Bulk Glassy Fe–Co–Ga–P–C–B Alloys with High Glass-Forming Ability, High Saturation Magnetization and Good Soft Magnetic Properties

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The effect of ferromagnetic metal Co on the glass-forming ability and magnetic properties for the $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ glassy alloys was investigated. The additions of 10 to 15 at%Co were found to be effective for the extension of the supercooled liquid region (ΔT_x) defined by the difference between the glass transition temperature (T_g) and crystallization temperature (T_x). The ΔT_x value is 37 K for the $\text{Fe}_{75}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy and increases to 48 K for the 10, 12.5 and 15 at%Co alloys. The liquidus temperature (T_l) of the 10, 12.5 and 15 at%Co alloys decreased by the addition of Co and the reduced glass transition temperature (T_g/T_l) increased. The largest T_g/T_l is 0.61 for the $\text{Fe}_{65}\text{Co}_{10}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy. These glassy ribbon alloys exhibit good soft magnetic properties of 1.15 to 1.33 T for saturation magnetization and 2.4 to 3.6 A/m for coercive force. Based on the large ΔT_x and high T_g/T_l values, we tried to prepare bulk glassy $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5, 15$) rods in a cylindrical form with different diameters. The glassy single phase was obtained in the diameter of 1.5 mm in the composition range of 10 to 15 at%Co.

(Received August 9, 2000; Accepted October 24, 2000)

Keywords: bulk glassy alloy, high glass-forming ability, high saturation magnetization, soft magnetization properties, large supercooled liquid region, iron-cobalt base system

1. Introduction

Amorphous ferromagnetic alloys have been investigated for several years for potential use as electrical transformers, motors, high-frequency switching power supplies, and other electrical energy conversion devices because of their good soft magnetic properties. However, the shapes of amorphous ferromagnetic alloys have been usually limited to sheet, wire and film because of their low glass-forming ability, leading to the restriction of their application fields. For instance, for the Fe-based amorphous alloy films, typically 25 ~ 30 μm thick, although the saturation magnetization is high and the soft magnetic properties are also good, the commercialization has been limited to transformers so far. The main three factors of limiting application are thinness of gauge, postanneal brittleness and stress sensitivity.¹⁾ The thin amorphous films are difficult to handle and thus the transformers can not be constructed by the ordinary method which has been used for conventional 0.3 mm thick crystalline Fe–Si laminas. In addition, the reduced thickness of the films causes a decrease in the core packing density since air gaps are left between the large number of thin films needed to build up the core, and this decreases the efficiency of the transformer. Therefore, it is very important to search a bulk Fe-based glassy alloy with high saturation magnetization and high glass-forming ability. There is no doubt that the advent of bulk glassy ferromagnetic alloys would be of tremendous benefit.

For the last several years, Inoue group has found multicomponent glassy alloys in the Fe–(Al, Ga)–(P, C, B, Ge, Si) and Fe–(Nb, Mo, Zr, W)–B alloy systems which exhibit a large supercooled liquid region reaching 58 to 88 K before crystallization and can be produced in a cylindrical form with diameters of 2 to 6 mm by copper mold casting.^{2–6)} However, these bulk glassy alloys have a disadvantage of relatively lower Fe concentrations less than 73 at% leading to saturated magneti-

zation values below 1.1 T. But more recently, a bulk glassy $\text{Fe}_{75}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy in the diameter of 1 mm with high saturation magnetization of about 1.28 T has been synthesized by Inoue group.⁷⁾ Based on this result, we examined the effect of the dissolution of ferromagnetic transition metal Co in the Fe–Ga–(P, C, B) alloy system with the aim of synthesizing a new bulk glassy alloy with high glass-forming ability, high saturation magnetization and good soft magnetic properties. This paper is intended to present a new Fe-based alloy system $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ with high saturation magnetization and good soft magnetic properties, in which bulk glassy alloys with diameters up to 1.5 mm are formed by copper mold casting. The effect of Co on the glass-forming ability and magnetic properties of the $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ glassy alloys is also discussed.

