Effects of Cu substitution for Fe on the glass-forming ability and soft magnetic properties for Fe-based bulk metallic glasses

Lintao Dou [a], Haishun Liu [a,*], Long Hou [a], Lin Xue [a,b,c], Weiming Yang [a,b], Yucheng Zhao [a], Chuntao Chang [b,**], Baolong Shen [c,***]

[a] School of Sciences, State Key Laboratory for Geomechanics and Deep Underground Engineering, China University of Mining and Technology, Xuzhou 221116, China
[b] Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[c] School of Materials Science and Engineering, Southeast University, Nanjing 211189, China

ARTICLE INFO

ABSTRACT

The effects of Cu substitution for Fe on the glass-forming ability (GFA) and soft magnetic properties for $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) bulk metallic glasses (BMGs) are investigated. It is found that the investigated BMGs exhibit large GFA as well as excellent soft magnetic properties, and proper substitution of Fe by Cu improves the saturation magnetization, coercive force, and effective permeability without obvious deterioration of the GFA.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Recently, bulk metallic glasses (BMGs) have attracted considerable attention due to their unique properties and potential applications [1–4]. Among them, Fe-based BMGs are more attractive and promising for engineering application due to their good soft magnetic properties [5] and much lower cost [6] compared to other BMGs [7–10]. However, the low packing density resulted from low glass-forming ability (GFA) of the currently commercialized Fe-based metallic glasses has increased Joule heat losses and prevented them from taking over the market for step down transformers, etc. [11]. Therefore, it poses a serious challenge to develop Fe-based BMGs with large GFA and good magnetic performance concurrently. To improve the GFA, multiple metallic elements have been alloyed to substitute Fe; as a result, it inevitably leads to the deterioration of magnetic properties, especially saturation magnetization [12]. Up to date, several compositions of Fe-based BMGs with large GFA have been reported [6,13,14]. However, such alloys contain a large amount of rare earth metal element and low Fe content, which leads to a decrease of saturation magnetization below 1 T [14], and even exhibit paramagnetic state at room temperature [6,13]. Meanwhile, some Fe-based ferromagnetic BMGs have been reported with high saturation magnetization above 1.5 T; however, their GFA is relatively poor [15,16]. Minor additions of elements with a large negative heat of mixing and/or a prominent atomic size mismatch with the main constituents in BMGs have been proven effective in enhancing GFA [10]. However, there is little coverage on the effect of an element with a positive heat of mixing with main constituents.

In this paper, we focus on Cu with a positive heat of mixing with the main constituents Fe ($+13$ kJ/mol) [17] in $Fe_{72}B_{20}Si_4Nb_4$ BMG, and the effects of its substitution for Fe, and finding it improves soft magnetic properties, but does not obviously reduce the GFA.

2. Experimental

Multi-component $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) ingots were prepared by arc melting the mixtures of Fe (99.99%), Cu (99.99%), and Nb (99.99%) metals, together with B (99.5%) and Si (99.999%) crystals in an argon atmosphere. The alloy ribbons and cylindrical rods were produced by a melt-spun method and a copper mold casting method, respectively. The structures of as-quenched samples were identified by X-ray diffraction (XRD) with Cu Kα radiation. The thermal stability of

* Corresponding author. Tel.: +86 139 12006872; fax: +86 516 83591591.
** Corresponding author. Tel.: +86 135 12977595; fax: +86 574 87617212.
*** Corresponding author. Tel.: +86 574 87913392; fax: +86 574 87617212.
E-mail addresses: liuhaishun@126.com (H. Liu), ctchang@nimte.ac.cn (C. Chang), blshen@seu.edu.cn (B. Shen).

the glassy samples was examined using a NETZSCH 404 C differential scanning calorimeter (DSC) under a flow of high purity argon. Magnetic properties including saturation magnetization (M_s), coercive force (H_c), and effective permeability (μ_e) at 1 kHz were measured by 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 at room temperature, respectively. All of the samples for magnetic property measurements were annealed for 300 s at the temperature of T_g−50 K for improving soft-magnetic properties through structural relaxation. The final results were obtained by averaging over 10 experimental values.

3. Results and discussion

Fig. 1 shows the XRD patterns for $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) as-cast rods. Each pattern contains only one broad maximum without any additional sharp Bragg peaks; the diffraction images did not show any traces of crystalline. This is a characteristic for fully amorphous samples.

