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SOFT MAGNETIC Fe-BASED METALLIC GLASSES PREPARED BY FLUXING AND WATER-QUENCHING

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Abstract. $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.20}Si_{0.05}]_{96}Nb_4$ soft magnetic bulk metallic glasses were prepared by fluxing and water-quenching in a silica tube. Dimension of the bulk metallic glass specimens was up to 7.7 mm in diameter, which is about 1.5 times larger than those prepared by Cu mold-casting. The critical cooling rate of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.20}Si_{0.05}]_{96}Nb_4$ alloys with fluxing for forming a metallic glass phase was 150 - 170 K/s, which was considerably smaller than that without fluxing. Saturation magnetization was 1.13 T, and coercivity was lower than 20 A/m. Fluxing suppresses heterogeneous nucleation by isolating the nucleation sites from the molten alloys and improves their glass-forming ability.

1. INTRODUCTION

Ferromagnetic metallic glasses are promising materials as cores for transformers or yokes of electromagnets since they possess excellent soft magnetic properties, such as ultra low coercivity, high saturation magnetization and high permeability. Fe-based metallic glasses are the most desired among many glassy alloys, but it is difficult to prepare Fe-based bulk metallic glasses since high cooling rate of 10^5 - 10^6 K/s is required. Hence, several large Fe-based bulk metallic glasses containing less than 50 at.% of Fe have been reported [1,2], but they are paramagnetic at room temperature. For further industrial applications, ferromagnetic bulk metallic glasses are required. Recently, it was found that (Fe,Cu,Ni)-based Cu mold-cast bulk metallic glasses have a large supercooled liquid region [3-7]. These metallic glasses also exhibit good soft magnetic properties and high fracture strength of 3000 - 5200 MPa [8-11], however, the dimension of the mold-cast metallic glasses is less than 5 mm in diameter.

An alternative method to prepare bulk metallic glasses is fluxing, i.e., melting an alloy immersed in flux, and followed by water-quenching. It is considered that the critical cooling rate of Pd-based bulk metallic glasses becomes slow by fluxing since heterogeneous nucleation cites, such as oxides or compounds with a high melting point, are isolated from the molten alloy during fluxing. As a consequent, larger specimens are successfully obtained with fluxing than Cu mold-casting without fluxing [12]. From viewpoint of Gibbs free energy of oxides [13], $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.20}Si_{0.05}]_{96}Nb_4$ alloys were chosen and subjected to fluxing and water-quenching to avoid reaction between molten alloys and B_2O_3 flux.

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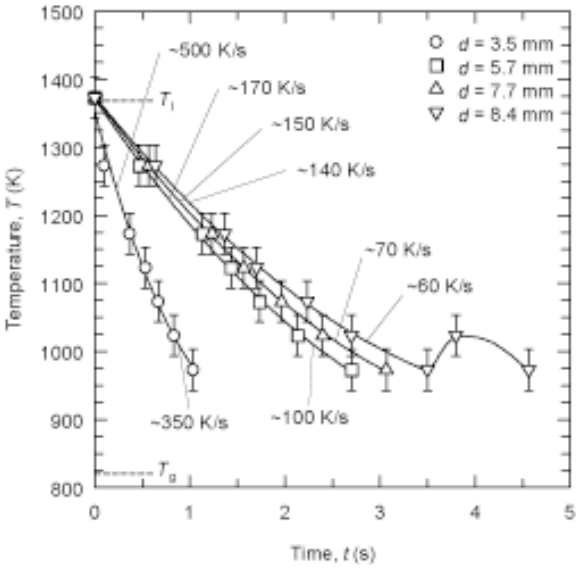

Fig. 1. Cooling curves for the specimens with 3.5 - 8.4 mm in diameter during quenching.

