FeSiBP Bulk Metallic Glasses with Unusual Combination of High Magnetization and High Glass-Forming Ability

Akihiro Makino, Takeshi Kubota, Chuntao Chang, Masahiro Makabe, and Akihisa Inoue

1 Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
2 Tohoku University, Sendai 980-8577, Japan

Among many kinds of bulk metallic glasses (BMGs), Fe-based BMGs with good magnetic properties, high strength and low materials cost should have great potential for wide variety of applications. However, the glass-forming metal elements such as Al, Ga, Nb, Mo, Y and so forth in the Fe-based BMGs significantly decrease saturation magnetization (J_s) which is a essential property as soft magnetic materials and also increase the material cost.

The coexistence of high Fe content and high glass-forming ability (GFA) has been earnestly desired from academia to industry. We report a novel Fe_{75}Si_{15}B_{10}P_{5} (at%) bulk metallic glass with unusual combination of high J_s of 1.51 T due to high Fe content and high GFA leading to a glassy rod with a diameter of 2.5 mm despite not-containing any glass-forming metal elements. This alloy composed of familiar and low-priced elements, also exhibiting very excellent magnetic softness and rather high strength, has a great advantage for engineering and industry, and thus should make a contribution to conservation of earth resources and environment through energy saving.

1. Introduction

Fe-metalloid (B, C, Si, P)-based ferromagnetic bulk metallic glasses (BMGs) containing glass-forming metal elements such as Al, Ga, Nb, Mo, Y and so forth have been developed.1-6) These alloys have a GFA leading to the formation of BMG rods with diameters of mm-order prepared by Cu-mold casting with much lower cooling rates than that of melt-spinning used for the production of the Fe-metalloid-based amorphous alloy ribbons with a thickness of less than about 50 μm without glass transition. The development of BMGs overcame the great disadvantage of the melt-spun amorphous ribbons. However, the glass-forming metal elements in BMGs result in a remarkable decrease in saturation magnetization (J_s) from 1.5–1.6 T of the representative Fe-Si-B amorphous alloys widely utilized by industries7) to less than about 1.3 T. The magnetic elements such as Co and Ni also have some beneficial effects on the GFA in most cases,8,9) however, the addition of these elements to Fe-based BMGs significantly decreases J_s in the same manner as the glass-forming elements; the substitution of Co for Fe at 50 at% in (Fe_{0.75}Si_{0.15}B_{0.15})_{90}Nb_4 significantly increases the critical rod-size of 1.5 mm to 5 mm in diameter, which is the largest size among the soft magnetic BMGs produced by Cu-mold casting, however, rapidly decreases to 1.1 T.10) The low J_s of the BMGs is a great disadvantage as soft magnetic materials. In addition, these metal elements are rare and expensive, and Al, Nb, Mo and Y also decrease the productivity due to their easy oxidation. It should be, thus, better to avoid the use of these metal elements for high J_s as well as conservation of earth resources and low material cost. Therefore, the development of Fe-based BMGs without any metal elements other than Fe and with relatively high Fe content have been desired for the last one decade, however, has been left unsolved matter over many years. We report a novel Fe_{75}Si_{15}B_{10}P_{5} bulk metallic glass with unusual combination of high J_s of 1.51 T due to high Fe content and high GFA leading to a glassy rod with a diameter of 2.5 mm despite not-containing any glass-forming metal elements.

2. Experimental

Fe-Si-B-(P) ingots were prepared by induction melting the mixture of pure metals of Fe (99.98 mass%), pre-melted Fe-P (99.9 mass%), and pure metalloid of crystal B (99.5 mass%) and Si (99.999 mass%) in an argon atmosphere. The alloy compositions represent nominal atomic percent. Amorphous or glassy alloys were produced in a ribbon form by the single roller melt-spinning method and in rod forms by the Cu-mold casting method. The as-spun and as-cast structures were examined by X-ray diffraction (XRD). The glass transition temperature (T_g) and crystallization temperature (T_x) were estimated by a differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s and the liquidus temperature (T_l) was also estimated by a thermogravimetry differential thermal analyzer at a cooling rate of 0.17 K/s. The density (ρ) was measured by the Archimedean method using a pycnometer with Helium gas at 298 K. Cross section of bulk rod with 2.5 mm in diameter was etched for 30 s at room temperature in a solution of 1% hydrofluoric acid and 99% distilled water, and was observed by an optical microscopy. J_s was measured under an applied field of 800 kA/m with a vibrating sample magnetometer. The coercivity (H_c) was measured under a field of 1 kA/m with a DC B-H loop tracer. The specimens for coercivity measurement were heated under a vacuum atmosphere of less than 2 × 10^{-4} Pa at a heating rate of 0.67 K/s and isothermal annealed at prescribed temperature for 0.6 or 7.2 ks, and then cooled to 295 K by the furnace cooling. Mechanical properties of Young’s modulus, compressive fracture strength, elastic strain, and...
Fe₈₀(SiₓB₇P₃₄)₂₄

