

Design of high strength Fe–(P, C)-based bulk metallic glasses with Nb addition

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Received 12 November 2010; accepted 26 May 2011

Abstract: Bulk metallic glass (BMG) rods $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ ($x=1, 2, 3, 4$ and 5) with diameter of 1 or 2 mm were synthesized by copper mold casting. The effects of Nb substitution for Mo on the structure, thermal and mechanical properties of $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ alloys were studied by X-ray diffraction, differential scanning calorimetry and compressive testing. The results show that the substitution of Nb for Mo leads to a decreased glass forming ability, but with plasticity of 1.0%, the fracture strength of $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ alloy increases up to 4.0 GPa. The improvement of the fracture strength is discussed in terms of the enhancement of atomic bonding nature and the favorite formation of a network-like structure due to the substitution of Nb for Mo.

Key words: Fe–(P, C)-based bulk metallic glass; Nb; forming ability; mechanical properties

1 Introduction

The design of high-performance materials with both high strength and good plasticity has been a long-term target pursued in material research. Recent research of bulk metallic glasses (BMGs) which are characterized by high strength, large elastic strain and improved corrosion resistance compared with their crystalline counterparts has become a hot topic in the development of advanced structural materials [1]. Among the BMG systems, Fe-based BMGs are more attractive for potential applications due to their good magnetic properties, ultrahigh strength, excellent corrosion resistance and relatively low material cost [2–6]. However, the Fe-based BMGs always show almost no plastic strain (less than 0.2%) at room temperature, which strictly limits the scope of their applications.

Recently, Fe–(P, C)-based BMGs with a spot of plasticity have been developed by varying the composition, while these alloys with enhanced plasticity always lose some strength [7–10]. For example, the $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ BMG alloy exhibits a plastic strain around 5.2%, but the ultimate strength decreases to 2.8 GPa [10]. Therefore, it is necessary to improve the strength of the plastic Fe–(P, C)-based BMGs for engineering applications.

More recently, it is found that the large Poisson ratio Nb (0.40) is one of the important factors in designing ultrahigh strength Fe–B-based BMGs in the Fe–Nb–B ternary system. As indicated, the $\text{Fe}_{71}\text{Nb}_6\text{B}_{23}$ BMG holds a record of high strength of about 4.85 GPa and plastic strain of 1.6% [11]. However, the mechanisms of the addition of Nb on the thermal stability and mechanical properties are still far from being clearly understood. Stimulated by this, the alloy composition through the substitution of Nb for Mo in $\text{Fe}_{71}\text{Mo}_5\text{P}_{12}\text{C}_{10}\text{B}_2$ BMG alloy is tailored [7] to design high strength Fe–P–C-based BMGs with good plasticity.

2 Experimental

Multi-component alloy ingots with composition of $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ ($x=1-5$, molar fraction) were prepared by arc melting the mixture of Fe (99.9%), Mo (99.9%), Nb (99.5%), C (99.999%) and B (99.95%) and industrial Fe–P alloy (72.6% Fe, 25.3% P and other impurities in remainder) under a Ti-gettered argon atmosphere. Sample rods with diameters from 1 or 2 mm were produced by suck mould casting. The structure of the as-cast alloys was identified by XRD (Philips X'Pert PRO) using $\text{Cu K}\alpha$ radiation. The structure of Nb-bearing alloy was further examined on a JEM 2010F (JEOL)

transmission electron microscopy (TEM). Thermal behaviors related to glass transition, crystallization and melting events were investigated with a differential scanning calorimeter (PE, DSC-7) and differential thermal analysis (PE, DTA-7) under flowing purified argon at a heating rate of 20 K/min. The uniaxial compression test using a specimen with size of $d1\text{ mm} \times 2\text{ mm}$ was performed on 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 morphology of fractured surface of samples was examined with a scanning electron microscope (SEM, FEI-Sirion 200).

