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# Fe-based bulk metallic glasses with a larger supercooled liquid region and high ductility

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#### ABSTRACT

Bulk metallic glasses (BMGs) with compositions of  $Fe_{61.5-x}Co_3Mo_{14}C_{15}B_6Er_{0.5}M_x$  (x=2, 3; M=Ni, Nb) were fabricated by copper mold casting using raw industrial materials. The X-ray diffraction (XRD), differential scanning calorimetry (DSC), mechanical tester and scanning electron microscope (SEM) were employed to check the phase constituent, the thermal stability, the mechanical properties and the fracture surfaces of as-cast samples. The results indicate that the BMGs with diameters of 1.5–3 mm were fabricated for the alloys investigated. The largest supercooled liquid region (SLR) up to 76 K was found for  $Fe_{58.5}Co_3Mo_{14}C_{15}B_6Er_{0.5}Ni_3$  BMG. The BMGs with Ni addition exhibit not only high fracture strengths reaching 3770 MPa for x=2 and 3980 MPa for x=3 alloys, respectively, but also apparently plastic strains up to 0.67% and 0.93%, respectively. The fracture surfaces of the  $Fe_{61.5-x}Co_3Mo_{14}C_{15}B_6Er_{0.5}Ni_x$  (x=2, 3) alloys with plasticity show narrow ridges characteristic of venous patterns combining with tearing flow between the ridges. While the Nb containing alloys show not only a lower SLR below 60 K but also a lower stress below 2400 MPa, as well as almost no plastic strain before fracture.

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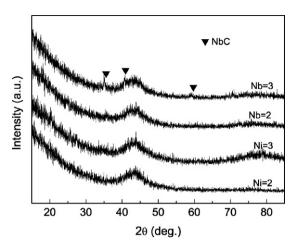
#### 1. Introduction

Since the first Fe-(Al, Ga)-metalloid BMG was discovered by Inoue et al. [1], a larger number of Fe- and Co-based BMGs have been developed [2-5]. In recent years, several Fe-based BMGs or amor $phous\ steels\ with\ larger\ glass\ forming\ ability\ (GFA)\ were\ discovered$ by the Poon and Liu groups [6-9]. Those BMGs are nonmagnetic materials and should be considered to use as structural ones, which are required to have certain plasticity from the application points of view. Therefore, many current investigations have focused on the plasticity improvement on Fe-based BMGs [10-14]. Gu et al. [13] presented a study of how plasticity correlates with elastic properties by systematic change of Er elements in Fe-Mo-C-B-Er alloy system. The ductility can also be improved by partially replacing elements that create ionic and covalent bonds with other elements that favour metallic cohesion [14]. However, the interaction between metal-metalloid atomic pairs may play important role in the improvement of the ductility for Fe-based BMGs due to larger amount of carbon and boron addition. Stimulated by this idea, two elements Ni and Nb were chosen due to their different bonding energy with carbon, the largest amount of metalloid element in  $Fe_{61.5}Co_3Mo_{14}C_{15}B_6Er_{0.5}$  alloy. Experimental results show that Ni and Nb elements have different effect on the ductility and SLR improvement for  $Fe_{61.5}Co_3Mo_{14}C_{15}$   $B_6Er_{0.5}$  BMG.

#### 2. Experimental

 $Fe_{61.5-x}Co_3Mo_{14}C_{15}B_6Er_{0.5}M_x$  (x = 2, 3; M = Ni, Nb) alloys were designed and the ingots were prepared by melting appropriate amount of Fe (99.5%), Co (99.9%), Fe-Mo intermediate alloy (39.329% Fe+59.85% Mo+0.06% C+others), Fe-B alloy (81.17% Fe+18.48% B+0.35% C+others), graphite powder (99.8%), Er (99.9%), Ni ((99.95%) and Nb (99.5%) in an arc melting furnace under an argon atmosphere. Cylindrical samples with 1.5-3 mm in diameters were cast by injection casting of the molten alloys into a copper mold. The amorphicity and thermal properties of ascast samples were examined by X-ray diffraction (XRD) and high temperature differential scanning calorimetry (DSC), respectively. A heating rate of 20 K/min was employed for DSC experiments. Measurements of the stress-strain curves of the BMG samples with 2 mm in diameter and 4 mm in length under compressive loading were carried out using an Instron testing machine under strain rate of  $10^{-4} \, s^{-1}$ . At least five samples for each composition were used in order to get reliable results. The resulting fracture surfaces were observed by using a scanning electron microscope (SEM).

