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Ferromagnetic Co–Fe–Zr–B amorphous alloys with glass transition and good high-frequency permeability

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A Co-based amorphous phase with glass transition and supercooled liquid region before crystallization was formed in $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ alloys containing more than 14 at % Fe. The crystallization temperature (T_x) is 899 K for the Co–Zr–B alloys and remains unchanged in the Fe concentration range up to 20%. The glass transition temperature (T_g) decreases with increasing Fe content, and the $\Delta T_x(=T_x-T_g)$ increases from 25 K at 14% Fe to 34 K at 21% Fe. The amorphous alloys with glass transition crystallize with a single stage precipitation of bcc Fe(Co) and Co_3ZrB_2 phases. The Co-rich amorphous alloys exhibit good soft magnetic properties, i.e., saturation magnetization of 0.58–0.83 T, low coercivity of 4.7–8.3 A/m, and high permeability of 5500–18 300 in the frequency range of $1-10^3$ kHz and low magnetostriction between -1.5×10^{-6} and $+10\times10^{-6}$ including zero. The success in synthesizing the soft magnetic amorphous alloys with high stability of supercooled liquid is promising for the future development of ferromagnetic Co-based bulk amorphous alloys.
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The search for Fe- and Co-based amorphous alloys with a wide supercooled liquid range is important because of the possibility of forming bulk amorphous alloys with good soft magnetic properties. Recently, Fe-based amorphous alloys with a wide supercooled liquid region above 50 K have been found in Fe–(Al, Ga)–(P, C, B, Si),[1–4] Fe–(Co, Ni)–Zr–B,[5] Fe–(Co, Ni)–(Zr, Nb)–B,[6] and Fe–(Co, Ni)–(Zr, Nb)–(Mo, W)–B[7] systems. The maximum value of the supercooled liquid region defined by the difference between T_g and T_x reaches 67 K[8] for the Fe-based alloys containing Al and Ga elements and 88 K[6,7] for the Fe-based alloys containing Zr and B elements. These Fe-based amorphous alloys are prepared in a bulk form with diameters up to 6 mm[7] and also exhibit good soft magnetic properties, i.e., saturation magnetization (I_s) of 1.1 T, coercivity (H_c) of 3–6 A/m, and permeability (μ') of 7000 at 1 kHz for the Fe–(Al, Ga)–(P, C, B, Si) bulk amorphous alloys[3,4,9] and I_s of 0.96 T, H_c of 2–6 A/m, and μ' of 18 000 for the Fe–(Co, Ni)–Zr–B amorphous alloys.[5,10] However, little is known about a Co-based amorphous alloy with a supercooled liquid region before crystallization. More recently, we have found that Co-based amorphous alloys with glass transition and supercooled liquid region are formed in Co–Fe–M–B (M=Zr, Nb) systems and exhibit good soft magnetic properties with high μ' in the high frequency range up to 1 MHz. This letter is intended to present the composition ranges in which an amorphous phase with glass transition and supercooled liquid region is formed in $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ systems by melt spinning and the thermal stability and magnetic properties of the Co-based amorphous alloys.

Multicomponent Co-based alloys with composition $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ ($x=0-21$ at %) were examined because a wide supercooled liquid region in $(Fe, Co, Ni)_{100-x-y}Zr_xB_y$ system was obtained for $Fe_{56}Co_7Ni_7Zr_{10}B_{20}$. Their alloy ingots were prepared by arc melting the mixtures of pure metals and pure B crystal in an argon atmosphere. Rapidly solidified ribbons with a cross section of 0.02×1 mm^2 were prepared from the ingots by melt spinning. The amorphous nature was examined by x-ray diffractometry and transmission electron microscopy. Thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Magnetic properties of I_s, H_c, and μ' were measured at room temperature with a vibrating sample magnetometer, a B–H loop tracer and an impedance analyzer, respectively. The saturated magnetostriction was also measured by a capacitance method. Electrical resistivity measurement was made by the four-probe technique.

