Soft Magnetic Properties and Wide Supercooled Liquid Region of Fe-P-B-Si Base Amorphous Alloys

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The glass transition phenomenon was observed in the temperature range before crystallization for amorphous $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$ alloys. The temperature interval of the supercooled liquid region (ΔT_x) is defined by the difference between glass transition temperature (T_g) and crystallization temperature (T_x) and the largest $\Delta T_x (= T_x - T_g)$ value is 36 K for $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$ where the crystallization reaction takes place through a single stage. The ΔT_x value increases by the dissolution of Al and/or Ga and the largest value is 46 K for $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and 49 K for $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$. The effectiveness of additional Al and/or Ga elements is interpreted to result from the formation of a higher degree of dense random packed structure by dissolving the Al and Ga elements with larger atomic sizes. These Fe-based amorphous alloys exhibiting the glass transition phenomenon crystallize through a single-stage exothermic reaction due to the precipitation of five crystalline phases $\alpha\text{-Fe}$, Fe_3B , Fe_2B , Fe_3P and FeP . The long-range atomic rearrangement necessary for the nearly simultaneous precipitation of the five crystalline phases seems to cause the appearance of the supercooled liquid region through the retardation of the precipitation reaction. The Fe-based amorphous alloys exhibit good soft magnetic properties of 1.14 to 1.34 T for saturation magnetization, 1.1 to 6.4 A/m for coercive force and 19000 to 22000 for permeability at 1 kHz in the annealed state for 600 s at 723 K. The synthesis of the Fe-based amorphous alloys exhibiting good soft magnetic properties and a wide supercooled liquid region is important for future development of a new type of soft magnetic material.

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Keywords: iron-based amorphous alloy, glass transition, supercooled liquid region, soft magnetic properties, single-stage crystallization, rapid solidification

I. Introduction

In addition to nonferrous bulk amorphous alloys with large glass-forming ability⁽¹⁾⁻⁽⁶⁾, it has recently been reported⁽⁷⁾⁻⁽¹¹⁾ that multicomponent Fe-based amorphous alloys consisting of three groups of Fe, (Al, Ga) and (P, B, C, Ge, Si) exhibit a wide supercooled liquid region before crystallization and have a large glass-forming ability leading to the formation of bulk amorphous alloy samples with diameters above 1 mm. Subsequently, multicomponent Co-based amorphous alloys consisting of Co, (Al, Ga) and (P, B, C) have also been found⁽¹²⁾ to exhibit the glass transition, followed by a supercooled liquid region before crystallization. These Fe- and Co-based amorphous alloys exhibiting the supercooled liquid region always contain metalloids of a nearly constant amount (≈ 20 at%) as well as simple metals of about 7 at%. These fixed composition ratios of the constituent elements with larger, intermediate and smaller atomic sizes imply that the atomic bonding nature and atomic spacing are important factors for formation of an amorphous phase exhibiting the glass transition resulting from the high thermal stability of the supercooled liquid. Thus, the Fe- and Co-based amorphous alloys exhibiting the glass transition phenomenon always contain P, B and C elements. Little is known about the influence of the elimination of C on the appearance of the glass transition and

supercooled liquid region for the Fe- and Co-based amorphous alloys. Considering that the free energies for formation of carbides between Fe or Co and C elements at 1273 K are -0.080 kJ/mol for Fe_3C and $+8.4$ kJ/mol for Co_3C ⁽¹³⁾, these atomic pairs without largely negative bonding pairs are expected to be eliminated for the formation of an amorphous phase with the supercooled liquid region before crystallization. The elimination of C implies the decrease in the metalloid content and hence allows us to expect the increase in saturation magnetization. This paper is intended to present the composition ranges in which an amorphous phase exhibiting the glass transition is formed in rapidly solidified $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$, $\text{Fe}_{75}\text{Al}_5(\text{P}, \text{B}, \text{Si})_{20}$ and $\text{Fe}_{73}\text{Al}_5\text{Ga}_2(\text{P}, \text{B}, \text{Si})_{20}$ alloys and to examine the thermal stability, crystallization behavior and magnetic properties of their amorphous alloys.

