Thermal and Magnetic Properties of Fe₅₆Co₇Ni₇Zr₁₀₋ₓNbₓB₂₀
Amorphous Alloys with Wide Supercooled Liquid Range

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Amorphous alloys with a wide supercooled liquid region of 45 to 85 K were found to be formed in Fe₅₆Co₇Ni₇Zr₁₀₋ₓNbₓB₂₀ (x=0 to 10 at%) alloys by melt spinning. The glass transition temperature (Tg) and the crystallization temperature (Tc) increase by the dissolution of 2 to 4% Nb. The degree of increase is larger for Tc than Tg, leading to the maximum ΔTc (= Tc − Tg) of 85 K for the 2%Nb alloy. The ΔTc value is about 20 K larger than the largest value for the newly developed Fe–(Al, Ga)–(P, C, B, Si) amorphous alloys. The crystallization occurs through a single stage, amorphous → α+γ–Fe+Zr+Fe₅₆ NbₓB₂₀ for the alloys containing less than about 6% Nb and through two stages, amorphous → amorphous + γ–Fe+Zr+CoₓNbₓB₂₀+NiₓNb for the alloys containing more than 8% Nb. The change in the crystallization process for the Nb-rich alloys probably reflects the disappearance of Fe₅₆(Nb, Zr) precipitates because of the weaker bonding of Fe–Nb pair as compared with Fe–Zr one. As the Nb content increases, the saturation magnetization (I₆) and permeability (μs) of the annealed alloys decrease while the coercive force (Hc) remains almost unchanged. The good soft magnetic properties are obtained for the alloys containing less than 2% Nb subjected to annealing for 300 s at 800 K and the I₆, Hc and μs at 1 kHz are 0.96 T, 2.0 A/m and 19100, respectively, for the 0% Nb alloy and 0.73 T, 1.1 A/m and 25000, respectively, for the 2% Nb alloy. The success of synthesizing the new amorphous alloys with a wide supercooled liquid region more than 80 K and with good soft magnetic properties is promising for future development as soft magnetic bulk amorphous alloys.

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I. Introduction

Since the findings of new amorphous alloys with large glass-forming ability in Mg–Ln–TM⁵⁰, Ln–Al–TM⁵¹ and Zr–Al–TM⁵² (Ln=lanthanide metal, TM=transition metal) systems has been published from 1988 to 1991, significant attention has been paid to the new multicomponent amorphous systems in which bulk amorphous alloys can be prepared by a copper mold casting process. The bulk amorphous alloys had been limited to the non-ferromagnetic Mg–⁷⁰, Ln–⁹⁰ and Zr–⁴¹ base systems. Subsequently, a search of bulk amorphous alloys with ferromagnetism at room temperature was carried out in the framework of the three empirical rules for the achievement of large glass-forming ability⁴⁴–⁴⁶. As a result, ferromagnetic bulk amorphous alloys have been found in the Fe–(Al, Ga)–(P, B, C, Si, Ge)⁴⁷ and (Nd, Pr)–Fe–(Al, Ga)⁴⁸–⁴⁹ systems. The former Fe-based bulk amorphous alloys are obtained in the diameter range up to 2 mm and exhibit good soft magnetic properties of 1.1 to 1.3 T for saturation magnetization (I₆), 2 to 5 A/m for coercive force (Hc) and 5000 to 7000 for permeability (μs) at 1 kHz. On the other hand, the latter Nd- and Pr-based bulk amorphous alloys are prepared in the diameter range up to 12 mm and have rather good hard magnetic properties, i.e., intrinsic coercive force (I₆) of 250 to 600 kA/m, remanence (Bₖ) of 0.1 to 0.2 T and maximum energy product (BH)ₘₚ of 10 to 20 kJ/m³. Considering that the soft magnetic properties of the Fe-based bulk amorphous alloys are comparable to those of commercial Fe–Si–B sheet amorphous alloys, the appearance of Fe-based amorphous alloys with larger glass-forming ability is expected to cause a further extension of application field of soft magnetic amorphous alloys. More recently, based on the three empirical rules⁵⁰–⁵² for the achievement of large glass-forming ability, we have searched a new Fe-based amorphous alloy with a wider supercooled liquid region, namely, a larger glass-forming ability, and succeeded⁵³ in finding new multicomponent Fe-based amorphous alloys with the largest ΔTc value of 73 K in (Fe, Co, Ni)₅₂Zr₁₀B₂₀ system. Subsequently, we have examined the effect of the partial replacement of Zr by Nb corresponding to the further increase in the degree of the satisfaction of the three empirical rules and noticed that the replacement by 2 at% Nb causes a significant increase in ΔTc to 85 K. This paper is intended to present the compositional dependence of Tc, T₆, ΔTc, crystallization behavior and magnetic properties for Fe₅₆Co₇Ni₇Zr₁₀₋ₓNbₓB₂₀ amorphous alloys and to investigate the reason for the increase in the thermal stability of the supercooled liquid region for the 2%Nb-con-
II. Experimental Procedure