Fig. 2(a) shows DSC curves of the melt-spun $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) BMGs. All the related thermal stability parameters are summarized in Table 1. It can be seen that glass transition temperature T_g and crystallization temperature T_x decrease simultaneously with Cu substitution, and they decrease from 842 to 820 K and from 882 to 855 K respectively; however, the supercooled liquid region ΔT_x increases gradually from 40 to 45 K with 0.2% Cu substitution, and then decreases constantly with increasing Cu substitution, decreases to 35 K under 1.0% Cu substitution. Fig. 2(b) shows the cooling DSC curves of the same Fe-based BMGs system, which demonstrates that the $Fe_{72}B_{20}Si_4Nb_4$ BMGs exhibit relatively high T_l and T_e of 1479 and 1406 K, respectively, as well as a relatively large temperature interval (T_l-T_e) of 73 K, implying that this composition does not lie in the vicinity of an eutectic point, and the substitution of Cu did not exert much influence on these physical quantities. Meanwhile, even after the substitution of Cu, the reduced glass transition temperature (T_g/T_l) [18] and γ parameter [$T_x/(T_g+T_l)$] [19] are determined to belong to the ranges of 0.583–0.599 and 0.372–0.381, respectively. This concludes that although the Cu element has positive heat of mixing with the main constituents Fe, the GFA shows very weak dependence on the thermal stability data in the present system, which is in agreement with the results in the literature [20]. In addition, it is noteworthy that every DSC exhibits only one endothermic event of the glass transition from the amorphous solid into the supercooled and a
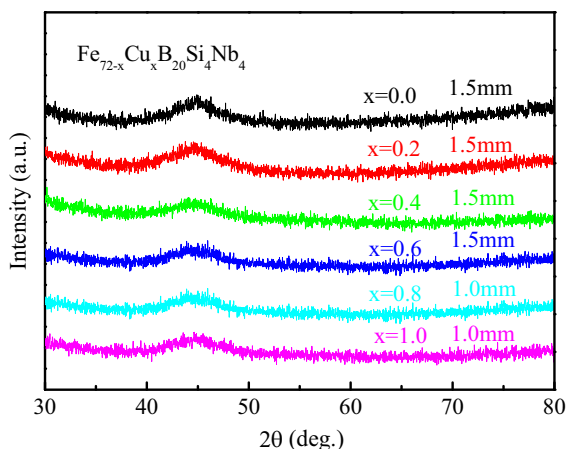
Fig. 2. DSC traces for cast $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) alloys: (a) measured at a heating rate of 40 K/min and (b) measured at a cooling rate of 4 K/min.

Table 1
Thermal stability data for cast $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) alloys: glass transition temperature T_g, crystallization temperature T_x, extension of the supercooled liquid region ΔT_x, liquid temperature T_l, melting temperature T_m, the reduced glass transition temperature T_{rg} and the γ parameter.

Atomic fraction x	T_g (K)	T_x (K)	ΔT_x (K)	T_l (K)	T_m (K)	T_{rg}	γ
0.0	842	882	40	1479	1406	0.599	0.380
0.2	840	885	45	1480	1406	0.597	0.381
0.4	824	865	41	1480	1406	0.586	0.375
0.6	820	859	39	1480	1406	0.583	0.373
0.8	820	857	37	1480	1406	0.583	0.372
1.0	820	855	35	1480	1405	0.584	0.372

following crystallization exothermic reaction, further confirming the glassy nature of the rods.

Fig. 3(a) shows the magnetic hysteresis loops of $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) BMGs, and corresponding saturation magnetization M_s of these alloys as a function of Cu substitution is also shown in Fig. 3(b). As can be seen, M_s increases with increasing Cu substitution, attains a broad maximum at $x=0.6$, and decreases rapidly with further Cu substitution. It is evident that the alloy with 0.6% Cu substitution exhibits the highest M_s of 1.245 T in the investigated Fe-based BMGs, which is consistent with the recently reported [11].

The TEM micrograph, corresponding selected area electron diffraction (SAED) pattern and HRTEM of the sample are shown in Fig. 4 (a) and (b). No crystalline phase is observed. The inset corresponding to SAED patterns exhibits a single diffraction halo, and no sharp

Fig. 1. XRD patterns of the cast $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) alloys rods with critical diameters.