2. Experimental Procedure

Multicomponent $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloys were examined in the present study. The ingots were prepared by induction melting a mixture of pure Fe, Co and Ga metals, prealloyed Fe–C and Fe–P ingots, and pure B crystal in a purified argon atmosphere. Their compositions are nominally expressed in atomic percentage. From the master alloy ingot, a ribbon with a cross section of about $0.020 \times 1.0 \text{ mm}^2$ was prepared by melt spinning. Cylindrical rods with diameters up to 1.5 mm and a length of 35 mm were also made by copper mold casting in an argon atmosphere. The amorphousness of the ribbons and rods was examined by X-ray diffraction with Cu-K α and optical microscopy (OM). The specific heat associated with glass transition, supercooled liquid region and crystallization was measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). The liquidus temperatures (T_l) of alloys were measured by cooling the molten alloy samples at a cooling rate of 0.033 K/s with differential thermal analysis (DTA). Magnetic properties

of saturation magnetization and coercive force were measured with a vibrating sample magnetometer (VSM) and a B-H loop tracer.

3. Results

It has been confirmed in the X-ray diffraction patterns that the melt-spun $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy ribbons are composed of a glassy phase without any crystallinity over the whole composition range up to 20 at%Co. Figure 1 shows DSC curves of the melt-spun $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 5, 7.5, 10, 12.5, 15, 17.5, 20$) glassy alloys. With increasing temperature, these glassy alloys show the segment change of the glass transition, followed by a supercooled liquid region and then crystallization. The temperature interval of the supercooled liquid region (ΔT_x), which is defined by the difference between glass transition temperature (T_g) and the onset temperature of crystallization (T_x), increases to 48 K when the Co content increases to 10, 12.5 and 15 at%. The ΔT_x value is larger than that (37 K)⁷ for the $\text{Fe}_{75}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy. In addition, the internal equilibrium state in which the disordered structure can be fully relaxed during continuous heating at the rate of 0.67 K/s is maintained in the temperature interval of 25 K before crystallization for the 10, 12.5 and 15 at%Co alloys. Moreover, it is seen that the crystallization takes place through a single exothermic stage, in agreement with that for the previously reported glassy alloys with a large supercooled liquid region before crystallization.^{8,9} The further increase in Co content resulted in a two-stage crystallization, accompanying a decrease in the supercooled liquid region (ΔT_x). It is also noted that the Curie temperature marked with T_c in Fig. 1 increases gradually from 627 to 650 K when Co con-

tent increases to 15 at%. The T_c values are higher than those (597 to 622 K)^{5,7} of Fe-Al-Ga-P-C-B and Fe-Ga-P-C-B alloy systems.

Figure 2 shows hysteresis I-H loops of the as-quenched $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 5, 7.5, 10, 12.5, 15, 17.5, 20$) glassy alloys. The saturation magnetization (I_s) is 1.33 T for the $\text{Fe}_{70}\text{Co}_5\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy and decreases gradually with increasing Co content. When the Co content increases to 20 at%, the saturation magnetization (I_s) decreases to 1.15 T. The coercive force (H_c) remains almost constant and keep a low value of about 3.0 A/m. Therefore, it is said that these glassy alloys exhibit good soft magnetic properties. Here, it is pointed out that the saturation magnetization (I_s) of about 1.3 T remains almost unchanged when the Co contents change to 10, 12.5 and 15 at%. Otherwise, according to the DSC results shown in Fig. 1, the 10, 12.5 and 15 at%Co glassy alloys exhibit a large supercooled liquid region and then a single-stage crystallization, implying that there is a high possibility of forming a bulk glassy alloy by the copper mold casting method. Therefore, it is encouraging because this glassy alloy system keeps high I_s of 1.3 T, low H_c of 3.0 A/m and high T_c of 650 K, in addition to high possibility of forming a bulk glassy alloy in the wide composition range. Thus, we tried to prepare bulk glassy $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5, 15$) alloys by copper mold casting.

