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Co-Based Bulk Metallic Glasses with Good Soft-Magnetic Properties and High Strength

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Abstract. The thermal stability, glass-forming ability, soft-magnetic properties and mechanical properties of $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0–2) bulk metallic glasses were investigated. The 5.5 at% Nb addition was found to be effective in approaching alloy to a eutectic point, resulting in an increase in glass-forming ability. By copper mold casting, bulk metallic glass rods with diameters up to 5 mm were produced. Except for high glass-forming ability, the bulk metallic glasses also exhibit good soft-magnetic properties, i.e., low coercive force of 1.34–2.14 A/m, high effective permeability at 1 kHz of 2.26–3.06×10^4, and high fractures strength (σ_f) of 4010–4460 MPa. This Co-based bulk metallic glass system with high strengths and excellent soft-magnetic properties is promising for future applications as a new functional material.

Introduction

Ferromagnetic BMGs has been intensively studied mainly due to the potential applications related to their excellent soft magnetic properties and mechanical properties [1-4]. For Co-based amorphous alloys, It is known that CoFeSiB alloys with zero magnetostriction exhibit super-high permeability which has been subsequently developed as high-sensitivity sensor materials [5, 6]. However, the poor glass-forming ability (GFA) requiring high cooling rates to obtain the amorphous phase from the liquid state, resulting in the limitation of shape and dimension to be thin ribbon and wire forms. Therefore, it is demanded to develop new Co-based BMGs combination with higher GFA and good soft-magnetic properties. It has been reported that $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ glassy alloy exhibits the highest strength (σ_f=5185 MPa) among all known alloys [7], and $[(Co_{1-x}Fe_x)_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ glassy alloy with diameters in the range up to 4 mm were also synthesized successfully [8]. With the aim of developing a new Co-based BMGs with higher GFA, it is important to optimize Nb content which could enhance the GFA [9]. We modified the alloy compositions by the substituting Nb for Fe in $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0–2) system, as a result Co-based BMGs with diameters up to 5 mm were synthesized. In addition, these Co-based BMGs exhibited good soft-magnetic properties and high σ_f of 4010–4460 MPa. This paper intends to present the compositional dependence of GFA as well as the soft-magnetic properties and mechanical properties for this glassy alloy system.

Experimental Procedure

Alloy ingots with compositions of $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0–2) were prepared by arc melting the mixtures of pure Fe, Co and Nb metals and pure B and Si crystals in an argon atmosphere. The alloy compositions represent nominal atomic percentages. The cylindrical alloy rods with diameters up to 6 mm were produced by the copper mold casting method. Glassy structure was examined by X-ray diffraction (XRD) with Cu K_α radiation. Thermal stability associated with T_g, T_l and ΔT_x was examined by Netzsch 404C differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus temperature (T_l) was measured by cooling the molten alloy samples with DSC performed at a very low cooling rate of 0.067 K/s. Mechanical properties of σ_f were measured by compression testing with an UTM 5105 testing machine. The gauge dimension was 2 mm in diameter and 4 mm in length, and the strain rate was 5×10^{-4} s^{-1}. Vickers hardness (H_v) was measured with a hardness tester under a load of 9.8 N. Magnetic properties of saturation magnetization (I_s), coercive force (H_c), and effective permeability (μ_e) were measured with a vibrating sample magnetometer (VSM) under an applied field of 400 kA/m, a *B-H* loop tracer under a field of 800 A/m, and an impedance analyzer under a field of 1 A/m, respectively.

Results and Discussion

Fig. 1 (a) shows DSC curves of melt-spun $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0, 0.5, 1, 1.5 and 2) glassy alloy ribbons. Upon heating, all of these amorphous alloys exhibit distinct endothermic events characteristic of the glass transition, and T_g increase gradually from 861 K to 880 K as well as ΔT maintains about a constant value of 54 K with increasing Nb content. The crystallization of the Co-based glassy alloys occurs through two exothermic reaction for x=0, 0.5 and 1, and a mostly single exothermic reaction for x=1.5 and 2, as shown in Fig 1(b). Base on DSC data, the 5.5 at% Nb addition was found to be effective in approaching alloy to a eutectic point. In addition, the lowest T_l is 1342 K for the 5.5 at% Nb alloy, and the T_g/T_l lies in the range from 0.631 to 0.649. These behaviors indicate that the concentration ratio of Nb to Fe is crucial in improving the thermal stability of the supercooled liquid as well as the alloy composition approaching a eutectic point.