An amorphous phase without crystallinity was formed in rapidly solidified $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ ($x=0-21$ at %) alloys. Figure 1 shows DSC curves of the amorphous $Co_{72-x}Fe_xZr_8B_{20}$ ($x=0$, 7, 14, and 21 at %) alloys, respectively. No glass transition is observed in the Fe concentration range below 7 at %, but the increase in Fe content to 14 at % causes the appearance of glass transition, followed by a narrow supercooled liquid region in the temperature range below T_x. The amorphous alloys containing more than about 14 at % Fe exhibit the sequential transitions of amorphous solid, glass transition, supercooled liquid re-

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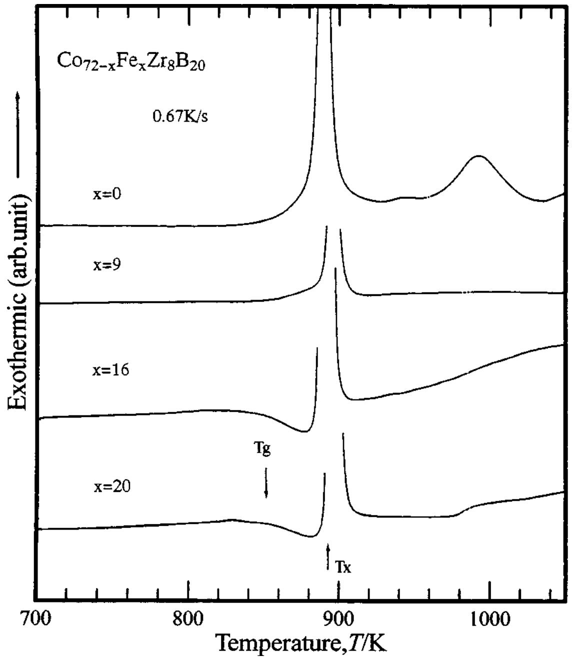

FIG. 1. DSC curves of amorphous $Co_{72}Zr_8B_{20}$, $Co_{63}Fe_9Zr_8B_{20}$, $Co_{56}Fe_{16}Zr_8B_{20}$, and $Co_{52}Fe_{20}Zr_8B_{20}$ alloys.

gion and then crystallization. It is to be noticed that a supercooled liquid state without transition stage is obtained in the temperature range of about 10 K for the $Co_{52}Fe_{20}Zr_8B_{20}$ amorphous alloy, as is evidenced for the magnified DSC curve in Fig. 2. The supercooled liquid region defined by the difference between T_g and T_x, $\Delta T_x(=T_x-T_g)$ is 25 K for $Co_{56}Fe_{14}Zr_{10}B_{20}$, 34 K for $Co_{49}Fe_{21}Zr_{10}B_{20}$, 39 K for $Co_{56}Fe_{16}Zr_8B_{20}$ and 43 K for $Co_{52}Fe_{20}Zr_8B_{20}$. Furthermore, the amorphous alloys with glass transition and supercooled liquid region have a single-stage crystallization process corresponding to the simultaneous precipitation of crystalline phases. The crystalline structure of the $Co_{52}Fe_{20}Zr_8B_{20}$ alloy consisted of bcc Fe(Co) and Co_3ZrB_2 phases. The single-stage crystallization agrees with that[11–14] for other amorphous alloys with a wide supercooled liquid region in Mg-,

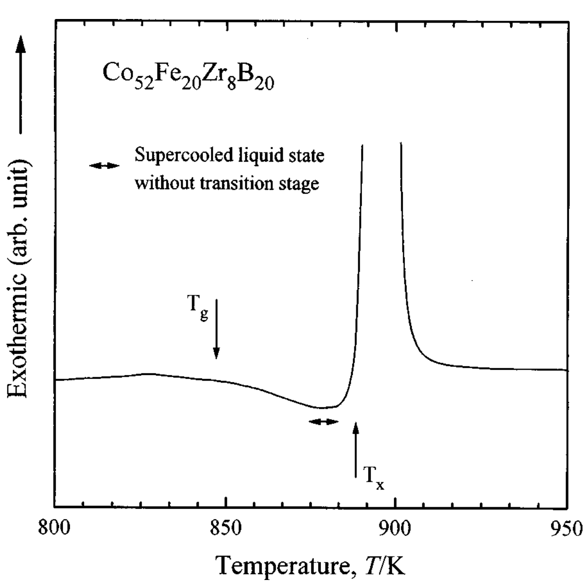

FIG. 2. Magnified DSC curve in the vicinity of supercooled liquid range for an amorphous $Co_{52}Fe_{20}Zr_8B_{20}$ alloy.

