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Enhanced glass forming ability of Fe-based amorphous alloys with minor Cu addition

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ABSTRACT

A novel approach was reported that allows us to enhance glass-forming ability (GFA) of Fe-based amorphous alloys with high saturation magnetization by minor substitution Cu, which has a large positive heat of mixing and similar atomic radius with the main constituent Fe. The minor Cu substitution (<1 at.%) can substantially increase the GFA of Fe-based amorphous alloys with the primary phase that is not α-Fe (110) type phase. Using this strategy, Fe-based amorphous alloys with both high saturation magnetization and good GFA were developed. Our results reveal that the formation of competing crystalline phases is beneficial for the GFA. We anticipate that this work may guide the way for designing new Fe-based amorphous alloys with high saturation magnetization and large GFA concurrently.

1. Introduction

Owing to the combination of high saturation magnetization, high permeability, and the low cost of manufacture [1], the high Fe content amorphous alloys, especially at.% of Fe > 83% [2,3], have attracted great research interests ever since their first synthesis. They are inherently strong and have promising applications in toroidal cores, choke coils, power transformers, etc. [4]. Unfortunately, most of them were limited to thin ribbons with thickness less than 15 μm, since the critical cooling rate that required to hinder the crystallization of these alloys was generally larger than order of 10^5–10^6 K/s [5]. Actually, the synthesis of Fe-based amorphous alloys with high glass-forming ability (GFA) has always been one of the most important scientific interests [6–9]. The widely used strategy to couple the attractive properties of Fe-based amorphous alloys with good GFA is introducing multiple metallic or metalloid elements with negative heat of mixing and/or a prominent atomic size mismatch with the main constituent Fe [10–12]. However, the reduction of Fe inevitably leads to the deterioration of magnetic properties, especially the saturation magnetization [8,13,14]. Therefore, it poses a serious challenge to develop Fe-based amorphous alloys with high saturation magnetization and good GFA concurrently.

In this paper, we report a novel approach that allows us to enhance GFA of high Fe content amorphous alloys by minor substitution of Cu, which has a large positive heat of mixing (+13 kJ/mol) [15] and similar atomic radius (0.124 nm) [16] with the main constituent Fe. Using this systematic approach, we can develop Fe-based amorphous alloys containing high iron content without deteriorating their good GFA and magnetic performance. Our approach reveals that the formation of competing crystalline phases is beneficial for the GFA, and might provide guidance to design new Fe-based amorphous alloys with high saturation magnetization and large GFA concurrently.

2. Experiments

Fe-based alloys ingots with nominal composition of $Fe_{72-x}B_{19.2}Si_{4.8}Nb_4Cu_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0$), $Fe_{84-x}Nb_2B_{14}Cu_x$ ($x = 0.0, 0.5, 1.0$ and 1.5) and $Fe_{86-x}B_7C_7Cu_x$ ($x = 0.0, 0.5, 0.7$ and 1.0) were prepared by arc-melting a mixture of pure Fe (99.99%), Nb (99.99%), B (99.5%), Si (99.999%), Cu (99.99%) and pre-alloyed Fe–C alloy in a highly purified argon atmosphere. The alloy ribbons and cylindrical rods were produced by single-roller using melt spinning method and copper mold casting method, respectively. The crystallization temperature (T_x) of as-quenched ribbons was measured by differential scanning calorimetry (DSC, NETZSCH 404C) with a heating rate of 0.67 K/s. Crystallization treatment was carried out by treating the as-quenched amorphous specimens at different temperatures under

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vacuum followed by water quenching. Microstructure was examined by X-ray diffraction (XRD, Bruker D8 Advance) with Cu $K\alpha$ radiation.

3. Results and discussion

Fig. 1 shows the effects of Cu substitution on the crystallization behavior in $Fe_{72-x}B_{19.2}Si_{4.8}Nb_4Cu_x$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0) alloys. The small Cu-addition yields two clearly separated peaks that assign to the first crystallization peaks T_{x1} and T_{x2}. The separation between the two peaks is practically insensitive to the further increase of the Cu content beyond a small, critical concentration ~ 0.3 at.%, as displayed in Fig. 1(a). It is known that the primary phase of the Cu-free glassy alloy is $Fe_{23}B_6$ phase. Although the first crystallization peak was the same from $x = 0.0$ to $x = 0.3$, as shown in Fig. 1(b), the primary phase changed into a mixture of $Fe_{23}B_6$ and bcc-Fe phases by increasing Cu content from $x = 0.1$ to 0.3, as shown in Fig. 1(c). However, from Fig. 1(d), the diffraction peaks of $x = 0.4$ alloy annealed for 600 s at 900 K correspond exclusively to the bcc-Fe phase. Therefore, the Cu-addition yields two separated the first crystallization peaks corresponding to the primary crystallization of bcc-Fe at T_{x1} and, subsequently, to the precipitation of $Fe_{23}B_6$ compounds at T_{x2}. The decrease of the onset temperature for the first crystallization stage reflects that the Cu substitution apparently lowers the configurational energy of the subcritical nucleus.

