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Effects of Cu substitution for Nb on magnetic properties of Fe-based bulk metallic glasses

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ABSTRACT

The effects of minor Cu substitution for Nb in $Fe_{72}B_{20}Si_4Nb_{4-x}Cu_x$ ($x = 0.0$, 0.1, 0.2, and 0.3) bulk metallic glasses (BMGs) on the magnetic properties were investigated. With increasing Cu content from $x = 0$ to 0.3, the critical diameters are kept constant at 1.5 mm for all Fe-based BMGs rods. Meanwhile, the increasing saturation magnetization from 1.19 to 1.27 T, and the decreasing coercive force from 2.5 to 1.5 A/m were found, with the effective permeability improved from 20,000 to 24,500. This work reveals the connection between the enhanced magnetic properties and Cu substitution. It may shed light on the design of Fe-based BMGs with better magnetic properties and larger glass-forming ability concurrently.

1. Introduction

In recent years, Fe-based bulk metallic glasses (BMGs) have attracted great attention because of their superior properties such as excellent magnetic properties and good mechanical properties, as well as their abundant natural resources and low materials costs [1–6]. Generally speaking, magnetic properties and glass-forming ability (GFA) are among the most concerned aspects in magnetic materials, physical science and related industries. Minor element substitution or addition is known as an important approach to tailor magnetic properties and GFA of BMGs [7]. For Fe-based BMGs, it has been accepted that great magnetic properties are originated from their high Fe content; meanwhile, it has also been reported that substitution of Fe element can improve GFA [3,8], accompanied with an unwanted decrease of magnetic properties [9,10]. Is it possible to obtain one improved property without decreasing the other, e.g. a better magnetic property with no decreased GFA? Among Fe-based BMGs, Fe-Si-B glassy alloy with high saturation magnetization has been widely used in motors, high frequency inductors and current transformers, etc. [11]. However, its critical diameter is limited to no more than 0.27 mm, which hinders the extension of its practical applications [12]. The atomic radii of Fe, Si, and B are 0.124, 0.117, and 0.09 nm [13], respectively, while it is 0.143 nm for Nb atom, which meets A. Inoue's empirical rules for high GFA [14]. Actually, significant improvement in GFA is expected through minor addition of Nb, thus Fe-Si-B-Nb BMGs were prepared and investigated [15,16]. Recently, elements with a positive mixing enthalpy with main component were demonstrated to promote the bonding of Fe—Fe pairs and enhance magnetic properties in Fe-based BMGs [17,18]. As we known, the mixing enthalpy between Cu and Fe is positive [13], suggesting a repulsive interaction between them. Therefore, improved magnetic properties are expected in the Cu-doped Fe-based BMGs. Meanwhile, it has been reported that Cu addition into the Fe-based BMGs can effectively increase the GFA while maintain or even strength the magnetic properties [19,20], which stimulates us conducting the exploration of partial substitution of Nb by Cu in Fe–Si–B–Nb BMG. Here, classic $Fe_{72}B_{20}Si_4Nb_4$ is adopted. This substitution is believed to be more economical, with expecting better magnetic properties and/or larger GFA.

In this paper, we demonstrated that the quaternary $Fe_{72}B_{20}Si_4Nb_4$ system with proper Cu substitution can dramatically improve both soft-magnetic properties and saturation magnetization, with almost the same high GFA. Besides, the effect of Cu substitution was interpreted in details. We believe this study can provide guideline for obtaining multicomponent amorphous alloys with higher saturation magnetization, lower coercive force and higher permeability.

