表: 著者の詳細

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Soft Magnetic Properties of Fe-Based Bulk Amorphous Alloys

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A large supercooled liquid region over 50 K before crystallization were obtained in amorphous Fe-(Al, Ga)-(P, C, B, Si), Fe-(Cr, Mo, Nb)- (Al, Ga)-(P, C, B) and (Fe, Co, Ni)-(Zr, Hf)-M-B (M = Ti, Hf, V, Nb, Ta, Cr, Mo, W) systems and their bulk glassy alloys were produced in a thickness range below 2 mm for the Fe-(Al, Ga)-(P, C, B, Si) system and 6 mm for the Fe-Co-(Zr, Nb, Ta)-(Mo, W)-B system by copper mold casting. The ring-shape glassy Fe-(Al, Ga)-(P, C, B, Si) alloys produced by copper mold casting exhibit much better soft magnetic properties than the ring-shape alloy made from the melt-spun ribbon as a result of the formation of a unique domain structure. The bulk Fe-(Al, Ga)-(P, C, B, Si) alloys were also produced by consolidating the amorphous powders using an electric-pulse-sintering method. The large elongation in the supercooled liquid region enables production of the bulk samples with relatively higher density and better soft magnetic properties than those of the sintered Fe-Si-B bulk amorphous sample. The bulk glassy (Fe, Co, Ni)12M4B20 (M = Zr, Hf) systems exhibit large supercooled liquid regions of 72 K for M = Zr, and of 82 K for M = Hf. The replacement of Zr or Hf by 2 at% Nb or Ta causes a further increase in the supercooled liquid region. The good combination of high glass-forming ability and good soft magnetic properties indicates the possibility of future development as a new bulk glassy magnetic material.

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Keywords: ferromagnetic bulk glassy alloy, rapid solidification, wide super cooled liquid region, soft magnetic properties

1. Introduction

To date, it has been found that bulk amorphous alloys in a number of alloy systems such as Ln-Al-TM,1) M2-Ln-TM,2) Zr-Al-TM,3) Ti-Zr-TM4,5) and Ti-Zr-Be-TM6) etc. (Ln = lanthanide metals, TM = transition metal) have a wide supercooled liquid region ($\Delta T_\text{c}$ = crystalization temperature ($T_\text{c}$) - glass transition temperature ($T_\text{g}$)) over 100 K before crystallization. The appearance of the high supercooled liquid region implies that the alloys have high resistance against crystallization. Consequently, these bulk amorphous alloys with large $\Delta T_\text{c}$ values have been confirmed to have an extremely large glass-forming ability (GFA), which enables the production of bulk amorphous samples. These bulk amorphous alloys have so unique properties that they will be expected to be very useful materials for industrial use. Practically, the Zr-based glassy alloy has been used as a high specific-strength material.

Recently, some kinds of Fe- and Co-based amorphous alloys with large $\Delta T_\text{c}$ combined with good soft magnetic properties have been found.7,8) We have already reported that the Fe-Al-Ga-P-C-B-Si glassy alloy has a wide $\Delta T_\text{c}$ of about 60 K and its maximum thickness to form a single amorphous phase was about 280 μm prepared by single-roller melt-spinning method.9) It has been also found that a wide supercooled liquid region exceeding 80 K before crystallization is obtained for amorphous alloys in Fe-Co-Ni-Hf-B systems.10) This paper summarizes the formation, thermal stability and magnetic properties of these new ferromagnetic bulk glassy alloys, and also describe the bulk Fe-Al-Ga-P-C-B-Si alloy produced by consolidating the amorphous powders.