II. Experimental Procedure

Multicomponent $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$, $\text{Fe}_{80-x}\text{Al}_x(\text{P}, \text{B}, \text{Si})_{20}$ and $\text{Fe}_{78-x}\text{Al}_x\text{Ga}_2(\text{P}, \text{B}, \text{Si})_{20}$ alloys were used in the present study. The ingots were prepared by induction melting a mixture of pure Fe, Al and Ga metals, pre-alloyed Fe-P ingots and pure B and Si crystals in a purified argon atmosphere. The compositions are nominally expressed in atomic per cent. From the master alloy ingot, a ribbon with a cross section of about 0.02×1.0 mm² was prepared by a single roller melt-spinning technique in an argon atmosphere. The molten alloy was ejected from the temperature which is higher by about 150 K than the

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melting temperature. The amorphicity of the melt-spun ribbon was examined by X-ray diffractometry with $\text{Cu-K}\alpha$ radiation and transmission electron microscopy (TEM). The TEM sample was prepared by thinning electrolytically the melt-spun ribbon at approximately 273 K in a solution of 10% perchloric acid and 90% methanol in volume ratio. The apparent specific heat (C_p) associated with Curie temperature (T_c), glass transition and crystallization was measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). Magnetization and coercive force under an applied field of 800 kA/m were measured at room temperature with a vibrating sample magnetometer (VSM). Hysteresis B-H loop under an applied field of 1.6 kA/m was also measured with a B-H loop tracer.

III. Results

Figure 1 shows the compositional dependence of as-quenched structure and temperature interval of supercooled liquid region for the melt-spun $\text{Fe}_{80}(\text{P}_{1-x-y}\text{B}_x\text{Si}_y)_{20}$ alloys. The numbers in the figure represent the temperature interval defined by the difference between glass transition temperature (T_g) and crystallization temperature (T_x), $\Delta T_x (= T_x - T_g)$. The amorphous single phase is formed in a wide composition range of 4 to 16 at%P, 2 to 12%B and 2 to 12%Si. No amorphous phase is formed in the Fe-P-B-Si alloys containing a large amount of Si. The amorphous alloys exhibiting a supercooled liquid region before crystallization are limited to the narrow composition range of 9 to 13%P, 3 to 5%B and 3 to 7%Si and the ΔT_x value is in the range of 17 to 36 K. It is seen that the glass transition phenomenon is observed in the Fe-P-B-Si alloys containing a larger amount of P among the three metalloid elements and the largest ΔT_x value is obtained for $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$. Furthermore, the

Fig. 1 Composition range in which an amorphous phase exhibiting the glass transition is formed in rapidly solidified $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$ alloys. The numbers represent the temperature interval of the supercooled liquid region defined by the difference between T_g and T_x , $\Delta T_x (= T_x - T_g)$.

effect of the three metalloid elements on the formation of an amorphous phase is the greatest for P, followed by B and then Si. In order to confirm the formation of an amorphous single phase in the $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$ alloys, the bright-field electron micrograph (a), selected-area electron diffraction pattern (b) and X-ray diffraction pattern (c) of the melt-spun $\text{Fe}_{80}\text{P}_{11}\text{B}_4\text{Si}_5$ alloy are shown in Fig. 2. The bright-field electron micrograph reveals only a featureless contrast and no appreciable contrast corresponding to a crystalline phase is seen. The electron and X-ray diffraction patterns consist only of halo rings and a broad peak, respectively. These results indicate clearly that the Fe-P-B-Si alloy is composed of an amorphous phase. Figure 3 shows the differential scanning calorimetric (DSC) curves of the $\text{Fe}_{80}\text{P}_{11}\text{B}_4\text{Si}_5$, $\text{Fe}_{80}\text{P}_{12}\text{B}_3\text{Si}_5$ and $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloys with the ΔT_x values of 26, 27 and 36 K, respectively. An endothermic reaction due to the glass transition marked with T_g is seen for the three alloys and a supercooled liquid region is scarcely observed in the temperature range just before crystallization only for the $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$ alloy. Furthermore, one can notice that only the $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloy with the supercooled liquid region crystallizes through a single exothermic reaction, indicating a close relation between the appearance of the supercooled liquid region and the single-stage crystallization reaction.

