Bulk Glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ Alloy with High Glass-Forming Ability and Good Soft Magnetic Properties

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A new Co-based bulk glassy alloy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ exhibiting a large supercooled liquid region before crystallization and good soft magnetic properties was synthesized by the copper mold casting method. The glass transition temperature (T_g) is 910 K and the supercooled liquid region (ΔT_x) reaches 70 K. The high thermal stability of the supercooled liquid enabled us to produce bulk glassy alloys with diameters up to 2 mm. These bulk glassy alloys exhibit good soft magnetic properties, *i.e.*, saturation magnetization of 0.5 T, very low coercivity of 0.9 A/m and very high permeability of 40000 at 1 kHz. It is noticed that the diameter of 2 mm is the largest value for Co-based bulk glassy alloys reported up to now. The success of forming the large-scale size Co-based bulk glassy alloy with high thermal stability of supercooled liquid and good soft magnetic properties is encouraging for future uses of bulk amorphous soft magnetic materials.

(Received June 12, 2001; Accepted August 15, 2001)

Keywords: cobalt-based bulk glassy alloy, large supercooled liquid region, soft magnetic properties

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 because 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.^{3,4)}

In the last decade, especially since 1995, Inoue group has devoted great efforts to the production of bulk Fe- and Co-based glassy alloys. As a result, bulk ferromagnetic Fe-based glassy 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)^{5–7)} and Fe–(Co, Ni)–(Zr, Nb, Ta, Mo, W)–B systems.^{8–10)} The critical thickness of Fe-based glassy alloys reaches 2 mm for Fe–(Al, Ga)–(P, C, B, Si, Ge)⁷⁾ and 6 mm for Fe–(Co, Ni)–(Zr, Nb, Ta, Mo, W)–B¹⁰⁾ system by the copper mold casting method. Recently, bulk glassy Fe–Ga–P–C–B and Fe–(Mo, Co)–Ga–P–C–B alloys of 1 to 2.5 mm in diameter with high saturation magnetization of 1.2 to 1.4 T have been synthesized by Inoue group.^{11–15)} Subsequently, ferromagnetic Co-based glassy alloys with large supercooled liquid region above 50 K were found in Co–Al–Ga–(Fe, Cr, V)–P–B–C–Si¹⁶⁾ and Co–Fe–(Zr, Nb, Ta, W)–B^{17,18)} systems. More recently, bulk glassy Co–Fe–(Zr, Nb)–B alloys of 1 mm in diameter with good soft magnetic properties have been synthesized.¹⁹⁾ Based on these encouraging results, we have investigated the effect of the dissolution of Ta element on the glass-forming ability in Co-based Co–Fe–B glassy alloys containing about 30 at%B. We have succeeded in finding a new alloy system of Co–Fe–Ta–B where the supercooled liquid region before crystallization (ΔT_x) is 70 K, the saturation magnetization (I_s) is 0.5 T and the effective perme-

ability (μ_e) at 1 kHz is 40000.²⁰⁾ Considering the previous data^{7,10–15,19)} that the ΔT_x value is roughly proportional to the glass-forming ability, the Co–Fe–Ta–B alloys are expected to be made into a bulk glassy form prepared by the copper mold casting method. This paper presents the production of bulk Co–Fe–Ta–B glassy alloys with diameters above 1.0 mm by copper mold casting and their thermal stability and magnetic properties in comparison with those for the melt-spun amorphous ribbon with a thickness of about 20 μm .

2. Experimental Procedure

A multicomponent alloy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ ingot was prepared by arc melting the mixture of pure Co, Fe, Ta metals, and pure B crystal in a purified argon atmosphere. The composition is 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 2 mm and a length of 40 mm were also made by copper mold casting in an argon atmosphere. The amorphicity of the ribbons and rods was examined by X-ray diffractometry 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 temperature (T_l) of the alloy was measured by cooling the molten alloy at a rate of 0.033 K/s with differential thermal analyzer (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

The $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ cylindrical rods with diameters of 1.0, 1.5 and 2 mm were prepared by the copper mold casting method. These rods have smooth surface and good metallic

Fig. 1 Transverse cross sectional structure of cast $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ rod with a diameter of 2 mm.

luster and no appreciable ruggedness corresponding to a crystalline phase is 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. Transverse cross sectional structure of the cast cylinder with a diameter of 2.0 mm is shown in Fig. 1. No contrast typical to a crystalline phase is seen over the whole cross section for all the samples except for some cast defects even in an etched state where the crystalline phase is easily detected. The featureless contrast indicates that these cast rods consist of a glassy phase. The formation of the glassy phase without crystallinity was also confirmed in the X-ray diffraction patterns taken from the transverse cross sections of the cast rods with diameters of 1.0, 1.5 and 2.0 mm. As shown in Fig. 2, the diffraction patterns consist only of a broad peak around $2\theta = 44$ degrees and no diffraction peak corresponding to a crystalline phase is seen. These identified results indicate that the bulk alloys in the diameter range up to 2.0 mm are composed of a glassy single phase.

The thermal stability of the cast glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ rods with diameters of 1.0, 1.5 and 2.0 mm was examined by DSC in comparison with that for the melt-spun glassy ribbon with a thickness of 20 μm . Figure 3 shows the DSC curves of the glassy rods. The T_g , T_x and ΔT_x values are measured to be 910 K, 980 K and 70 K, respectively, in agreement with those for the melt-spun ribbon. No appreciable difference in T_g , T_x , ΔT_x , and crystallization process is seen between the melt-spun ribbon and the three bulk rods.