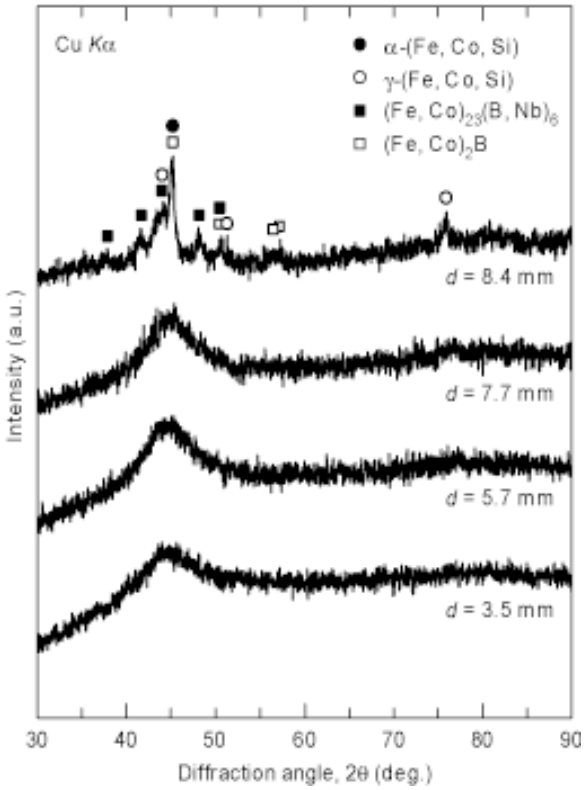

Fig. 2. XRD profiles taken from the transverse cross section of the bulk specimens with diameters of 3.5, 5.7, 7.7, and 8.4 mm.

In the present study, thermal and magnetic properties of fluxed $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.20}Si_{0.05}]_{96}Nb_4$ metallic glasses were investigated.

2. EXPERIMENTAL PROCEDURES

Ingots with nominal composition of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.20}Si_{0.05}]_{96}Nb_4$ were prepared by arc-melting in an Ar atmosphere. All the bulk glassy specimens were prepared by fluxing followed by water-quenching. B_2O_3, whose glass transition temperature (T_g) and melting temperature are 603K and 723K respectively, was chosen as a flux. Small pieces of the arc-melted ingots and B_2O_3 were put together in a dry and clean fused silica tube. The ingots and the flux were melted in an Ar flow and were kept at higher temperature than liquidus temperature (T_l) of the alloys for 100 - 200 s by using a torch, then they were cooled in air until recalescence accompanying crystallization was observed in the molten alloy. This heating and cooling cycle was repeated several times, and finally the system was quenched in water. Recalescence behavior and cooling rate of the specimen during quenching were monitored by using a digital video camera and a thermo-couple. For comparison, ribbons, whose dimension is 1.5 mm in width and 30 μm in thickness, were prepared by a melt-spinning technique using some pieces of the arc-melted ingots.

Microstructure of the specimens was examined by X-ray diffractometry (XRD). T_g, crystallization temperature (T_x), supercooled liquid region ($\Delta T_x = T_x - T_g$) and heat of crystallization (ΔH) were measured by a differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s. T_l was also determined by DSC measurement at a cooling rate of 0.033 K/s. Isothermal DSC measurements were also performed at 723K for the ribbons and the bulk glassy specimens to compare the degree of structural relaxation during water-quenching. Coercivity (H_c) was measured at room temperature by using a vibrating sample magnetometer (VSM) in an applied field of 500 kA/m.

3. RESULTS AND DISCUSSION

Change in temperature of the specimen during water-quenching after fluxing is shown for the sample diameter of 3.5, 5.7, 7.7, and 8.4 mm in Fig. 1. Recalescence accompanying crystallization of supercooled liquid was observed at about 1000K

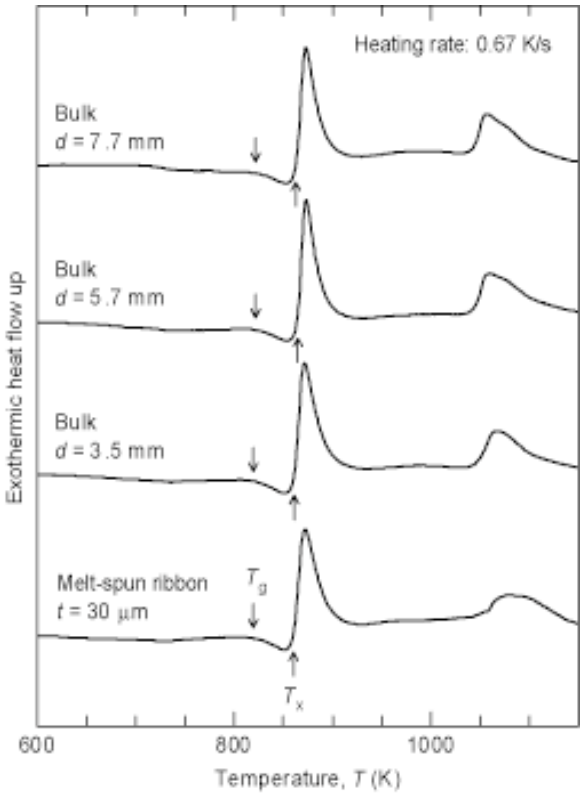

Fig. 3. DSC curves of the bulk specimens with diameters of 3.5, 5.7, and 7.7 mm. The data of the melt-spun tape are also shown for comparison.