We examined the effect of additional Al element on the thermal stability of the supercooled liquid region for $\text{Fe}_{80-x}\text{Al}_x\text{P}_{12}\text{B}_4\text{Si}_4$ alloys. The Al element was chosen based on the previous information⁽⁷⁾⁻⁽¹¹⁾ that the dissolution of Al element with a much larger atomic size as compared with the other constituent elements is effective for the increase in ΔT_x value. Figure 4 shows the changes in T_g , T_x and ΔT_x values as a function of Al content for

Fig. 2 Bright-field electron micrograph (a), selected-area electron diffraction pattern (b) and X-ray diffraction pattern (c) of a rapidly solidified $\text{Fe}_{80}\text{P}_{11}\text{B}_4\text{Si}_5$ alloy.

Fig. 3 DSC curves of amorphous $\text{Fe}_{80}\text{P}_{11}\text{B}_4\text{Si}_5$, $\text{Fe}_{80}\text{P}_{12}\text{B}_3\text{Si}_5$ and $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$ alloys exhibiting the glass transition.

Fig. 4 Changes in T_g , T_x and $\Delta T_x (= T_x - T_g)$ with Al content for amorphous $\text{Fe}_{80-x}\text{Al}_x\text{P}_{12}\text{B}_4\text{Si}_4$ alloys.

the $\text{Fe}_{80-x}\text{Al}_x\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloys. The T_g and T_x values decrease by the dissolution of a small amount of Al, show minimum values of 737 and 770 K, respectively, at 2%Al and then increase gradually with further increasing Al content. The resulting ΔT_x value shows a maximum value of 46 K at 4%Al. Consequently, the changes in the glass formation and ΔT_x with metalloid composition were examined for the alloy series $\text{Fe}_{76}\text{Al}_4(\text{P}, \text{B}, \text{Si})_{20}$. As shown in Fig. 5, the addition of 4%Al causes the significant extension of the composition

Fig. 5 Composition range in which an amorphous phase exhibiting the glass transition is formed in rapidly solidified $\text{Fe}_{76}\text{Al}_4(\text{P}, \text{B}, \text{Si})_{20}$ alloys. The numbers represent the ΔT_x values.

range in which the glass transition is observed and the increase in ΔT_x , in addition to the extension of the glass formation range to the B-rich composition region. The largest ΔT_x value is obtained for $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and the metalloid composition at which the largest ΔT_x value is obtained agrees with that for the $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$ alloys without Al element. It is therefore said that the dissolution of the optimum amount of Al element is very effective for the increase in the thermal stability of the supercooled liquid region before crystallization.

It has previously been reported that the simultaneous dissolution of Al and Ga elements causes a further increase in ΔT_x for the Fe-P-B-C⁽⁷⁾ and Fe-P-B-C-Ge⁽⁸⁾ amorphous alloys. Consequently, we examined the effect of the addition of 2 at.%Ga on the ΔT_x value for the Fe-Al-P-B-Si alloys. Figure 6 shows the changes in T_g , T_x and ΔT_x values as a function of Al content for $\text{Fe}_{78-x}\text{Al}_x\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloys. The Ga composition was chosen because 2 at.%Ga was an optimum content for the achievement of the largest ΔT_x value for the Fe-Al-P-B-C and Fe-Al-P-B-C-Ge alloys. The T_x increases gradually with increasing Al content and shows a maximum value at 6 at.%Al, while the T_g remains almost constant in the range up to 4%Al, increases with increasing Al content and shows a maximum at 6%Al. As a result, the ΔT_x value shows a maximum value of 49 K at 4%Al, as shown in Fig. 6. The addition of 2 at.%Ga causes an increase in ΔT_x by 4 K at the same Al content of 4%. Figure 7 shows the composition range in which an amorphous phase is formed in the $\text{Fe}_{74}\text{Al}_4\text{Ga}_2(\text{P}_{1-x-y}\text{B}_x\text{Si}_y)_{20}$ alloys and the compositional dependence of the ΔT_x values. Although the glass formation range is narrower as compared with the $\text{Fe}_{76}\text{Al}_4(\text{P}, \text{B}, \text{C})_{20}$ alloys, the ΔT_x value increases for almost all the alloys and the largest ΔT_x value is 49 K for $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$. The optimum metalloid composition at which the largest ΔT_x value is obtained in the Fe-P-B-Si system remains unchanged in the Fe-Al-P-B-Si and Fe-Al-Ga-P-B-Si

Fig. 6 Changes in T_g , T_x and ΔT_x with Al content for amorphous $\text{Fe}_{78-x}\text{Al}_x\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ alloys.

