Journal of Non-Crystalline Solids 410 (2015) 155–159

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Synthesis of CoCrMoCB bulk metallic glasses with high strength and good plasticity via regulating the metalloid content

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ARTICLE INFO

Article history:
Received 21 July 2014
Received in revised form 10 November 2014
Accepted 9 December 2014
Available online 27 December 2014

Keywords:
Metallic glass;
Mechanical property;
Elastic constant

ABSTRACT

CoCrMoCB bulk metallic glasses (BMGs) with large glass-forming ability (GFA), large supercooled liquid region and excellent mechanical properties were obtained through regulating the contents of B and C. Fully glassy rod of $Co_{50}Cr_{15}Mo_{14}C_{10}B_{11}$ with a diameter of 3.5 mm can be produced. The metalloid dependence of GFA in the present alloys was explained by the atomic packing density. Furthermore, the influence of metalloid on mechanical properties was explored. The high fracture strength of 4.5–5 GPa and outstanding plasticity of 1–3% can be observed. The contribution of C content to strength is larger than that of B content. In addition, the elastic moduli mainly depend on the B content, and the developed alloys possess high Poisson's ratio. In the view of atomic bonding characters, the reason for various effects of B and C contents on strength and elasticity is analyzed.

1. Introduction

Co-based bulk metallic glasses (BMGs) possess high strength and hardness, good resistance to corrosion and oxidation [1–6], thus making them promising structural materials. Nevertheless, the practical applications of Co-based BMGs are hindered by the low glass-forming ability (GFA) and the poor macroscopic plastic deformation [7]. Although extensive efforts have been devoted to develop new Co-based BMGs with enhanced GFA and plasticity, to the best of my knowledge, very few experiments show that Co-based BMGs possess the large GFA and outstanding plasticity simultaneously. For example, Shen et al. fabricated the $Co_{61}Nb_8B_{31}$ BMGs with large plastic strain up to 5%, but its critical diameter (d_c) is only 1.5 mm [4]; T. Zhang et al. discovered the more than one centimeter diameter $Co_{43}Fe_5Cr_{15}Mo_{14}C_{15}B_6Er_2$ BMGs with compressive strength 5200 MPa, nonetheless the plastic strain is near 0% [3]. In view of the present situation, it is necessary to further search for the Co-based BMGs with attractive combination of large GFA, high strength and good plasticity.

It has been clarified that the metalloid atoms locate in the interstitial position of the network-like atomic configurations in metal–metalloid-type glass alloys [8,9]. The atomic bonding character between metal–metalloid atoms is more covalent-like [2,10]. This has a strong influence on the activation energy barrier of the fundamental flow units or the global bonding strength [11,12], and additionally, affects the GFA and macroscopic mechanical properties of BMGs [13–17]. On the other hand, both the GFA and mechanical properties are also influenced by the degree of dense randomly packed atomic configuration [4,16–18]. Because of different electron configurations and various atomic radii among metalloid atoms (B, C, Si, P) and metal atoms, the contents of metalloid elements and metal elements could change the atomic bonding character and the degree of dense randomly packed atomic configuration [13–18]. In light of this, the contents of metalloid elements could play an important role in determining the GFA and macroscopic mechanical properties [4,13,14,17,19]. For example, the Fe–Si–B–P BMG with a critical diameter of 2.5 mm could be synthesized through adding proper amounts of metalloid elements (B, Si, P) [14]; Gu et al. studied the character of Fe – C/B/P bonds and interpreted the change of mechanical properties in FeMoPCB BMGs [13]. Consequently, tuning the contents of metalloid elements may be an effective method to design BMGs with specific properties.

Based on the above arguments, the $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ BMG was selected as the precursor alloy [20,27]. Through adjusting the contents of B and C, CoCrMoCB BMGs, which contain the total content of B and C (C_{B+C}) of 21 at.%, 23 at.%, 25 at.%, and 30 at.% and various ratios of B/C at the fixed C_{B+C} of 21 at.% and 25 at.% (as listed in Table 1), were fabricated. The influences of contents of B and C on the GFA and thermal properties were investigated. Furthermore, the contribution of B or C content to the strength and elastic moduli was quantitatively evaluated, and the physical mechanism was analyzed from the view of atomic bonding character.