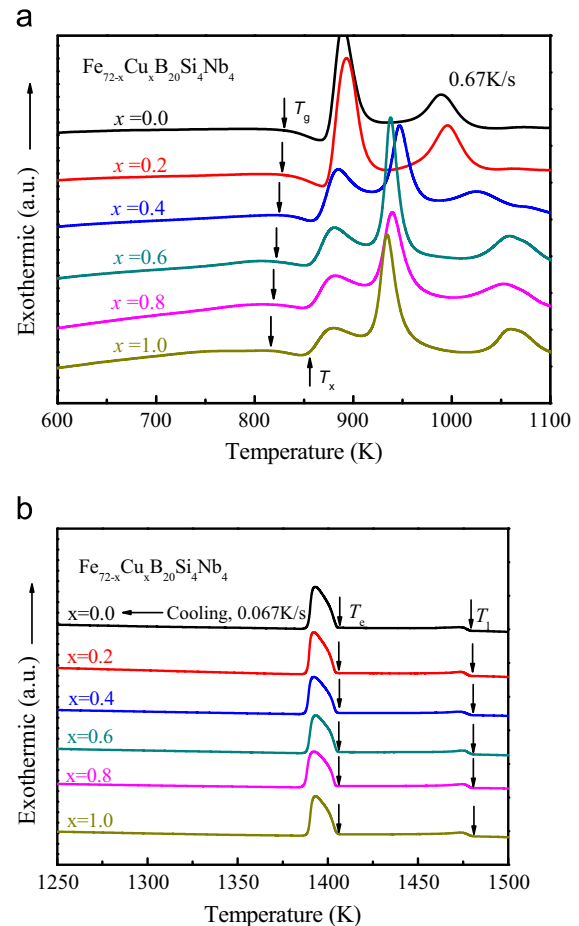diffraction rings are observed, which further confirms that the sample possesses a fully glassy structure. This indicates that the α-Fe nano-crystals could be excluded from the causes of the increment in M_s.
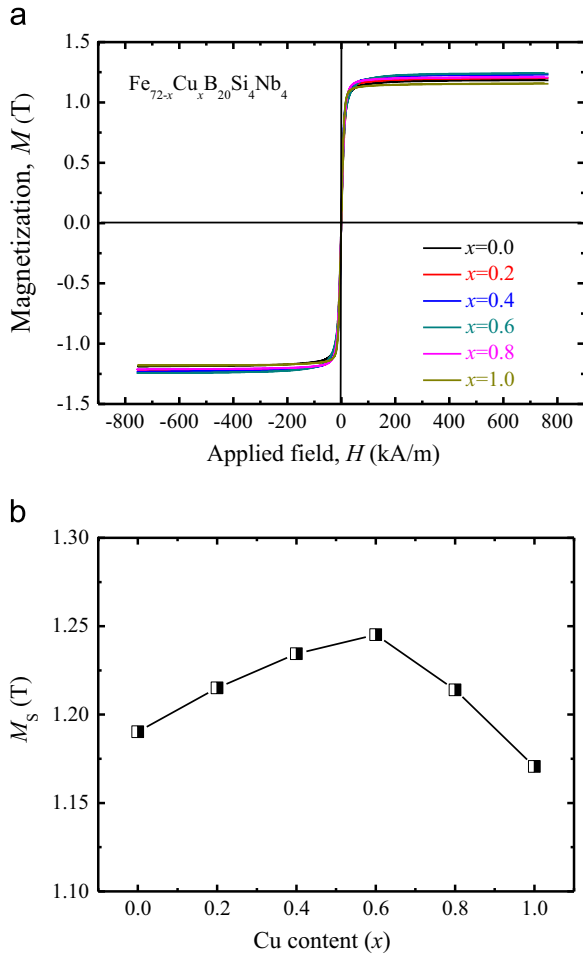
It is known that M_s is actually determined by the total magnetic moment in the amorphous structures, and Cu substitution for Fe indeed reduces the total concentration of Fe atoms in the alloy, which undoubtedly decreases M_s of corresponding BMGs. On the contrary, copper has a positive heat of mixing with Fe atoms, their atoms would impulse each other in the Cu-doped alloys [11], and it has been proven that proper additions of Cu could promote the bonding of Fe–Fe pairs [21], and leads to the increase of the number of the nearest-neighbor Fe atoms; according to Heisenberg [22], the atomic magnetic moment is assumed to be dependent on the number of the nearest-neighbor Fe atoms. From this perspective, Cu substitution for Fe can somewhat lead to an increment in the saturation magnetization as well. When minor Fe was substituted by Cu in the base alloy, the effect of the impulse between Cu and Fe atoms may be more obvious, the number of the nearest-neighbor Fe atoms increases, and M_s increases consequently; with excessive additions of Cu (> 0.6%), the effect of the reduction of Fe concentration atoms may become more dominant, resulting in the decrease of M_s. Therefore, M_s first reaches the maximum at the alloy with 0.6% Cu and then decreases at the alloy containing 1.0% Cu.