Fig. 7 Composition range in which an amorphous phase exhibiting the glass transition is formed in rapidly solidified $\text{Fe}_{74}\text{Al}_4\text{Ga}_2(\text{P}, \text{B}, \text{Si})_{20}$ alloys. The numbers represent the ΔT_x values.

systems. As examples, Fig. 8 shows the DSC curves of the $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{14}\text{B}_2\text{Si}_4$, $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{10}\text{B}_6\text{Si}_4$ amorphous alloys with ΔT_x values of 38, 49 and 42 K, respectively. The three alloys exhibit the glass transition, followed by the appearance of a supercooled liquid region and then a single exothermic reaction due to crystallization. It is again confirmed that the appearance of the wide supercooled liquid region is closely related to the single-stage crystallization process.

We examined the crystallized structure after the single-stage exothermic reaction for the $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloys by X-ray diffractometry. Figure 9 shows the X-ray diffraction patterns of the three amorphous alloys an-

Fig. 8 DSC curves of amorphous $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{14}\text{B}_2\text{Si}_4$, $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{10}\text{B}_6\text{Si}_4$ alloys exhibiting the glass transition.

Fig. 9 X-ray diffraction patterns of amorphous $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ alloys annealed for 600 s at 843, 823 and 833 K, respectively.

nealed for 600 s at temperatures between 823 and 843 K corresponding to the temperature region higher than the exothermic peak. As identified in Fig. 9, the diffraction

peaks consist of five phases α -Fe, Fe_3B , Fe_2B , Fe_3P and FeP for all the alloys and the crystallized phases are independent of the existence of Al and Ga elements. The identified results allow us to conclude that the single exothermic peak is due to the simultaneous precipitation of the five crystalline phases. That is, the appearance of the wide supercooled liquid region may be attributed to the simultaneous precipitation of the five kinds of crystalline phases from the supercooled liquid.

The $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloys exhibited ferromagnetism with Curie temperatures of 613, 599 and 594 K, respectively. Figure 10 shows the B-H hysteresis loops at room temperature for the three melt-spun amorphous alloys. The B-H loops indicate that these amorphous alloys have good soft magnetic characteristics. The saturation magnetization (B_s), coercive force (H_c) and squareness ratio

(B_r/B_s) are 1.13 T, 1.3 A/m and 0.29, respectively, for the Fe-P-B-Si alloy, 1.08 T, 13 A/m and 0.31, respectively, for the Fe-Al-P-B-Si alloy and 1.03 T, 19 A/m and 0.30, respectively, for the Fe-Al-Ga-P-B-Si alloy. Furthermore, the permeability at 1 kHz and the saturated magnetostriction were measured to be 5800 and 31×10^{-6} , respectively, for the Fe-P-B-Si alloy, 2600 and 30×10^{-6} , respectively, for the Fe-Al-P-B-Si alloy and 1900 and 21×10^{-6} , respectively, for the Fe-Al-Ga-P-B-Si alloy. It is well known that the annealing treatment in the temperature range between T_c and T_x causes a significant improvement of soft magnetic properties. The effect of annealing for 600 s at 723 K is shown in Fig. 11. Table 1 also summarizes the soft magnetic properties of the $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloys in the as-quenched and annealed (723 K, 600 s) states, together with the data

Fig. 10 B-H hysteresis loops of as-quenched amorphous $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ alloys.

Fig. 11 B-H hysteresis loops of amorphous $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{75}\text{Al}_5\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{73}\text{Al}_5\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ alloys annealed for 600 s at 723 K.

Table 1 Thermal stability and magnetic properties of the amorphous $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ alloys.

