Journal of Non-Crystalline Solids 476 (2017) 75–80

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Glass-forming ability, thermal properties, and corrosion resistance of Fe-based (Fe, Ni, Mo, Cr)-P-C-B metallic glasses

Siwen Wang[a], Yanhui Li[a], Xuewei Wang[a], Shinichi Yamaura[a,b,c], Wei Zhang[a,b,*]

[a] Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China
[b] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[c] Polytechnic University, Kodaira, Tokyo 187-0035, Japan

ARTICLE INFO

Keywords:
Fe-based bulk metallic glasses
Glass-forming ability
Supercooled liquid region
Corrosion resistance
Mechanical properties

ABSTRACT

Co-addition of appropriate Mo, Cr and Ni in the $Fe_{80}P_{12}C_4B_4$ alloy not only enhances the thermal stability of the supercooled liquid and glass-forming ability (GFA) but also reduces the glass transition temperature (T_g) of the Fe-based metallic glass. The $Fe_{55}Ni_{15}Cr_7Mo_3P_{12}C_4B_4$ bulk metallic glass (BMG) exhibits a low T_g of 690 K, large supercooled liquid region (ΔT_x) of 60 K, and high GFA with a critical diameter of 2.5 mm. The co-addition of Mo, Cr and Ni remarkably improves the corrosion resistance of the BMGs in 1 M HCl and 0.5 M H_2SO_4 solutions, which is superior compared to the SUS316L stainless steel. The alloys also possess high compressive yield strength of ~3.01 GPa with distinct plastic strain of ~1.2%. The good combination of low T_g, large ΔT_x, high GFA, excellent corrosion resistance and mechanical properties makes the developed (Fe, Ni, Cr, Mo)$_{80}P_{12}C_4B_4$ BMGs show great promise as anti-corrosion materials suitable for thermoplastic processing.

1. Introduction

Fe-based bulk metallic glasses (BMGs) are attractive in the BMG families from the standpoint of engineering applications owing to their high strength and hardness, good wear resistance, excellent soft magnetic properties, and relatively low material cost [1,2]. Over the last two decades, series of Fe-based BMGs have been developed, for instance, in Fe-(Al, Ga)-(P, C, B) [3], Fe-(Zr, Nb, Hf)-B [4], Fe-(Cr, Mo)-(P, C, B) [5], Fe-(Cr, Mo)-(Y, Ln)-(C, B) (Ln: lanthanides) [6], and Fe-P-C systems [7]. While most of them, especially for the Y- and Ln-free alloys, exhibit relatively low glass-forming ability (GFA) with a critical diameter for glass-formation (d_c) ≤ 3 mm. In addition, the Fe-based BMGs have a very limited plasticity at room temperature, which hinders their practical use as structural materials [8]. By taking the advantage of the viscous flow workability in the supercooled liquid region, the Fe-based BMGs can be made into functional devices with complex shapes by thermoplastic processing, and the metallic glass powders can be fabricated as protective coatings by thermal spraying, which extends the application areas of the Fe-based alloys [9,10]. In addition to the good GFA, the metallic glasses suitable for the thermoplastic processing should possess a low glass transition temperature (T_g) and a large supercooled liquid region (ΔT_x, the interval between the T_g and onset temperature of crystallization (T_x)) [10–12]. The alloy with a large ΔT_x usually possesses a low processing viscosity in the supercooled liquid state, which makes it easy for superplastic deformation or forming uniform and compact coatings [10,13,14]. A low T_g implies that the processing can be carried out at a low temperature, leading to the reductions of both equipment requirement and energy consume [10].

One of the typical applications for the thermoplastic processing of the metallic glasses is producing anti-corrosion bipolar plate for proton exchange membrane fuel cells by hot-pressing the Ni-based metallic glass sheet in the supercooled liquid state [13], or by thermal spray-coating the powders on Al-plate [14]. Although the excellent corrosion resistance of the Ni-based metallic glasses is beneficial to the service life of the bipolar plate in the acidic conditions, the low GFA, high T_g (~828 K), and high materials cost bring challenges to the industrialization. Fe-based metallic glasses with good corrosion resistance and proper properties for thermoplastic processing, i.e., low T_g and large ΔT_x, are hence expected to replace the Ni-based alloys in term of the low cost. While the previously developed Fe-based Fe-Cr-Mo-P-C-B [5], Fe-Cr-Mo-C-B-Y [15] and Fe-Co-B-Si-Nb-Cr [16] BMGs with high GFA, large ΔT_x and good corrosion resistance possess very high T_g (~936 K). The Fe-P-C [7] and Fe-P-C-B [17] BMGs show low T_g of ~690 K, whereas their ΔT_x are small (< 35 K), and the GFA and corrosion resistance are relatively poor. The Cr and Mo elements are