Figure 3 shows the outer surface appearance of the cast $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5, 15$) rods of 1.5 mm in diameter. These rods have smooth surface and good metallic luster and no appreciable ruggedness corresponding to a crystalline phase can be observed on the outer surface. In order to examine the formation of an amorphous phase and the absence of any crystalline phase in the rod samples, the cross sectional structure was examined by optical microscopy. No contrast typical to a crystalline phase can be observed over the whole cross section for all the samples with a diameter of 1.5 mm. The X-ray diffraction patterns taken from the trans-

Fig. 1 DSC curves of melt-spun $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 5, 7.5, 10, 12.5, 15, 17.5$ and 20 at%) glassy alloys.

Fig. 2 Hysteresis I-H loops of melt-spun $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 5, 7.5, 10, 12.5, 15, 17.5$ and 20 at%) glassy alloys.

Fig. 3 Outer shape of cast (a) $\text{Fe}_{65}\text{Co}_{10}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$, (b) $\text{Fe}_{62.5}\text{Co}_{12.5}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ and (c) $\text{Fe}_{60}\text{Co}_{15}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ glassy rods of 1.5 mm in diameter.

Fig. 4 DSC curves of cast $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5$ and 15 at%) glassy rods of 1.5 mm in diameter.

verse cross sections of the rod samples of 1.5 mm in diameter consist only of a broad peak around $2\theta = 44.5$ degrees and no diffraction peak corresponding to a crystalline phase is observed. These identified results indicate that the bulk alloys are composed of a glassy phase without crystallinity. Figure 4 shows the DSC curves of the glassy $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5, 15$) rods of 1.5 mm in diameter. No appreciable difference in T_c , T_g , T_x , ΔT_x , and crystallization process is observed between the melt-spun ribbon samples and the three bulk samples.

Fig. 5 Hysteresis I-H loops of cast $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5$ and 15 at%) glassy alloys of 1.5 mm in diameter.

The hysteresis I-H loops of the glassy $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5, 15$) rods of 1.5 mm in diameter are shown in Fig. 5. The I-H loop was measured by VSM because the conventional I-H loop tracer could not be used for the cylindrical bulk glassy alloy. As shown in the figure, the saturation magnetization (I_s) of the cast (a) $\text{Fe}_{65}\text{Co}_{10}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$, (b) $\text{Fe}_{62.5}\text{Co}_{12.5}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$, and (c) $\text{Fe}_{60}\text{Co}_{15}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ glassy rods of 1.5 mm in diameter are about 1.30, 1.28 and 1.27 T, respectively. Therefore, these bulk glassy alloys also exhibit high saturation magnetization.

4. Discussion

Here, we discuss the reason why the effect of addition of Co for the $\text{Fe}_{75}\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy is such distinct. The addition of Co is due to the satisfaction of the three empirical rules¹⁰⁻¹³ for the achievement of high glass-forming ability and the stabilization of the supercooled liquid. The three rules are: (1) multicomponent alloy systems consisting of more than three elements, (2) significantly different atomic size ratios above 12% among the constituent elements, and (3) large negative heats of mixing among the elements. It is well known^{14,15} that the Co element has large negative heats of mixing against the other constituent elements. There is a high tendency for Co to form various kinds of compounds such as Fe_xCo_y , Co_xGa_y , Co_xB_y and Co_xP_y . However, as is the case for the previously reported results on the addition of Al, Ge, Ga, Nb, Cr and Mo etc.,^{2,3,7,16} only α -Fe, Fe_3P , Fe_3B and Fe_3C crystallized phases are detected but we can not detect any kind of compounds containing Co as a main constituent element after annealing over the crystallization temperature, indicating that Co element is also dissolved into those crystallized phases. The dissolution of Co into the crystallized phases implies the necessity of the redistribution of Co from the supercooled liquid to the crystallized

Fig. 6 Change in liquidus temperature with Co content for $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 5, 7.5, 10, 12.5, 15, 17.5$ and 20 at%) alloys.