2. Experimental

$Fe_{72}B_{20}Si_4Nb_{4-x}Cu_x$ ($x = 0.0$, 0.1, 0.2, and 0.3) ingots were prepared by arc melting the mixtures of Fe (99.99%), Nb (99.99%), and Cu (99.99%) metals, together with B (99.50%) and Si (99.99%) crystals in an argon atmosphere. Melt-spun method and copper mold casting method were used to produce the alloy ribbons and cylindrical rods, respectively. The structures of as-quenched samples were examined

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by X-ray diffraction (XRD) with Cu K_α radiation. The thermal properties of these BMGs were investigated using a NETZSCH 404C differential scanning calorimeter (DSC) under a flow of high purity argon. The as-quenched ribbons were isothermally annealed at the temperature 50 K below the glass transition temperature for 600 s under vacuum followed by water quenching. Saturation magnetization (M_s) and coercive force (H_c) were measured with a vibrating sample magnetometer (VSM) under an applied field of 400 kA/m and a B-H loop tracer under a field of 800 A/m, respectively. Effective permeability (μ_e) at 1 kHz was measured by an impedance analyzer under a field of 1 A/m at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Fe_{72}B_{20}Si_4Nb_{4\text{-}x}Cu_x$ ($x = 0.0, 0.1, 0.2$, and 0.3) alloy rods with 1.5 mm in diameter. It is shown that all XRD patterns exhibit only one broad diffraction peak without visible crystal diffraction peaks, which is the characteristic of an amorphous structure.

The DSC traces of $Fe_{72}B_{20}Si_4Nb_{4\text{-}x}Cu_x$ ($x = 0.0, 0.1, 0.2$, and 0.3) alloy rods are shown in Fig. 2. The thermal stability parameters, including glass transition temperature T_g, crystallization temperature T_x, extension of the supercooled liquid region ΔT_x, liquidus temperature T_l, the eutectic temperature T_e, the reduced glass transition temperature $T_{rg} = T_g/T_l$ [21] and $\gamma = T_x/(T_g + T_l)$ [22] are summarized in Table 1. All DSC curves exhibit one characteristic endothermic event of glass transition, followed by a supercooled liquid region and crystallization exothermic reaction, further confirming the glassy structure in these alloys. All these Fe-based BMGs present high thermal stability with high crystallization temperatures above 880 K. It can be found that with the increase of Cu content, glass transition temperature T_g and crystallization temperature T_x decrease gradually from 842 to 838 K and from 882 to 880 K, respectively. Meanwhile, the supercooled liquid region ΔT_x increases from 40 to 42 K with Cu substitution, as shown in Fig. 2(a). Fig. 2(b) presents the cooling DSC curves of the same Fe-based BMG system, it can be seen that liquidus temperature T_l increases from 1479 to 1484 K while the eutectic temperature T_e is maintained at the 1406 K, demonstrating the substitution of Cu does not exert much influence on reduced glass transition temperature T_{rg} and γ parameter. In order to describe the GFA of metallic glasses, three important parameters including the critical diameter, the reduced glass transition temperature T_{rg}, and γ are adopted [21,22]. In details, 1.5 mm is determined as the critical diameter for all samples. At the same time, with increased Cu content from 0.0 to 0.3, T_{rg} and γ decrease slight from 0.569 to 0.565 and from 0.380 to 0.379, respectively. As no obvious variations are found for all these three parameters, it is believed that the relatively high GFA remains constant here, i.e. no decrease in GFA was observed with minor Cu substitution for Nb in the present system.

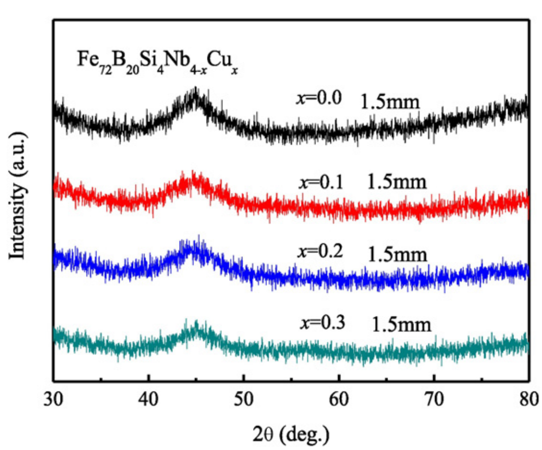

Fig. 1. XRD patterns of the $Fe_{72}B_{20}Si_4Nb_{4\text{-}x}Cu_x$ ($x = 0.0, 0.1, 0.2$, and 0.3) alloy rods under critical diameters.

