



Effects of metalloids on the thermal stability and glass forming ability of bulk ferromagnetic metallic glasses



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ABSTRACT

We prepared three types of bulk ferromagnetic glasses, Fe–Mo–P–C, Fe–Mo–Ga–P–B–C, and Fe–(Co, Sb, Cr, Mo, Ga)–P–B–C by a flux-melting and water-quenching technique. We systematically changed the content of both alloying metals and metalloids to improve the glass-forming ability (GFA) and thermal stability – the difference between crystallization temperature T_x and glass transition temperature T_g – of bulk ferromagnetic glasses. One of our flux-melted ferromagnetic alloys with optimized compositions has a critical cooling rate on the order of $\sim 10 \text{ K s}^{-1}$, suggesting that the flux treatments play an important role in improving the GFA. Tuning the thermal stability of supercooled liquid by modifying the content of alloying metalloids is more effective than by modifying the content of alloying metals. Adding 1 at.% alloying metalloids and metals can increase $T_x - T_g$ by $\sim 20 \text{ K}$ and 4 K , respectively. We found that upon increasing the content of alloying metalloids, $T_x - T_g$ increases and reaches a maximum where the GFA is highest. After $T_x - T_g$ reaches a maximum, a further increase in the content of alloying metalloids lowers the GFA whereas $T_x - T_g$ may either increase or decrease. Bulk ferromagnetic glasses can only be formed by modifying the content of metalloids within a narrow range, $\sim 2\text{--}6 \text{ at.}\%$, in our alloy systems. Our experimental results suggest that optimizing the content of metalloids is a powerful tool for improving the GFA and thermal stability of bulk metallic glasses.

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1. Introduction

Iron-based ferromagnetic metallic glasses have been extensively studied for four decades because they exhibit good soft magnetic properties that are suitable for applications in such energy conversion devices as electrical transformers and motors. Most of the ferromagnetic glasses prepared so far, however, are thin foils, typically $30\text{--}50 \mu\text{m}$ thick. It is believed [1] that using thick glassy ferromagnetic glasses as the starting materials for the above energy conversion devices would be of tremendous benefit than using thin ferromagnetic foils. Therefore, there has been increasing interests in developing bulk Fe-based metallic glasses. In the past decades, many bulk iron-based ferromagnetic glasses in such systems as Fe–(Al, Ga)–(P, C, B, Si, Ge) [2], (Fe, Co, Ni)–(Zr, Nb, Ta, Mo, W)–B [3], Fe–(Co, Cr, Mo, Ga, Sb)–P–B–C [1], and Fe–Ni–P–B [4] have been developed.

A common feature of the developed bulk metallic glasses is the presence of a wide region of supercooled liquid, i.e., a large difference between crystallization temperature, T_x , and glass transition

temperature, T_g . Study on the factors that determine T_x , T_g , and $T_x - T_g$ is of great importance, as briefly discussed below:

- (1) For practical applications of metallic glasses, the operation temperature cannot be too close (e.g., within $50\text{--}100 \text{ K}$) to T_g . This is because a significant structural relaxation, characterized by topological atomic ordering and chemical ordering, may occur when the temperature is close to T_g . This relaxation will change both the mechanical and magnetic properties of metallic glasses. Furthermore, the viscosity and strength of metallic glasses decrease significantly when the temperature is close to T_g .
- (2) The crystallization of metallic glasses is a kinetics transition. Leaving the metallic glasses at a temperature that is close to T_x may crystallize the amorphous structures, which often degrades the excellent mechanical and magnetic performance of metallic glasses. In addition, T_x also sets the upper temperature limit of magnetic annealing, which is often used to modify or improve the magnetic properties.
- (3) In many alloy systems, the value of $T_x - T_g$ correlates with the GFA of alloys [1,5]. Therefore, search of alloys with a large $T_x - T_g$ might guide the search of alloys with a high GFA.

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- (4) For some applications the as-prepared bulk metallic glasses must take various dimensions and morphologies. This can be done by heating the metallic glasses to within T_x and T_g and shaping them under a small applied pressure because of the extremely low viscosity within the T_x – T_g region. In practical manufacturing, one will need to heat the metallic glasses to within the T_x – T_g region. It is difficult to prevent the metallic glasses from crystallizing if the T_x – T_g region is narrow, e.g., below about 10–20 K. Therefore, shaping the bulk metallic glasses without losing their amorphous structure is practically possible only when there is a relatively large T_x – T_g region.