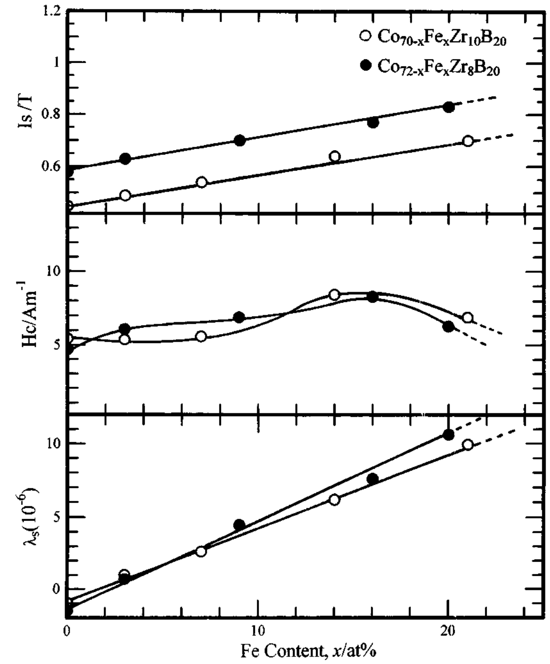

FIG. 3. Saturation magnetization (I_s), coercivity (H_c), and saturated magnetostriction (λ_s) as a function of Fe content for amorphous $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ alloys subjected to annealing for 600 s at 800 K.

lanthanide-, Zr-, and Pd-based systems, though only the Zr-base system containing Be has been reported[15] to show a spinodal decomposition. The single-stage mode seems to contribute to the appearance of the glass transition and supercooled liquid region.

Figure 3 plots I_s, H_c, and λ_s as a function of Fe content for the $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ ($x=0-21$ at %) amorphous alloys. The I_s increases almost linearly in the range of 0.45–0.83 T with increasing Fe content and with decreasing Zr content, while the H_c shows low values of 7 A/m in the range below 10% Fe and increases with a further increase in Fe content. The λ_s shows a negative value of -1.5×10^{-6} at 0% Fe and changes to positive values passing through zero around 2 at % Fe. The further increase in Fe content causes an increase in the positive λ_s, but the λ_s is less than 10×10^{-6} even at 20% Fe. It is therefore concluded that the Co-based amorphous alloys containing more than 14 at % Fe exhibit small λ_s as well as the glass transition and supercooled liquid region. It is characterized that the $Co_{72-x}Fe_xZr_8B_{20}$ ($x=16-20$ at %) amorphous alloys exhibit good soft magnetic properties of 0.77–0.83 T for I_s, 6.3–8.3 A/m for H_c, and 7.6–10 for λ_s, in addition to the glass transition phenomenon. Figure 4 shows the real and imaginary parts of permeability (μ' and μ''), respectively, as a function of frequency (f) for the $Co_{56}Fe_{16}Zr_8B_{20}$ amorphous ribbons of 1.0 mm in width. The μ' keeps high values of 17 100 to 5500 in the high frequency range up to 1 MHz and decreases with a further increase in frequency to 10 MHz. Similar frequency dependence was recognized for a wide ribbon of 15 mm in width. It is to be noticed that the frequency at which the maximum μ'' is obtained for the wide ribbon is as high as about 1 MHz. The $\mu''(f)$ data indicate that the Co–Fe–Zr–B alloy can keep high μ' values up to 1 MHz of the maximum μ'' point.

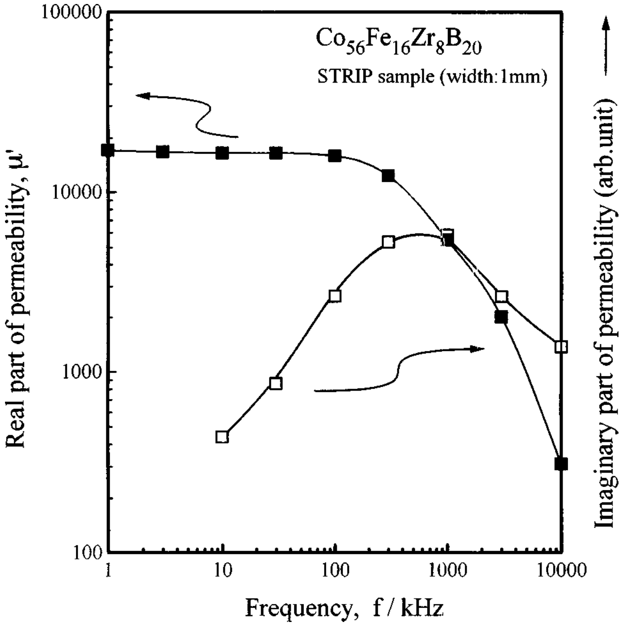

FIG. 4. Frequency dependence of real (μ') and imaginary (μ'') parts of permeability for amorphous $Co_{56}Fe_{16}Zr_8B_{20}$ alloy of 1 and 15 mm in width subjected to annealing for 600 s at 800 K.