It has previously been shown that the bulk glassy alloys have useful properties of high glass-forming ability (GFA), high mechanical strength, high elastic energy up to yielding, good workability, good bondability, etc. The Fe- and Co-based amorphous ribbons prepared by melt spinning exhibit good soft magnetic properties at room temperature.11,12) Based on the nonferrous alloy compositions with high GFA found before 1993, the second author has noticed the existence of three empirical roles for achievement of high GFA for metallic alloys.13,14) That is, (1) multicomponent alloy systems consisting of more than three elements, (2) significant difference in atomic size ratios above about 12% among the main three constituent elements, and (3) negative heats of mixing among the main three constituent elements. Based on the three empirical rules for high GFA, we have searched for Fe- and Co-based glassy alloys with a large supercooled liquid region because the high stability of the supercooled liquid against crystallization enables us to produce bulk glassy alloys. The compositional dependence of $\Delta T_\text{c}$ was examined for melt-spun Fe$_{90}$P$_{10}$B$_4$Si$_4$ glassy alloys.15) The glassy alloys with glass transition are formed in the range of 9 to 13 at.% P, 3 to 5 at.% B and 3 to 7 at.% Si and the largest $\Delta T_\text{c}$ of 36 K is obtained for Fe$_{90}$P$_{10}$B$_4$Si$_4$. We also examined the effect of additional Al and Ga on the increase of $\Delta T_\text{c}$ for the Fe-P-B-Si glassy alloys because the addition of their elements satisfies the three empirical rules. Figure 1 shows the compositional dependence of $\Delta T_\text{c}$ for the glassy Fe$_{74}$Al$_2$Ga$_2$(P, B, Si)$_{20}$ alloys.15) The addition of Al and Ga extends the composition range of glassy alloys and the largest $\Delta T_\text{c}$ increases to 49 K. These glassy alloys crystallize through a single exothermic reaction, accompanying the simultaneous
precipitation of five crystalline phases of $\alpha$-Fe, Fe$_3$P, Fe$_3$B, FeP and Fe$_7$B. This crystallization mode also indicates the necessity of long-range rearrangements of the elements. However, the long-range rearrangements are not always easy in the Fe-based glassy alloys with a higher degree of dense random packed structure, leading to a high stability of supercooled liquid.

These Fe-based glassy alloys exhibit good soft magnetic properties. Table 1 summarizes the saturated magnetization ($I_s$), residual magnetization ($I_r$), squareness ratio ($I_r/I_s$), coercive force ($H_c$) and effective permeability ($\mu_e$) at 1 kHz for the Fe–P–B–Si, Fe–Al–P–B–Si and Fe–Al–Ga–P–B–Si glassy alloys.\(^{15}\) The Fe-based glassy alloys have useful combined characteristics, i.e., good soft magnetic properties of high $I_s$ of 1.1 to 1.3 T, low $H_c$ of 1 to 5 A/m and high $\mu_e$ of 19000 to 22000 and high stability of supercooled liquid, which have not been reported for Fe-based amorphous alloys reported hitherto.

A larger supercooled liquid region has also been recognized for another system of Fe–Al–Ga–P–C–B\(^{16}\) which satisfies the three empirical rules. Figure 2 shows the DSC curves of the Fe$_{77}$Al$_{13}$Ga$_3$P$_{11}$C$_6$B$_4$\(^{16}\) and Fe$_{77}$Al$_{13}$Ga$_3$P$_{11}$C$_6$B$_4$M$_x$ (M = Nb, Mo, Cr or Co)\(^{17}\) glassy alloys. The large supercooled liquid region exceeding 60 K is observed and the addition of a small amount of Nb, Mo or Cr is effective for extension of the supercooled liquid region. The largest $\Delta T_s$ is 64 K for Fe$_{79}$Al$_{16}$Ga$_3$P$_{11}$C$_6$B$_4$Nb$_2$. These glassy alloys also crystallize through a single exothermic reaction accompanying the precipitation of five crystalline phases, in agreement with that for the Fe–Al–Ga–P–B–Si glassy alloys. It has subsequently been found that the replacement of P by only 1 at%Si causes further extension of the supercooled liquid region to 67 K.\(^{18}\) The use of the 1%Si-containing alloy has enabled us to produce bulk glassy alloys in a cylindrical form with larger diameters of 2 to 3 mm and in a sheet form of 1 mm in thickness, 5 mm in width and 70 mm in length. The bulk glassy alloys in the Fe–Al–Ga–P–C–B and Fe–Al–Ga–P–C–B–Si systems have been reported to have the $T_c$ of 580 to 610 K from the thermomagnetic data. By using the Fe$_{70}$Al$_{13}$Ga$_3$P$_{6.65}$C$_{5.75}$B$_{4.6}$Si$_{1.5}$ alloys with $\Delta T_s$ above 60 K, a ring-shape glassy alloy with a thickness of 1 mm, an outer diameter of 10 mm and an inner diameter of 6 mm was formed by the copper mold casting method,\(^{19}\) as shown in Fig. 3. This bulk alloy has a good luster for typical metallic amorphous alloys and no distinctive contrast revealing the precipitation of crystalline phase is seen. Figure 4 shows the optical micrograph, SEM image, the bright field image and the

\[\text{Table 1} \quad \text{Soft magnetic properties of Fe–P–B–Si, Fe–Al–P–B–Si and Fe–Al–Ga–P–B–Si amorphous alloys.}\]

