(Fe, Co)–(Hf, Nb)–B Glassy Thick Sheet Alloys Prepared by a Melt Clamp Forging Method

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Glassy Fe₅₈Co₄Hf₆B₃₀ and Fe₆₀Co₃₀Hf₆Nb₂B₁₂ alloys in a thick sheet form were prepared by a meltclamp forging method. Their thickness was 0.78 mm and 0.49 mm, respectively. The glassy sheets have nearly the same values of glass transition temperature (Tg), onset temperature of crystallization (Tc) and Curie temperature (Tc) as those for the melt-spun ribbon samples. The Tg, Tc and Tc were 826 K, 895 K, and 598 K respectively for the Fe₅₈Co₄Hf₆B₃₀ alloy, and 799 K, 841 K and 638 K respectively for the Fe₆₀Co₃₀Hf₆Nb₂B₁₂ alloy. The same thermal properties between the forged and the melt-spun samples are presumably due to the formation of a similar glassy structure. The success of manufacturing Fe-based glassy thick sheets by the forging method is encouraging for future progress as a new engineering material.

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1. Introduction

It is well known that Fe- and Co-based amorphous alloys exhibit good soft magnetic properties and have been utilized¹ in many application fields. However, these soft magnetic amorphous alloys have usually been prepared in a thin sheet form with thickness below 40 μm or in a wire form with a diameter range below 120 μm.² Such a limitation in thickness resulting from their low glass-forming ability has prevented the further extension of application fields as magnetic materials. Great effort has been devoted to search a new ferromagnetic amorphous alloy with higher glass-forming ability in the last few decades. Recently, Inoue et al. have succeeded in finding a number of glassy alloys with high glass-forming ability in Ln-Al-TM,³ Mg-Ln-TM,⁴ Zr-Al-TM⁵ and Pd-Cu-Ni-P⁶ (Ln: lanthanide metal, TM: transition metal) systems and in preparing bulk glassy alloys with maximum diameters up to about 72 mm by the copper mold casting method.⁶ Although these bulk glassy alloys had been limited to nonferrous type without ferromagnetism, the findings of the above described bulk glassy alloys enabled us to derive the three empirical rules for achievement of high glass-forming ability.⁷–¹⁰ That is, (1) multi-component alloys consisting of more than three elements, (2) significant difference in atomic size ratios above 12% among the main constituent elements, and (3) negative heat of mixing among their elements. Based on the three empirical rules, we have subsequently searched ferromagnetic Fe- and Co-based glassy alloys with high glass-forming ability leading to the production of a bulk glassy alloy. As a result, we have found that multicomponent glassy alloys in Fe-(Co, Ni)-(Zr, Nb, Ta)-B, Fe-Co-(Zr, Nb)-(Mo, W)-B and Co-Fe-(Zr, Nb)-B systems exhibit a large supercooled liquid region reaching 80 K before crystallization¹¹–¹３ and can be produced in a cylindrical form with diameters up to about 5 mm by copper mold casting.¹⁴ In addition, it has been reported that the ring form bulk glassy alloy with an outer diameter of 10 mm, an inner diameter of 6 mm and a thickness of 1 mm in Fe-Al-Ga-P-C-B-Si system is formed by copper mold casting and exhibits excellent soft magnetic properties.¹⁵ Although there have been two methods of forming Fe-based bulk glassy alloys, i.e., (1) copper mold casting and (2) pulse current sintering,¹⁶ it is important to develop a new preparation method for fabrication of a bulk glassy Fe-based alloy.

We have tried to prepare a glassy thick sheet form by the melt clamp forging method and succeeded in producing (Fe, Co)–(Hf, Nb)–B glassy alloys in a thick sheet form. This paper presents the structure and the thermal stability of supercooled liquid region of Fe₅₈Co₄Hf₆B₃₀ and Fe₆₀Co₃₀Hf₆Nb₂B₁₂ glassy alloys in a thick sheet form prepared by the melt clamp forging method.

2. Experimental Procedure

Multicomponent alloys with compositions of Fe₅₈Co₄Hf₆B₃₀ and Fe₆₀Co₃₀Hf₆Nb₂B₁₂ were prepared by arc melting a mixture of each pure metals and pure boron crystal in an argon atmosphere. Their compositions are nominally represented as atomic percentage. The thick sheet samples of these alloys were prepared by the melt clamp forging method. The forging equipment used in the present study is illustrated in Fig. 1. The glassy structure of forged samples was examined by X-ray diffraction and optical and scanning electron microscopy (OM and SEM). The samples for X-ray diffraction were in powder form, crushed in an agate mortar, in order to confirm the structure of the interior part of the thick sheets. The thermal stability associated with glass transition, supercooled liquid region and crystallization was examined at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). Every measurement was conducted in a room temperature.

3. Results and Discussion

The thick sheet samples were produced from 20 g of each master alloys, and the thickness of the forged Fe₅₈Co₄Hf₆B₃₀ sample is 0.78 mm and of the Fe₆₀Co₃₀Hf₆Nb₂B₁₂ sample is 0.49 mm. These were probably forecasted to be determined
by temperature, viscosity and cooling speed of each molten alloys or other function, these will be clarified by further detail research.

Figure 2 shows X-ray diffraction patterns of the forged Fe58Co14Hf6B20 and Fe60Co20Hf6Nb2B12 glassy alloys. The XRD patterns consist only of broad peaks, indicating the formation of a glassy phase in the thick sheets. Figures 3 and 4 show optical micrographs and SEM images of the cross section of the forged Fe58Co14Hf6B20 and Fe60Co20Hf6Nb2B12 glassy alloys. No distinct contrast revealing the precipitation of a crystalline phase is seen for both sheets.

Figure 5 shows DSC curves of the forged Fe58Co14Hf6B20 and Fe60Co20Hf6Nb2B12 glassy thick sheets, together with the data of the melt-spun ribbon. The glass transition tempera-

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**Fig. 1** Schematic illustration of a newly designed forging equipment to prepare a bulk glassy alloy in a thick sheet form.

**Fig. 2** XRD patterns of the forged thick sheets. (a) Fe58Co14Hf6B20 and (b) Fe60Co20Hf6Nb2B12.

**Fig. 3** Optical micrographs of the cross sections of the forged thick sheets. (a) Fe58Co14Hf6B20 and (b) Fe60Co20Hf6Nb2B12.

**Fig. 4** SEM images of the cross sections of the forged thick sheets. (a) Fe58Co14Hf6B20 and (b) Fe60Co20Hf6Nb2B12.
4. Summary

The glassy Fe_{58}Co_{14}Hf_{8}B_{20} and Fe_{60}Co_{20}Hf_{8}Nb_{2}B_{12} alloy sheets of 0.78 mm and 0.49 mm in thickness, respectively, were prepared by the melt clamp forging method. These sheets are composed of a glassy phase and have a large supercooled liquid region of 69 K and 49 K, respectively, which are nearly the same as those of the melt-spun ribbons. It is therefore interpreted that the glassy alloy in a thick sheet form has the similar glassy structure as that for the melt-spun thin ribbon.

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