Fig. 1 The compositional dependence of as-quenched structure, supercooled liquid region (Δ₄₇) for melt-spun alloys (a), and the critical rod-diameter (Dcı) produced by Cu-mold casting in Fe₇₆(SiₓB₇P₃₄)₂₄ (x + y + z = 1) alloy system.

fracture strain were measured with an Instron testing machine. The specimen dimension was 1.5 mm in diameter and 3 mm in length, and the strain rate was 5.0 × 10⁻⁴ s⁻¹. The characteristics of the fractured surface was studied by scanning electron microscopy (SEM). All the measurements were carried out at room temperature.

3. Results and Discussion

Figure 1 shows (a) the compositional dependence of as-quenched structure and supercooled liquid region (Δ₄₇) for melt-spun alloys and (b) the critical rod-diameter produced by Cu-mold casting in Fe₇₆(SiₓB₇P₃₄)₂₄ (x + y + z = 1) alloy system, respectively. The number in Fig. 1(a) represents the temperature interval (Δ₄₇), known to be one of the indicators for GFA. The T₄₀ and Tₓ were shown in Fig. 1(a) and (b), “glassy” and “amorphous” alloys are distinguished by the presence of glass transition. An amorphous phase was observed in a wide compositional range except higher Si, B and P contents than around 8%. Obvious glass transition was observed at the limited quaternary compositions in the amorphous-forming region and the large Δ₄₇ of over 40 K is observed in the range of x = 0.3–0.5, y = 0.2–0.5 and z = 0.2–0.4. The largest Δ₄₇ is 52 K for Fe₇₆Si₉B₉₆P₄₈ and Fe₇₆Si₉B₁₀P₅. The rod with a diameter of 2.5 mm was obtained for the above mentioned alloys and Fe₇₆Si₉B₁₀P₅ alloy, as shown in Fig. 1(b). Comparing Fig. 1(a) and Fig. 1(b), it can be noted that critical diameter (Dcı) coincides with Δ₄₇.

Figure 2 shows (a) the optical micrograph and (b) the XRD pattern taken from the cross section of the as-cast Fe₇₆Si₉B₁₀P₅ rod with a diameter of 2.5 mm. The XRD pattern reveals only typical halos, and no peaks corresponding to crystalline phases are visible. It is thus to be noticed that a single glassy phase is formed in the diameter range up to 2.5 mm.

It is important in applications as engineering materials to clarify the magnetic and mechanical properties of the Fe-metalloids BMGs. The Hₑ of Fe₇₆Si₉B₁₀P₅ glassy alloy with Δ₄₇ of 52 K and Fe₇₆Si₉B₁₅ amorphous alloy without glass transition as a function of annealing temperature is shown in Fig. 3. The extremely low Hₑ of 0.8 A/m at 653 K and rapidly increases with increasing annealing temperature above 653 K, even though an amorphous structure should remain in the temperature range, which is considerably lower than the crystallization temperature of 841 K. On the other hands, the Hₑ of the Fe₇₆Si₉B₁₀P₅ glassy alloy reaches a minimum value of 0.8 A/m at 748 K, 10 times smaller than the minimum Hₑ of 8.0 A/m for the amorphous alloy, and then slightly increases to 1.4 A/m at 773 K just below the glass transition temperature of 780 K. The ρ in as-quenched state was 7111 kg/m³ for the Fe₇₆Si₉B₁₅ amorphous alloy and 7054 kg/m³ for the glassy alloy. The ρ of
the glassy alloy significantly increases from 7054 kg/m$^3$ to 7207 kg/m$^3$ by 2.17% upon the optimum annealing at 748 K. This change is considered to originate from the glass transition from the as-quenched amorphous phase with some inhomogeneity to a glassy phase with a higher degree of atomic density of dense random packed structure. On the contrary, the $\beta$ of the amorphous alloy little changes by 0.22% with annealing because of lack of glass transition. Considering the minimum values of $H_c$ and the annealed structure for the alloys, as described above, the extremely low $H_c$ of 0.8 A/m for the glassy alloy can be explained as due to the dense packed glassy structure. Taking account of the difference in the optimum annealing temperature for $H_c$, 748 K for the glassy alloy and 653 K for the amorphous alloy, we can see that the Fe$_{76}$Si$_9$B$_{10}$P$_5$ glassy alloy exhibits the higher thermal stability of magnetic softness, which should indicate the higher stability of the glassy phase than the amorphous phase.

