Effect of minor Cu addition on phase evolution and magnetic properties of \{[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}\}_{100-x}Cu_x\} alloys

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Abstract. \{[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}\}_{100-x}Cu_x (x = 0, 1, 1.5 and 2) alloys with different rapid solidification conditions were prepared by copper mold casting and melt spinning. The structures, the thermal and the magnetic properties were studied by X-ray diffraction, differential scanning calorimetry and vibrating sample magnetometry, respectively. Minor Cu addition obviously depresses the glass-forming ability of the alloys (critical glassy diameter \(d_c < 1\) mm) compared with \{[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}\}_{99.75}Cu_{0.25} (d_c = 3\) mm). The effect of Cu addition on the evolution of crystalline phases corresponding to different rapid solidification conditions was evaluated. The existence of (Fe,Co), (Fe,Co)\(_3\)B, (Fe,Co)\(_2\)B and (Fe,Co)\(_{23}\)B\(_6\) crystalline phases in \{[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}\}_{100-x}Cu_x\} alloys influences the saturation magnetization compared with the corresponding glassy alloys.

1. Introduction
Since the first ferromagnetic metallic glass, Fe-C-P, was found in 1965 [1], Fe- and Co-based amorphous alloys and the resulting crystalline alloys, produced through crystallization of the corresponding glassy precursors, are regarded as attractive industrial alloys because of their excellent soft magnetic properties [2]. Based on their magnetic advantages, many kinds of products consisting of ferromagnetic metallic glasses have been widely used in our life, such as anti-theft labels in supermarkets and libraries and high efficient magnetic transformers [3,4]. Multi-component glassy alloys decrease the critical cooling rate of glass formation, and promote successfully the formation of bulk metallic glasses (BMGs), which give ferromagnetic metallic glasses potential application as advanced structural material because of their high strength and good corrosion resistance [5-8].

Recently, (Fe-Co)-B-Si-Nb BMGs are regarded as one of the most excellent candidates combining the advantages of functional and structural materials because of their high glass-forming ability (GFA), good mechanical and magnetic properties [9]. Minor addition of Cu in the corresponding glassy precursors is well known as a good method to increase the soft magnetic properties resulting in ultrafine crystalline alloys, such as in case of FINEMET alloys [10]. In the (Fe-Co)-B-Si-Nb alloy system, many researchers also elucidate the influence of minor addition of Cu on GFA, mechanical and magnetic properties of resulting alloys. Jia et al. reported on the GFA of \{[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}\}_{100-x}Cu_x (x = 0, 0.5, 0.6, 0.7 and 1.0) alloys [11]. Shen et al. revealed that in situ formation of (Fe,Co) and (Fe,Co)\(_2\)B\(_6\) microcrystalline grains during the solidification process can improve the ductility of the \{[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}\}_{99.75}Cu_{0.25}\}...
BMG composite [12]. Inoue et al. reported on the effect of crystallization of Fe–Co–B–Si–Nb–Cu glassy alloys on their soft magnetic properties by heat treatment [13]. In this paper, we report on the effect of Cu addition in {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} alloys (x = 0, 1, 1.5 and 2) on GFA and the evolution of crystalline phases corresponding to different rapid solidification conditions. The relationship between the phase constituents and the magnetic properties is also studied.

2. Experimental procedure

Alloy ingots of {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} (x = 0, 1, 1.5 and 2) were produced by induction-melting mixtures of pure Fe (99.9 mass %), Co (99.9 mass %), Si (99.99 mass %), B (99.9 mass %) Nb (99.9 mass %) and Cu (99.9 mass %) in a quartz cup under a high-purity argon atmosphere. The master alloys were remelted in quartz tubes and then the melting liquid was injected into a water-cooled copper mold in a high-purity argon atmosphere to produce rod-shaped specimens (1, 2, 3 and 5 mm), respectively. In order to control the rapid solidification condition for every sample, we chose the same injection temperature of 1523 K to insure the comparability for all as-cast rods. The temperature of the melting of the alloys was measured by an infrared temperature monitor. In addition, ribbons were produced by single-roller melt spinning. The phases of ribbons and rods were examined using a Philips PW 1050 X-ray diffractometer (XRD) with Co-K\(_\alpha\) radiation at a scanning rate of 0.6 degrees/minute. The thermal stability and the melting behavior of the specimens were evaluated with a NETZSCH DSC 404 C differential scanning calorimeter (DSC) at heating and cooling rates of 0.33 K/s. For magnetic measurements, M-H hysteresis loops were measured with a vibrating sample magnetometer (VSM) at ambient temperature. The Curie temperature (\(T_c\)) for glassy samples was determined from the endothermic transition in the DSC curves of the corresponding samples [12,13].