The flux-melting technique was originally used to process bulk non-ferromagnetic Pd₄₀Ni₄₀P₂₀ glasses [6]. Later, this technique was used to develop bulk Pd–Cu–P [7], Pd–Ni–Cu–P [8], and Pd–Ni–Fe–P glasses [9]. None of these bulk glasses is ferromagnetic at room temperature. Depending on the applied field, bulk Pd₄₀Ni_{40–x}Fe_xP₂₀ ($x = 17.5$) glass exhibits a field-induced ferromagnetic-like state that separates the superparamagnetic state within 30–60 K and the spin-glass state within 5–30 K [10]. We have successfully used the flux-melting technique to process bulk ferromagnetic glasses in Fe–(Co, Cr, Mo, Ga, Sb)–P–B–C [11] and Fe–Ni–P–B [4] alloys. The flux-melting removes most heterogeneous nucleants in the alloy melt, enabling us to achieve a large undercooling upon melt-solidifying. In fact, the crystal nucleation rate in our bulk Fe–Ni–P–B glass prepared by flux-melting is four orders of magnitude smaller than that in previously studied glassy Fe–Ni–P–B ribbon [4]. In addition, our bulk ferromagnetic glasses have extremely soft ferromagnetic properties [11]. The coercivity H_c and maximum permeability μ_m of our bulk glassy Fe_{65.5}Cr₄Mo₄Ga₄P₁₂B_{5.5}C₅ alloy are ~ 0.4 A m^{–1} (5 mOe) and 2.8×10^5 , respectively [11], comparable to those found in annealed zero-magnetostriction cobalt-based alloys. The total power loss of our bulk glassy Fe_{65.5}Cr₄Mo₄Ga₄P₁₂B_{5.5}C₅ alloy is about one order of magnitude lower than that of rapidly quenched Fe-based glassy ribbons [11].

In most previous studies, the thermal stability and GFA of bulk ferromagnetic metallic glasses are often improved by modifying the content of alloying metal elements [12,13]. This usually degrades the fundamental magnetic properties of glassy alloys. For example, depending on the content of Fe, Co, and Ni elements, the saturation magnetization of [(Fe_{1–x–y}Co_xNi_y)_{0.75}B_{0.20}Si_{0.05}]₉₆Nb₄ glassy alloys can range from 1.3 to 0.3 T [14]. Some metal elements, such as V, Nb, and Zr, often largely decrease the saturation magnetization and Curie temperature of iron-based glassy alloys [15]. For example, all amorphous Fe–Zr alloys have a Curie temperature below room temperature [15]. In contrast, metalloid elements – such as P, B, and C – do not largely degrade the fundamental magnetic properties of iron-based glassy alloys [15]. In this paper, bulk Fe–Mo–P–C, Fe–Mo–Ga–P–B–C, and Fe–(Co, Sb, Cr, Mo, Ga)–P–B–C glassy alloys were synthesized and characterized. The critical cooling rate for glass formation is derived from a model and compared with the experimentally measured cooling rate. The content of both metalloid (P, B, C) and metal (Cr, Mo, Ga) alloying elements was modified to improve the thermal stability and GFA. Our previous studies indicate [16] that bulk ferromagnetic glasses based on these metal and metalloid alloying elements have both high saturation induction (~ 1 T) and high Curie temperature (above ~ 400 K), which are often required for practical applications in magnetic devices. Our experimental results suggest that the thermal stability and GFA of bulk ferromagnetic glassy alloys can be largely improved by modifying the content of metalloids.