\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Composition & $\mu_e$ & $H_c$ (A/m) & $I_s$ (T) & $I_r$ (T) & $I_r/I_s$ & $\lambda_4$ (10$^{-6}$) & $T_c$ (K) & $T_s$ (K) & $\Delta T_s$ (K) \\
\hline
Fe$_{80}$P$_{12}$B$_4$Si$_4$ & 5800 & 1.3 & 1.10 & 0.32 & 0.29 & 31 & 753 & 789 & 36 \\
Fe$_{76}$Al$_{14}$P$_{12}$B$_4$Si$_4$ & 2600 & 12.7 & 0.96 & 0.30 & 0.31 & 30 & 738 & 780 & 46 \\
Fe$_{74}$Al$_{16}$Ga$_3$P$_{12}$B$_4$Si$_4$ & 1900 & 19.1 & 0.91 & 0.27 & 0.30 & 21 & 737 & 786 & 49 \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Composition & $\mu_e$ & $H_c$ (A/m) & $I_s$ (T) & $I_r$ (T) & $I_r/I_s$ & $\lambda_4$ (10$^{-6}$) & $T_c$ (K) & $T_s$ (K) & $\Delta T_s$ (K) \\
\hline
Fe$_{80}$P$_{12}$B$_4$Si$_4$ & 22000 & 1.1 & 1.34 & 0.46 & 0.34 & & & & \\
Fe$_{76}$Al$_{14}$P$_{12}$B$_4$Si$_4$ & 21000 & 2.6 & 1.24 & 0.43 & 0.35 & & & & \\
Fe$_{74}$Al$_{16}$Ga$_3$P$_{12}$B$_4$Si$_4$ & 19000 & 6.4 & 1.14 & 0.40 & 0.35 & & & & \\
\hline
\end{tabular}
selected-area diffraction pattern at the central region of the cast sample observed by TEM. These photographs show only the featureless contrast and the halo pattern based on the homogeneous amorphous phase. It is, therefore, concluded that the cast bulk ring sample consists only of amorphous single phase. The glassy ring also has smooth outer surface and good metallic luster. The feature of the DSC curves of the ring-shape glassy alloy is the same as that for the melt-spun ribbon.

The glassy alloys in cylinder and ring forms also exhibited good soft magnetic properties. The hysteresis $I$-$H$ loop of the as-cast Fe–Al–Ga–P–C–B–Si glassy ring with a thickness of 1 mm is shown in Fig. 5, in comparison for the data of the ring shape with a thickness of 0.02 mm made from melt-spun ribbon. The ring-shape glassy alloy exhibits high $I_s$ of 1.2 T, low $H_c$ of 2.2 A/m and rather low saturated magnetostriiction ($\lambda_s$) of $21 \times 10^{-6}$. The maximum permeability ($\mu_{\text{max}}$) is as

![Fig. 5 Hysteresis $I$-$H$ loops of the as-cast ring-shape Fe$_{70}$Al$_{15}$Ga$_3$P$_{5.65}$C$_{5.75}$B$_{4.6}$Si$_{13}$ glassy alloy with a thickness of 1 mm, an inner diameter of 6 mm and an outer diameter of 10 mm. The data of the ring-shape sheet with a thickness of 0.02 mm made from the melt-spun glassy ribbon are also shown for comparison.](image)

![Fig. 4 Optical micrograph, SEM image, bright field image and selected-area diffraction pattern at the central region of the cast sample observed by TEM.](image)
high as 110000. The $H_c$ and $\mu_{\text{max}}$ values are superior to those (3.7 A/m and 27000) for the melt-spun ring-shape alloy. The remarkable improvement of the soft magnetic properties has been demonstrated so as to result from the significant difference in magnetic domain structure. Figure 6 shows the micrographs of the magnetic domain structures for the bulk ring sample and the ring shape sheet sample. The domain structure for the bulk sample looks like a coarse concentric circle pattern in spite of vague outline. On the other hand, that for the sheet sample forms a fine radial pattern clearly. This indicates that the concentric circle pattern is more favorable to magnetize at the circumference direction than the fine radial pattern in the low magnetic field. The reason is that, at the concentric circle pattern, not all of the domain wall displacements are needed on account of a part of the easy axis having already fitted toward that direction. The difference in the magnetic domain pattern between the bulk sample and the sheet sample arises presumably due to the difference in distribution of inner stress caused by the preparation methods and their sample thicknesses. A detailed investigation of the relation between the domain structure and inner stress for these samples will give rise to some insight in the clarification of the reason for the achievement of the large $\mu_{\text{max}}$ and low $H_c$ of the ring-shape bulk Fe-based glassy alloys.

