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The effect of Cu on the plasticity of Fe–Si–B–P-based bulk metallic glass

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A $(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{99.9}Cu_{0.1}$ bulk metallic glass exhibits strength of 3.3 GPa and a large plastic deformation of about 3.1% in compression. A well-developed vein pattern on the fracture surface and easily distinguishable highly dense multiple shear bands on the side surface of the rod specimen near the fracture surface were observed. The unusual deformation behavior could be due to the existence of a large number of α-Fe nanocrystals (less than 10 nm) embedded in a glassy matrix.

Keywords: Bulk metallic glass; Plasticity; α-Fe; Shear band

Fe-based bulk metallic glasses (BMGs) with high strength, excellent magnetic softness and relatively low material cost offer a great potential for a wide variety of applications [1–4]. However, the Fe-based BMGs basically exhibit very poor ductility, almost no plastic strain during deformation at room temperature. This is much inferior to that of non-ferrous BMGs [4–7]. This poor plasticity and catastrophic fracturing hinder the use of the BMGs in new structural applications. Previous studies have revealed that glassy alloys deform in homogeneously through shearing [8,9]. Recently, great efforts have been made to improve the plastic deformation ability of many types of BMGs and the compressive ductility has been improved to a large extent by promoting multiple shearing in Zr- [10,11], Cu- [12,13], Ni- [14,15], Ti- [16–18], Mg- [19], and Pd-based [20] BMG composites containing second dendrite or particle phase, or fine pore phase in their BMG matrices. Similar to the situation of crystalline metallic materials, the coexistence of high strength and high ductility is desirable for structural applications. Although, Yao and Zhang [21] have reported a $Fe_{40}Ni_{40}P_{14}B_6$ alloy with a plastic strain of up to 5.2%, the yield strength and the ultimate strength decrease to ~2.32 and ~2.80 GPa, respectively, with the decrease of the Fe content. Therefore, it is necessary to improve the plasticity of the Fe-based BMGs with higher strength for structural applications by controlling the structure.

We recently reported that the addition of P significantly increases the glass-forming ability (GFA) of the ordinary melt-spun Fe–Si–B amorphous alloys, which are less than 100 μm thick. The representative $Fe_{76}Si_9B_{10}P_5$ alloy [22], without any glass-forming metal elements such as Al, Ga, Nb, Mo, and Y, shows high glass-forming ability leading to a rod specimen having a diameter of 2.5 mm by Cu-mold casting as well as a high yielding stress of 3.3 GPa followed by a plastic deformation of 0.7% in compression. The plastic deformation is rather large compared to the Fe-based BMGs having higher strength than 3 GPa [5,6]. Moreover, the Fe-metalloid BMGs also show very low material cost compared to the previously reported Fe-based BMGs with glass-forming metal elements.

We have studied the effect of small amounts of Cu, which are well known to have a large negative mixing enthalpy with Fe [23], and non-solubility into Fe in solid [24], on the structure and mechanical properties of the Fe-metalloid BMGs. In this paper, we report a new $(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{99.9}Cu_{0.1}$ BMG having an unusual combination of large plastic deformation (about 3.1%) and high strength (3.3 GPa).

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$(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{100-x}Cu_x$ ($x = 0$ and 0.1) alloy ingots were produced by induction melting mixtures of pure Fe (99.998 mass%), Si (99.99 mass%), B (99.9 mass%) and pre-alloyed Fe–P (99.9 mass%) with known analyzed composition, in a high purity argon atmosphere. From the master alloy, ribbons and cylindrical rods were produced by melt-spinning and copper mold casting under air atmosphere in the same processing conditions, and the temperature was controlled with a digital radiation temperature sensor [17]. The structure of the specimens was examined by X-ray diffractometry (XRD), with Cu-K_α radiation, and transmission electron microscopy (TEM). Thermal stability associated with glass transition (T_g) and crystallization (T_x) behaviors of the glassy samples was evaluated by differential scanning calorimetry (DSC) at a heating rate of $0.67\ K\ s^{-1}$. The mechanical properties of yield stress, fracture stress and compressive strain were measured by compression testing with an Instron testing machine. The dimensions of samples for compression testing were 1.5 mm (circumferentially) and 3 mm (longitudinally), and the strain rate was $5 \times 10^{-4}\ s^{-1}$. The deformation and fracture behavior were examined by scanning electron microscopy (SEM).

