Journal of Alloys and Compounds 504S (2010) S78–S81

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Enhancement of plasticity of Fe-based bulk metallic glass by Ni substitution for Fe

S.F. Guo[a,b], N. Li[a], C. Zhang[a], L. Liu[a,*]

[a] State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, 430074 Wuhan, People's Republic of China
[b] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:
Received 4 July 2009
Received in revised form 7 January 2010
Accepted 10 February 2010
Available online 18 February 2010

Keywords:
Amorphous materials
Thermal analysis
Mechanical property

ABSTRACT

Bulk metallic glasses (BMGs) $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ (x = 0, 0.1 and 0.2) with a diameter of 3 mm were synthesized by copper mold casting. The effect of Ni substitution for Fe on the structure, thermal and mechanical properties has been studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and compressive testing. It was found that the substitution of Ni for Fe enhances the glass forming ability, and improves the plasticity of $Fe_{71}Mo_5P_{12}C_{10}B_2$ BMG as indicated by the increase in the plastic strain from 3.1% (x = 0) to 5.2% (x = 0.2). The improvement of the plasticity is discussed in term of the reduction of glass transition temperature and the supercooled liquid region due to the substitution of Ni for Fe.

1. Introduction

Recently, the improvement of the room temperature plasticity of bulk metallic glasses (BMGs) has become a hot topic in the development of advanced structural materials [1,2]. Unlike other BMG systems, Fe-based BMGs are more attractive for engineering application due to the combination of ultrahigh strength, excellent corrosion resistance and relatively low material cost [3–8]. However, the majority of the Fe-based BMGs show almost no plastic strain at room temperature (usually less than 0.2%), which strictly limits the scope of their applications. Recently, it has been found that the Poisson's ratio and the value of G/K (G and K are the shear modulus and bulk modulus, respectively) are important factors in designing Fe-based BMGs to alleviate the brittleness [9–11]. By varying the composition, shear bands are easily initiated and multiplied under external loading for the BMGs with a higher Poisson's ratio or lower G/K ratio. Using these strategies, Gu et al. [12] have developed ductile FeMoPCB BMGs with the maximum plastic strain up to 3.6%. In addition to the elastic parameters, it was also found that the atomistic interaction between constituents plays an important role in the plasticity of Fe-based BMGs [9].

In this work, we tune the alloy composition by the substitution of Ni for part of Fe in FeMoPCB BMG system with the aim to improve its plasticity. Element Ni is chosen due to the following considerations: (i) compared to Fe, Ni has a higher Poisson's ratio (0.31) and lower G/K ratio (0.42), therefore, the substitution of Ni for Fe could increase the Poisson's ratio of the alloy system; (ii) the substitution can improve the glass forming ability of Fe-based BMG as reported previously [13]; (iii) Ni has a smaller negative mixing enthalpies with metalloid elements (P, C and B) than Fe, which may decrease atomistic interaction, consequently enhance the plasticity. Based on these considerations, a novelty FeNiMoPCB BMG was developed, which indeed shows a high glass forming ability and extended plasticity.

2. Experimental

Multi-component master alloys with compositions of $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ (at.%) where x = 0, 0.1 and 0.2 were prepared by arc melting of raw materials under a Ti-gettered argon atmosphere. The raw materials include pure Fe (99.9%), Ni (99.99%), Mo (99.9%), C (99.999%) and B (99.95%) and industrial Fe–P alloy which consists of 72.6% of Fe, 25.3% of P and other impurities in remainder. Sample rods with diameters of 1 and 3 mm were produced by suck mould casting. The structure of the as-cast alloys was identified by X-ray diffraction (XRD, Philips X'Pert PRO) using Cu Kα radiation. The thermal behaviors related to glass transition, crystallization and melting events of the as-cast alloys were investigated with a differential scanning calorimeter (PerkinElmer, DSC-7) and differential thermal analysis (PerkinElmer, DTA-7) under flowing purified argon at a heating rate of 20 K/min. The uniaxial compression test was performed with a Zwick/Roell testing machine at a strain rate of 10^{-4} s^{-1}. At least five specimens were tested for each composition to ensure that the results were reproducible. The compression specimens with a diameter of 1 mm and a length of 2 mm were cut from the cast rods, and the ends were polished carefully to ensure parallelism. The morphology of fractured and the lateral surface of samples were examined with a scanning electron microscope (SEM, FEI-Sirion 200).