* Corresponding author.
E-mail address: wzhang@dlut.edu.cn (W. Zhang).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.09.028
Received 8 June 2017; Received in revised form 7 September 2017; Accepted 11 September 2017
Available online 19 September 2017

favorable to the improvement of corrosion resistance, but the excessive Cr/Mo leads to the increase of T_g and even deterioration of GFA [15,18]. It will be of significance to achieve the best combination of low T_g, high GFA, and excellent corrosion resistance by optimizing the Cr and Mo contents. In addition, substitution of Fe with proper Ni in the Fe-based BMGs is useful to reduce the T_g and increase the ΔT_x and GFA [12,19]. It is then predicted that combined addition of appropriate Mo, Cr and Ni is an effective way to obtain the Fe-based BMGs with high GFA, large ΔT_x, good corrosion and low T_g. In this work, an $Fe_{80}P_{12}C_4B_4$ metallic glass possessing a low T_g of 694 K were selected as the base alloy, and the effects of Mo, Cr and Ni additions on the thermal stability, GFA, corrosion resistance and mechanical properties were investigated.

2. Experimental procedure

Alloy ingots of (Fe, Ni, Cr, Mo)$_{80}$P$_{12}$C$_4$B$_4$ in at.% were prepared by induction melting the mixture of Fe (99.9 mass%), Mo (99.9 mass%), Cr (99.9 mass%), Ni (99.99 mass%), C (99.999 mass%), B (99.5 mass%) and Fe_3P precursor (99.9 mass%) under a high-purified argon atmosphere. The mass losses were < 0.2 mass%. Ribbons with a width of 2 mm and thicknesses of 20 μm were prepared by single-roller melt spinning with a linear velocity for copper wheel of 40 m/s. Cylindrical rods with diameters of 1–3 mm were fabricated by copper mold casting. The structure of the samples was examined by X-ray diffraction (XRD) with Cu-K_α radiation using a D8 Focus (Bruker). The thermal properties associated with the glass transition, supercooled liquid region and crystallization of the samples were measured by differential scanning calorimetry (DSC, Q100, TA Ins.) from 373 to 873 K at a heating rate of 0.67 K/s. The ribbons were heated to the respective onset temperature of each crystallization peak under the same heating rate as the DSC test, held isothermally for 60 s, and subsequently quenched into water to study the crystallization products corresponding to each crystallization peak. A series of isothermal DSC measurements were carried out at temperatures between 688 and 743 K to investigate the crystallization behavior. The ribbons were first heated to the desired annealing temperature at a heating rate of 0.67 K/s and then held isothermally for a certain period of time until the completion of crystallization. The liquidus temperature (T_l) was measured with a differential thermal analyzer (DTA, Q600, TA Ins.) at a heating rate of 0.33 K/s. At least three tests were repeated for each determination of the thermal parameters. The maximum variation in the temperature measurements is less than ± 1 K. The corrosion behaviors of the alloys were evaluated by electrochemical measurements and immersion tests in 1 M HCl and 0.5 M H_2SO_4 solutions open to air, respectively. The samples (ribbons for electrochemical tests and φ1.5 mm rods for immersion) were firstly mechanically polished and subsequently exposed to air for 24 h for a consistent surface condition. The electrochemical measurements were conducted in a three-electrode cell with a platinum counter electrode and an Ag/AgCl reference electrode at 298 K. Potentiodynamic polarization curves were measured using electrochemical workstation (Interface1000, Gamry) at a potential sweep rate of 50 mV/min after open-circuit immersion of samples for about 20 min when the open-circuit potentials became almost steady. The corrosion rates were estimated from the weight losses of the samples after immersion in the solutions at 298 K for 168 h. The mechanical properties of the alloys were measured using an Instron 5581 mechanical testing machine under the compressive load. The gauge dimension for the mechanical test specimen was 2 mm in diameter and 4 mm in height, and the strain rate was fixed as $5.0 \times 10^{-4}\,s^{-1}$. The fracture morphology of the specimen were observed by scanning electron microscope (SEM, JSM-5600LV, JEOL). At least three samples for each composition were repeated in the corrosion and mechanical measurements.