2. Experimental procedures

In order to obtain batches of several compositions and ensure compositional homogeneity, master alloy ingots were pre-melted by induction melting the mixtures of pure metals with purities above 99.9% and then prepared by arc melting under a Ti-gettered argon atmosphere. The alloy ingots were re-melted in quartz tubes by

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.12.005
0022-3093/

Table 1
GFA, thermal properties, density and C_g of CoCrMoCB BMGs.

Alloy	d_c (mm)	T_g (K)	T_x (K)	ΔT_x (K)	ρ (g/cm^3)	C_g
$Co_{50}Cr_{15}Mo_{14}C_{18}B_3$	2	801	873	72	8.283 ± 0.003	0.677
$Co_{50}Cr_{15}Mo_{14}C_{15}B_6$	2	810	885	75	8.300 ± 0.005	0.682
$Co_{50}Cr_{15}Mo_{14}C_{10}B_{11}$	3.5	827	907	80	8.348 ± 0.002	0.693
$Co_{48}Cr_{15}Mo_{14}C_{16}B_7$	2	825	900	75	8.272 ± 0.003	0.687
$Co_{46}Cr_{15}Mo_{14}C_{15}B_{10}$	2	843	917	74	8.169 ± 0.006	0.677
$Co_{46}Cr_{15}Mo_{14}C_{10}B_{15}$	2	856	941	85	8.228 ± 0.002	0.688
$Co_{41}Cr_{15}Mo_{14}C_{15}B_{15}$	2	871	947	76	8.121 ± 0.004	0.680

induction heating and injected into copper molds to form rod-shaped samples in diameters ranging from 1 to 4 mm and in length of ~45 mm. Microstructure of as-cast rods was determined by X-ray diffraction (XRD) using Dmax2500PC X-ray diffractometer with Cu Kα radiation. Thermal properties of samples were characterized by a NETZSCH DSC 404C differential scanning calorimeter (DSC) at a heating rate of 0.33 K/s. Uniaxial compressive testing was performed at a strain rate of 8×10^{-4} s^{-1} on SANS 5504 testing machine at room temperature. The cylindrical testing samples with a gauge aspect ratio of 2:1 were cut from as-cast 1 mm rods. The testing sample ends were polished to provide parallel and flat surfaces which are orthogonal to the loading axis. The density was measured by Archimedes's method using a Sartorius balance (with a resolution of 0.1 mg). An Olympus Panametric-NDT5703PR ultrasonic testing device was used to determine the elastic properties of glassy samples with 2 mm in diameter and 4 mm in length. The deformed and fracture specimens were observed by Camscan 3400 scanning electron microscopy (SEM).

3. Results

Fig. 1 shows the XRD patterns of representative as-cast rods of CoCrMoCB alloys with critical diameters. All the samples are confirmed to be fully amorphous by the broad diffraction peaks in the patterns within the resolution of XRD. Staring from the $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ alloy with a d_c of 2 mm [20,27], the substitution of 5 at.% B for C can remarkably improve the d_c to 3.5 mm. However, the substitution of B for Co has no influence on the d_c (still 2 mm). Additional studies reveal that the d_c can keep 2 mm till the C_{B+C} exceeds 30 at.% or the C content (C_C) exceeds 18 at.% in the case of the $C_{B+C} = 21$ at.%. This result indicates that the present alloys possess large composition range for glass formation.

The glass transition and crystallization behavior of these glass alloys are shown in Fig. 2. Thermal parameters, i.e., the glass transition temperature (T_g) and the onset temperature of crystallization, are listed in Table 1. As can be seen in Fig. 2, the alloys demonstrate distinct glass transitions followed by wide supercooled liquid regions which are larger than 70 K and enlarged through the substitution of B for C.

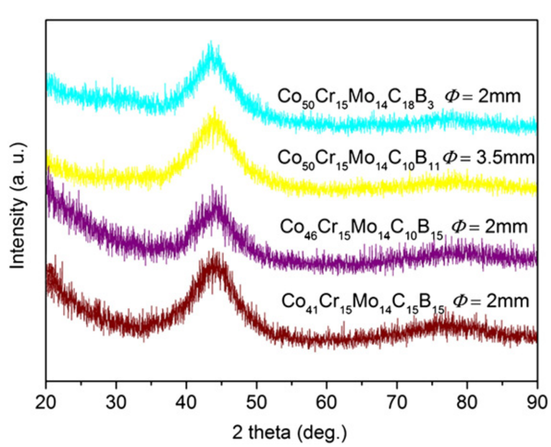

Fig. 1. X-ray diffraction patterns of CoCrMoCB BMGs.

