Bulk Glassy Alloys in (Fe, Co, Ni)–Si–B System

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Multicomponent $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys were found to exhibit a distinct glass transition, followed by a supercooled liquid region before crystallization in a rather wide composition range of 7.5 to 45 at%Co and 7.5 to 60 at%Ni. The largest value of the supercooled liquid region defined by the difference between the glass transition temperature (T_g) and crystallization temperature (T_x), $\Delta T_x (= T_x - T_g)$ was 54 K for $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$. Furthermore, the high reduced glass transition temperature (T_g/T_m) above 0.60 was obtained in the range of 15 to 30 at%Co and 37.5 to 52.5 at%Ni in the series of $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$. The use of $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ with a large ΔT_x of 54 K and a high T_g/T_m of 0.65 enabled us to produce bulk glassy rods with diameters up to 1.2 mm. The T_g , T_x , saturated magnetization ($4\pi I_s$), and coercive force (H_c) of the as-cast 1.2 mm rod alloy are 780 K, 834 K, 0.90 T, and 3.0 A/m, respectively. In addition, the cast glassy rod exhibits Young's modulus of 110 GPa, compressive fracture strength of 2800 MPa and fracture elongation of 1.9%. It is noticed that the thermal stability, magnetic properties and mechanical properties are nearly the same as those for the melt-spun glassy ribbon. The first synthesis of Fe–Si–B base bulk glassy alloys with good soft magnetic properties and high mechanical strength is promising for the future development as a new type of engineering material.

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1. Introduction

It is known that Fe-based amorphous alloys are one of the most important engineering materials because of their useful functional properties.¹⁾ There has been a strong demand to develop a new Fe-based amorphous alloy with useful magnetic properties as well as high glass-forming ability. Since an amorphous Fe–P–C alloy was synthesized in 1967,²⁾ a number of Fe-based amorphous alloys have been formed for the subsequent 15 years.¹⁾ However, all Fe-based amorphous alloys have required high cooling rates above 10^4 K/s and thus the maximum sample thickness has been limited to thin sheets with a thickness less than about 50 μm .¹⁾ The enclosed situation has been explored by the first success of synthesizing Fe-based bulk glassy alloy rods with diameters up to 2 mm in Fe–(Al, Ga)–(P, C, B) system by the copper mold casting process in 1995.^{3,4)} It has subsequently been reported that Fe-based bulk glassy alloys are formed in Fe–(Nb, Cr, Mo)–(Al, Ga)–(P, C, B),⁵⁾ (Fe, Co, Ni)–(Zr, Hf, Nb)–B,⁶⁾ (Nd, Pr)–Fe–(Al, Si),⁷⁾ Fe–Co–Ln–B (Ln = lanthanide metal),^{8,9)} Fe–Si–C–B,¹⁰⁾ Fe–(Cr, Mo)–Ga–(P, C, B),¹¹⁾ Fe–Nb–B,¹²⁾ Fe–(Cr, Mo)–(C, B)¹³⁾ and Fe–Ga–(P, C, B)¹⁴⁾ systems. In the subsequent search on a new Fe-based bulk glassy alloy, we have found that (Fe, Co, Ni)–Si–B glassy alloys have a large supercooled liquid region over 50 K and can be produced in a bulk form with a thickness below 1.2 mm. Considering that the (Fe, Co, Ni)–Si–B glassy alloys are the most dominant system among practical soft magnetic amorphous materials, the finding is expected to lead to a further extension of their bulk glassy alloys as a bulk-type soft magnetic material. This paper is intended to present the formation, thermal stability, mechanical properties and magnetic properties of the bulk glassy (Fe, Co, Ni)–Si–B alloys.

2. Experimental Procedure

Multicomponent Fe-based alloys with compositions of $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ were prepared by arc melting the mixtures of Fe(99.9%), Co(99.9%) and Ni(99.8%) metals, Si(99.999%) and B(99.8%) crystals in an argon atmosphere. The alloy components represented the nominal atomic percentage. Ribbon samples with a cross section of $0.04 \times 2 \text{ mm}^2$ were produced by the melt spinning technique in an argon atmosphere. Bulk cylindrical rod samples with diameters up to 3 mm were also prepared by the copper mold casting method in an argon atmosphere. The glassy phase was identified by X-ray diffraction and transmission electron microscopic (TEM). The thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The saturated magnetization and intrinsic coercive force were measured with a vibrating sample magnetometer (VSM) and a B–H loop tracer at room temperature, respectively. The density was measured by the Archimedian method at 298 K. The mechanical properties were measured with an Instron-type testing machine at room temperature. The shape and structure in the transverse cross section were examined by an optical microscopy (OM).

