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Effect of replacing Nb with (Mo and Zr) on glass forming ability, magnetic and mechanical properties of FeCoBSiNb bulk metallic glass

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ABSTRACT

In this work, effects of replacing Nb with either Mo or Zr on glass forming ability (GFA), thermal stability, magnetic and mechanical properties of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ bulk metallic glass were studied. The rod and ribbon samples were prepared using copper mold casting and melt spinner respectively. The replacement of Mo instead of Nb does not affect the crystallization behavior but the GFA is decreased. However an increases in plasticity up to 4% and saturation magnetization (M_s) by 10% is observed for the equal atomic percentage of Mo, with further increase in the Mo content GFA still decreases ($d_c = 1$ mm) and M_s remains the same. In case of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}$ Zr_4 three distinct crystallization events were observed, the glass transition (T_g) and on set of crystallization (T_x) were decreased by 18 K and 23 K respectively. The GFA decreased drastically however the M_s remains the same.

1. Introduction

After the discovery of first ferromagnetic glass in Fe-P-C system by P. Duwez et al. in 1967 [1], several other Fe-based bulk metallic glass (BMG) systems were developed [2–5] for structural and functional applications. Fe-based BMGs are well known for its attractive combination of structural and magnetic properties, moreover these alloys are widely used in industries because of low price and good glass forming ability (GFA) [6]. Fe-Co-B-Si-Nb system was first introduced by Inoue et al. in 2004 [7], $[(Fe_{0.5}Co_{0.5})_{0.75}$ $Si_{0.05}B_{0.20}]_{96}Nb_4$ system is widely studied because of its high strength, excellent soft magnetic properties and high GFA [7]. These Fe-based BMGs do not exhibit strain hardening and can sustain almost no plastic deformation. This brittle behavior under mechanical loading severely limits the applications of Fe-based BMGs as engineering materials. Great efforts have been made recently for improving the plastic deformability of monolithic BMGs or BMG composites. Addition of small amount of Cu up to 0.5 at.% proved to improve the plasticity and magnetic property of this Fe-Co-B-S-Nb system [8]. Yang et al. [9] showed that addition of Mo improves the GFA and also the plastic strain in Fe-P-C system. Xu et al. [10] reported new Fe-Co system having large supercooled liquid region up to 65 K with addition of Mo. Recently, Guo et al. [11] showed that the plasticity of Fe BMGs can be improved by promoting the formation of α-Fe dendrites. Yao et al. [12] revealed that addition of Zr promotes the formation of α-Fe and decreases the $Fe_{23}B_6$ phase. In comparison with Nb, Zr atoms have higher negative heat of mixing with Fe and Co atoms, i.e. −25 and −41 kJ/mol respectively, whereas Mo has lower negative heat of mixing with both Fe and Co atoms: −2 and −5 kJ/mol, respectively. Moreover, the atomic radius of Zr (208 pm) is higher than the atomic radius of Mo (190 pm) or Nb (198 pm). This increases the atomic mismatch and may improve the GFA of this alloy system. Motivated by these studies we decided to replace Nb with Mo and Zr in $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ BMG system. In this present work we will discuss the changes in GFA, magnetic properties and mechanical properties caused due to the addition of Mo and Zr to the Fe-Co-B-Si-Nb glass.

2. Experimental details

The master alloys with the composition of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{100\text{-}x,y}$ (Nb_x, Zr_x, Mo_y) (x = 4) (y = 4, 5, 6)

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were prepared by melting together the mixtures of pure metals and metalloids in induction meting under a protective Ar atmosphere. In this process, induction melting was preferred in order to assure a good homogeneity of the entire master alloy. Pieces of the master alloys were remelted in quartz tubes and subsequently injected into a water-cooled copper mold and copper wheel under a high purity Ar atmosphere to produce rod-shaped and ribbon specimens. Thermal behaviors of glassy samples were evaluated with a NETZSCH DSC 404C differential scanning calorimeter (DSC). The structural characterization of the as-cast rods, as well as the crystallized sample, was performed by X-ray diffraction (XRD) using a Panalytical X'Pert PRO D3290 diffractometer with Co-Kα radiation ($\lambda = 0.17889$ nm). For magnetic measurements, DC M − H hysteresis loops were measured with a vibrating sample magnetometer (VSM) at ambient temperature. The coercivity was measured using a Foerster Coercimat-type device under a DC magnetic field, which can be continuously changed from −250 mT to +250 mT. Cylindrical specimens of 1 mm diameter and 2 mm length were prepared from the as-cast samples and tested with an INSTRON 8562 testing facility in constant strain rate mode (strain rate = $1 \times 10^{-4}s^{-1}$) at room temperature. Both ends of the samples were carefully polished to make them parallel to each other prior to the compression test. The accuracy of the measured data lies within ±2.5 K in the case of DSC measurements, ± 0.1 A/m for coercivity, and ±80 A/m (~1 Oe) for VSM measurements and ±20 MPa for the stress-strain measurements.

3. Results and discussions

Following the experimental route as described above, the maximum diameter of the fully glassy rods obtained for the $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{100-y}$ (Mo_y) (y = 4, 5, 6) alloys are 1.5 mm, 1.5 mm and 1 mm respectively. The addition of Zr instead of Nb reduces the glass forming ability drastically, only the ribbons were amorphous.