Table 1 summarizes $T_x$, $T_g$, $D_{cr}$, $\Delta T_x$, $T_g/T_1$, $\gamma$ and magnetic properties ($J_s$, $H_c$) for the Fe$_{76}$Si$_9$B$_{10}$P$_5$ BMG and the typical Fe-based ferromagnetic BMGs previously reported. Here, $\Delta T_x$, $T_g/T_1$ and $\gamma (= T_x/(T_g + T_1))$ are adopted as the parameters, and the larger all the parameters, the higher is the GFA. The Fe$_{76}$Si$_9$B$_{10}$P$_5$ BMG has the relatively high $\Delta T_x$ of 52 K, comparable to the other BMGs, and higher $T_g/T_1$ of 0.62 and $\gamma$ of 0.41 than those of the other Fe-based BMGs, which are probably one of the reasons for the high GFA of the Fe$_{76}$Si$_9$B$_{10}$P$_5$ BMG leading to the 2.5 mm-diameter specimen.

The Fe$_{76}$Si$_9$B$_{10}$P$_5$ BMG exhibits the highest $J_s$ of 1.51 T among the previously reported Fe-based BMGs due to the high Fe content of 76% and without any metal elements except Fe as well as high GFA leading to the 2.5 mm-diameter specimen.

The P-added Fe-based amorphous and glassy alloys have been investigated for four decades ago. The measured Young modulus is 175 GPa. SEM observations show that the fracture under compression occurs in a shear mode. On the specimen surfaces, it is noted that many localized shear bands near the fracture plane were observed, as shown in Fig. 4(c). The shear bands have a relatively high density near the fracture plane. The activation of the shear bands should be a direct evidence for the compressive plasticity of the Fe$_{76}$Si$_9$B$_{10}$P$_5$ BMG.
quaternary alloy exhibit the glass transition were reported. However, bulk glassy rod specimen with over 0.5 mm of a
diameter have been not yet found, even though
4. Conclusions

(1) The large $\Delta T_s$ of over 40 K is observed in the range of $x = 0.3–0.5$, $y = 0.2–0.5$ and $z = 0.2–0.4$ for Fe$_{74}$Si$_{10}$B$_{16}$P$_{6}$ ($x + y + z = 1$) alloy system. The largest $\Delta T_s$ is 52 K for Fe$_{76}$Si$_{8}$B$_{9}$P$_{6}$ and Fe$_{76}$Si$_{8}$B$_{10}$P$_{5}$.

(2) Fe$_{76}$Si$_{9}$B$_{10}$P$_{5}$, Fe$_{76}$Si$_{9}$B$_{10}$P$_{5}$ and Fe$_{76}$Si$_{9}$B$_{10}$P$_{5}$ alloys have high GFA leading to a glassy rod with a diameter of 2.5 mm despite not-containing any glass-

(3) The higher $J_s$ of 1.51 T than those of the previously reported Fe-based BMGs was obtained for Fe$_{76}$Si$_{9}$B$_{10}$P$_{5}$ alloy due to the high Fe content of 76% and without any metal elements except Fe.

(4) The extremely low $H_c$ of 0.8 A/m and the high strength of 3.3 GPa and the plastic strain to final failure of 0.7% were obtained for Fe$_{76}$Si$_{9}$B$_{10}$P$_{5}$.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, “Materials Science of Bulk


REFERENCES