The hysteresis I-H loops of the glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ rods with diameters of 1.0, 1.5 and 2.0 mm are shown in Fig. 4, where the data of the melt-spun glassy ribbon are also shown 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 glassy alloy. As shown in the figure, the saturation magnetization (I_s) of the glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ rods with diameters of 1.0, 1.5 and 2.0 mm are 0.51 T, 0.50 T and 0.49 T, respectively. No distinct difference in the hysteresis I-H loops measured by VSM is seen between the bulk rods and the melt-spun ribbon. Here, it is reasonable to consider that the cast bulk glassy rods have nearly the same soft magnetic properties as those for the melt-spun glassy ribbon from

Fig. 2 X-ray diffraction patterns of cast $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glassy rods with diameters of 1.0, 1.5 and 2.0 mm. The data of the melt-spun ribbon are also shown for comparison.

Table 1 Thermal stability and magnetic properties of the cast $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glassy rods with diameters of 1.0, 1.5 and 2.0 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

	I_s/T	H_c/Am^{-1}	μ_e (1 kHz)	T_g/K	$\Delta T_x/\text{K}$	T_g/T_l
Ribbon	0.51	0.9	4×10^4	910	70	0.61
$\phi 1.0 \text{ mm}$	0.51	—	—	910	70	0.61
$\phi 1.5 \text{ mm}$	0.50	—	—	910	70	0.61
$\phi 2.0 \text{ mm}$	0.49	—	—	910	70	0.61

the similarity in the I-H loops between the melt-spun ribbon and the cast bulk rods.

Table 1 summarizes magnetic properties of I_s and H_c as well as thermal stability of T_g , ΔT_x and reduced glass transition temperature (T_g/T_l) of the glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ rods with diameters of 1.0, 1.5 and 2.0 mm. The data of the melt-spun ribbon are also shown for comparison. Although the I_s was slightly lower for the bulk sample, no distinct difference in the T_g , ΔT_x and T_g/T_l was observed among the bulk and ribbon samples. Therefore, it is concluded that these bulk alloys are composed only of a glassy phase with high glass-forming ability and excellent soft magnetic properties. Within the author's knowledge, the diameter of 2 mm is the largest value for Co-based bulk glassy alloys reported up to now.

4. Discussion

We discuss the reason why the supercooled liquid of the $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glassy alloy has high stability against crystallization. It has been pointed out²¹⁻²³ that all the alloys with high thermal stability of supercooled liquid sat-

Fig. 3 DSC curves of cast $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glassy rods with diameters of 1.0, 1.5 and 2.0 mm. The data of the melt-spun ribbon with a thickness $20\ \mu\text{m}$ are also shown for comparison.

Fig. 4 Hysteresis I-H loops of cast $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glassy rods with diameters of 1.0, 1.5 and 2.0 mm. The data of the melt-spun ribbon are also shown for comparison.

isfy the following three empirical rules for achievement of high glass-forming ability, *i.e.*, (1) the multicomponent alloy system consisting of more than three elements, (2) the significantly different atomic size ratios above 12% among the constituent elements, and (3) large negative heats of mixing among the elements. The atomic radius changes in the order of $\text{Co} > \text{Ta} > \text{Fe} \gg \text{B}$ ²⁴⁾ and the predicted heat of mixing has negative values of 36 kJ/mol for equiatomic

Co-Ta pair, 34 kJ/mol for Co-B pair, 15 kJ/mol for Fe-Ta pair, 38 kJ/mol for Fe-B pair, and 39 kJ/mol for Ta-B pair.²⁵⁾ The Co-Fe-Ta-B system also satisfies the three empirical rules. The satisfaction of the rules causes the formation of a highly dense random packed structure, in the framework of geometrical and chemical points of view, in which the diffusivity of the constituent elements is suppressed and the liquid/solid interfacial energy is increased. Even in the supercooled liquid structure, long-range atomic rearrangements are required for the single-stage precipitation of the crystalline phases. However, the atomic rearrangements are difficult in the specialized liquid with low diffusivity. The difficulty seems to be the reason for the appearance of the glass transition and large supercooled liquid region before crystallization. Furthermore, it is pointed out that the high reduced glass transition temperature of 0.61 resulting from the decrease in T_i due to the high stability of supercooled liquid is an important factor for the high glass-forming ability in the prediction of thermodynamic aspect.

5. Summary

We found that a $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ alloy exhibits a large supercooled liquid region of 70 K before crystallization. By using the alloy, the formation of a bulk glassy alloy in a cylindrical form was examined by the copper mold casting method. The cast bulk glassy alloys with a length of about 40 mm were produced in the diameter range up to 2.0 mm. These cast glassy alloys have high thermal stability with the glass transition temperature of 910 K and the large supercooled liquid region of 70 K. The magnetic properties measured by VSM are nearly the same as those for the melt-spun glassy ribbon. The combination of high glass-forming ability as well as excellent soft magnetic properties for the glassy $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ alloy is encouraging for the future uses of Co-based bulk glassy alloys as bulk soft magnetic materials with the feature of extremely low coercive forces below 1 A/m.

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