3. Results

Figure 1 shows the composition range in which glassy alloys with glass transition before crystallization are formed in the $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ alloy systems by melt spinning and the compositional dependence of T_g . As seen in Fig. 1, the amorphous alloys are formed over the whole composition range. However, the appearance of the glass transition is limited to the range of 7.5 to 45 at%Co and 7.5 to 60 at%Ni. The T_g tends to increase from 750 to 780 K with increasing Fe and Co contents. As examples, Fig. 2 shows DSC curves of the melt-spun $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys exhibiting the

Fig. 1 Composition range in which a glassy phase in $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ system is formed by melt spinning and compositional dependence of T_g .

Fig. 3 Compositional dependence of the supercooled liquid region, $\Delta T_x (= T_x - T_g)$ for melt-spun $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys.

Fig. 2 DSC curves of melt-spun $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys.

glass transition and supercooled liquid region. One can see one or two exothermic peaks due to crystallization, indicating the absence of a close relation between the appearance of glass transition and the crystallization stage. Figure 3 shows the compositional dependence of $\Delta T_x (= T_x - T_g)$ for the $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys. The largest ΔT_x value of 54 K is obtained for $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ and the ΔT_x decreases with an deviation from the optimum composition. It is noticed that the large ΔT_x value exceeding 50 K is obtained in the rather wide composition range of 22.5 to 30 at%Co and

Fig. 4 Compositional dependence of the reduced glass transition temperature (T_g/T_m) for melt-spun $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys.

45 to 52.5 at%Ni.

It has been reported that the glassy alloy with ΔT_x over 50 K can be made into a bulk form with diameters above 1 mm.^{15,16)} With the aim of obtaining the further detailed information on the glass-forming ability, we evaluated the reduced glass transition temperature (T_g/T_m) by the measurement of melting temperature (T_m). Figure 4 shows the compositional dependence of T_g/T_m for the $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ glassy alloys. The high T_g/T_m values exceeding 0.60 are obtained in the composition range of 15 to 30 at%Co and 37.5 to 52.5 at%Ni in which an increase in Ni content causes a decrease in T_g/T_m .

The high T_g/T_m values exceeding 0.60 allow us to expect the formation of a bulk glassy alloy even by use of an ordinary non-fluxed melt. Figure 5 shows optical micrographs of the transverse cross section of the $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ rod samples with diameters of 1.2 and 2 mm prepared by the copper mold casting method. No contrast corresponding to a

Fig. 5 Optical micrographs of the transverse cross section of the cast $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ rods with diameters of 1.2 and 2 mm.

crystalline phase is seen over the whole cross section for the 1.2 mm sample, though casting-induced pores distinguished as dark spots are observed. However, the increase of diameter to 2 mm leads to the precipitation of a crystalline phase in the central region with a diameter of 1 mm. Thus, the formation of the glassy phase is limited to the outer surface region with a thickness of about 0.5 mm. Figure 6 shows the DSC curves of the resulting cast rod sample with a diameter of 1.2 mm, together with the data of the melt-spun ribbon with a cross section of $0.04 \times 2 \text{ mm}^2$. The T_g , T_x and heat of crystallization (ΔH_x) of the rod sample are 780 K, 834 K and 3.26 kJ/mol, respectively, in agreement with those for the ribbon sample. In addition, there is no appreciable difference in the number of exothermic peaks in the temperature range up to 950 K. Figure 7 shows the hysteresis curve of the cast glassy $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ rod sample with a diameter of 1.2 mm, together with the data of the glassy alloy ribbon. The saturated magnetization ($4\pi I_s$) and coercive force (H_{cj}) are 0.90 T and 3.0 A/m, respectively, for the cast rod sample and 0.92 T and 3.4 A/m, respectively, for the melt-spun ribbon sample. Although the slightly smaller $4\pi I_s$ value for the rod sample arisen from the demagnetization correction

Fig. 6 DSC curve of the cast $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ glassy rod with a diameter of 1.2 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