Fig. 5 shows the coercive force H_c and effective permeability μ_e of $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) BMGs

Fig. 3. (a) DC hysteresis loops for $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) alloys. (b) Variations of saturation magnetization as function of the Cu content x.
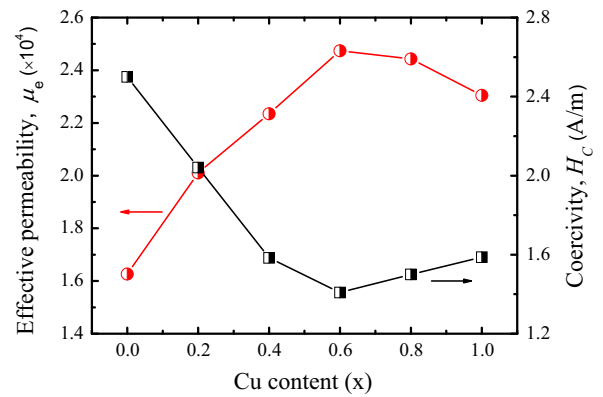

Fig. 5. The coercive forces and effective permeability of $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) alloys.
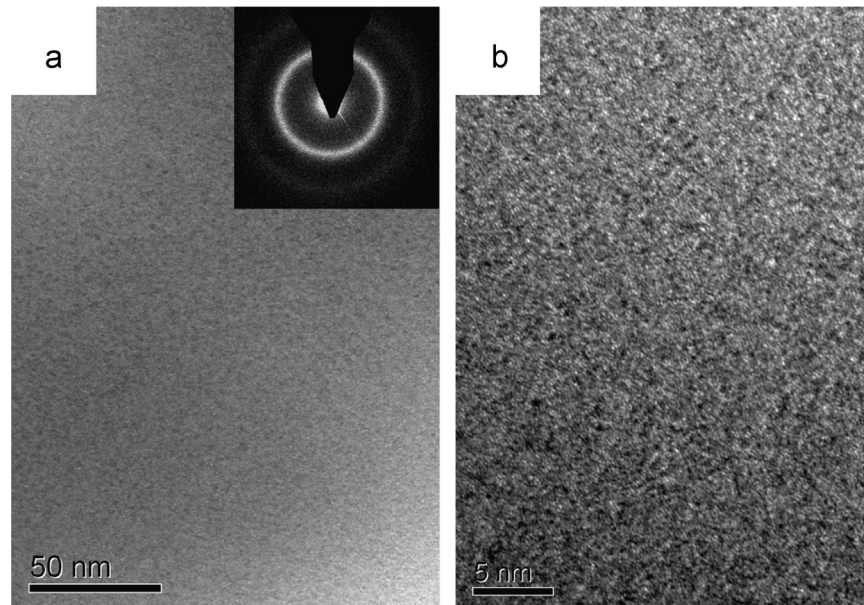

Fig. 4. (a) TEM micrograph, corresponding selected area electron diffraction (SAED) pattern and (b) HRTEM image of the $Fe_{71.4}Cu_{0.6}B_{20}Si_4Nb_4$ sample.

annealed at the temperature of T_g−50 K. It can be seen that H_c and μ_e exhibit an approximate inverse variation relationship with Cu substitution; every glassy alloy shows a relatively low H_c and a relatively high μ_e, indicating its good soft magnetic properties. It can also be seen that H_c decreases from 2.5 A/m to a minimum of 1.4 A/m with no Cu substitution for the alloy with $x=0.6$, and then increases with further Cu substitution; meanwhile, μ_e increases from 16,200 to 24,700 with 0.6% Cu substitution, and then decreases with further Cu substitution. It has been proven that the coercive force H_c can be estimated by the following equation $H_c \approx \alpha(K/(\mu_0 M_s)) + \beta(\sqrt{(\lambda_s \sigma)/(\mu_0 M_s)^2})$ with α and β are the constants, K the magnetic anisotropy, μ_0 the vacuum permeability, λ_S the effective magnetostriction, and σ the average absolute value of the residual stresses [23,24]. It is well known that σ decreases rapidly first and then becomes close to 0 after annealing at the temperature of T_g−50 K. The variation in H_c can be attributed to the effect of M_S. Increase of M_S results in the decrease of H_c with increasing Cu substitution; meanwhile, the decrease of M_S results in the increase of H_c with subsequently further Cu substitution. Accordingly, H_c would first decrease and then increase. Conversely, μ_e increases from 16,200 to 24,700 with 0.0–0.6% Cu substitution, and then decreases with further Cu substitution.