phases for the progress of crystallization. The redistribution is not always easy for Co element with high melting temperature and large negative heats of mixing. The redistribution of Co and the other solute elements such as Ga, P, C and B may be concluded to lead to the retardation of precipitation of the crystallized phases. In addition, as shown in Fig. 6, one can notice that the liquidus temperatures T_l for the 10, 12.5 and 15 at% alloys are very low and exhibit a “deep eutectic” phase diagram. Moreover, the reduced glass transition temperatures (T_g/T_l) of the three alloys are between 0.60 to 0.61. These results also predict that this alloy system has a higher glass-forming ability when the Co contents are 10, 12.5 and 15 Co at%, especially for 10 Co at% alloy.

5. Summary

A new glassy $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ alloy system with

high glassy-forming ability, high saturation magnetization and good soft magnetic properties was synthesized in the wide composition range of 10, 12.5 and 15 at%Co. The large ΔT_x and high T_g/T_l have enabled us to form bulk glassy alloy rods in the diameter of 1.5 mm by the copper mold casting method in the wide composition range. These cast glassy alloy rods also exhibit high saturation magnetization of 1.30 T and high Curie temperature of 650 K. The combination of high glass-forming ability as well as high saturation magnetization and good soft magnetic properties for the glassy $\text{Fe}_{75-x}\text{Co}_x\text{Ga}_5\text{P}_{12}\text{C}_4\text{B}_4$ ($x = 10, 12.5, 15$) alloys is encouraging for the future application of Fe-based bulk glassy alloys to bulk soft magnetic materials.

REFERENCES

- 1) D. Raskin and C. H. Smith: *Amorphous Metallic Alloys*, Ed. by T. E. Luborsky, Butterworths, London, (1983), chap. 20, pp. 381–400.
- 2) A. Inoue and J. S. Gook: *Mater. Trans., JIM*, **36** (1995), 1180–1183.
- 3) A. Inoue and J. S. Gook: *Mater. Trans., JIM*, **36** (1995), 1282–1285.
- 4) A. Inoue, Y. Shinohara and J. S. Gook: *Mater. Trans., JIM*, **36** (1995), 1427–1433.
- 5) A. Inoue, A. Murakami, T. Zhang and A. Takeuchi: *Mater. Trans., JIM*, **38** (1997), 189–196.
- 6) A. Inoue, Tao Zhang and Akira Takeuchi: *Appl. Phys. Lett.*, **71** (1997), 464–466.
- 7) B. L. Shen, H. Koshiba, T. Mizushima and A. Inoue: *Mater. Trans., JIM*, **41** (2000), 873–876.
- 8) A. Inoue: *Advanced Materials and Processing*, Ed. by K. S. Shin, J. K. Yoon and S. J. Kim, The Korean Inst. Metals and Materials, Seoul, (1995), pp. 1849–1858.
- 9) A. Inoue: *Sci. Rep. Inst. Tohoku Univ.*, **A42** (1996), 1–11.
- 10) A. Inoue, T. Zhang and T. Masumoto: *J. Non-Cryst. Solids*, **156–158** (1993), 473–480.
- 11) A. Inoue: *Mater. Trans., JIM*, **36** (1995), 866–875.
- 12) A. Inoue: *Mater. Sci. Forum*, **179–181** (1995), 691–700.
- 13) A. Inoue: *Nanostructured and Non-Crystalline Materials*, M. Vazque and A. Hemando, Ed. Singapore: World Scientific, (1995), pp. 15–24.
- 14) F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Moedema and A. H. Niessen: *Cohesion in Metals*, Elsevier Science Publishers B. V., Amsterdam, (1988), pp. 261–267.
- 15) T. Nishizawa and K. Ishida: *Binary Alloy Phase Diagrams*, Ed. by T. B. Massalski, ASM International, Materials Park, Ohio (1990), pp. 761–766.
- 16) B. L. Shen, H. Koshiba, H. Kimura and A. Inoue: *Mater. Trans., JIM*, **41** (2000). (in press)