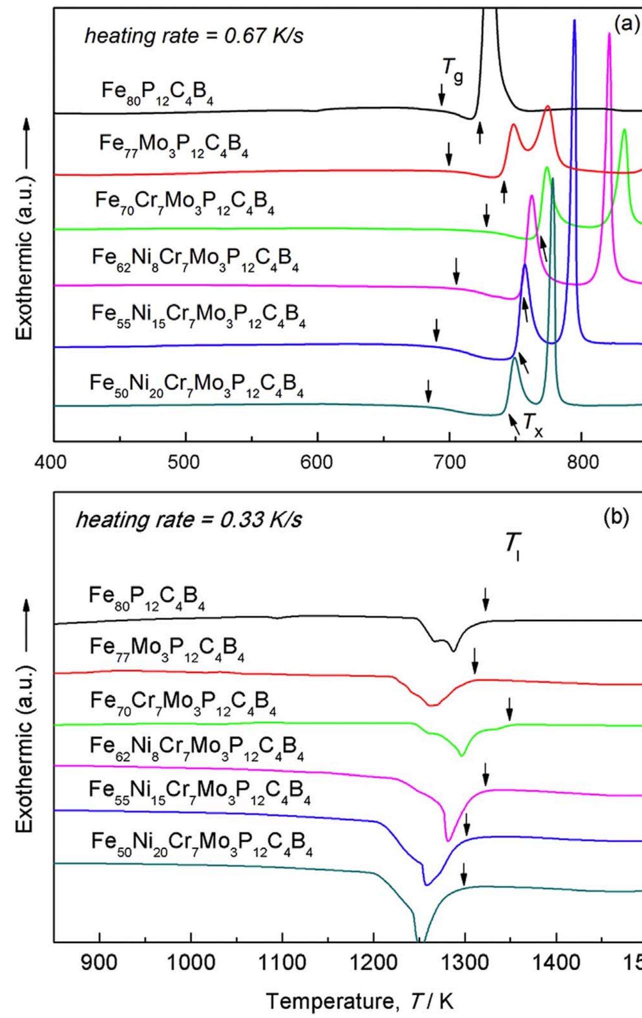

Fig. 1. DSC (a) and DTA (b) curves of (Fe, Ni, Mo, Cr)$_{80}$P$_{12}$C$_4$B$_4$ metallic glasses.

3. Results

A fully glassy structure was confirmed for the as-spun (Fe, Ni, Cr, Mo)$_{80}$P$_{12}$C$_4$B$_4$ ribbon samples according to the XRD results. Fig. 1 shows the DSC (a) and DTA (b) curves of the metallic glasses, and the T_g, T_x and T_l are marked in the figures by arrows. During the continuous heating, the alloys all exhibit a clear endothermic glass transition followed by a supercooled liquid region, and then exothermic peaks corresponding to crystallization (see Fig. 1(a)). The additions of 3 at.% Mo and 3 at.% Mo + 7 at.% Cr shift the T_g and T_x of the alloy towards higher temperatures, and extend the ΔT_x from 29 to 37 and 42 K, respectively. The further addition of 8–20 at.% Ni in the $Fe_{70}Cr_7Mo_3P_{12}C_4B_4$ alloy reduces the T_g to 684 K without greatly decreasing the T_x, and hence extends the ΔT_x up to 60 K. The extended ΔT_x suggests that the co-addition of Mo, Cr and Ni improves the thermal stability of the supercooled liquid of the alloy effectively. From the DTA curves, it is detected that the addition of Mo + Cr increases the T_l of the base alloy from 1323 to 1349 K, while co-addition of Mo, Cr and Ni decreases the T_l to 1299 K (see Fig. 1(b)). Table 1 lists the T_g, ΔT_x, T_l, and GFA indicators, i.e., T_{rg} ($= T_g / T_l$) [20], γ ($= T_x / (T_l + T_g)$) [21] and S ($= \Delta T_x / (T_l - T_g)$) [10] values of the present alloys. It is seen that the ΔT_x, γ, and S values rise simultaneously with the addition of Mo, Cr and Ni until the Ni content reaches 20 at.%, which indicates an increased GFA.

Cylindrical rods with different diameters were produced by copper mold casting to evaluate the GFA of the (Fe, Ni, Cr, Mo)$_{80}$P$_{12}$C$_4$B$_4$ alloys. Fig. 2 presents the XRD patterns of the as-cast rods with diameters