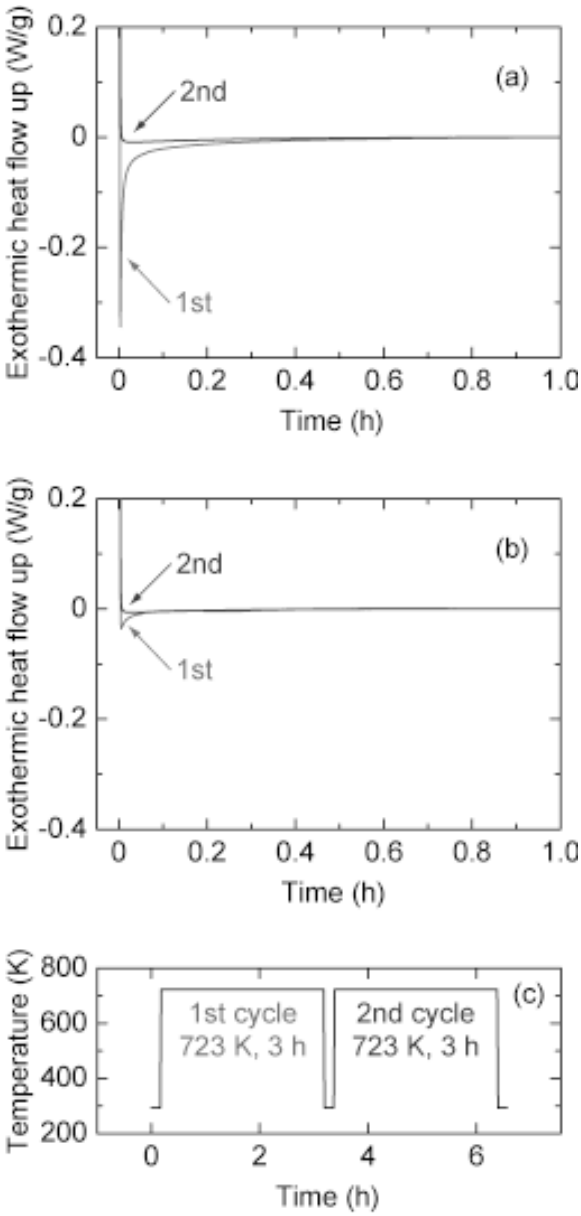

Fig. 4. Isothermal DSC curves of (a) the ribbons and (b) the bulk glassy specimen of 4.6 mm in diameter. The temperature history of the heat treatment used in these measurements is also depicted in (c).

for 8.4 mm diameter specimen, while the others were water-quenched without recalescence. Therefore, it is expected that the specimens with diameter up to 7.7 mm have a fully glassy phase. The cooling rate is estimated to be about 150 K/s at 1200K and about 70 K/s at 1000K for 7.7 mm specimen. The cooling rate decreases with increasing diameter of the specimens. XRD patterns taken from transverse cross sections of the specimens are shown in Fig. 2. The patterns for 3.5 - 7.7 mm diameter specimens consist only of a halo and no diffraction peaks from crystals are found. Therefore, they consist of a single glassy phase. On the other hand, the specimen with 8.4 mm in diameter, in which recalescence was clearly observed during water-quenching, is composed of some crystalline phases, such as α-(Fe,Co,Si), γ-(Fe,Co,Si), $(Fe,Co)_{23}(B,Nb)_6$ ($Cr_{23}C_6$-type), and $(Fe,Co)_2B$.