Recently, the bulk glassy alloys have been prepared by consolidating amorphous alloy powders using an electric-pulse-sintering (SPS) method in the temperature range of the supercooled liquid region. Figure 7 shows the outer morphology of the disk shape Fe$_{70}$Al$_3$Ga$_2$P$_{9.65}$C$_{5.75}$B$_{4.6}$Si$_3$ alloy sample with 18 mm in diameter and 1 mm in thickness prepared by the sintering method. The sample prepared by sintering also consists only of amorphous phase. The magnetic properties and relative density of the cast and sintered Fe-based bulk glassy alloys, melt-spun ribbon and sintered Fe$_{78}$Si$_9$B$_{13}$ bulk are summarized in Table 2. The relative density of the sintered bulk glassy sample is about 99%, which is much higher than 94% of the sintered Fe–Si–B bulk sample prepared by the same method. Figure 8 shows the DSC and TMA curves of Fe$_{70}$Al$_3$Ga$_2$P$_{9.65}$C$_{5.75}$B$_{4.6}$Si$_3$ glassy alloy ribbon. A large elongation can be observed in $\Delta T_c$ region. It is, therefore, considered that the high density of the sintered Fe-based glassy alloy is presumably due to its viscous flow occurred in the supercooled liquid region.

Figure 9 shows the hysteresis $I$–$H$ loop of the sintered bulk amorphous sample. The data on the bulk amorphous Fe$_{78}$Si$_9$B$_{13}$ alloy prepared by the same method under the condition without precipitation are also shown for comparison.
The soft magnetic properties of the sintered bulk sample are much better than those of the bulk Fe–Si–B sample, though these are not so good as those of the casting and melt-spin samples. Generally speaking, the conventional bulk amorphous alloys prepared by powder metallurgy do not have good soft magnetic properties because a homogeneous structure cannot be obtained for its low glass forming ability and low deformability. It is, therefore, concluded that the sintered bulk Fe-based glassy alloy has higher structural homogeneity.

3. Bulk Glassy (Fe, Co, Ni)_{70}(Zr, Hf, Nb, Ta)_{10}B_{20} Soft Magnetic Alloys

In addition to the Fe–(Al, Ga)–(P, C, B, Si) glassy alloys, the (Fe, Co, Ni)–Zr–B glassy alloys also exhibited a large supercooled liquid region before crystallization. The large $\Delta T_x$ values above 65 K are obtained in the wide Fe-rich composition range of 3 to 20 at%Co and 3 to 28 at%Ni, as shown in Fig. 10. The $\Delta T_x$ are larger than those for the previously reported Fe-based glassy alloys. Bulk glassy alloys in the Fe–Co–Zr–M–B (M = Nb or Ta) systems in a cylindrical form of 3 and 5 mm in diameters were prepared by the copper mold casting method. These bulk glassy alloys exhibit smooth outer surface and good metallic luster. No contrast revealing the precipitation of a crystalline phase is seen over the whole outer surface.

The new Fe-based glassy alloys also exhibited good soft magnetic properties. The ferromagnetic characteristics are obtained in the wide composition range except the Ni-rich corner for the (Fe, Co, Ni)$_{70}$Zr$_{10}$B$_{20}$ glassy alloys. The $H_c$ decreases gradually from 6 to 3 A/m with increasing the Fe content and the Fe-rich glassy alloys with $\Delta T_x$ above 65 K exhibit low $H_c$ below 5 A/m. The composition dependence of $I_x$, $\mu_e$ at 1 kHz and $\lambda_6$ is summarized in Fig. 11. The $I_x$ increases from 0.3 to 0.9 T with increasing the Fe content, while the $\lambda_6$ shows zero in the Co-rich composition range and increases monotonously to $15 \times 10^{-8}$ with increasing the Fe content. The compositional dependence of $\mu_e$ is complicated and the maximum of about 20000 is obtained in the Fe- and Co-rich composition ranges. From the compositional dependence of the above-described soft magnetic properties, it is recognized that the new glassy alloys exhibit good soft magnetic properties of $I_x$ above 0.9 T, $H_c$ of 3 to 4 A/m, $\lambda_6$ of 12–15 $\times 10^{-6}$ and $\mu_e$ of 20000 in the Fe-rich range and $I_x$ of 0.5 T, $H_c$ of 6 A/m, nearly zero $\lambda_6$ and $\mu_e$ of 20000 in the Co-rich range.

