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Super-high hardness of (Fe,Co)-B-Si-Zr/Hf bulk glassy alloys

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ABSTRACT

In this work, the alloying effect of similar atom substitution of Co for Fe on the glass-forming ability as well as mechanical and magnetic properties of $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ (x, y = 0, 5, 10, 15, 20 and 25) glassy alloys has been studied. Our experiments show that the substitution of Co for Fe causes a decrease in the glass-forming ability. By increasing the content of Co, the critical glass formation size gradually decreases from 2.5 mm to 1 mm. Nano-indentation results indicate that both the Young's modulus and hardness increase with increasing Co content in the bulk glassy alloys. The $Fe_{51.7}Co_{20}B_{16.7}Si_{8.3}Zr_{3.3}$ bulk glassy alloy exhibits a microhardness, $H_v = 13.5$ GPa, and a Young's modulus, $E = 230$ GPa, the microhardness being the highest among all the Fe-based metallic bulk materials reported to date. All of the glassy alloys exhibit good soft magnetic properties with high saturation magnetization (1.12–1.33 T) and low coercive force (0.6–5.2 A/m).

1. Introduction

Iron-based amorphous alloys are of great interests for their excellent soft magnetic and mechanical properties [1]. However, Fe-based amorphous alloys generally have poor glass-forming ability (GFA), which limits their industrial applications. In the last decade, great efforts have been made to overcome the size limitation imposed by the high cooling rates needed in the production of Fe-based metallic glasses [2]. Since the first $Fe_{73}Al_5Ga_2P_{10}C_4B_4Si_2$ bulk glassy alloy was synthesized [3], several families of Fe-based bulk glass alloys have been successfully developed. Among them, Fe-B-Si-ETM (Early Transition Metals, ETM = Nb, Zr, Hf, and Ta) quaternary bulk glassy alloys exhibit large GFA, high fracture strength, and good soft magnetic properties [4–9]. Similar atom substitution is an effective method to enhance the GFA of glass alloys. The replacement of Fe by Co has result in not only the enhanced GFA and mechanical strength, but also the decreases of coercive force (H_c) in Fe-B-Si-Nb bulk glassy alloys [10]. The maximum critical diameter of glass formation of $d_c = 5$ mm is achieved in $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ bulk glassy alloys with high fracture strength (σ_f) of 4210 MPa [11,12].

In our previous works [4,6], $Fe_{71.7}B_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5}B_{16.7}Si_{8.3}Hf_{2.5}$ bulk glassy alloys with high GFA ($d_c = 2.5$ mm), good soft magnetic and mechanical properties were developed using the cluster-plus-glue-atom model. This letter reports the alloying effects of similar atom substitution in $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ alloy systems, and the discovery of super-high hardness and elastic modulus.

2. Experimental

Multi-component alloy ingots with compositions of $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ (x, y = 0, 5, 10, 15, 20 and 25) were prepared by arc melting a mixture of pure Fe (99.999 wt%), Si (99.999 wt%), B (99.5 wt%), Co (99.99 wt%), Zr (99.95 wt%) and Hf (99.95 wt%) in a Ti-gettered argon atmosphere. Alloy rods with different diameters were prepared by copper mold suction casting. Ribbons with a width of 1.5 mm and a thickness of about 20–30 μm were prepared by single-roller melt spinning at a tangential wheel speed of 40 m/s. The structures of as-cast ribbons and rods were examined by a Bruker D8 Focus X-ray diffractometer (XRD) with Cu-K_α radiation. The thermal behavior of the glassy alloys was measured by Differential Thermal Analysis (DTA) at a heating rate of 0.67 K/s. The B_s and coercive force (H_c) were tested by a MATS-2010SD Hysteresis-graph. Nano-indentation experiments were carried out by a NHT2+MST nano-indenter at a

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constant strain rate of 0.05 s^{-1} and a maximum load of 200 mN with glassy rods. Hardness and modulus were calculated by using the method proposed by Oliver and Pharr [13]. The Vickers hardness (H_v) measurement was conducted on the 1.0 mm diameter rod samples under a load of 500 g.

3. Results and discussions

X-ray diffraction reveals that the ribbon samples of $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ (x, y = 0, 5, 10, 15, 20 and 25) alloys are amorphous. Fig. 1 presents the X-ray diffraction patterns of the as-cast rod samples of $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ alloys. The results indicate that d_c decreased with increasing Co content in the two series of alloys, which is indicative of reduction of GFA. At the composition of $Fe_{46.7-x}Co_{25}B_{16.7}Si_{8.3}Zr_{3.3}$, the 1 mm diameter rod sample partially crystallizes into a mixture of α-(FeCo) and $(Fe,Co)_2B$ phases. This result comes to be different from those observed in the (Fe,Co)-B-Si-Nb/Ta glassy alloys of similar compositions [14,15].