Multicomponent alloys with composition Fe56Co7Ni5Zr10-nNb28 were examined in the present study because the Fe56Co7Ni5Zr10B20 amorphous alloy had the widest supercooled liquid region before crystallization. Their master ingots were prepared by arc melting the mixture of pure Fe, Co, Ni, Zr and Nb metals and pure B crystal in an argon atmosphere. The alloy compositions represent the nominal atomic percentage of the mixture. Rapidly solidified ribbons with a cross section of 0.015 × 1.0 mm² were prepared by melt spinning the master ingots in an argon atmosphere. The amorphous structure was confirmed by X-ray diffractometry and transmission electron microscopy. Thermal stability associated with glass transition, supercooled liquid region and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The saturation magnetization and residual magnetization at room temperature were measured in a maximum applied field of 1260 kA/m with a vibrating sample magnetometer (VSM). The coercive force was measured with a B-H loop tracer. Permeability was evaluated at 1 kHz with an impedance analyzer.

III. Results

Figure 1 shows the X-ray diffraction patterns of the melt-spun Fe56Co7Ni5Zr10-xNb28 (x=0, 2, 4, 6, 8 and 10 at%) alloys. Only a broad peak is seen at a wave vector (Kx=4π sin θ/λ) of about 30.2 nm⁻¹ (2θ=44 deg) and no diffraction peak corresponding to a crystalline phase is seen for all the alloys. The X-ray diffraction data indicate clearly that these melt-spun alloys are composed of an amorphous phase. Figure 2 shows the DSC curves of the melt-spun Fe56Co7Ni5Zr10-xNb28 (x=0, 2, 4, 6, 8 and 10 at%) amorphous alloys. It is to be noticed that a glass transition, followed by a wide supercooled liquid region is observed distinctly in the temperature range before crystallization for all the alloys. However, the crystallization behavior changes from a single stage to two stages for the alloy composition around 7 at%Nb. Based on these DSC curves, the glass transition temperature (Tg), the onset temperature of crystallization (Tc) and the temperature interval of supercooled liquid region (∆Tg, Tc - Tg) for the Fe-Co-Ni-Zr-Nb-B amorphous alloys were plotted as a function of Nb content in Fig. 3. The Tg and Tc are 814 and 887 K, respectively, for the 0%Nb alloy. They increase by the dissolution of Nb to show maximum values of 828 and 912 K, respectively, for the alloys containing 2 to 4 at%Nb and then decrease significantly with a further increase in Nb content. The degree of increase in Tg is larger than that in Tc, leading to the increase in ∆Tg from 73 K for the 0%Nb alloy to 85 K for the 2%Nb alloy. Here, it is important to point out that the Fe56Co7Ni5Nb10B20 amorphous alloy also exhibits the glass transition and a wide supercooled liquid

Fig. 1 X-ray diffraction patterns of the melt-spun Fe56Co7Ni5Zr10-xNb28 (x=0, 2, 4, 6, 8 and 10 at%) alloys.