3 Results and discussion

Figure 1 displays the XRD patterns of the as-cast $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ ($x=1, 2, 3, 4$ and 5) samples with diameter of 1 or 2 mm. It can be clearly seen that the $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ ($x=1, 2$ and 3) samples exhibit only one broad peak, indicating these alloys are composed of an amorphous structure (see Fig. 1). Although it is known that Nb can stabilize the supercooled liquid and enhance the glass forming ability (GFA) of Fe-(B, Si)-based BMGs [12–13], the partial substitution of Mo by Nb gradually decreases the GFA of the present Fe-(P, C)-based BMGs due to the strong interattraction between Nb and metalloid element C [14]. This presumption can be confirmed by the fact that when Nb substitutes more than 3% Mo (molar fraction), NbC phase is easily precipitated even in the rod with diameter

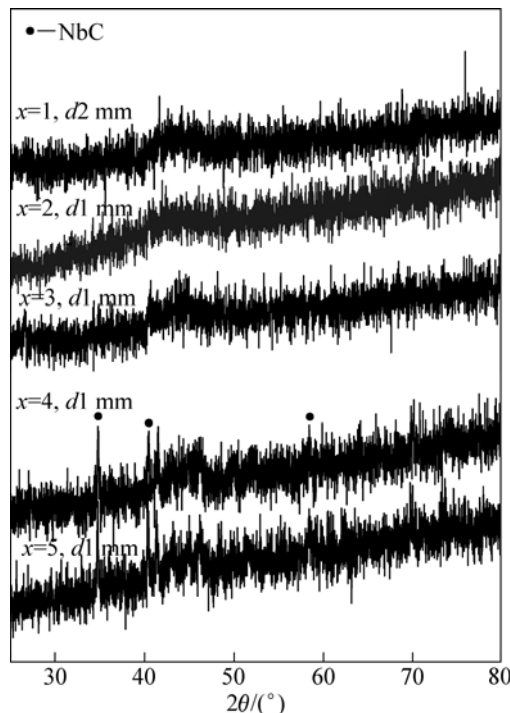


Fig. 1 XRD patterns of as-cast $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ alloys with diameter of 1 and 2 mm

of 1 mm as indicated in the XRD patterns.

Figure 2(a) shows the DSC curves of the as-cast $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ ($x=1, 2$ and 3) alloys with a diameter of 1 mm. The curves reveal a distinct glass transition followed by a supercooled liquid region before crystallization for all the BMGs. Thermal properties including glass transition temperature T_g , onset crystallization temperature T_x and supercooled liquid region $\Delta T_x = T_x - T_g$ are listed in Table 1. It can be seen that T_g , T_x and ΔT_x decrease gradually with increasing Nb content. Figure 2(b) shows the DTA curves, which illustrates 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 all alloys is almost identical, T_l increases gradually with the increase

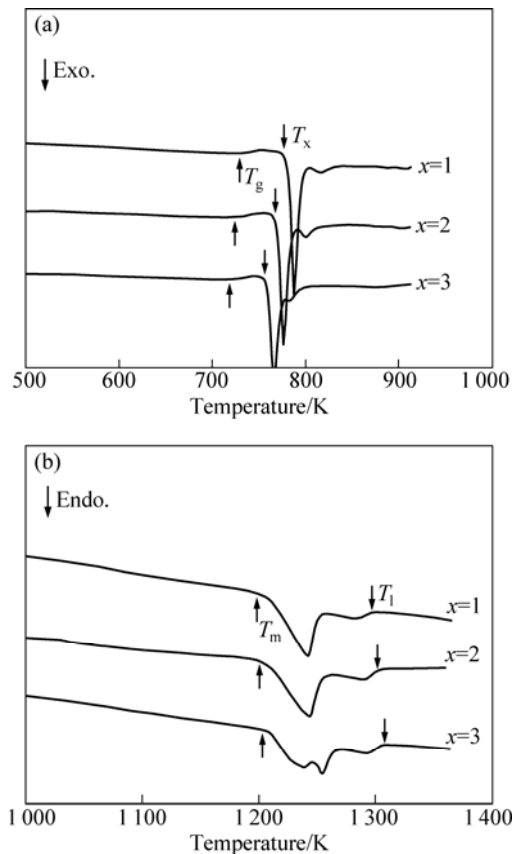


Fig. 2 DSC curves showing glass transition and crystallization (a) and DTA curves showing melting events (b) of as-cast $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ glassy alloys at heating rate of 20 K/min

Table 1 Thermal properties of as-cast $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ alloys

Alloy	d/mm	T_g/K	T_x/K	$\Delta T_x/\text{K}$	T_m/K	T_l/K	T_{rg}
$x=1$	2	729	777	48	1 198	1 296	0.578
$x=2$	1	724	766	42	1 200	1 302	0.556
$x=3$	1	719	757	38	1 205	1 305	0.551

of Nb content, indicating that the substitution of Nb for Mo makes the alloy far away from the eutectic composition and results in poor GFA [15]. Moreover, the alloy with lower values of ΔT_x and T_{fg} implies lower liquidus-solidus interracial energy and thermal stability, which results in the precipitation of the competition crystalline phase during rapid solidification.