The electrical resistivity (ρ_{RT}) of the $Co_{56}Fe_{16}Zr_8B_{20}$ amorphous alloys is 1.70 $\mu\Omega$ m, which is higher as compared with 1.34 $\mu\Omega$ m for $Co_{70.3}Fe_{4.7}B_{10}Si_{15}$,[16] 1.37 $\mu\Omega$ m for $Fe_{78}B_{13}Si_9$ (METGLAS 2605S-2),[17] and 1.42 $\mu\Omega$ m for the Co–Fe–Ni–Si–B METGLAS 2714A alloy.[17] Consequently, the excellent high-frequency permeability for the present alloys is probably due to the decrease in eddy current loss resulting from the higher ρ_{RT}. Thus the present Co-based amorphous alloys have good soft magnetic properties and high stability of supercooled liquid against crystallization. The high stability allows us to expect that a bulk amorphous alloy with a diameter above 1 mm is formed in the Co–Fe–Zr–B alloys by various casting processes.

Finally, we discuss the reason why the $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ amorphous alloys containing 14%–20% Fe exhibit the high stability of supercooled liquid. It has recently been pointed out[12,13,18] that all the alloys having the high stability of supercooled liquid against crystallization satisfy the three empirical rules for achievement of large glass-forming ability, i.e., (1) the multicomponent system consisting of more than three elements, (2) the different atomic size ratios above about 12% among the main constituent elements, and (3) the negative heats of mixing among their elements. The atomic radius changes in the order of $Zr \gg Co > Fe \gg B$[19] and the predicted heat of mixing has negative values of 60 kJ/mol for equiatomic Co–Zr pair, 34 kJ/mol for Co–B pair, 37 kJ/mol for Fe–Zr pair, 38 kJ/mol for Fe–B pair, and 102 kJ/mol for Zr–B pair.[20] The Co–Fe–Zr–B system also satisfies the three empirical rules. The satisfaction of the rules causes the formation of a highly dense random packed structure, in the framework of geometrical and chemical points of view, in which the diffusivity of the constituent elements is suppressed and the liquid/solid interfacial energy is increased. Even in the supercooled liquid structure, long-range atomic rearrangements are required for the single-stage precipitation of the crystalline phases. However, the atomic rearrangements are difficult in the specialized liquid with low diffusivity. The difficulty seems to be the reason for the appearance of the glass transition and supercooled liquid region before crystallization.

It was shown that no glass transition was observed in the Co–Zr–B system. Thus, the addition of more than about 14 at % Fe is necessary for the appearance of the glass transition and supercooled liquid. Although the reason for the necessity of Fe remains unknown, it may be due to the increase in the degree of satisfaction of the empirical rules. The increase is expected from the data[17] that the heats of mixing and the atomic sizes among Co, Zr, and B elements are different from those among Fe, Zr, and B elements.

In conclusion, new Co-based amorphous alloys with glass transition and supercooled liquid region were synthesized in $Co_{70-x}Fe_xZr_{10}B_{20}$ and $Co_{72-x}Fe_xZr_8B_{20}$ containing more than 14 at % Fe. The maximum ΔT_x is 43 K for $Co_{52}Fe_{20}Zr_8B_{20}$. The crystallization occurs with a single-stage precipitation of bcc Fe(Co) and Co_3ZrB_2. The Co-based amorphous alloys exhibit good soft magnetic properties. The H_c shows low values of 4.7–8.3 A/m. The λ_s is -1.5×10^{-6} at 0% Fe and increases to $+10\times10^{-6}$ at 20% Fe. The μ' is 17 100 at 1 kHz and keeps the high values above 5500 in the frequency range up to 1 MHz. The synthesis of the Co–Fe–Zr–B amorphous alloys indicates the possibility that a bulk amorphous alloy with good soft magnetic properties is produced by a casting process.

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