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**Fig. 1.** XRD patterns of as-cast  $Fe_{61.5-x}Co_3Mo_{14}C_{15}B_6Er_{0.5}M_x$  (x = 2, 3 with M = Ni and Nb) alloys with 2 mm in diameter.

#### 3. Results

The alloy compositions studied are found to form 1.5–3 mm diameter glassy samples. Fig. 1 shows the XRD patterns of as-cast samples with 2 mm in diameter. All the diffraction patterns consist of a broad peak in 2 theta region of  $40-50^{\circ}$  except for Nb = 3 alloy, on which NbC phase was observed. This indicates that the GFA for Nb = 3 alloy is lower than 2 mm in diameter. Further experiments show that it can be cast into 1.5 mm rod. While the GFA for Ni = 3 alloy is near 3 mm in diameter. Further increase in Ni content will lead to the decrease of the GFA. The GFA for others is about 2 mm in diameter.

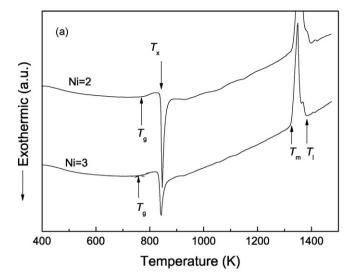
Thermal stability determined by DSC is shown in Fig. 2(a and b) for Ni and Nb doping alloys with 2 mm in diameter. All the BMGs show distinct glass transition temperature ( $T_{\rm g}$ ) and crystallization temperature ( $T_{\rm x}$ ). The larger supercooled liquid region (SLR) characterized by the temperature interval between  $T_{\rm x}$  and  $T_{\rm g}$  was observed for Ni containing alloys. The largest SLR up to 76 K was observed which is corresponding to the GFA of Ni = 3 alloy. This alloy also presents the lowest liquidus  $T_{\rm l}$ , indicating that it is more near the eutectic temperature during composition change. While the reduced glass transition temperature  $T_{\rm rg}$  can not reflect the GFA due to the highest  $T_{\rm rg}$  value is corresponding to the lowest GFA for Nb = 3 alloy. Those results for the glassy alloys studied are summarized in Table 1.

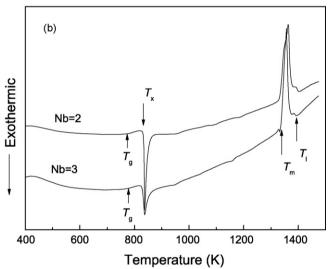
The mechanical properties under compression are shown in Fig. 3. It is obvious that the Ni containing alloys present larger fracture strength and high plastic strain up to  $3770\,\mathrm{MPa}$  and 0.67% for Ni=2 alloy (Fig. 3c) and  $3980\,\mathrm{MPa}$  and 0.93% for Ni=3 alloy (Fig. 3d), respectively. While the lower stress and no plastic strain were observed for Nb containing alloys (Fig. 3a and b).

The typical outer morphologies of the fractured samples for Ni and Nb containing alloys are shown in Fig. 4(a and b), respectively. It is obvious that the fracture under compression occurs in a shear mode for Ni containing alloy. The compressive fracture surface has

Table 1 Thermal properties (heating rate of  $20\,\text{K/min})$  for  $Fe_{61.5-x}Co_3Mo_{14}C_{15}B_6Er_{0.5}M_x$  BMGs

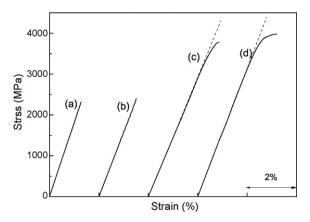
Alloys	<i>T</i> <sub>g</sub> (K)	<i>T</i> <sub>x</sub> (K)	$\Delta T_{\rm x}$ (K)	T <sub>m</sub> (K)	<i>T</i> <sub>1</sub> (K)	$T_{\rm rg}$
M = Ni, x = 2	766	839	73	1334	1394	0.55
M = Ni, x = 3	757	833	76	1327	1378	0.55
M = Nb, $x = 2$	773	832	59	1331	1401	0.55
M = Nb, x = 3	778	826	48	1335	1390	0.56





**Fig. 2.** DSC traces for as-cast  $Fe_{61.5-x}Co_3Mo_{14}C_{15}B_6Er_{0.5}M_x$  (x = 2, 3) alloys, (a) M = Ni and (b) M = Nb.

an angle about 43° with respect to the stress axis (Fig. 4a), which is widely observed on the fracture surface of Zr- and Cu-based metallic glasses. While the sample for Nb containing alloys were broken into pieces under compression (Fig. 4b), which is often observed



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