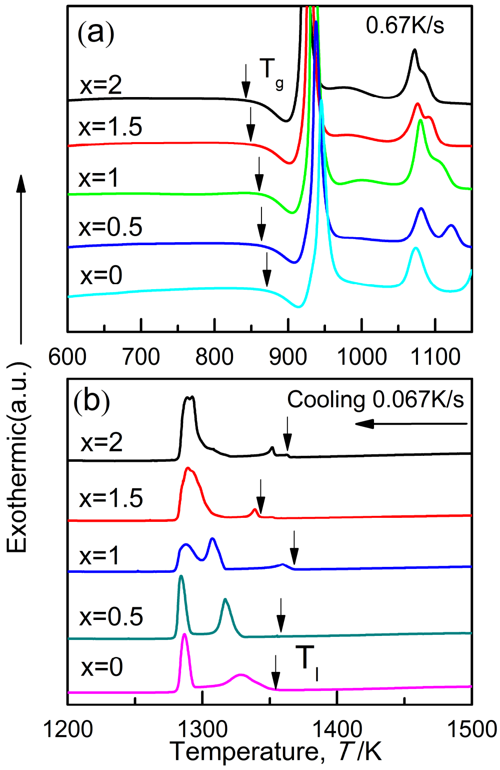

Fig. 1 DSC curves of melt-spun $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0, 0.5, 1, 1.5 and 2) glassy alloy ribbons.

The glassy alloy rods were fabricated at all alloy compositions in this Co-based BMG system. Fig. 2 shows XRD patterns for those cast alloy rods. Only broad peaks without crystalline peaks can be seen for these bulk samples, indicating the amorphous state of these samples. The critical diameter for formation of a glassy single phase was 3.5, 4, 4.5, 5 and 4.5mm for x=0, 0.5, 1, 1.5, and 2, respectively. Insert figure shows outer surface and morphology of the cast glassy alloy rods with diameters of 3–5 mm. For all rod samples the outer surface is smooth and lustrous, and neither apparent volume reductions can be recognized on their surfaces resulting from any crystalline phases.

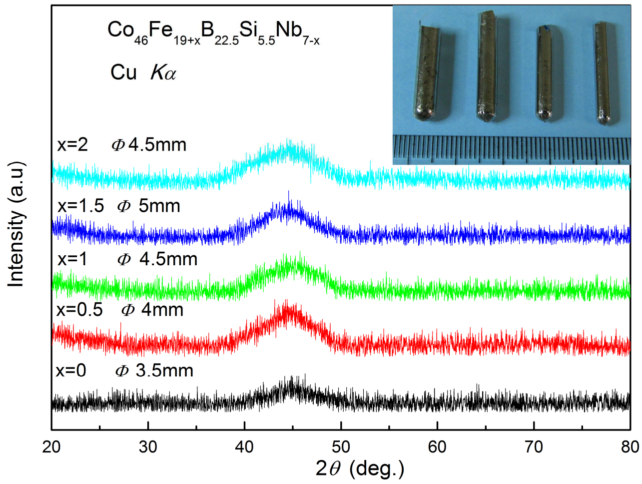

Fig. 2 XRD patterns of the cast $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0, 0.5, 1, 1.5 and 2) alloy rods with critical diameters of 3.5, 4, 4.5, 5 and 4.5 mm, respectively. Insert: Outer surface and morphology of the cast BMG rods.

We also measured the soft-magnetic properties of this BMG system. Fig. 6 shows Typical *I–H* loops measured with VSM and *B–H* loops (inset) of the $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0–2) glassy alloys measured at room temperature. This Co-based BMG system also exhibits good soft magnetic properties including low H_c of 1.34–2.14 A/m and high μ_e of 2.26–3.06×10^4 as shown in the inset figure. It is seen that the I_s decreases from 0.70 T to 0.53 T with the increasing of Nb content from 5 to 7 at%. The origin of excellent soft magnetic properties can be attributed to the low number density of the domain-wall pinning sites, resulting from the high degree of amorphicity and structural homogeneity proceeding from the high GFA [10].