Figure 3 shows the engineering stress—strain curves of the BMG sample with diameter of 1 mm with different Nb contents. The corresponding mechanical properties of the samples and some other Fe-based BMGs are listed in Table 2. Here the yield strength σ_y is defined by the stress of deviation from the linear relation in the stress—strain curve. The substitution of Nb for Mo gradually increases the fracture strength and plastic strain in Fe—Mo—P—C—B system. Interestingly, with further increase in Nb contents up to 3%, the $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ alloy exhibits high fracture strength up to 4.0 GPa and plastic strain of 1.0%. Such high strength and good plasticity gathering in the integral whole are not common in Fe-based BMGs. The results show that the strength is enhanced by the substitution of Nb for Mo in Fe—Mo—P—C—B system. One of the reasons for the ultrahigh strength is that the mixing enthalpies between Nb and metalloid elements atomic pairs is higher than those of Mo (those of Nb—P, Nb—C and Nb—B pairs are -89.5 , -102 and -54 kJ/mol, respectively, but those of Mo—P, Mo—C and Mo—B atomic pairs are -53.5 , -67 and -34 kJ/mol, respectively) [18]. As a result, a highly dense packed structure with strong bonding nature is obtained in the as-cast Fe—Mo—Nb—P—C—B glassy alloy system. Another reason is thought to be that the easier formation of network-like atomic configurations in which trigonal prisms consisting of Fe and metalloids element are connected with each other through a glue

atom of Nb [11, 19], therefore, raising the high strength.

In addition, the enhanced plasticity and strength are also observed in some BMGs containing a small volume of nanocrystals, which can not be determined by ordinary XRD. Figure 4 shows the HRTEM micrograph of the $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ sample. It can be seen that there is no trace of nanocrystalline phases in the sample within the resolution of the TEM apparatus. It is concluded that there may be some special microstructure features related to the mixing enthalpies or network-like atomic configurations in these BMGs, which can accommodate both the strength and plasticity. However, the detailed mechanism for the simultaneously enhanced plasticity and strength still needs to be further investigated.

It should be mentioned that the plastic strain of the $\text{Fe}_{71}\text{Mo}_5\text{P}_{12}\text{C}_{10}\text{B}_2$ alloy can be achieved to 3.6% [7]. However, with higher Poisson ratio of Nb additions, the plasticity of the BMGs is not as initially thought. It needs more careful consideration to improve the plasticity of

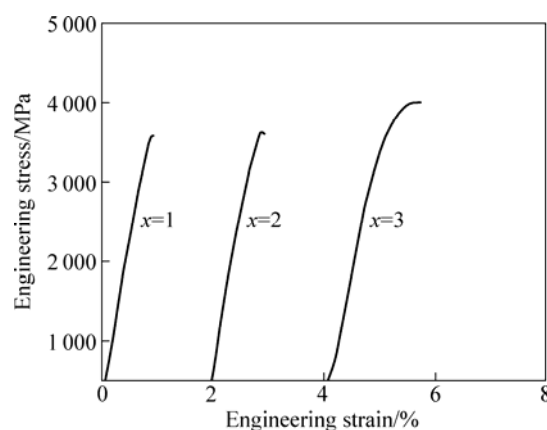


Fig. 3 Engineering stress—strain curves of bulk glassy $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ rod with diameter of 1 mm under room-temperature compression

Table 2 Mechanical properties of present and some other Fe-based BMGs [16–17]

