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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_{x}Zr_{10}B_{20} and Co_{72-x}Fe_{x}Zr_{8}B_{20} alloys containing more than 14 at % Fe. The crystallization temperature (T_c) 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 ΔT_c (= T_c − 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_{2}Zr_{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 × 10^{-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. © 1998 American Institute of Physics.

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 systems. The maximum value of the supercooled liquid region defined by the difference between T_g and T_c reaches 67 K for the Fe-based alloys containing Al and Ga elements and 88 K 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 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_{x}Zr_{10}B_{20} and Co_{72-x}Fe_{x}Zr_{8}B_{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_{x}Zr_{10}B_{20} and Co_{72–x}Fe_{x}Zr_{8}B_{20} (x=0–21 at %) were examined because a wide supercooled liquid region in (Fe, Co, Ni)_{100–x}Zr_{x}B_{20} system was obtained for Fe_{50}Co_{50}Zr_{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 mm² 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_{x}Zr_{10}B_{20} and Co_{72–x}Fe_{x}Zr_{8}B_{20} (x=0–21 at %) alloys. Figure 1 shows DSC curves of the amorphous Co_{72–x}Fe_{x}Zr_{8}B_{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_g. The amorphous alloys containing more than about 14 at % Fe exhibit the sequential transitions of amorphous solid, glass transition, supercooled liquid re-
region 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$_{8}$B$_{20}$ 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$_{16}$Zr$_{8}$B$_{20}$, 39 K for Co$_{49}$Fe$_{21}$Zr$_{10}$B$_{20}$, and 43 K for Co$_{52}$Fe$_{20}$Zr$_{8}$B$_{20}$. 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$_{8}$B$_{20}$ alloy consisted of bcc Fe-Co and Co$_3$ZrB$_2$ phases. The single-stage crystallization agrees with that for other amorphous alloys with a wide supercooled liquid region in Mg-, lanthanide-, Zr-, and Pd-based systems, though only the Zr-based system containing Be has been reported 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 \( \lambda_s \) as a function of Fe content for the Co$_{70}$Fe$_{20}$Zr$_{10}$B$_{20}$ and Co$_{72}$Fe$_{20}$Zr$_{8}$B$_{20}$ \((x = 0-21 \text{ at } \%)\) 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 \( \lambda_s \) shows a negative value of \(-1.5 \times 10^{-6}\) 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 \( \lambda_s \), but the \( \lambda_s \) is less than \(10 \times 10^{-6}\) even at 20% Fe. It is therefore concluded that the Co-based amorphous alloys containing more than 14 at % Fe exhibit small \( \lambda_s \) as well as the glass transition and supercooled liquid region. It is characterized that the Co$_{72}$Fe$_{16}$Zr$_{8}$B$_{20}$ \((x = 16-20 \text{ at } \%)\) 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 \( \lambda_s \), in addition to the glass transition phenomenon. Figure 4 shows the real and imaginary parts of permeability \((\mu' \text{ and } \mu'')\), respectively, as a function of frequency \((f)\) for the Co$_{56}$Fe$_{16}$Zr$_{8}$B$_{20}$ amorphous ribbons of 1.0 mm in width. The \( \mu' \) 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 \( \mu'' \) 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 \( \mu' \) values up to 1 MHz of the maximum \( \mu'' \) point.
the main constituent elements, and a component system consisting of more than three elements, mixing among their elements. The atomic radius changes in an unfavorable way against crystallization satisfy the three empirical rules for the alloys having the high stability of supercooled liquid. It has recently been pointed out that all systems having negative values of the heats of mixing and the atomic sizes among Co, Zr, and B elements are different from those among Fe, Zr, and B elements.

Finally, we discuss the reason why the Co-based amorphous alloys with glass transition and supercooled liquid region were synthesized in Co$_{70-x}$Fe$_x$Zr$_8$B$_{20}$ and Co$_{70-x}$Fe$_x$Zr$_{18}$B$_{20}$ containing more than 14 at % Fe. The maximum $\Delta T_s$ is 43 K for Co$_{70}$Fe$_{20}$Zr$_{18}$B$_{20}$. The crystallization occurs with a single-stage precipitation of bcc Fe(Co) and Co$_3$ZrB$_2$. The Co-based amorphous alloys exhibit good soft magnetic properties. The $H_f$ shows low values of 4.7–8.3 A/m. The $\lambda$ is $-1.5 \times 10^{-6}$ at 0% Fe and increases to $+10 \times 10^{-6}$ at 20% Fe. The $\mu'$ 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.

In conclusion, new Co-based amorphous alloys with glass transition and supercooled liquid region were synthesized in Co$_{70-x}$Fe$_x$Zr$_{18}$B$_{20}$ and Co$_{70-x}$Fe$_x$Zr$_{18}$B$_{20}$ containing more than 14 at % Fe. The maximum $\Delta T_s$ is 43 K for Co$_{70}$Fe$_{20}$Zr$_{18}$B$_{20}$. The crystallization occurs with a single-stage precipitation of bcc Fe(Co) and Co$_3$ZrB$_2$. The Co-based amorphous alloys exhibit good soft magnetic properties. The $H_f$ shows low values of 4.7–8.3 A/m. The $\lambda$ is $-1.5 \times 10^{-6}$ at 0% Fe and increases to $+10 \times 10^{-6}$ at 20% Fe. The $\mu'$ 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.