Based on the present and previous results [17], the effect of Cu on the process of primary phase in the alloy is schematically presented as shown in Fig. 2. The initial amorphous phase is the chemically uniform amorphous solid solution and the primary phase of the Cu-free glassy alloy is $Fe_{23}B_6$ phase. As the amount of Cu goes up, the concentration of Cu in the clusters increases, and their structure becomes more like fcc. Because Cu has a large positive heat of mixing with respect to Fe [15], Fe atoms are rejected from Cu clusters and would pileup at the Cu/amorphous interface [18]. Then heterogeneous nucleation at the Cu/amorphous interface would be chemically more favorable than homogeneous nucleation inside the amorphous phase. The heterogeneous nucleating potential barrier is smaller than homogeneous nucleating potential barrier [19]. Meanwhile, the Cu particle in amorphous alloys has the nearest neighbor structure similar to the fcc–Cu. The fcc–Cu (111) and bcc α-Fe (110) have very good matching [20]. Therefore, α-Fe (110) will be nucleated on the fcc–Cu (111) surface which can provide a low interfacial energy, i.e., Cu substitution can facilitate the segregation of α-Fe (110) phases. In addition, the $Fe_{23}B_6$ phase has a complex face-centered cubic structure with a large lattice parameter of more than 1 nm including 96 atoms [21], and its precipitation from the network-like glassy structure requires high energy and long-range atomic rearrangements of constituent elements. The competitive formation of the $Fe_{23}B_6$ and α-Fe (110) leads to the glassy phase upon the devitrification is drastically impeded. In consequence, the formation

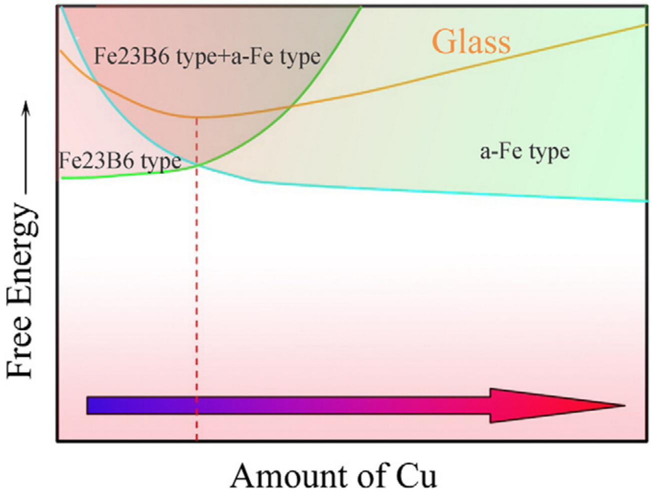

Fig. 2. The free energy diagram for $Fe_{72-x}B_{19.2}Si_{4.8}Nb_4Cu_x$ alloys.

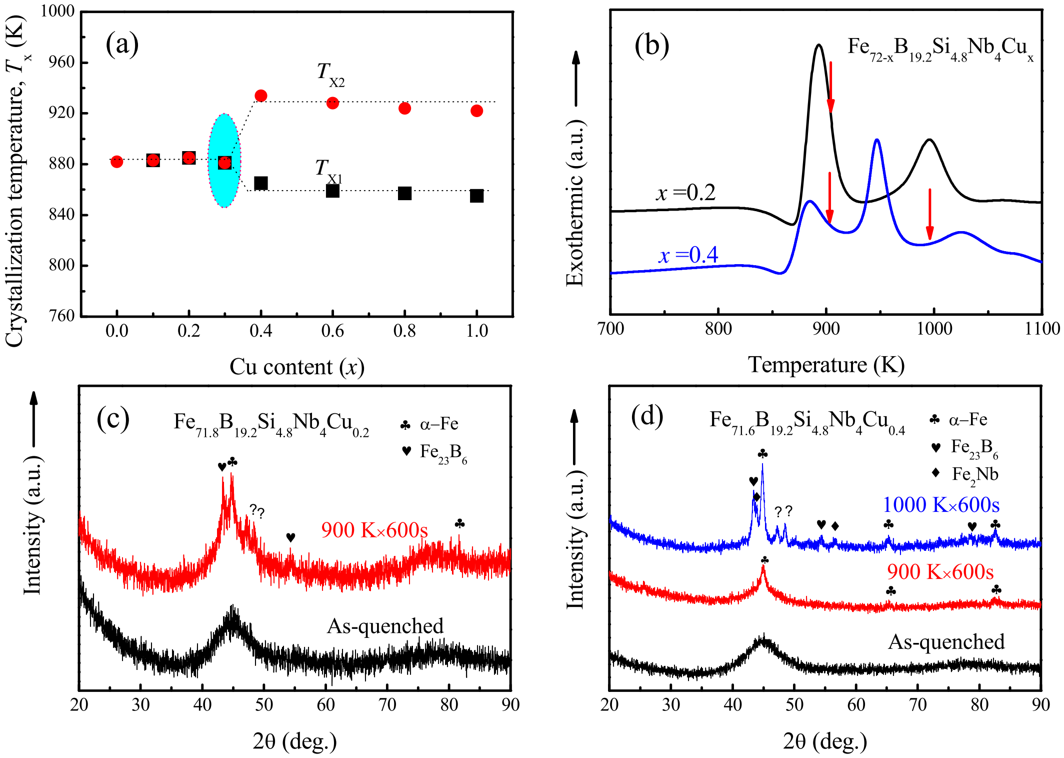

Fig. 1. Effects of Cu on the crystallization behavior in $Fe_{72-x}B_{19.2}Si_{4.8}Nb_4Cu_x$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0) alloys. (a) Onset temperatures for crystallization, T_x, vs. Cu content. (b) DSC curves of the melt-spun $Fe_{71.8}B_{19.2}Si_{4.8}Nb_4Cu_{0.2}$ and $Fe_{71.6}B_{19.2}Si_{4.8}Nb_4Cu_{0.4}$ amorphous ribbons. (c) XRD patterns of the melt-spun $Fe_{71.8}B_{19.2}Si_{4.8}Nb_4Cu_{0.2}$ samples as quenched and annealed for 600 s at 900 K. (d) XRD patterns of the melt-spun $Fe_{71.6}B_{19.2}Si_{4.8}Nb_4Cu_{0.4}$ samples as quenched, annealed for 600 s at 900 K and 1000 K.