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-cast $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ samples (x = 0, 0.1 and 0.2) of 3 mm in diameter. It can be observed that the Ni-bearing alloys are basically amorphous, while the Ni-free alloy shows a few of Fe_3P crystalline peaks superimposed on the broad hump, indicating

* Corresponding author. Tel.: +86 27 87556894; fax: +86 27 87554405.
E-mail addresses: sfguo2005@163.com, lliu2000@mail.hust.edu.cn (L. Liu).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.02.058

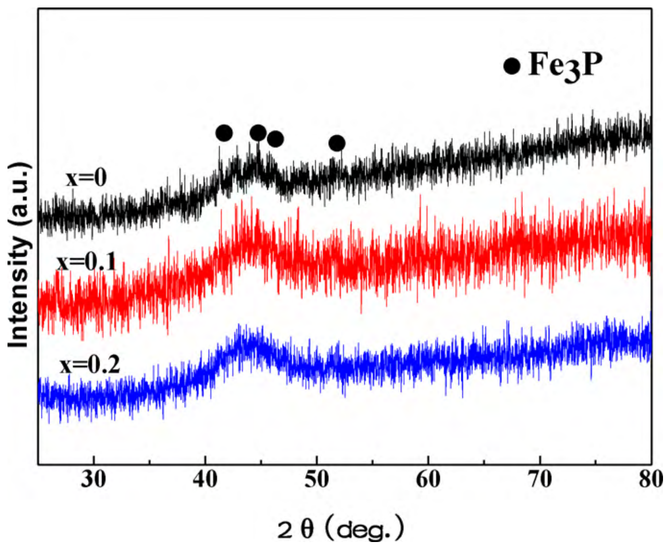

Fig. 1. XRD patterns of the as-cast $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ (x = 0, 0.1 and 0.2 at.%) alloys with 3 mm in diameter.

that the substitution of an appropriate amount of Ni for Fe can improve the glass forming ability (GFA) of the Fe-based system. However, further increase in Ni up to 0.3 deteriorates the GFA, because crystalline phases were precipitated even for the 1.5 mm rod (not shown here).

Fig. 2(a) shows the DSC curves of the three as-cast alloys with a diameter of 1 mm, which are of fully amorphous structure. The curves reveal a distinct glass transition followed by a wide supercooled liquid region before crystallization for all the BMGs. The glass transition, onset crystallization temperature (T_x) and supercooled liquid region (ΔT_x ($=T_x - T_g$)) are summarized in Table 1. It can be seen that both T_g and T_x decrease gradually with increasing Ni content. Fig. 2(b) shows the DTA curves, which illustrate the melting reaction of different alloys. The melting temperature T_m, liquids temperature T_l and the reduced glass transition temperature T_{rg} ($=T_g/T_l$) are also included in Table 1. Although the T_m of the three alloys is almost identical, the T_l decreases gradually with the increase of Ni content and the interval between T_m and T_l (i.e., $\Delta T_m = T_l - T_m$) reduces monotonously, demonstrating that the substitution of Ni for Fe makes the alloy close to the eutectic composition.

Fig. 3 shows the engineering stress–strain curves of the three BMG (⌀1 mm) with different Ni contents. All the samples exhibit an extremely high strength and significantly plasticity. The yield stress σ_y, fracture strength σ_f, and plastic strain ε_p of the BMGs are listed in the last three columns in Table 1. Here the yield stress is defined by the deviation from the linear relation in the stress–strain cure. It can be seen that the substitution of Ni for Fe increases the plastic strain from 3.1% (x = 0) up to 5.2% (x = 0.2), but reduces slightly the yield and fracture strength. The plastic strain obtained in this study for the Ni-bearing BMG (x = 0.2) is much larger than that of most Fe-based BMGs reported [3–8] and comparable to that of $Fe_{75}Mo_5P_{10}C_{7.5}B_{2.5}$ [14] and $Fe_{40}Ni_{40}P_{14}B_6$ BMGs [15]. It is noted that the present Ni-free BMG does not achieve the plastic strain as reported in literature [12]. This maybe result from the low