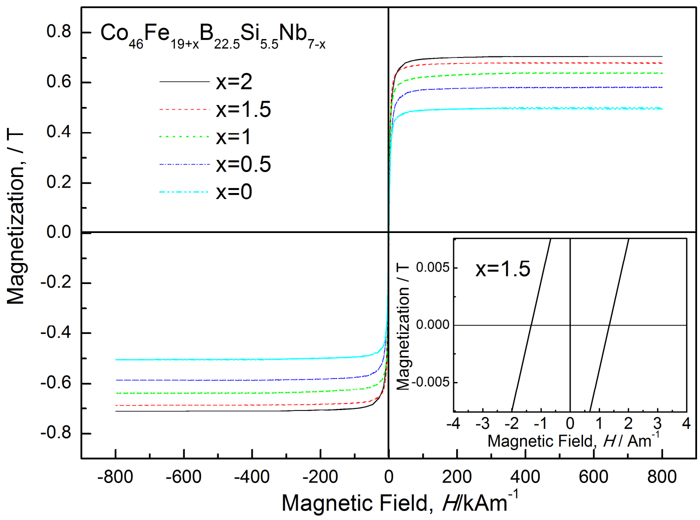

Fig. 3 *I–H* hysteresis loops of the cast $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0, 0.5, 1, 1.5 and 2) glassy alloy ribbons annealed for 300 s at the temperature of T_g−50 K.

The compressive stress-strain curves of the $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=1, 1.5) glassy alloy rods with a diameter of 2 mm were measured as shown in Fig. 4. These glassy alloys exhibit elastic deformation up to a strain of about 0.02, followed by a yield behavior, and then final fracture. These BMGs of x=0, 0.5, 1, 1.5, and 2 exhibit high σ_f value of 4260, 4460, 4390, 4330 and 4010 MPa, and high H_v values of 1196, 1150, 1114 and 1110, respectively. Macro-hardness measurements have been performed using Vickers hardness indenter as shown in insert figure. A number of slip-steps markings are seen in the vicinity of the indentation for the alloys. The generation of slip-steps markings as well as the absence of appreciable crack also indicates the ductility of these Co-based BMGs.

Here we discuss the reasons why the Co-based glassy alloys exhibit a high GFA and high σ_f. One reason is the optimization of concentration ratio of Nb to Fe decrease T_l as well as the alloy composition approaching a eutectic point. The increasing thermal stability of the supercooled liquid enhanced the GFA. In addition, it has been pointed out that heat of mixing play important roles in bulk glassy alloy formation [11]. The mixing enthalpies between Nb and Fe, or Co atomic pairs are −16 and −25 kJ/mol, respectively. Moreover, the mixing enthalpies between Nb and B, or Si atomic pairs are as large as −39 kJ/mol, respectively [12]. The large mixing enthalpies between Nb and B, Si result in the increase of the thermal stability of the supercooled liquid. The high values of σ_f are interpreted to result from strong bonding nature among the constituent elements as is expected from the mixing enthalpies with large negative values.