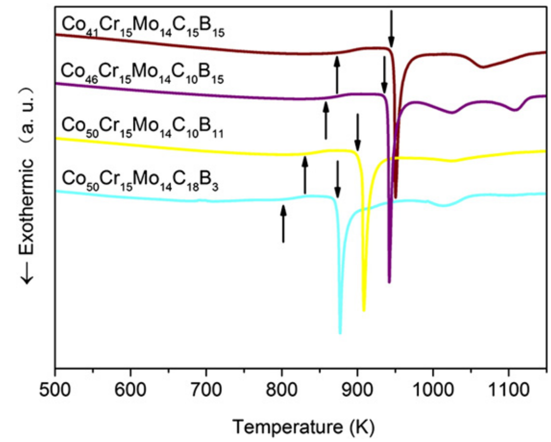

Fig. 2. DSC curves of CoCrMoCB BMGs at a heating rate of 0.33 K/s.

Meanwhile, T_g can significantly rise with the increase of C_{B+C} or the increase of B at the given C_{B+C}.

In order to characterize the influences of B and C elements on mechanical properties and elastic properties, uniaxial compressive tests and elastic moduli measurements are conducted at ambient temperature. Fig. 3 shows stress–strain curves of the CoCrMoCB alloy rods with 1 mm in diameter. As one can see, all alloys exhibit similar deformation behaviors, i.e., the stress–strain relation is linear up to the elastic strain limit of ~2% followed by a plastic deformation. Compressive strength (σ_c), yield strength (σ_y), plastic strain (ε_p) and elastic moduli are tabulated in Table 2. The CoCrMoCB alloys possess high σ_c of 4500–5100 MPa, σ_y of 4300–4800 MPa and large ε_p of 1–3%. Meanwhile, the alloys exhibit shear modulus (G) of ~80 GPa, Young's modulus (E) of ~220 GPa and bulk modulus (K) of ~225 GPa. Except for ε_p, both mechanical properties and elastic constants increase with the increasing C_{B+C}. Furthermore, in the fixed C_{B+C} the addition of C can considerably enhance σ_c and σ_y while its influence on G, E, and K is slight. On the contrary, the substitution of B can significantly improve G, E, and K but slightly degrade the strength.

As a typical sample, the deformed and fracture specimens of $Co_{50}Cr_{15}Mo_{14}C_{10}B_{11}$ BMG were characterized by SEM. Fig. 4(a, b, c) shows the lateral morphology of the specimen which was subjected to compression strain of about 1% but unloaded prior to failure. Multiple shear bands are clearly observed, which are composed of the primary shear bands inclined by about 45° to the direction of applied load and the secondary shear bands formed by the branching and interaction of the primary shear bands [1,19]. In addition, several cracks are visible on the surface. After the failure, the specimen shattered into several small pieces (Fig. 4(d)). In the fracture surface, it is found that the

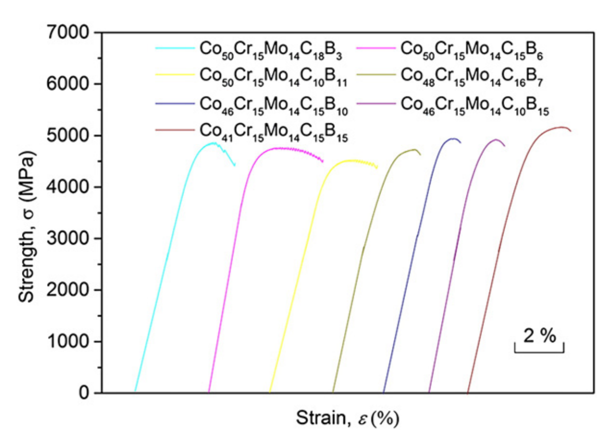

Fig. 3. Compressive stress–strain curves of CoCrMoCB glassy rods.