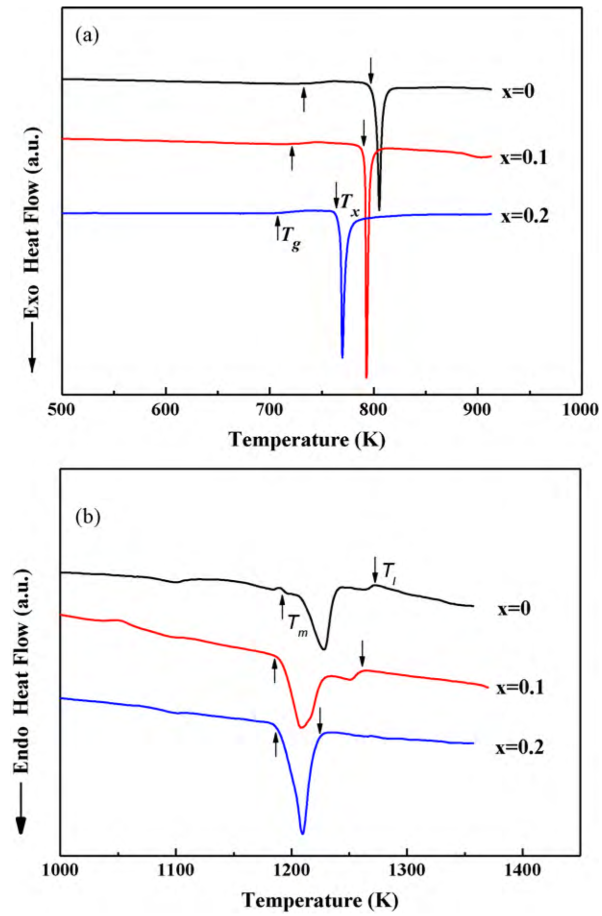

Fig. 2. (a) DSC curves showing the glass transition and crystallization of the as-cast $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ (x = 0, 0.1 and 0.2 at.%) glassy alloys at a heating rate of 0.33 K/s. (b) DTA curves showing melting events for the same alloys

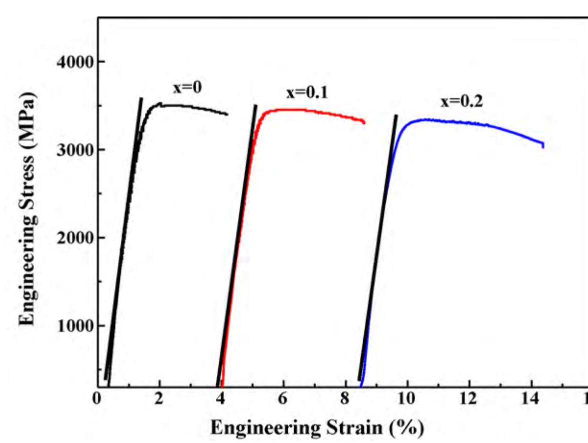

Fig. 3. Engineering stress–strain curves of bulk glassy $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ (x = 0, 0.1 and 0.2 at.%) rod with 1 mm in diameter under room temperature compression.

Table 1
Thermal and mechanical properties of the as-cast $(Fe_{1-x}Ni_x)_{71}Mo_5P_{12}C_{10}B_2$ (x = 0, 0.1 and 0.2 at.%) alloys.

Alloy	D (mm)	T_g (k)	T_x (k)	ΔT_x (k)	T_m (k)	T_l (k)	ΔT_m	T_{rg}	σ_y (GPa)	σ_f (GPa)	ε_p (%)
x = 0	~3	731	797	66	1192	1270	78	0.58	2.5	3.4	3.1
x = 0.1	3	720	786	66	1186	1263	77	0.57	2.45	3.3	3.9
x = 0.2	3	707	762	55	1187	1223	46	0.58	2.4	3.1	5.2