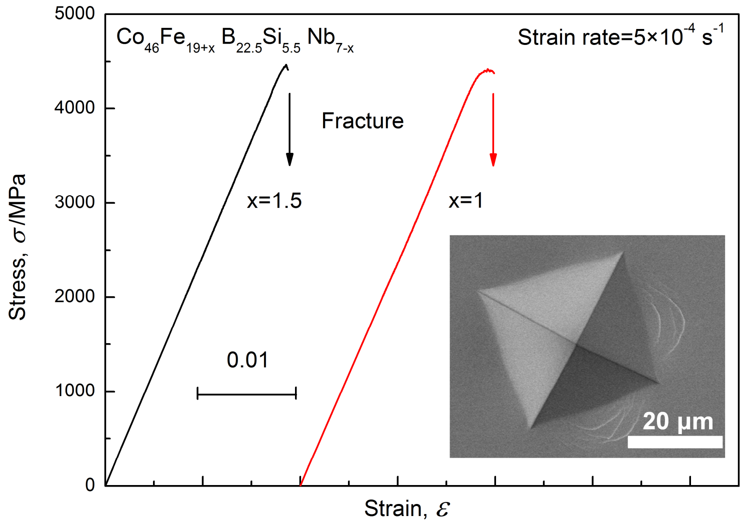

Fig. 4 Compressive stress−strain curves of $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=1 and 1.5) alloys rod with a diameter of 2 mm. Insert: SEM image of the as-cast $Co_{46}Fe_{20.5}B_{22.5}Si_{5.5}Nb_{5.5}$ BMG rod with a slip marking generated by indentation of a Vickers indenter with a load of 9.8 N.

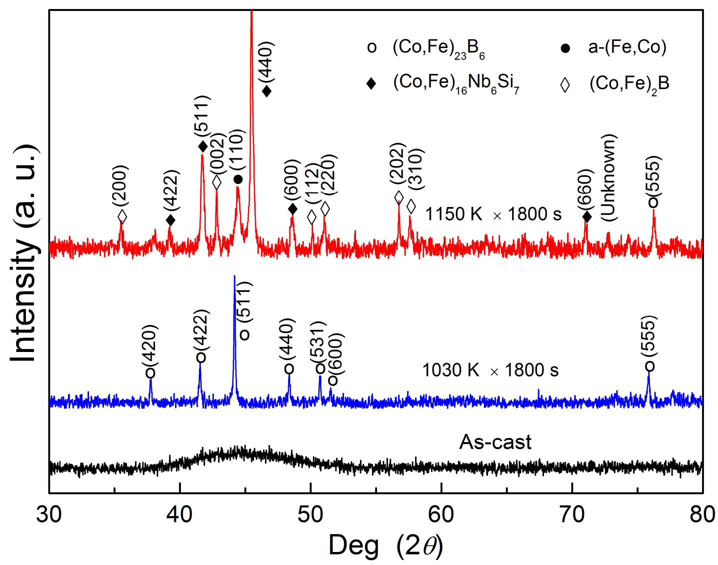

Fig. 5 XRD patterns of the $Co_{46}Fe_{20.5}B_{22.5}Si_{5.5}Nb_{5.5}$ glassy alloy samples annealed for 1800 s at temperatures of 1030 and 1150 K, respectively.

Summary Meantime, we have checked the primary crystalline phase of $Co_{46}Fe_{20.5}B_{22.5}Si_{5.5}Nb_{5.5}$ glassy alloy annealed at temperatures of 1030 K and 1150 K as shown in Fig. 5. It is seen that a complex face-centered cubic $(Co,Fe)_{23}B_6$ phase are identified after annealing at 1030 K for 1800 s, and after annealing at 1150 K the α-(Fe,Co), $(Co,Fe)_{16}Nb_6Si_7$ and $(Co,Fe)_2B$ phases were identified. It has been pointed out that $(Fe,M)_{23}B_6$ phase precipitated from a unique network-like structure, in which distorted trigonal prisms consisting of Fe and B are connected with each other through glue atoms of Nb [13]. The similarities of the primary crystallization phase and the alloy components allow us to presume the formation of the similar network-like atomic configurations that can act as the origins for high resistance against plastic yielding. Furthermore, crystallization of the $(Co,Fe)_{21}Nb_2B_6$ phase from the network-like structure requires long-range atomic rearrangements of constituent elements, which also improves the thermal stability of supercooled liquid, hence enables the formation of a larger BMG by the copper mold casting process.

Thermal stability, glass-forming ability, soft-magnetic properties and mechanical strengths of Co-based $Co_{46}Fe_{19+x}B_{22.5}Si_{5.5}Nb_{7-x}$ (x=0–2) glassy alloys in melt-spun and cast states were examined in this study. Bulk glassy alloy rods with diameters up to 5 mm were fabricated by the copper mold casting method. This Co-based BMG system exhibits excellent soft magnetic and high σ_f over 4000 MPa. The high GFA and super-high σ_f is associated with the high thermal stability of the supercooled liquid, the strong bonding forces among the constituent elements. This Co-based BMG system exhibit high strength combined with excellent soft-magnetic properties, which is promising for future applications new structural and functional materials.

Acknowledgements

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