Fig. 2 Differential scanning calorimetric curves of the amorphous Fe56Co7Ni5Zr10-xNb28 alloys.
region.

With the aim of clarifying the reason for the change in the crystallization behavior around 7 at%Nb, the X-ray diffraction patterns of the Fe$_{56}$Co$_{20}$Ni$_{15}$Zr$_{10}$-$_{x}$Nb$_{x}$B$_{20}$ (x = 2, 4, 8 and 10 at%) alloys heated for 600 s at temperatures above the exothermic peaks were examined. The X-ray diffraction patterns (Fig. 4) were identified to consist of α-Fe, γ-Fe, Fe$_2$Zr and Fe$_{28}$Nb$_{6}$B$_{18}$ phases for the 2 and 4 at% Nb alloys with a single exothermic peak, a γ-Fe phase for the 8 and 10 at% Nb alloys heated to 883 K corresponding to the temperature just above the first exothermic peak and γ-Fe, Co$_2$Nb$_2$B$_2$ and Ni$_3$Nb phases for the 8 and 10 at% Nb alloys heated to 1028 to 1047 K just above the second exothermic peak. From the identification, it is concluded that the crystallization occurs with a single stage (amorphous → α-Fe + γ-Fe + Fe$_2$Zr + Fe$_{28}$Nb$_{6}$B$_{18}$) for the alloys containing less than about 6 at% Nb, and with two stages (amorphous → γ-Fe + amorphous → γ-Fe + Co$_2$Nb$_2$B$_2$ + Ni$_3$Nb) for the alloys containing more than 8 at% Nb. It is to be noticed that the two-stage crystallization occurs when the Fe$_2$(Nb, Zr) phase is not formed. It has been reported that the predicted negative heat of mixing for an equiatomic alloy is 37 kJ/mol for Fe-Zr, 38 kJ/mol for Fe-B, 102 kJ/mol for Zr-B, 23 kJ/mol for Fe-Nb, 79 kJ/mol for Nb-B, 37 kJ/mol for Co-Nb and 45 kJ/mol for the Ni-Nb systems. These values suggest that the bonding force for the Fe-Nb pair is considerably weaker as compared with any other atomic pairs. The weakest bonding force of Fe-Nb pair is thought to allow the generation of isolated Fe-Fe bonding pairs, leading to the change in the crystallization process from a single stage to two stages due to the additional precipitation of the γ-Fe phase in the alloys containing more than 8 at% Nb. This is possibly the first evidence for the appearance of a wide supercooled liquid region exceeding 45 K in amorphous alloys where the crystallization occurs with two distinct stages where temperature interval is as large as about 150 K.