3. Results and discussion

In order to evaluate the effect of minor Cu addition to the {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} base alloy on the GFA, ribbons of {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} (x = 0, 1, 1.5 and 2) alloys were produced. XRD measurements indicate that all ribbons are amorphous. (The patterns are not shown here.) Figure 1(a) shows the crystallization of these ribbons. The addition of Cu changes the shape of the crystallization peaks. The glass transition temperature (\(T_g\)) is obviously shifted to lower temperature with the addition of Cu, which indicates that the introduction of Cu decreases the thermal stability of the supercooled liquid in the resulting metallic glasses. For comparison, {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} (x = 1, 1.5 and 2) rods with different diameters were also produced. The results of XRD measurement show that crystalline phases can be found in all rods. The comparison of the released heat of crystallization (\(\Delta H_{cry}\)) between the glassy ribbon and as-cast rods for the same alloy (one sample shown in Fig. 1(b)) also indicates minor Cu addition lowers the GFA of the alloys. The critical diameter (\(d_c\)) of fully glassy {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} is 3 mm under our experimental conditions.

Table 1. Thermal stability data and magnetic properties of {[(Fe\(_{0.5}\)Co\(_{0.5}\)Si\(_{0.05}\)B\(_{0.20}\)Nb\(_{0.04}\)]\(100-x\)Cu\(_{x}\)} (x = 0, 1.0, 1.5 and 2) glassy ribbons. \(d_c\), \(T_g\), \(T_c\), \(T_m\), \(T_{\gamma}\) and \(M_s\) are critical diameter, glass transition onset temperature, onset temperature of crystallization, melting temperature during the cooling process, liquidus temperature during the cooling process, Curie temperature and saturation magnetization, respectively; \(\Delta T_c\) is equal to \(T_c - T_g\), and \(\gamma\) is equal to \(T_{\gamma}/(T_c + T_g)\).

| x  | \(d_c\)/mm | \(T_g\)/K | \(T_c\)/K | \(\Delta T_c\)/K | \(T_m\)/K | \(T_{\gamma}\)/K | \(M_s\)/emu/\(g\) |
|----|------------|----------|----------|----------------|--------|------------|------------------|
| 0  | 3          | 818      | 852      | 34             | 1380   | 1268       | 0.59             | 0.388 | 700 | 108 |
| 1.0| <1         | 756      | 813      | 57             | 1357   | 1109       | 0.56             | 0.385 | 692 | 102 |
| 1.5| <1         | 764      | 812      | 48             | 1399   | 1107       | 0.55             | 0.375 | 688 | 102 |
| 2.0| <1         | 785      | 812      | 27             | 1385   | 1104       | 0.57             | 0.374 | 688 | 101 |
Figure 1. (a) DSC curves of \( \{(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{Si}_{0.05}\text{B}_{0.20}\text{Nb}_{0.04}\}_{100-\text{Cu}} \) \( (x = 0, 1, 1.5 \text{ and } 2) \) glassy ribbons (heating rate of 0.33 K/s). \( T_g, T_x \) and \( T_c \) are glass transition temperature, onset temperature of crystallization and Curie temperature, respectively; (b) DSC curves of \( \{(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{Si}_{0.05}\text{B}_{0.20}\text{Nb}_{0.04}\}_{98} \) Cu_{2} ribbon and as-cast rods with diameters of 1 and 2 mm at the same heating rate. \( \Delta H_{\text{cry}} \) is the released heat of crystallization.