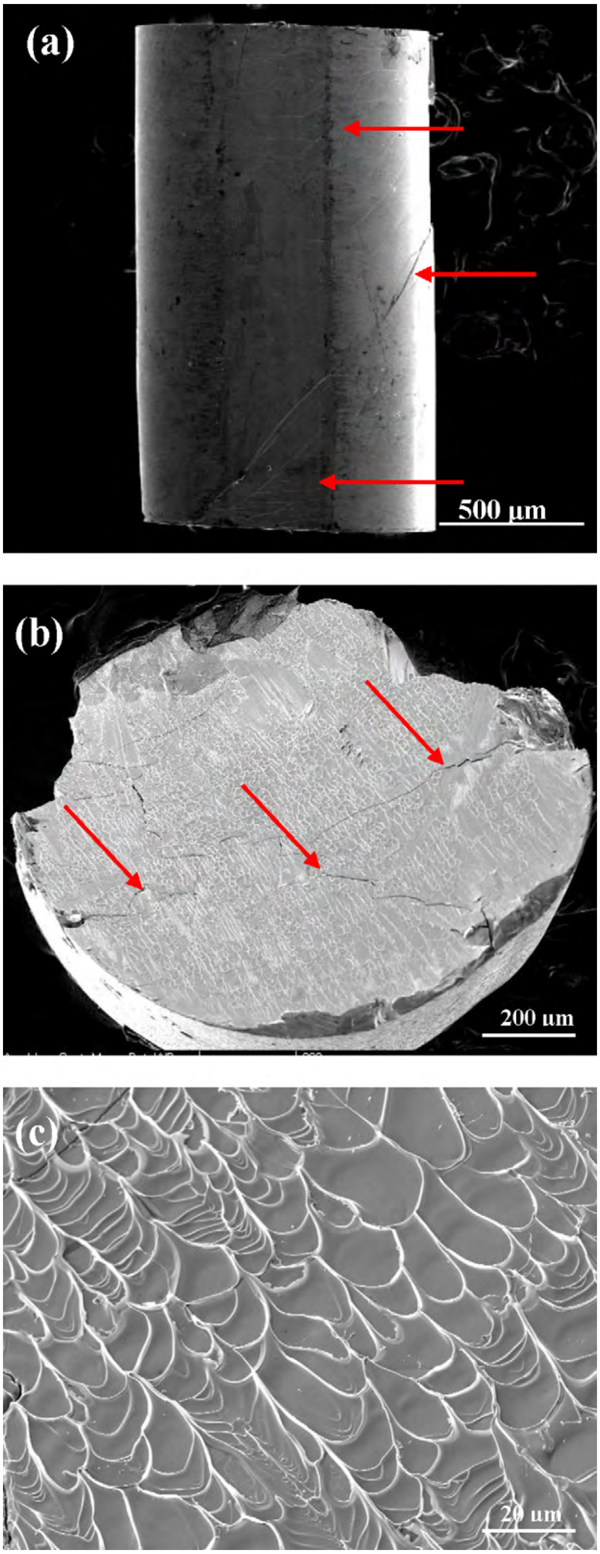

Fig. 4. SEM images of the lateral surface of $(Fe_{0.8}Ni_{0.2})_{71}Mo_5P_{12}C_{10}B_2$ BMG loaded to plastic strain of about 2% (a), and the fracture morphologies shown different magnifications (b and c).

machine stiffness (23,300 N/mm) applied, which is considered to have a significant effect on the obtainable plasticity [16].

Fig. 4 shows the SEM images of the lateral and fracture surfaces of the $(Fe_{0.8}Ni_{0.2})_{71}Mo_5P_{12}C_{10}B_2$ BMG. A number of shear bands can be observed on the whole lateral surface as indicating by the arrows in Fig. 4(a). More importantly, the fracture of the BMG under compression was found to take place in a shear mode, instead of smashing fracture of most of the brittle Fe-based BMGs (see Fig. 4(b)). The fracture surface reveals robust plastic flow patterns, which is usually observed in ductile BMGs. Furthermore, some remarkable cracks existed on the fractured surface (see Fig. 4(b)), but did not shatter the sample, demonstrating that the present BMG containing Ni is pretty tough. Applying the plastic fracture theory to metallic glasses, the fracture toughness K_c can be estimated by using $r_p = (1/6\pi)(K_c/\sigma_y)^2$, where r_p is the plastic zone size or approximately the square root of the plastic zone area size and σ_y is the yield strength [12,17]. Taking the average value of r_p about 10 µm from the micrograph shown in Fig. 4(c) and σ_y of 2.4 GPa from Fig. 3, K_c is calculated to be about 33 MPa m$^{1/2}$, which is larger than that reported in other Fe-based BMGs [18].

The above results show that the plasticity of Fe-based BMG, to some extent, is enhanced by the substitution of Ni for Fe in FeMoPCB system. This phenomenon is considered to be related to the bonding nature of the constituent elements proposed by Liu et al. [19]. The mixing enthalpies between metalloid elements and Ni atomic pairs are smaller than the Fe pairs (e.g., the mixing enthalpy for Ni–P, Ni–C, and Ni–B pairs is −34.5, −39, −24 kJ/mol, respectively, but the mixing enthalpy for Fe–P, Fe–C, and Fe–B atomic pairs are −39.5, −50, −26 kJ/mol, respectively). This could result in a loose structure with weaker atomic interaction, which, in turn, enhance the atomic movement, and finally cause the improvement of the plasticity of the Ni-bearing BMG.