The as-cast $(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{100-x}Cu_x$ ($x = 0$ and 0.1) alloys have a relatively high GFA leading to critical diameter of rod specimens (2.5 mm), which have been characterized by XRD analysis as glassy alloy. These alloys have a wide super-cooled liquid region (ΔT_x) of 48 and 46 K, respectively, which is a GFA parameter defined by the temperature interval between the glass transition temperature and crystallization temperature (summarized in Table 1). With increasing Cu content, the critical diameter and ΔT_x of the alloy rods decrease significantly to 2 mm and 33 K, respectively, for 0.4% Cu-added specimens. We measured the mechanical properties of these Fe-based glassy alloy rods, which are 1.5 mm in diameter and 3 mm long, by compression testing. Figure 1 shows the compressive true stress–strain curves of $(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{100-x}Cu_x$ ($x = 0$ and 0.1) BMGs. The yield stress, defined by a deviation of 0.2% from the linear relation in the stress–strain curve, and the elastic strain are 3.25 GPa and about 1.9%, respectively, for both alloys. After yielding, the alloys exhibit a maximum stress of 3.3 GPa and this stress gradually decreases with further increase in strain. The plastic strain is around 0.7% for the alloy without Cu and increases significantly to around 3.1% for the 0.1% Cu-added alloy. The plasticity of the Cu-added alloy is relatively large as Fe-based BMGs, which is well known to be brittle in nature [6]. As shown in the inset of Figure 1, the distinguishable serrated characteristics attributed to the formation of shear bands were not observed. The relative smooth flow behavior should be closely related to the highly dense multiple shear bands, which will be shown in Figure 3. This result demonstrates that the ductility of the Fe-metalloids glassy alloys can be significantly improved by addition of an extremely small amount of Cu.

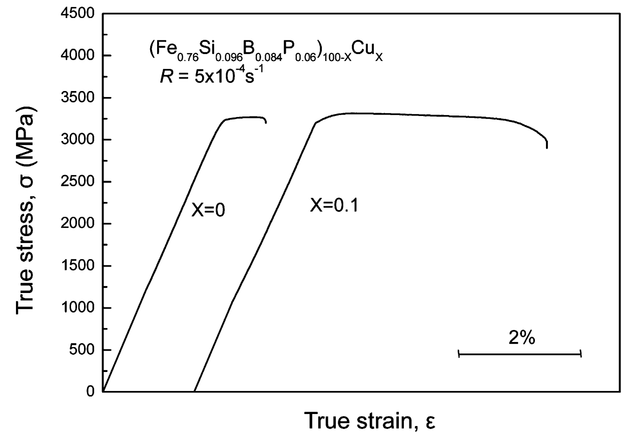

Figure 1. Compressive true stress–strain curves of as-cast $(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{100-x}Cu_x$ ($x = 0$ and 0.1) bulk glassy rod specimens with a diameter of 1.5 mm.

Figure 2 shows SEM images revealing surface appearance (a), the vein pattern on the fracture surface (b), and the multiple shear bands on the side surface of the Cu-added glassy rod (c). The fracture surface exhibits a well-developed vein pattern usually observed in the non-ferrous BMGs with good ductility. Moreover, the density of multiple shear bands on the side surface of the rod sample is extremely high, as shown in Figure 2c. The small spacing between the shear bands is 10–50 μm, which should be closely related to the absence of the serrated characteristics in the stress–strain curve and a large plastic deformation for the Cu-added alloy already shown in Figure 1. In general, plastic deformation of glassy alloys is highly localized into shear bands, followed by rapid propagation of these shear bands and a sudden fracture. Therefore, the highly dense multiple shear bands result in large plastic deformation [25].

The origin of the unusual ductile fracture behavior of the Cu-added Fe-based BMGs is very interesting. Figure 3a and b show the high resolution TEM images and the selected area electron diffraction (SAED) patterns taken from the cross-section of the as-cast rod specimens with and without Cu. The dispersion of a large number of α-Fe nanocrystals with diameters less than 10 nm in the glassy matrix phase was observed in the TEM image, and a (200) peak from α-Fe was found in the SAED pattern for the Cu-added alloy. An enlarged image of Figure 3b is shown in Figure 3c.

Table 1. The glass transition temperature (T_g), the crystallization temperature (T_x), the critical diameter (D_{cr}) and the parameters for GFA (ΔT_x, T_g/T_l and γ) for $(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{100-x}Cu_x$ ($x = 0$ and 0.1)

Composition	T_g (K)	T_x (K)	ΔT_x (K)	T_l (K)	T_g/T_l	γ	D_{cr} (mm)
$x = 0$	783	831	48	1340	0.6201	0.3688	2.5
$x = 0.1$	785	831	46	1346	0.5832	0.3684	2.5