Fig. 7 Hysteresis B - H curve of the cast $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ glassy rod with a diameter of 1.2 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

was made, the present data indicate that the cast glassy rod possesses good soft magnetic properties which are nearly the same as those for the melt-spun glassy alloy ribbon. Furthermore, it is important to point out that the Young's modulus (E), compressive fracture strength ($\sigma_{c,f}$) and fracture elongation (ε_p) for the glassy rod with a diameter of 1.2 mm are 110 GPa, 2800 MPa and 1.9%, respectively, being nearly the same level as those ($E = 105 \text{ GPa}$, tensile fracture strength $\sigma_{t,f} = 3100 \text{ MPa}$ and tensile elongation $\varepsilon_{t,f} = 2.1\%$) for the glassy ribbon. The good mechanical properties indicate the possibility that the Fe–Co–Ni–Si–B bulk glassy alloys can develop as a new type of high-strength material combined with soft magnetic properties.

4. Discussion

We discuss the reason for the increase in the thermal stability of the supercooled liquid against crystallization in the vicinity of $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$. There have been a num-

ber of data on the thermal stability of Fe–Si–B, Co–Si–B and Ni–Si–B, Fe–Co–Si–B, Fe–Ni–Si–B and Ni–Co–Si–B amorphous alloys.^{17–20} However, no glass transition has been found in the ternary and quaternary alloys, in agreement with the present results. Furthermore, little has been reported about the thermal stability of the pentenary Fe–Co–Ni–Si–B amorphous alloys, though some data on the magnetic properties have been presented. From the previous and present data, it is concluded that the simultaneous addition of Fe, Co and Ni elements is essential for the appearance of the glass transition and supercooled liquid region as well as the achievement of the high glass-forming ability. It has been pointed out that the alloys with high glass-forming ability and a large supercooled liquid region have higher packing densities as compared with ordinary amorphous alloys which require high cooling rates above 10^5 K/s for the formation of an amorphous phase.^{21,22} Although there have been no data on the density and local atomic configurations in the Fe–Co–Ni–Si–B system, it is expected that the simultaneous addition of Fe, Co and Ni elements causes an increase in the packing density as well as the necessity of more longer range rearrangement of the constituent elements for the progress of crystallization reaction. Thus, the difficulty in the rearrangements of the more species of constituent elements in the higher degree of dense random packed liquid may be the reason for the enhancements of the thermal stability of the supercooled liquid as well as the glass-forming ability.

5. Summary

With the aim of developing a new Fe-based bulk glassy alloy with useful functional properties, we examined the glass-forming ability, thermal stability, magnetic properties and mechanical properties of the $\text{Fe}_{75-x-y}\text{Co}_x\text{Ni}_y\text{Si}_8\text{B}_{17}$ alloys. The results obtained are summarized as follows;

(1) Glassy alloys with glass transition before crystallization were formed in the composition range of 7.5 to 45 at%Co and 7.5 to 60 at%Ni. The largest ΔT_x was 54 K for $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$ and the deviation of alloy component from the optimum composition caused a decrease of ΔT_x .

(2) The high reduced T_g/T_m values exceeding 0.60 were obtained in the range of 15 to 30 at%Co and 37.5 to 52.5 at%Ni and the largest T_g/T_m was 0.65 for $\text{Fe}_{30}\text{Co}_{30}\text{Ni}_{15}\text{Si}_8\text{B}_{17}$.

(3) By use of the alloy with the largest T_g/T_m , bulk glassy

alloy rods with diameters up to 1.2 mm were prepared by the copper mold casting process.

(4) The T_g , T_x , ΔH_x , $4\pi I_s$ and H_{cj} of the 1.2 mm rod alloy were 780 K, 834 K, 3.26 kJ/mol, 0.90 T, and 3.0 A/m, respectively, in agreement with those for the corresponding melt-spun ribbon.

(5) The bulk glassy alloy rod with a diameter of 1.2 mm also exhibited a high $\sigma_{c,f}$ of 2800 MPa and an elongation of 1.9% which were nearly the same as the tensile fracture strength of 3100 MPa and tensile elongation of 2.1% for the melt-spun glassy ribbon. The rather good mechanical properties indicate the possibility that the Fe–Si–B base bulk glassy alloys become significant as a new functional material.

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