Alloy	Engineering value			True value			Reference
	σ_y/GPa	$\sigma_{\max}/\text{GPa}$	$\varepsilon_p/\%$	σ_y/GPa	$\sigma_{\max}/\text{GPa}$	$\varepsilon_p/\%$	
$\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$	2.8	4.0	1.0				Present work
$\text{Fe}_{71}\text{Mo}_3\text{Nb}_2\text{P}_{12}\text{C}_{10}\text{B}_2$	2.5	3.6	0.5				Present work
$\text{Fe}_{71}\text{Mo}_4\text{Nb}_1\text{P}_{12}\text{C}_{10}\text{B}_2$	—	3.5	—				Present work
$\text{Fe}_{71}\text{Mo}_5\text{P}_{12}\text{C}_{10}\text{B}_2$				2.45	3.15	3.6	[7]
$(\text{Fe}_{0.9}\text{Co}_{0.1})_{76}\text{Mo}_4(\text{P}_{0.45}\text{C}_{0.2}\text{B}_{0.2}\text{Si}_{0.15})_{20}$					3.37	1.7	[8]
$\text{Fe}_{75}\text{Mo}_5\text{P}_{10}\text{C}_{8.3}\text{B}_{1.7}$				2.5	3.0	4.4	[2]
$\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$	2.23	2.8	5.21				[10]
$\text{Fe}_{77}\text{Ga}_3\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5}$	2.98	3.16	0.3				[3]
$\text{Fe}_{75}\text{Mo}_5\text{P}_{10}\text{C}_{7.5}\text{B}_{2.5}$	3.08	3.28	5.5				[16]
$\text{Fe}_{71}\text{Nb}_6\text{B}_{23}$	—	4.85	1.6				[15]
$\text{Fe}_{56.05}\text{Co}_{13.45}\text{Nb}_{5.5}\text{B}_{25}$		4.5	0.6				[17]

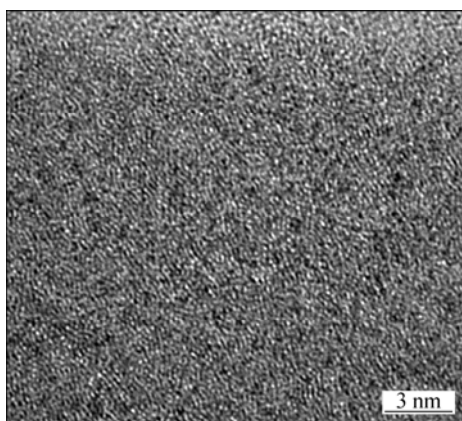


Fig. 4 HRTEM micrograph of $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ sample

BMGs by only concerning the Poisson ratio of the alloying elements. Empirically, it is thought that the Nb has a higher Poisson ratio (0.40) than Mo (0.31), which may increase the plasticity of BMGs during the substitution. However, the present investigation is invalid since Mo has a lower shear modulus G (20 GPa) and G/K (K is bulk modulus) value (0.09) than Nb (38 GPa and 0.22, respectively), which may be a more sensitive indicator for correlating with plasticity than the Poisson ratio [20]. Furthermore, the formation of high electron bonding energy for Nb–C pairs makes it difficult to start the shear slip under compressive deformation, indicating that the atomistic interaction must also be considered in designing plastic Fe-based BMGs [21].

Figure 5(a) shows the SEM image of the fracture surface of the $\text{Fe}_{71}\text{Mo}_4\text{Nb}_1\text{P}_{12}\text{C}_{10}\text{B}_2$ BMG, which nearly fails in the elastic regime with no observable plasticity (less than 0.5%). A number of small fracture planes appear to be declined by about 90° to the direction of applied load. This easy initiation of fracture at many sites is due to the high stress level exceeding 3.5 GPa, which is similar to $(\text{Fe}_{0.75}\text{B}_{0.15}\text{Si}_{0.1})_{96}\text{Nb}_4$ and $[(\text{Fe}_{0.8}\text{Co}_{0.2})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ BMGs [3, 9, 22]. At high magnification (see Fig. 5(b)), the cleavage surface indicated by the arrow in Fig. 5(a) shows a dimple-like structure resulting from the inflection and intersection of parallel nanowave that usually occurs in brittle Fe- and Mg-based BMGs [11, 23]. Unlike most of the brittle Fe-based BMGs that always fail in a fragmentation mode, the fracture of the $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ BMG under compression occurs in a shear sliding mode as shown in Fig. 5(c). The shear fracture surface reveals robust plastic flow patterns, which is usually observed in plastic BMGs (see Fig. 5(d)). The substitution of Nb for Mo enables the BMG to change in the critical shear fracture strength caused by the unique structure, which seems to result in the simultaneous achievement of high strength and good plasticity.