In addition, it is suggested that the simultaneous reduction of glass transition temperature T_g and supercooled liquid region ΔT_x due to the substitution of Ni for Fe may also play an important role in the enhancement of plasticity in the present Fe-based BMG. It has been reported that the glass transition temperature T_g is closely related to the shear modulus, which affects significantly the plasticity of an amorphous alloy [20,21]. The DSC results show that the T_g of the alloy with Ni substitution decreases from 731 to 707 K, reflecting the decrease in shear modulus. This means that the shear deformation could easily occur in the Ni-bearing BMG. In general, the activation barrier for viscous flow is proportional to shear modulus [22]. The viscous flow also inosculates with the plastic deformation of BMG. Furthermore, the supercooled liquid region ΔT_x reflects how the crystallization can be kinetically avoided, it may have the same trend as the effective activation energy for crystallization. For a given system, the deformation-induced microstructural change could take place easily in the metallic glass with narrow ΔT_x in the process of mechanical deformation. This could probably cause the structural heterogeneity with the formation of nanocrystals or nanoclusters, which leads to a large plastic deformation [23,24]. Therefore, the T_g and ΔT_x may serve as a simple rule of thumb for assessing the plasticity of a given BMG system. However, more work is needed in order to clarify this prediction.

4. Conclusions

Bulk metallic glasses FeNiMoPCB system with a diameter of 3 mm were synthesized by copper mold casting. The substitution of Ni for Fe can enhance the plasticity of the Fe-based BMG up to 5.2%. The enhancement of the plasticity results from the decrease in glass transition temperature and supercooled liquid region due to the substitution of Ni for Fe.

Acknowledgements

This work is financially supported by National Nature Science Foundation of China under Grant No. 50871042 and 50828101 and State Key Lab of Advanced Metals and Materials, University of Science and Technology Beijing (2008F-02). Authors are grateful to the Analytical and Testing Center, Huazhong University of Science & Technology for technical assistances.

References

[1] A.R. Yavari, J.J. Lewandowski, J. Eckert, MRS Bull. 32 (2007) 8.
[2] Y.H. Liu, G. Wang, R.J. Wang, D.Q. Zhao, M.X. Pan, W.H. Wang, Science 315 (2007) 1385.
[3] A. Inoue, B.L. Shen, A.R. Yavari, A.L. Greer, J. Mater. Res. 18 (2003) 1487.
[4] V. Ponnambalam, S.J. Poon, G.J. Shiflet, J. Mater. Res. 19 (2004) 1320.
[5] Z.P. Lu, C.T. Liu, J.R. Thomson, W.D. Porter, Phys. Rev. Lett. 92 (2004) 245503.
[6] B.L. Shen, A. Inoue, Appl. Phys. Lett. 85 (2004) 4911.
[7] Q.J. Chen, J. Shen, D.L. Zhang, H.B. Fan, J.F. Sun, J. Mater. Res. 22 (2007) 358.
[8] S.F. Guo, L. Liu, X. Lin, J. Alloys Compd. 478 (2009) 226.
[9] X.J. Gu, A.G. McDermott, S.J. Poon, G.J. Shiflet, Appl. Phys. Lett. 88 (2006) 211905.
[10] X.J. Gu, S.J. Poon, G.J. Shiflet, J. Mater. Res. 22 (2007) 344.
[11] J.H. Yao, J.Q. Wang, Y. Li, Appl. Phys. Lett. 92 (2008) 251906.
[12] X.J. Gu, S.J. Poon, G.J. Shiflet, M. Widom, Acta Mater. 56 (2008) 88.
[13] C.T. Chang, B.L. Shen, A. Inoue, Appl. Phys. Lett. 89 (2006) 051912.
[14] T. Zhang, F.J. Liu, S.J. Pang, R. Li, Mater. Trans. JIM 48 (2007) 1157.
[15] K.F. Yao, C.Q. Zhang, Appl. Phys. Lett. 90 (2007) 061901.
[16] Z. Han, W.F. Wu, Y. Li, Y.J. Wei, H.J. Gao, Acta Mater. 57 (2009) 1367.
[17] X.K. Xi, D.Q. Zhao, M.X. Pan, W.H. Wang, Y. Wu, J.J. Lewandowski, Phys. Rev. Lett. 94 (2005) 125510.
[18] C.H. Shek, G.M. Lin, K.L. Lee, J.K.L. Lai, J. Non-Cryst. Solids 224 (1998) 244.
[19] F.J. Liu, Q.W. Yang, S.J. Pang, C.L. Ma, T. Zhang, Mater. Trans. JIM 49 (2008) 231.
[20] W.L. Johnson, K. Samwer, Phys. Rev. Lett. 95 (2005) 195501.
[21] L. Zhang, L.L. Shi, J. Xu, J. Non-Cryst. Solid 355 (2009) 1005.
[22] J.C. Dyre, Rev. Mod. Phys. 78 (2006) 953.
[23] Z. Liu, K.C. Chan, L. Liu, J. Alloys Compd. 487 (2009) 152.
[24] J.C. Lee, K.W. Park, K.H. Kim, E. Fleury, B.J. Lee, M. Wakeda, Y. Shibutani, J. Mater. Res. 22 (2007) 3087.