Figures 5 and 6 show hysteresis I-H loops of Fe$_{56}$Co$_{20}$Ni$_{15}$Zr$_{10}$-$_{x}$Nb$_{x}$B$_{20}$ amorphous alloys in as-quenched and annealed (300 s, 800 K) states, respectively. It is seen that the replacement of Zr by Nb for the as-quenched samples causes a decrease in $I_e$ from 0.92 T at 0 at% Nb to 0.54 T at 10 at% Nb through 0.74 T at 2 at% Nb and an increase in $H_e$ from 5.2 A/m at 0 at% Nb to 41.3 A/m at 10% Nb through 5.5 A/m at 2% Nb. On the other hand, the annealed samples exhibit a monotonous decrease in $I_e$ from 0.96 T at 0% Nb to 0.61 T at 10% Nb as well as a nearly constant low $H_e$ of about 1.1 A/m in the whole Nb content range. It is thus to be noticed that the $H_e$ decreases significantly by the optimal annealing treatment. Figures 5 and 6 also show that the annealing causes a marked increase in the squareness ratio defined by the ratio of residual magnetization ($I_e$) to $I_e$ for the alloys con-
taining 4 to 10% Nb. Although the total amount of Fe and Co elements remains constant, it is seen that the $I_s$ for the annealed samples shows a decrease of 0.21 T only by the dissolution of 2 at% Nb. The significant decrease probably reflects the lowering of Curie temperature with increasing Nb content. Figure 7 shows changes in effective permeability ($\mu_e$) at 1 kHz and saturated magnetostriction ($\lambda_s$) as a function of Nb content for the Fe$_{59}$Co$_{20}$Ni$_{10}$Zr$_{10-x}$Nb$_x$B$_{20}$ amorphous alloys in as-quenched and annealed states, together with those of $I_s$ and $H_c$. The $\mu_e$ increases significantly by annealing and reaches 19100 at 0 at% Nb and 25000 at 2 at% Nb. With a further increase in Nb content, the $\mu_e$ decreases gradually to 14800 at 10 at% Nb. The compositional dependence is analogous to that for $I_s$. It is also confirmed that the $H_c$ of the alloys containing more than 4 at% Nb decreases significantly from about 45 A/m to about 1 A/m by annealing. The $\lambda_s$ keeps a relatively low level of about 10$^{-6}$ in the whole Nb content range and remains almost unchanged in the as-quenched and annealed states. The $\lambda_s$ value is considerably lower than that of conventional Fe-Si-B amorphous alloy ribbons. The lower $\lambda_s$ is thought to be one of the reasons for the simultaneous achievement of lower $H_c$ and higher $\mu_e$ as compared with Fe-Si-B amorphous alloys. Although the reason for the significant change in $H_c$ in the vicinity of 3 at% Nb for the as-quenched samples with nearly the same $\lambda_s$ values remains unknown, it may be related to the decrease in the glass-forming ability resulting from the decrease in $\Delta T_g$. From the compositional dependence of the thermal stability of the supercooled liquid and the magnetic properties, it is concluded that the Fe$_{59}$Co$_{20}$Ni$_{10}$Zr$_{10-x}$Nb$_x$B$_{20}$ amorphous alloys containing 0 to 2 at% Nb have the combination of large glass-forming ability and good soft magnetic properties.
IV. Discussion

It was shown in Figs. 2 and 3 that the replacement of Zr by 2 to 4 at% Nb causes the significant extension of the supercooled liquid region defined by the difference in $T_g$ and $T_s$ through the increase in $T_s$, exceeding the degree of the increase in $T_L$ as a function of Nb content. It is to be noticed that the largest $\Delta T_s$ value of 86 K for the 2 at% Nb alloy is larger by about 20 K than the largest value (66 K)\(^{(30)}\) for Fe-based amorphous alloys reported up to date. The significant increase in $\Delta T_s$ allows us to expect that the new Fe–Co–Ni–Zr–Nb–B alloy has a large glass-forming ability which enables the production of bulk amorphous alloys with diameters above several millimeters by the copper mold casting process. Consequently, it is important to discuss the reasons for the significant extension of the supercooled liquid region before crystallization by the dissolution of 2 to 4 at% Nb. It has been previously pointed out that the appearance of the wide supercooled liquid region of 73 K\(^{(28)}\) for the Fe–Co–Ni–Zr–B alloys without Nb is due to the satisfaction of the three empirical rules for the achievement of large glass-forming ability, namely, (1) the multicomponent system consisting of more than three constituent elements, (2) the significantly different atomic size ratios above about 12% among the three main constituent elements, as is evidenced from the change Zr $\gg$ Fe $\gg$ Co $\approx$ Ni $\gg$ B\(^{(30)}\), and (3) the large negative heats of mixing among the main constituent elements, as is evidenced from the negative enthalpies of mixing of 37 to 72 kJ/mol for Fe–Zr, Co–Zr and Ni–Zr pairs, 33 to 38 kJ/mol for Fe–B, Co–B and Ni–B pairs and 102 kJ/mol for Zr– B pair\(^{(29)}\). The addition of an appropriate amount (2 to 4 at%) of Nb is expected to cause an enhancement of the degree of the satisfaction of the three empirical rules. That is, the atomic size changes more continuously in the order of Zr $\gg$ Nb $\gg$ Fe $\approx$ Co $\approx$ Ni $\gg$ B\(^{(31)}\) and additional atomic pairs of Fe–Nb, Co–Nb, Ni–Nb and Nb–B with large negative heats of mixing generate for the Nb-containing alloys. However, the heat of mixing is 23 to 45 kJ/mol for the Fe–Nb, Co–Nb and Ni–Nb pairs and 79 kJ/mol for the Nb–B pair\(^{(29)}\), being considerably smaller than those for the corresponding Fe–Zr, Co–Zr, Ni–Zr and Zr–B pairs. The weaker bonding nature of the main Fe–Nb atomic pair seems to result in the decrease in $\Delta T_s$ for the alloys containing more than 8 at% Nb owing to the primary precipitation of the $\gamma$-Fe phase resulting in a change from a single-stage crystallization process to a two-stage process. This change indicates clearly the importance of an attractive bonding nature among the constituent elements for the achievement of a wide supercooled liquid region before crystallization in addition to the significantly different atomic size ratios.