〈As-quenched〉 Composition		μ_e	$H_c(\text{A/m})$	$B_s(\text{T})$	$B_r(\text{T})$	B_s/B_r	λ_s	$T_g(\text{K})$	$T_x(\text{K})$	$\Delta T_x(\text{K})$
$\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$		5800	1.3	1.10	0.32	0.29	31×10^{-6}	753	789	36
$\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$		2600	12.7	0.96	0.30	0.31	30×10^{-6}	738	780	46
$\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$		1900	19.1	0.91	0.27	0.30	21×10^{-6}	737	786	49
〈Annealed for 600 s at 723 K〉 Composition		μ_e	$H_c(\text{A/m})$	$B_s(\text{T})$	$B_r(\text{T})$	B_s/B_r				
$\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$		22000	1.1	1.34	0.46	0.34				
$\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$		21000	2.6	1.24	0.43	0.35				
$\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$		19000	6.4	1.14	0.40	0.35				

of the as-quenched Fe-based amorphous alloys. In comparison between the as-quenched and annealed states, one can clearly notice that the annealing causes the increases in the magnetization at 1600 A/m (B_{1600}) to 1.13–1.34 T, residual magnetization (B_r) to 0.40–0.46 T and the squareness ratio defined by B_r/B_{1600} to 0.34–0.35 and the decrease in H_c to 1.1–6.4 A/m. Furthermore, the permeability at 1 kHz also increases significantly by about 4 to 9 times upon annealing and the high permeabilities exceeding 19000 are obtained for the three annealed samples. These soft magnetic properties are comparable to those for Fe–Si–B amorphous alloys which have been used in various application fields⁽¹⁴⁾. The increase in the temperature interval of the supercooled liquid to above 50 K enables the production of bulk amorphous alloys with a thickness above 1 mm⁽⁹⁾ and neither glass transition nor supercooled liquid region before crystallization is observed for the commercial Fe–Si–B amorphous alloys with the maximum sample thicknesses below about 0.05 mm⁽¹⁵⁾. Consequently, the present Fe–Al–Ga–P–B–Si amorphous alloys are attractive for a new type of soft magnetic material with the features of large glass-forming ability, easy deformability in the supercooled liquid and good soft magnetic properties.

IV. Discussion

1. Reason for the appearance of a wide supercooled liquid region before crystallization

We discuss the reason why the widest supercooled liquid region is obtained for the $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloy with the single-stage crystallization process. It has previously been proposed^{(1)–(6)} that the wide supercooled liquid region is obtained for multicomponent alloys with the following three empirical rules, i.e., (1) multicomponent alloy systems consisting of more than three constituent elements, (2) significantly different atomic size ratios above 12% among main constituent elements, and (3) negative heats of mixing among main constituent elements. The atomic sizes of the constituent elements decrease in the order $\text{Al} > \text{Ga} > \text{Fe} > \text{Si} > \text{P} > \text{B}$ and the heats of mixing have large negative values among the three group elements Fe, (Al, Ga) and (P, B, Si). Consequently, the present Fe–Al–Ga–P–B–Si alloys satisfy the three empirical rules for the achievement of large glass-forming ability and the appearance of a wide supercooled liquid region. In the amorphous alloys which satisfy the three empirical rules, a higher degree of dense random packed structure with low atomic diffusivity and large liquid/solid interfacial energy is formed⁽¹⁶⁾ and hence the precipitation of a crystalline phase is retarded through the suppression of nucleation and growth reactions of a crystalline phase. The single-stage precipitation of the five crystalline phases also implies the necessity of long-range atomic rearrangements for the precipitation of the crystalline phases from the homogeneously mixed supercooled liquid. The necessity also causes the retardation of the precipitation reaction, leading to the increase

in the thermal stability of supercooled liquid before crystallization. This presumption is also supported from the previous experimental results^{(1)–(6)} that a wide supercooled liquid region is always obtained for the amorphous alloys with a single-stage crystallization reaction.

