range. As a result, the H_c and μ_e are significantly improved to excellent values of under 1 A/m and over 40000, respectively. In particular, the $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ alloy with the widest ΔT_x has both the high glass-forming ability and good soft magnetic properties, *i.e.*, the high reduced glass transition temperature (T_g/T_i) of 0.60, the low coercive force of 0.24 A/m, the low saturated magnetostriction of 1.8×10^{-6} and the high effective permeability of 42100 at 1 kHz.

Subsequently, the $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ ring shape alloy with an outer diameter of 7 mm, an inner diameter of 3 mm and

Fig. 2 Changes in B_s , H_c , μ_e at 1 kHz and λ_s as a function of Fe content for the glassy $\text{Co}_{63-X}\text{Fe}_X\text{Ta}_{5.5}\text{B}_{31.5}$ alloys as-quenched and annealed for 600 s at 870 K.

Fig. 3 Outer morphology of the bulk $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ sample in a ring form with a thickness of 1 mm.

a thickness of 1 mm was formed by the copper mold casting method, as shown in Fig. 3. This exhibits a smooth outer surface and metallic luster. The fracture surface of the bulk sample also shows a very smooth surface like that of oxide glasses, as shown in Fig. 4. The optical micrograph of the cross-section also reveals a featureless contrast in an etched state using aqua regia.

Figure 5 shows the XRD patterns for the bulk samples prepared by copper mold casting. The data of the melt-spun ribbon sample with a thickness of 20 μm are also shown for comparison. Both patterns consist only of a broad peak at a wave vector ($K_p = 4\pi \sin \theta / \lambda$) of about 31 nm^{-1} .

Fig. 4 SEM image of the cross-section for the bulk $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ sample in a ring shape form.

Fig. 5 XRD pattern of the bulk $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ alloy in a ring form. The data of corresponding melt-spun ribbon with a thickness of $20\text{ }\mu\text{m}$ is also shown for comparison.

Fig. 6 DSC curve of the bulk $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ sample with a thickness of 1 mm . The DSC curve for the melt-spun ribbon with a thickness of $20\text{ }\mu\text{m}$ is also shown for comparison.

Fig. 7 D.C. B-H curves of the bulk glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ alloy in a ring form in as cast state and annealed state for 1800 s at 870 K .

The DSC curves of the cast bulk and the melt-spun ribbon are shown in Fig. 6. The T_g , T_x and ΔT_x for both samples are 907 K , 979 K and 72 K , respectively.

Figure 7 shows the D.C. B-H curves of the cast bulk $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ sample in as-cast and annealed (1800 s , 870 K) states. These curves are plotted in the two applied magnetic field ranges: (a) $\pm 1500\text{ A/m}$ and (b) $\pm 50\text{ A/m}$. The B_s of 0.47 T for the as-cast bulk sample is slightly larger than that of 0.45 for the melt-spun ribbon sample, as shown in Fig. 2. On the other hand, H_c of the bulk sample is 3.7 A/m begin smaller 7.4 A/m for the ribbon sample. The different of magnetic properties between these samples is caused by a difference in the cooling rates. Since a cooling rate of a melt-spinning method is faster than that of casting method, large stress is induced to influence magnetic properties. The H_c and μ_{max} are significantly improved by the annealing treatment, and B_s also slightly increase to 0.49 T which is the same as the melt-spun ribbon.

Figure 8 shows initial magnetization and enlarged D.C. B-H curves in the applied magnetic field range of $\pm 2\text{ A/m}$ for the same cast bulk $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ sample in annealed (1800 s , 870 K) states. The H_c of the annealed sample shows an extremely low value of 0.25 A/m , which is nearly the same as that of the melt-spun ribbon. The μ_{max} also shows the very high value of 460000 . The strain caused by casting seems to

Fig. 8 Initial magnetization and enlarged D.C. B-H curves of the bulk glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ alloy in a ring form in annealed state for 1800 s at 870 K.

be almost released by the annealing treatment.

It is concluded that a Co-based bulk glassy alloy with excellent soft magnetic properties and low saturated magnetostriction can be produced by choosing the alloy composition of $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$.

4. Summary

The glassy ring form bulk Co–Fe–Ta–B alloy was prepared by a copper mold casting method. These glassy samples have a wide ΔT_x exceeding 70 K, which is the same as that of the corresponding melt-spun ribbon. The B_s , H_c and $\mu_{\max}$ for the

$\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ ring shape bulk glassy alloy were 0.49 T, 0.25 A/m and 460000, respectively. The excellent soft magnetic properties for these alloys are ascribed to high structural homogeneity in the high glass-forming system. We hope that the Co–Fe–Ta–B glassy alloys are practically very useful because of their excellent soft magnetic properties combined with high glass-forming ability.

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REFERENCES

- 1) A. Inoue, K. Ohtera, K. Kita and T. Masumoto: *Jpn. J. Appl. Phys.* **27** (1974) 2248–2251.
- 2) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans., JIM* **30** (1989) 965–972.
- 3) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans., JIM* **31** (1990) 177–183.
- 4) A. Peker and W. L. Johnson: *Appl. Phys. Lett.* **63** (1993) 2342–2344.
- 5) A. Inoue: *Mater. Sci. Forum* **179–181** (1995) 691–700.
- 6) T. Mizushima, A. Makino and A. Inoue: *J. Appl. Phys.* **83** (1998) 6329–6331.
- 7) A. Inoue, T. Zhang, T. Itoi and A. Takeuchi: *Mater. Trans., JIM* **38** (1997) 359–362.
- 8) A. Inoue, H. Koshida, T. Itoi and A. Makino: *Appl. Phys. Lett.* **73** (1998) 744–747.
- 9) T. Mizushima, K. Ikarashi, S. Yoshida, A. Makino and A. Inoue: *Mater. Trans., JIM* **40** (1999) 1019–1022.
- 10) P. Villars, A. Prince and H. Okamoto: *Handbook of Ternary Alloy Phase Diagrams*, (ASM International, OH, 1995) pp. 5484–5485.