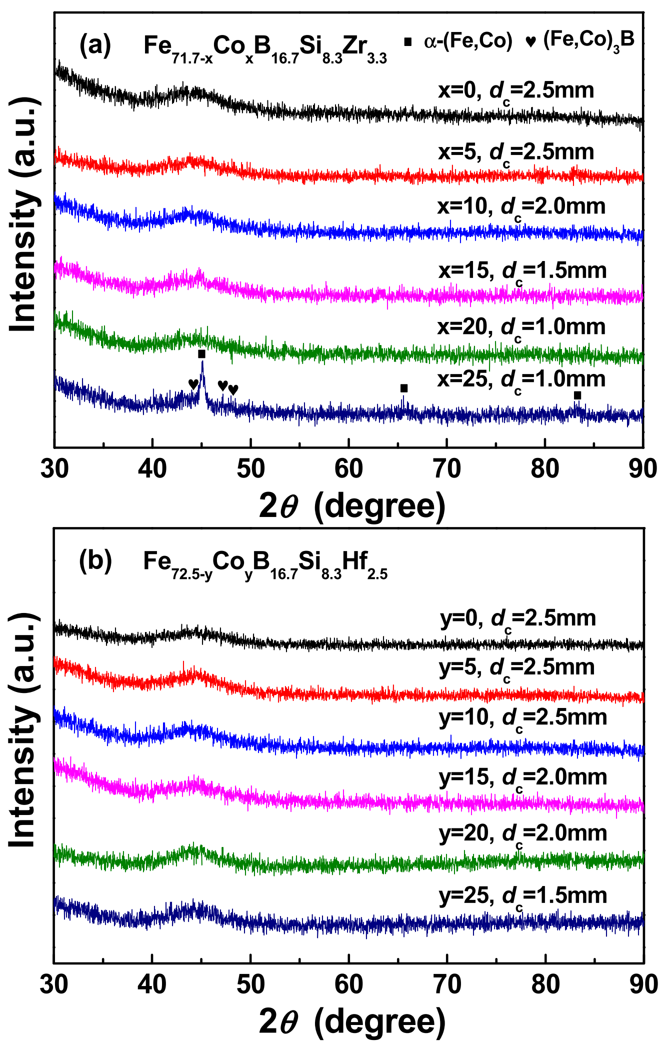

Fig. 1. XRD patterns of (a) $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and (b) $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ (x, y = 0, 5, 10, 15, 20 and 25) as-cast rods with critical diameter sizes (d_c).

Fig. 2 shows the DTA traces of $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ (x, y = 0, 5, 10, 15, 20 and 25) glass alloys. The glass transition temperature (T_g), onset crystallization temperature (T_x), melting temperature (T_m), and liquidus temperature (T_l) are marked with the arrows in Fig. 2. The measured temperature data are summarized in Table 1. It is found that both T_g and T_x of the $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ glassy alloys shift to lower temperature with the increasing content of Co. In the $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ series of alloys, however, T_g and T_x first increase and then decrease with increasing Co content. Both T_m and T_l decrease with increasing Co content in the two alloy systems. The melting behavior of the present glass alloys is similar with the case of (Fe,Co)-B-Si-Nb and (Fe,Co,Ni)-B-Si-Ta [14,15]. The supercooled liquid region $\Delta T_x = T_x$-T_g and the reduced glass transition temperatures $T_{rg} = T_g/T_l$ are calculated to assess the thermal stability and/or GFA of the alloys. The calculation results are included in Fig. 3 and Table 1. With the increase of Co content from x = 0 to 25, the glass transition become weak, and ΔT_x gradually decreases from 41 to 23 K for $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and 35 to 25 K for $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ glassy alloys, respectively. The decrease of ΔT_x reflects the decreased thermal stability of the undercooled liquids of the glass forming alloys. The variation of ΔT_x follows the same tendency as the change of d_c. Unexpectedly, the T_{rg} first increases and then decreases with increasing Co content in two serials alloys, and the T_{rg} for all Co-bearing glassy alloys are greater than that for Co-free glassy alloys. Accordingly, ΔT_x rather than T_{rg} is suitable for the GFA assessment of $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ alloys.

The averaged load-displacement (*P-h*) curves of nano-indentations for $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ bulk glassy alloys are presented in Fig. 4. The Vickers hardness (H_v) and calculated nano-indentation hardness (H_N) and elastic modulus (E) are displayed in Table 1. The H_v, H_N and E show an increasing tendency with increasing Co content in $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ glassy alloys. In particular, the H_v, H_N and E are measured to be 1348 ± 19, 16948 ± 53 MPa and 226 ± 1 GPa, respectively, for $Fe_{51.7}Co_{20}B_{16.7}Si_{8.3}Zr_{3.3}$ glassy alloy, which are the highest among the known Fe-based bulk glassy alloys.

The B_s and H_c of the $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ glass ribbons are summarized in Table 1. These Fe-based glassy alloys exhibit good soft magnetic properties, i.e., high B_s of 1.12–1.33 T and low H_c of 0.6–5.2 A/m. The alloying addition of Co is found to result in lowered saturation magnetization of the glassy alloys. According to the classical localized electron model, the replacement of Fe by Co atoms in the amorphous structures would lead to reduced exchange interaction energy because Co has a smaller atomic magnetic moment than Fe [16]. This would explain the decreasing tendency of the saturation magnetization with increasing Co content in these glassy alloys.

Fig. 5 summarizes the H_v and E data of the $Fe_{71.7-x}Co_xB_{16.7}Si_{8.3}Zr_{3.3}$ and $Fe_{72.5-y}Co_yB_{16.7}Si_{8.3}Hf_{2.5}$ glassy alloy rods together with the previous reported for other typical Fe-based bulk glassy alloys [11,12,17–20]. It is concluded that the new $Fe_{51.7}Co_{20}B_{16.7}Si_{8.3}Zr_{3.3}$ glassy alloy possess the highest H_v among all Fe-based bulk glassy alloys reported to date. With the empirical hardness-strength relationship for bulk glassy alloys, $H_v \approx 3.2\sigma$ [21], the $Fe_{51.7}Co_{20}B_{16.7}Si_{8.3}Zr_{3.3}$ glassy alloys would also deliver a super-high strength. The high values of H_v can be attributed to the strong bonding nature among the constituent elements, as is expected from their strongly negative enthalpies of mixing [14]. The