The replacement of Zr by 2 at%Nb or Ta for Fe$_{56}$Co$_{12}$Ni$_7$Zr$_{10}$B$_{20}$ glassy alloys caused a further increase in $\Delta T_x$ from 72 to 87 K. Furthermore, the 2%Nb-containing alloy exhibits an improved $\mu_e$ of 25000 in the maintenance of nearly the same low $H_c$ and $\lambda_6$ values as those for the 10%Zr alloy. Table 3 summarizes the $I_x$, $H_c$, $\mu_e$ and $T_c$ of the Fe$_{56}$Co$_{12}$Ni$_7$Zr$_{10}$M$_2$B$_{20}$ (M = Ti, Hf, V, Nb, Ta, Cr, Mo or
W) glassy alloys. The best combination of soft magnetic properties is obtained for the Ti-, Nb-, Ta- and Cr-containing alloys and their $I_e$, $H_{cr}$, $\mu_e$ and $T_c$ are in the ranges of 0.75 to 0.82 T, 1.1 to 2.7 A/m, 10040 to 25000 and 503 to 531 K, respectively.

The wide supercooled liquid region and the good soft magnetic properties have been also obtained for (Fe, Co, Ni)–Hf–B alloys. The $\Delta T_c$ reaches a maximum value of 82 K at the composition of Fe$_{50}$Co$_{25}$Ni$_{15}$Hf$_{10}$B$_{20}$. This alloy exhibits good soft magnetic properties of $I_e$ of 0.82 T, $H_{cr}$ of 2.5 A/m, $\lambda_e$ of $10^{-6}$ and $\mu_e$ of 17800. We also have made the partial replacement of Hf by 2 at% Nb or Ta to improve the glass-forming ability of the Fe$_{50}$Co$_{25}$Ni$_{15}$Hf$_{10}$B$_{20}$ alloy. Figure 12 shows DSC curves of the Fe$_{50}$Co$_{25}$Ni$_{15}$Hf$_{10}$B$_{20}$ (M = Hf, Nb or Ta) amorphous alloys. One can see a distinct glass transition, followed by a wide supercooled liquid region in the temperature range before crystallization for these alloys. The $\Delta T_c$ increases to large values exceeding 90 K by the addition of 2 at% M, being larger by about 10 K than the largest value for (Fe, Co, Ni)–Zr–M–B (M = Nb or Ta) alloys. Table 4 summarizes $I_e$, $H_{cr}$, $\mu_e$ at 1 kHz and $\lambda_e$ for the Fe$_{50}$Co$_{25}$Ni$_{15}$Hf$_{10}$B$_{20}$ amorphous alloys, which were subjected to annealing for 300 s at 800 K just below $T_c$. It is seen that the replacement of Hf by M elements causes a decrease of $I_e$. The $I_e$ decreases by 0.06 to 0.11 T only by the addition of 2 at% M. The $\mu_e$ values also slightly decrease, even though they keep the high values of 15500 to 16500. Additionally, the $H_{cr}$ also exhibits a low value of 1.0 A/m. From the compositional dependence of the thermal stability of the supercooled liquid and the magnetic properties, it is concluded that the Fe$_{50}$Co$_{25}$Ni$_{15}$Hf$_{10}$B$_{20}$ (M = Nb or Ta) amorphous alloys have the useful characteristics of high glass-forming ability and good soft magnetic properties.

4. Conclusions

By using the three empirical rules as a guiding principal for obtaining bulk glassy alloys, Fe–(Al, Ga)–(P, C, B, Si) and (Fe, Co, Ni)–(Zr, M)–B systems with high $\Delta T_c$ of 60–90 K and good soft magnetic properties were obtained. The maximum diameter is 2.2 mm for Fe$_{77}$Al$_{12}$Ga$_{10}$P$_{2.4}$C$_{2}$B$_{7.5}$Si$_{2}$ and 5 mm for Fe$_{65}$Co$_{7}$Zr$_{10}$Mo$_{5}$W$_{2}$B$_{15}$ by copper mold casting. The sintered bulk Fe$_{65}$Al$_{12}$Ga$_{10}$P$_{2.4}$C$_{2}$B$_{7.5}$Si$_{2}$ alloy with the relative density of 99% can be produced. The success of forming the ferromagnetic bulk glassy alloy is promising for future development as a new type of magnetic materials.

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