2. Experimental methods

To synthesize bulk ferromagnetic glassy alloys we first prepared a Fe_{82.7}C_{17.3} (at.%) alloy by mechanical alloying. The mechanical alloying was performed in a SPEX 8000 ball mill located inside an argon-filled glove box with less than 0.1 ppm oxygen. 10 g of elemental Fe (–22 mesh, 99.998%) and graphite pieces (99.9995%) were mixed and mechanically alloyed for 30 h in a tungsten carbide (WC) vial together with a WC ball weighing 12.6 g. The mechanically alloyed powders were placed in a fused silica tube together with dehydrated B₂O₃ (99.9995%). The silica tube was heated to 1423 K inside the glove box to purify the mechanically alloyed powders. The purified products were then mixed with commercially available Fe (–22 mesh, 99.998%), Co (–100 mesh, 99.8%), Sb (6 mm shot, 99.999%), Cr (–200 mesh, 99.95%), Mo (–200 mesh, 99.9%), Ga (2–4 mm splatter, 99.9999%), Fe₂B (–35 mesh, 99%), and FeP (–200 mesh, 99.5%) to obtain the desired compositions. The above mixtures were placed in a fused silica tube together with dehydrated B₂O₃. The silica tube was evacuated via a mechanical pump, filled with pure argon to a pressure slightly higher than 1.013×10^5 Pa, and then heated slowly to 1623 K to melt the mixtures. Following melting, the B₂O₃ floated on the surface of the melt. The tube was then evacuated at 1623 K to emerge bubbles from the melt to purify the alloy melt. When the bubbling ceased, the tube was evacuated to a pressure below 0.13 Pa, then re-filled with high-purity argon to a pressure slightly above 1.013×10^5 Pa, and finally quenched in water. The as-quenched bulk metallic glasses are in the form of spheres with a diameter of 2–3 mm, or rods with a diameter of 4 mm and a length of 5–20 mm. One of our alloys, Fe_{94–x}Mo₄Ga₂(P₁₂B₄C₄)_{x/20} ($x = 22$) has been cast into a glassy rod with a maximum diameter of 5 mm.

The as-prepared glassy alloys were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). The XRD experiments were carried out in a SCINTAG copper-anode powder X-ray diffractometer having a solid-state Peltier-cooled detector. The DSC measurements were performed in a PERKIN–ELMER DSC-7 instrument. Temperature calibration of the DSC was performed by using indium (99.99%) and zinc (99.999%). The samples were placed in aluminum pans and heated at a rate of 20 K min^{–1}. For each sample, a second run was recorded as a baseline for the data from the first run. The DTA tests were carried out in a PERKIN–ELMER DTA-1700 analyzer using ~ 50 – 100 mg samples held in boron nitride pans. Sn, (99.99%), Zn (99.999%), Al (99.999%), and Ag (99.9999%) were used to calibrate the temperature in DTA. Argon flowing at the rate of 40 ml min^{–1} was used to purge the samples during the DSC and DTA measurements.

The cooling rate was obtained by measuring the temperature–time relationship during cooling an alloy melt. 0.67 g of (Fe₆₆Cr₄Mo₄Ga₄P₁₂C₅)_{94.5/95}B_{5.5} alloy together with 0.33 g of B₂O₃ was placed into a silica tube with an inside diameter of 4 mm and an outside diameter of 5 mm. A thermal couple was inserted into a smaller silica tube with an inside diameter of 2 mm and an outside diameter of 3 mm. The smaller-diameter silica tube (containing the thermal couple) was then embedded in the larger-diameter silica tube (containing the alloy and B₂O₃). The two tubes were heated to 1503 K to melt the alloy and B₂O₃, and then quenched in water. During the water quenching, the melt temperature was recorded as a function of time to obtain cooling rates.

3. Results

Fig. 1 shows the temperature dependence of cooling rate measured for our (Fe₆₆Cr₄Mo₄Ga₄P₁₂C₅)_{94.5/95}B_{5.5} alloy. The cooling rate

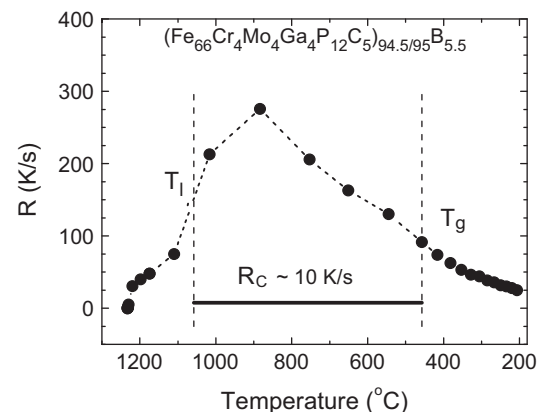


Fig. 1. Temperature dependence of cooling rate achieved during quenching flux-melted (Fe₆₆Cr₄Mo₄Ga₄P₁₂C₅)_{94.5/95}B_{5.5} alloys in water. Two vertical dashed lines represent liquidus (T_l) and glass transition (T_g) temperatures whereas horizontal solid line represents the critical cooling rate R_c .

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