2. Reason for the achievement of high permeability

It has previously been reported⁽¹⁷⁾ that the highest permeability of conventional Fe–Si–B amorphous alloys in the annealed state is about 12000 around $\text{Fe}_{78}\text{Si}_{10}\text{B}_{12}$. It is to be noticed that the present μ_e values exceed largely the highest value for the Fe–Si–B amorphous alloys without glass transition which have been widely used⁽¹⁴⁾ for application. With the aim of investigating the reason for the difference, we examined the saturated magnetostriction (λ_s) for the annealed $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$, $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ alloys. The λ_s values of the three alloys are 31×10^{-6} , 30×10^{-6} and 21×10^{-6} , respectively, which are smaller by about 6 to 36% than that (33×10^{-6})⁽¹⁸⁾ for the $\text{Fe}_{78}\text{Si}_{10}\text{B}_{12}$ amorphous alloy. There is a clear tendency for μ_e to increase with decreasing λ_s . The tendency is also interpreted from the theoretical relation between μ_e and λ_s ⁽¹⁹⁾⁽²⁰⁾. Thus, the high μ_e values for the present Fe-based amorphous alloys are concluded to result from the low λ_s . There have been no systematic data on the influence of each metalloid element on λ_s for Fe-based amorphous alloys and hence the reason why the present Fe-based amorphous alloys exhibit the small λ_s values remains unclear. The accumulation of the information on the composition dependence of λ_s will shed light on the clarification of the reason for the smaller λ_s values of the present Fe-based amorphous alloys as compared with the Fe–Si–B amorphous alloys.

V. Summary

With the aim of searching a new ferromagnetic Fe-based amorphous alloy with a wide supercooled liquid region before crystallization, we examined the formation range, thermal stability and magnetic properties of melt-spun $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$, $\text{Fe}_{80-x}\text{Al}_x(\text{P}, \text{B}, \text{Si})_{20}$ and $\text{Fe}_{78-x}\text{Al}_x\text{Ga}_2(\text{P}, \text{B}, \text{Si})_{20}$ amorphous alloys. The results obtained are summarized as follows:

(1) An amorphous phase exhibiting the glass transition phenomenon was formed in the composition range of 7 to 12 at%P, 3 to 5%B and 3 to 7%Si in the $\text{Fe}_{80}(\text{P}, \text{B}, \text{Si})_{20}$ alloys. The largest ΔT_x value of 36 K was obtained for the $\text{Fe}_{80}\text{P}_{12}\text{B}_4\text{Si}_4$ amorphous alloy where the crystallization takes place through a single stage.

(2) The ΔT_x value increases to 46 K for $\text{Fe}_{76}\text{Al}_4\text{P}_{12}\text{B}_4\text{Si}_4$ and 49 K for $\text{Fe}_{74}\text{Al}_4\text{Ga}_2\text{P}_{12}\text{B}_4\text{Si}_4$ and these amorphous alloys also crystallize through a single-stage reaction. The effectiveness of additional Al and Ga elements on the increase in ΔT_x is due to the formation of a higher degree of dense random packed structure resulting from the satisfaction of the three empirical rules for the achievement of large glass-forming ability and the appearance of a wide supercooled liquid region.

(3) The crystallized structure of the three amorphous

alloys with the maximum ΔT_x and single-stage crystallization process consists of five crystalline phases α -Fe, Fe₃B, Fe₂B, Fe₃P and FeP. The long-range atomic rearrangements required for the precipitation of the five crystalline phases also play an important role in the appearance of the wide supercooled liquid region through the retardation of the precipitation reactions.

(4) These Fe-based amorphous alloys with the glass transition phenomenon exhibit soft magnetic properties of 1.03 to 1.13 T for B_s , 1.3 to 19.1 A/m for H_c and 1900 to 5800 for μ_e at 1 kHz in the as-quenched state. The annealing for 600 s at 723 K caused a significant improvement of soft magnetic properties as is evidenced from the achievement of 1.14 to 1.34 T for B_s , 1.1 to 6.4 A/m for H_c and 19000 to 22000 for μ_e at 1 kHz.

The ferromagnetic Fe-based amorphous alloys with good soft magnetic properties and a wide supercooled liquid region are very attractive because of the expectation of the formation of bulk amorphous alloys with good workability in the supercooled liquid region.

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