Fig. 3 shows DSC curves of the bulk metallic glassy specimens and the as-spun ribbons measured at a heating rate of 0.67 K/s. Although the cooling rates during quenching were different for each specimen as shown in Fig. 1, the profiles of the DSC curves are almost the same, i.e. T_g, T_x, ΔT_x, and ΔH are approximately 821K, 862K, 41K, and 53 J/g. The as-spun ribbons and a bulk glassy specimen of 4.6 mm in diameter were subjected to two cycles of isothermal DSC measurement at 723K, which is about 120K lower temperature than T_g. The specimens were rapidly heated up to 723K at a heating rate of 8.33 K/s before the isothermal

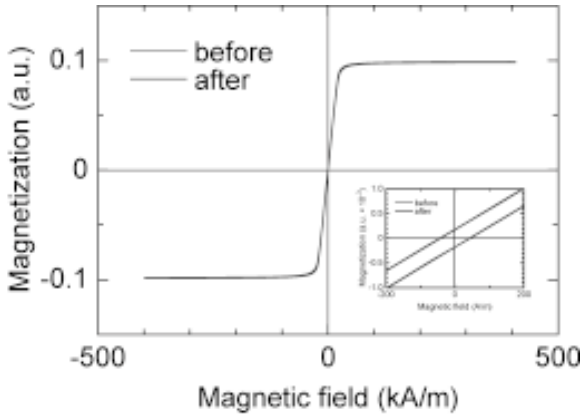

Fig. 5. Magnetization curves at room temperature of the bulk glassy specimen of 4.6 mm in diameter before and after the isothermal DSC measurements. The enlarged curves near the origin are shown in the inset. Both magnetization curves are almost identical because of the accuracy of VSM measurement.

measurement for 3 h, and followed by cooling at a rate of 8.33 K/s. By repeating this procedure twice for the same specimens, isothermal DSC curves of the specimens before and after structural relaxation were measured. Figs. 4a and 4b show the results of isothermal DSC measurement for the ribbons and the 4.6 mm diameter bulk specimen respectively. The heating and cooling procedure used in this experiment is also depicted in Fig. 4c. Part of the DSC curves for the first one or two minutes should be ignored, because the isothermal measurement was not stable. In those DSC curves, the ends of the isothermal DSC curves, where the glassy specimens were almost completely relaxed at 723K, were taken as the origins for the first and second cycles. As structural relaxation proceeds in the specimens, the gap between the first and second DSC curves decreases. Because the ribbons were more rapidly quenched than the bulk specimen, the gap for the ribbons is considerably larger than the bulk specimen. Moreover, it took longer time to reach fully relaxed state at 723K.

Fig. 5 shows the magnetization curves of the bulk glassy specimen of 4.6 mm in diameter before and after the isothermal DSC measurements, i.e. structural relaxation at 723K for 6 h. Both the profile of the magnetization curves and H_c of the specimen hardly changed, although the specimen was experienced structural relaxation. Taking into consideration of demagnetizing field, H_c of the bulk specimen is actually lower than 40 A/m and is different from the previously reported values [14,15]. More precise measurements are required in order to clarify the effect of structural relaxation on coercivity of soft magnetic bulk metallic glasses.

When the ingots were not subjected to fluxing and water-quenching, the maximum diameter of the Cu mold-cast bulk glassy specimens is 5.0 mm [14]. As mentioned above, the maximum diameter of the bulk specimen with a glassy phase is 7.7 mm. Therefore it is confirmed that fluxing is much effective for increasing glass-forming ability (GFA). From the cooling curves of 7.7 mm and 8.4 mm diameter specimen, shown in Fig. 1, the critical cooling rate for a glassy phase can be estimated to be approximately 150 - 170 K/s at around 1200K and 60 - 70 K/s at around 1000K. It is well known that the critical cooling rate of typical Fe-based metallic glassy alloys produced by melt-spinning is about 10^4 - 10^5 K/s. Therefore, it should be noted that the critical cooling rate of alloys subjected to flux treatment is about 10^2 - 10^3 times slower than that of Fe-based metallic glass melt-spun alloys.

4. CONCLUSIONS

(i) The large bulk glassy $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.20}Si_{0.05}]_{96}Nb_4$ alloy specimen with the diameter of 7.7 mm was successfully synthesized by water-quenching of the melt immersed in the molten flux of B_2O_3. (ii) The specimen size is approximately 1.5 times larger than that of the maximum diameter of the copper mold-cast one, and this specimen is the thickest among any Fe-based ferromagnetic glassy alloys formed until now. (iii) The critical cooling rate for a glassy phase significantly decreases by one-third after the flux treatment. (iv) Magnetic properties of the bulk specimen of 4.6 mm in diameter hardly changed although the specimen were subjected to structural relaxation. (v) The flux treatment technique improves GFA by suppressing heterogeneous nucleation.

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