Figure 2. XRD patterns of \( \{(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{Si}_{0.05}\text{B}_{0.20}\text{Nb}_{0.04}\}_{98} \) Cu_{2} rods in diameters of 1, 2, 3 and 5 mm, respectively.

Figure 3. The dependence of phase constituents decided by sample dimension for the saturation magnetization \( (M_s) \) for the \( \{(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{Si}_{0.05}\text{B}_{0.20}\text{Nb}_{0.04}\}_{98} \) Cu_{2} alloy.

The melting and solidification behavior of every alloy was also studied because these thermal characteristics are associated with the GFA of the master alloy. The thermal stability data, such as \( T_g, T_x, \Delta T_x, T_m, T_t \) etc., are listed in Table 1. The values of \( T_g/T_t \) decrease from 0.59 at \( x = 0 \) to 0.56 at \( x = 1 \). According to the Turnbull’s rule [14], the decrease of GFA influenced by the addition of Cu is easy to understand. Furthermore, the heats of mixing of Fe-Cu and Co-Cu are 13 kJ/mol and 6 kJ/mol, respectively. Some results also referred that a positive mixing heat is not of great benefit to the glass formation [15].

For each as-cast rod under different rapid solidification conditions, i.e. specimens with different diameters, respectively, we evaluated the phase constituents by XRD. The results indicate that the phase constituents for the as-cast rods with different Cu addition but same diameter are completely same, which means that the precipitated phases are decided by the rapid solidification condition, but
are not influenced by the alloy composition when the amount of Cu added is between 1 % to 2 %. Hence, as a typical example we chose a sample with 2 at. % Cu to give the following explanation of the phase evolution. Fig. 2 shows XRD patterns of the as-cast rods of the \( [(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}]_{23}Cu_2 \) alloy with diameters \( (d) \) of 1, 2, 3 and 5 mm, respectively. The \( \alpha-(Fe,Co)B \) phase, a metastable orthorhombic phase [16], only appears under a certain range of cooling rate \( (d < 3 \text{ mm for bulk samples}) \). This phase is the primary crystalline phase precipitated in the glassy matrix during the solidification process, which is different from \( (Fe,Co) \) or \( Fe_{23}B \) as the primary phase in some reports [12,13]. Furthermore, under a slower cooling rate \( (d = 3 \text{ mm and 5 mm}) \) the \( \alpha-(Fe,Co) \) phase comes out together with \( (Fe,Co)_{23}B_6 \) and \( (Fe,Co)_2B \), and these same crystalline phase constituents are even found in the ingot after the arc melting.

The hysteresis loops of \( [(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}]_{23}Cu_x \) \( (x = 0, 1, 1.5 \text{ and 2}) \) glassy ribbons were measured using VSM. The saturation magnetization \( (M_s) \) of these ribbons at 15000 Oe is listed in Table 1. Similar to the change of \( T_c \), minor Cu addition to the \( [(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}]_{23}Cu_x \) alloy depresses \( M_s \) of the resulting glassy alloys. Fig. 3 shows the dependence of phase constituents decided by sample dimension for \( M_s \) in the \( [(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}]_{23}Cu_2 \) alloy. The precipitation of the \( \alpha-(Fe,Co)B \) phase in glassy matrix slightly decreases \( M_s \). However, the appearance of the \( \alpha-(Fe,Co) \) phase is beneficial for the improvement of \( M_s \) of the as-cast alloys under slower cooling conditions.

4. Conclusions
The minor addition of Cu in \( [(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.20}]_{0.96}Nb_{0.04}]_{23}Cu_x \) \( (x = 0, 1, 1.5 \text{ and 2}) \) alloys lowers the GFA of the resulting alloys and no bulk metallic glasses with the addition of Cu can be produced. During the solidification process the primary crystalline phase is the \( \alpha-(Fe,Co)B \) metastable phase, which is replaced by \( \alpha-(Fe,Co), (Fe,Co)_{23}B_6 \) and \( (Fe,Co)_2B \) phases under slower cooling conditions. The precipitation of \( \alpha-(Fe,Co) \) is beneficial for the improvement of \( M_s \) of as-cast rods.

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