V. Summary

With the aim of searching a new amorphous alloy with a wide supercooled liquid region before crystallization and good soft magnetic properties, the compositional dependence of $T_g$, $T_s$, $\Delta T_s$, crystallization behavior and magnetic properties was examined for the alloy series of Fe$_{58}$Co$_{11}$Ni$_{17}$Zr$_{10}$–xNb$_x$B$_{30}$ ($x = 0$ to 10 at%). The results obtained are summarized as follows.

(1) The glass transition and subsequent supercooled liquid region were observed in the temperature range before crystallization for all the alloys. The $T_s$ and $T_g$ are 814 and 887 K, respectively, for the 0 at% Nb alloy, increase by the dissolution of Nb and show maximum values of 828 and 912 K, respectively, for the alloys containing 2 to 4 at% Nb. The degree of the increase in $T_s$ as a function of Nb content is larger than that for $T_g$, leading to the maximum $\Delta T_s$ of 85 K for the 2 at% Nb alloy. This value is about 20 K larger than the largest value for Fe-based amorphous alloys reported up to date.

(2) The crystallization takes place with a single stage (amorphous $\rightarrow \alpha$-Fe $+$ $\gamma$-Fe $+$ Fe$_2$Zr $+$ Fe$_2$Nb$_2$B$_3$) for the alloys containing less than about 6 at% Nb, and two stages (amorphous $\rightarrow \gamma$-Fe $+$ amorphous $\rightarrow \gamma$-Fe $+$ Co$_2$Nb$_2$B$_3$ and Ni$_3$B) for the alloys containing more than about 8 at% Nb without precipitating Fe$_2$Zr and Fe$_2$Nb. The temperature interval of the two exothermic peaks corresponding to the two-stage crystallization is as large as about 150 K. It is to be noticed that the wide supercooled liquid region exceeding 30 K appears even for the alloys with the distinct two-stage crystallization processes.

(3) The $I_s$, $H_s$ and $\mu_s$ at 1 kHz in the optimally annealed state are 0.96 T, 2.0 A/m and 19100, respectively, for the Fe–Co–Ni–Zr–B alloy. However, the $I_s$ and $\mu_s$ decrease with increasing Nb content while $H_s$ remains almost unchanged. The resulting $I_s$, $H_s$ and $\mu_s$ are 0.75 T, 1.1 A/m and 25000 for the 2 at% Nb alloy and 0.61 T, 1.1 A/m and 14800 for the 10 at% Nb alloy. Thus, the alloys containing less than about 3 at% Nb exhibit the good combination of the wide supercooled liquid region and good soft magnetic properties. The finding of the new amorphous alloys with the two characteristics is important for the future development of bulk amorphous alloys in the application of soft magnetic materials.

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