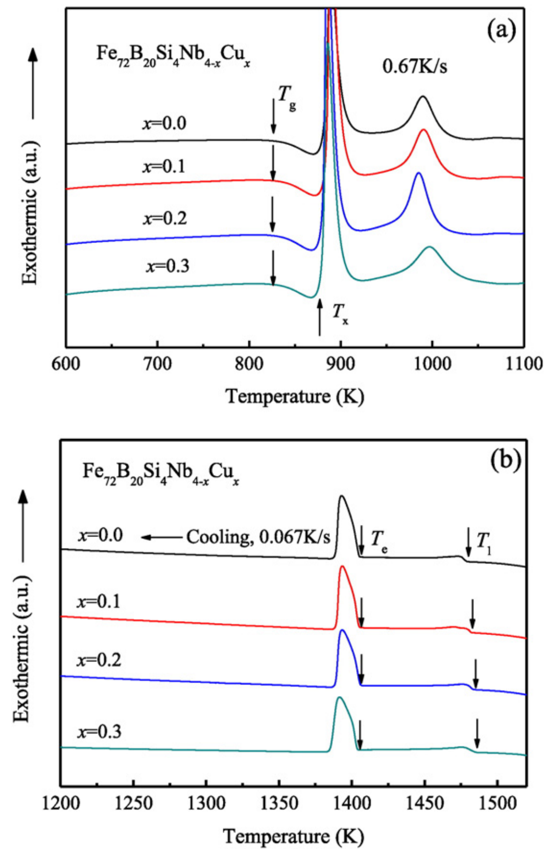

Fig. 2. DSC traces for $Fe_{72}B_{20}Si_4Nb_{4\text{-}x}Cu_x$ ($x = 0.0, 0.1, 0.2$, and 0.3) alloy rods. (a) Heating rate of 40 K/min; (b) cooling rate of 40 K/min.

Fig. 3(a) exhibits the magnetic hysteresis loops of $Fe_{72}B_{20}Si_4Nb_{4\text{-}x}Cu_x$ ($x = 0.0, 0.1, 0.2$, and 0.3) glassy ribbons, the corresponding saturation magnetization M_s as a function of Cu content are also given in Fig. 3(b). It can be seen that saturation magnetization M_s increases monotonically from 1.19 to 1.27 T with increasing Cu content from 0.0 to 0.3, indicating the improved saturation magnetization M_s without decreased GFA. As we all know, the magnetic moment is an important parameter characterizing the magnetism, and the saturation magnetization value reflects the amount of total magnetic moment for magnetic materials [23]. The increment in the saturation magnetization with Cu substitution is explained as follows. Partial substitution of Cu (with atomic radius 0.128 nm) for Nb (with a larger atomic radius of 0.143 nm) [13] means the decrease of atomic distance between Fe atoms. Subsequently, the exchange-coupling interaction of Fe atoms is enhanced, which results in an increased total magnetic moment of the alloy [20,24]. Besides, it is known that the positive mixing enthalpies between Fe—Cu pairs are + 13 kJ/mol [19]. Because of this positive mixing enthalpy, the repulsive interaction between Fe and Cu atoms is generated, which promotes the bonding of Fe—Fe pairs that finally results in the increment of the nearest-neighbor Fe atoms [20]. According to Heisenberg [18,20],

Table 1
Thermal stability data for cast $Fe_{72}B_{20}Si_4Nb_{4-x}Cu_x$ ($x = 0.0, 0.1, 0.2$, and 0.3) alloy rods.

Atomic fraction x	T_g (K)	T_x (K)	ΔT_x (K)	T_l (K)	T_e (K)	T_{rg}	γ
0.0	842	882	40	1479	1406	0.569	0.380
0.1	840	881	41	1482	1406	0.567	0.379
0.2	838	881	42	1483	1406	0.565	0.379
0.3	838	880	42	1484	1406	0.565	0.379