4. Conclusion

The effect of substitution of Fe by Cu on glass formation and magnetic properties of $Fe_{72-x}Cu_xB_{20}Si_4Nb_4$ BMGs ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) was studied, and it can be concluded that:

(1) Transition temperature T_g and crystallization temperature T_x constantly decrease simultaneously with Cu substitution; however, the supercooled liquid region ΔT_x increases with 0.2% Cu substitution, and then decreases with further Cu substitution.
(2) The studied BMGs exhibit relatively high T_l and T_e as well as relatively large temperature interval ($T_l - T_e$); the substitution of Cu does not exert much influence on these physical quantities.
(3) The saturation magnetization M_s and effective permeability μ_e increase with little Cu substitution, and decrease rapidly as Cu

substitution $> 0.6\%$, and coercive forces H_c show an approximate inverse variation. The alloy with 0.6% Cu substitution exhibits the best soft magnetic properties.

References

[1] A.L. Greer, Science 267 (1995) 1947.
[2] A. Inoue, Acta Mater. 48 (2000) 279.
[3] W.M. Yang, H.S. Liu, X.Q. Yang, L.M. Dou, J. Low Temp. Phys. 160 (2010) 148–155.
[4] K. Zhang, H. Li, L. Li, X.F. Bian, Appl. Phys. Lett. 102 (2013) 1907.
[5] W.M. Yang, H.S. Liu, L. Xue, J.W. Li, C.C. Dun, J.H. Zhang, Y.C. Zhao, B.L. Shen, J. Magn. Magn. Mater. 335 (2013) 172–176.
[6] Z.P. Lu, C.T. Liu, J.R. Thompson, W.D. Porter, Phys. Rev. Lett. 92 (2004) 2455031.
[7] B.L. Shen, M. Akiba, A. Inoue, Appl. Phys. Lett. 88 (2006) 131907.
[8] J.W. Li, W.M. Yang, M.X. Zhang, G.X. Chen, B.L. Shen, J. Non-Cryst. Solids 365 (2013) 42–46.
[9] A. Inoue, B.L. Shen, H. Koshiba, H. Kato, A.R. Yavari, Nat. Mater. 2 (2003) 661–663.
[10] M. Stoica, V. Kolesar, J. Bednarčic, S. Roth, H. Franz, J. Eckert, J. Appl. Phys. 109 (2011) 054901.
[11] J.E. Gao, H.X. Li, Z.B. Jiao, Y. Wu, Y.H. Chen, T. Yu, Z.P. Lu, Appl. Phys. Lett. 99 (2011) 052504.
[12] J.W. Li, W.M. Yang, D. Estéves, G.X. Chen, W.G. Zhao, Q.K. Man, Y.Y. Zhao, Z.D. Zhang, B.L. Shen, Intermetallics 46 (2014) 85–90.
[13] V. Ponnambalam, S.J. Poon, G.J. Shiflet, J. Mater. Res. 19 (2004) 1320.
[14] S. Lee, H. Kato, T. Kubota, K. Yubuta, A. Makino, A. Inoue, Mater. Trans. 49 (2008) 506–512.
[15] L. Xue, H.S. Liu, L.T. Dou, W.M. Yang, C.T. Chang, A. Inoue, X.M. Wang, R.W. Li, B.L. Shen, Mater. Des. 56 (2014) 227–231.
[16] M.X. Zhang, A.D. Wang, W.M. Yang, B.L. Shen, J. Appl. Phys. 113 (2013) 17A337.
[17] A. Takeuchi, A. Inoue, Mater. Trans. 46 (2005) 2817.
[18] G.B. Fratucello, P. Vavassori, J. Magn. Magn. Mater. 260 (2003) 480–486.
[19] D. Turnbull, Contemp. Phys. 10 (1969) 473–488.
[20] W.M. Yang, H.S. Liu, C.C. Dun, J.W. Li, Y.C. Zhao, B.L. Shen, J. Non-Cryst. Solids 361 (2013) 82–85.
[21] Z.B. Jiao, H.X. Li, J.E. Gao, Y. Wu, Z.P. Lu, Intermetallics 19 (2011) 1502–1508.
[22] W. Heisenberg, Z. Phys. 49 (1928) 619.
[23] H. Kronmüller, Philos. Mag. B 48 (1983) 127–150.
[24] P. Agudo, M. Vázquez, J. Appl. Phys. 97 (2005) 023901.