4 Conclusions

1) Fe–Mo–Nb–P–C–B based bulk metallic glass rods with diameter of 1 or 2 mm are synthesized by copper mold casting method. The substitution of Nb for

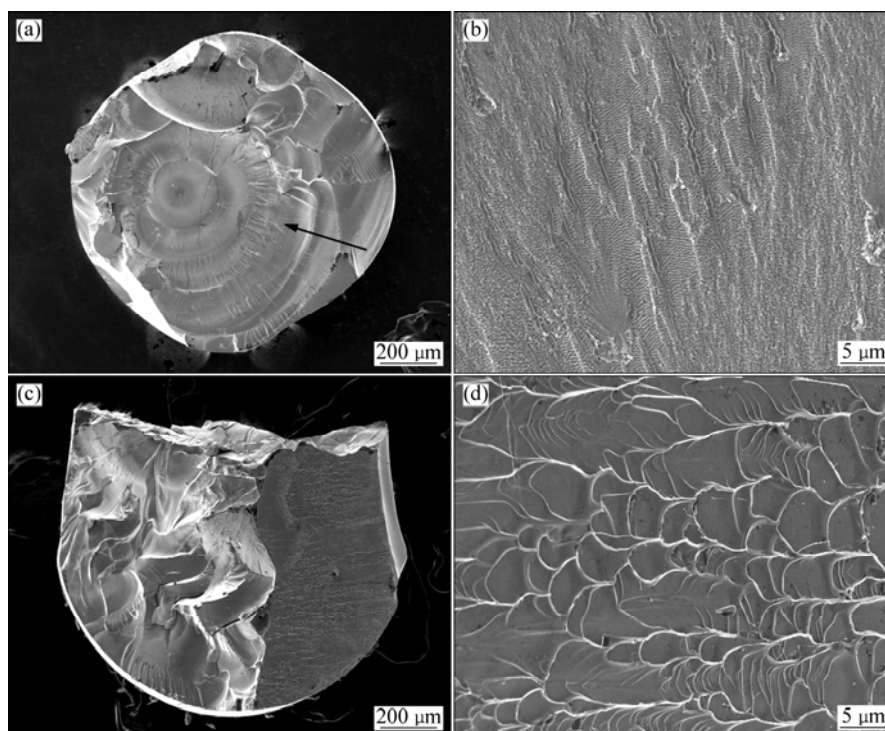


Fig. 5 Morphologies of fractured surface of $\text{Fe}_{71}\text{Mo}_4\text{Nb}_1\text{P}_{12}\text{C}_{10}\text{B}_2$ BMG (a, b) and $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ BMG (c, d)

Mo makes the alloy far away from the eutectic composition and results in the decrease of the glass forming ability.

2) The substitution of Nb for Mo can enhance the fracture strength of the $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ bulk metallic glass up to 4.0 GPa due to the strong banding nature and the formation of the network-like structure.

3) The high strength and plasticity of the present Fe-(P, C)-based BMG with Nb addition are encouraging the future development of new type Fe-based BMG alloys which can be used for structural materials.

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高强度 Fe-(P, C)基块体金属玻璃的形成

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摘 要: 采用铜模吸铸法制备不同直径的 $\text{Fe}_{71}\text{Mo}_{5-x}\text{Nb}_x\text{P}_{12}\text{C}_{10}\text{B}_2$ ($x=1\sim5$) 合金棒。利用 X 射线衍射、差热分析和压缩测试等手段分别研究 Nb 替换 Mo 对 $\text{Fe}_{71}\text{Mo}_5\text{P}_{12}\text{C}_{10}\text{B}_2$ 合金的结构、热稳定性及室温力学性能的作用。结果表明: 随着 Nb 含量的增加, 合金的玻璃形成能力有所降低, 而断裂强度逐步增加; $\text{Fe}_{71}\text{Mo}_2\text{Nb}_3\text{P}_{12}\text{C}_{10}\text{B}_2$ 金属玻璃的断裂强度高达 4.0 GPa, 且具有 1% 的室温压缩塑性。Fe-P-C 基块体金属玻璃断裂的强度提高的原因主要是由于 Nb 替换 Mo 有利于形成似网格状结构且增强原子间结合力。

关键词: Fe-(P, C)基块体金属玻璃; 铌; 形成能力; 力学性能

(Edited by FANG Jing-hua)