3.1. Thermal stability and magnetic properties

Fig. 1 shows the DSC traces measured for all the samples at a heating rate of 20 K/min. The temperatures T_g, and T_x, which are marked in the DSC curves, are the glass transition temperatures and the onset temperatures of crystallization, respectively. The addition of Mo instead of Nb did not affect the crystallization behavior, but the glass transition T_g and the onset temperature of crystallization T_x decreases gradually up to 12 K with increase in Mo content. However the addition of Zr completely changes the crystallization behavior, three distinct crystallization exothermic peaks are observed in contrast to the single exothermic peak observed in the case of alloy with Nb. The thermal stability data as T_g, T_x, ΔT_x, and T_l etc., for both Mo and Zr added alloys are listed in Table 1. The phase evaluation is almost same in Nb and Mo containing alloys, in both the glasses complex $Fe_{23}B_6$ phase forms during the first crystallization [13]. Whereas in the Zr added glass the first phase that precipitates is α-Fe, upon further annealing $Fe_{23}B_6$, FeB, Fe_2B, ZrB_2 phases forms (see Fig. 2). This precipitation of α-(Fe,Co) in Zr added glass maybe promoted by the difference in the electronegativity of the atoms: larger electronegativity difference means stronger metal-metalloids bonds. Zr atoms has the lowest electronegativity (1.33) when compared to Nb (1.60) and Mo (2.16) and hence Mo and Nb added glass has stronger metal-metalloids covalent bond and better GFA. In contrast, the Zr added glass has weaker metal-metalloid bonds and therefore is easy to form the primary phase and thus the GFA is lower [14].

Fig. 3 depicts the hysteresis loops for $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{100-x,\,y}$ (Nb_x, Zr_x, Mo_y) (x = 4) (y = 4, 5, 6) glasses in as cast conditions. In order to avoid the effects due to the sample geometry all the hysteresis loops measurements were done for the samples having same dimensions, in case of coercivity measurement samples with dimensions of 1 mm × 20 mm diameter and length respectively were used. The addition of 4 at.% of Mo increases the M_s value from 108 emu/g to 118 emu/g (see Table 1), however with further increase in Mo at.% the M_s started to decrease slowly. In case of Zr addition no change in the M_s values were observed. The coercivity values were found to increase from 4 A/m to 6 A/m with increase in Mo content, whereas the Zr added glassy ribbons shows a coercivity of 12 A/m. The higher coercivity values for the ribbons is due to the surface irregularities in the ribbons.

3.2. Mechanical properties

Fig. 4 shows a typical room temperature compressive true stress-true strain curves of 1 mm diameter as-cast $[FeCoBSi]_{96}Nb_4$ (black lines) and $[FeCoBSi]_{96}Mo_4$ (red lines) samples. The Nb containing alloy exhibits a high yield strength of $\sigma_y = 3800 \pm 20$ MPa, fracture strength of $\sigma_f = 4000 \pm 20$ MPa and plasticity of 1%. In case of the alloy containing 4% Mo the yield strength of $\sigma_y = 3500 \pm 20$ MPa, fracture strength of $\sigma_f = 3800 \pm 20$ MPa and a high plastic strain of 4%. In addition, the Young's modulus obtained from the linear fitting of the stress-strain curves are $E = 185 \pm 5$ GPa and 154 ± 5 GPa for Nb an Mo containing glasses respectively.

All the stress-strain curves showed numerous serrations, in the plastic deformation region, which should be an indicative of the formation and propagation shear bands [15]. Upon fracture the samples shatter apart in to many pieces, the fractured surfaces of the samples were examined in SEM (the results are not shown). The sample containing Nb shows numerous primary and secondary shear bands, but all of them stopped in a premature stage leading to the cleavage failure. In case of the alloy containing Mo combination of both river like patterns and cleavages are observed. This combination of both ductile and brittle failure may be due to the formation of soft zones because of the Mo addition. Moreover the Mo has lower shear modulus G (20 GPa) and Shear modulus (G) to bulk modulus (B) ratio (0.09), which may increase the Poisson ratio of the current FeCoBSiMo system and thereby leading to a larger

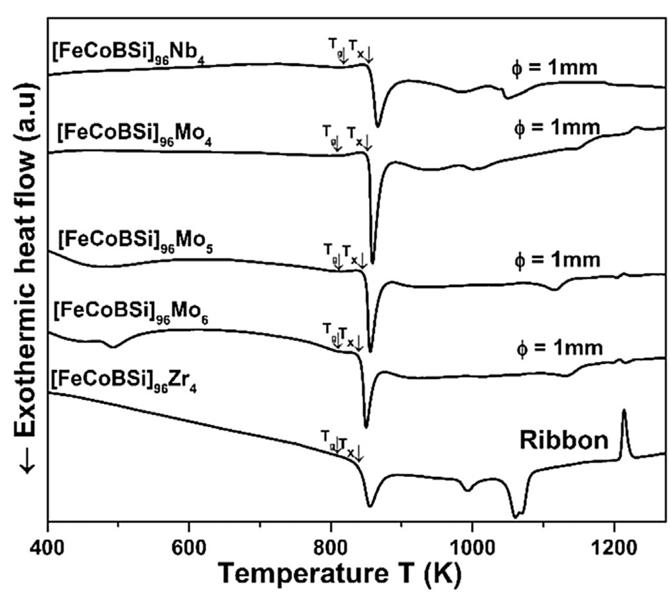

Fig. 1. DSC curves for $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{100-x,\,y}$ (Nb_x, Zr_x, Mo_y) (x = 4) (y = 4, 5, 6) glasses.