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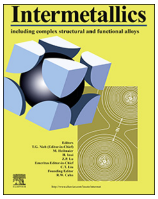

Effect of boron addition on thermal and mechanical properties of Co-Cr-Mo-C-(B) glass-forming alloys

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ABSTRACT

In this work, we investigated the effect of boron addition on glass-forming ability and mechanical properties of Co-Cr-Mo-C alloys. The starting alloy was $(Co_{0.65}Cr_{0.13}Mo_{0.22})_{80}C_{20}$ derived from the $Co_{65}Cr_{13}Mo_{22}$ ternary eutectic composition. This alloy is almost fully crystalline and exhibits brittle mechanical properties. Replacing carbon with boron allows obtaining bulk metallic glasses (BMGs) and bulk metallic glass composites. The designed alloys show very high strength (~4100 MPa), wide super-cooled liquid region (~100 K) and large endothermic enthalpy of the supercooled liquid region (~35 J/g), indicating high thermal stability. The electronegativity difference and supercooled liquid region of the present alloys are comparable to rare-earth elements containing BMGs. The physical properties of the present alloys corresponded well with the alloy design strategy based on the unified parameter using the glass transition temperature, fracture strength, and molar volume. Furthermore, we propose the optimum compositional condition for glass formation by controlling the carbon-to-boron ratio and the influence of carbon on phase formation in this alloy system is discussed.

1. Introduction

Compared with crystalline metallic materials, bulk metallic glasses (BMGs) exhibit higher strength and specific strength due to their disordered atomic structure and structural uniformity [1–4]. Especially, it has been reported that ferrous element-based BMGs such as Fe-, Co-, and Ni-based BMGs show much higher fracture strength values of about 3000–6000 MPa [4–8] than that of Ti-, Zr-, and Cu-based BMGs which is in range of 1700–2000 MPa for Ti-based BMGs, 1500–1800 MPa for Zr-based BMGs, and 1900–2500 MPa for Cu-based BMGs [9–16]. However, the glass-forming ability (GFA) of ferrous element-based BMGs is inferior to that of the other BMGs, which have been reported as centimeter-scale BMGs [9–13]. Recently, it has been found that minor addition of rare-earth elements (RE) with large atomic radius is an effective approach for improving the GFA and thermal stability of Co- and Fe-based BMGs [17–22]. Unfortunately, these Co- and Fe-based BMGs with RE additions are extremely brittle at room temperature and also quite expensive. In general, alloys with compositions close to deep eutectics exhibit good GFA in a given system because the kinetic process of crystallization in the undercooled liquid of the alloys is more sluggish, so that the critical cooling rate for glass formation can be reduced [17,23]. For ferrous element-based alloys, the GFA can also be significantly improved by the addition of metalloids such as C, B, and Si with very small atomic radius [24–26], and it is widely recognized that the metalloid elements are essential for the formation of BMGs, which mostly have a metalloid element content around 20 at.% [26]. However, although almost all ferrous element-based BMGs possess a large amount of metalloids, it is still unclear which element is more effective. Therefore, investigations concerning the optimized ratio of the metalloid elements and their influence on the GFA and mechanical properties of BMGs are of great importance for understanding the role of the metalloid elements and for developing new BMGs with excellent properties.

Along this line, the $Co_{65}Cr_{13}Mo_{22}$ ternary eutectic alloy has been selected as a precursor alloy in this work [27]. 20 at.% carbon were added to the ternary eutectic alloy and thus $Co_{52}Cr_{10.4}Mo_{17.6}C_{20}$ was

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used as starting alloy for the investigations. To understand the effect of the metalloid ratio on the microstructural evolution and physical properties, boron has been partially substituted for carbon. In order to find an optimum composition for high GFA and good mechanical and thermal properties, the alloy composition was systematically changed to establish different atomic ratios between carbon and boron, and to study the impact of the carbon-to-boron ratio on the GFA of the Co-Cr-Mo-C-B system. Therefore, the aim of the present work is to investigate the role of the carbon-to-boron ratio (1:1, 2:1, 3:1, 3:2) on the GFA, mechanical properties, and thermal stability by substituting carbon with boron and to finding the optimum atomic ratio between carbon and boron for obtaining alloys with high GFA.

2. Experimental procedures

$Co_{52}Cr_{10.4}Mo_{17.6}C_{20\text{-}x}B_x$ alloy ingots with different carbon-to-boron ratios (x = 5, 6.7, 8, 10, and 20 at. %) were fabricated by arc-melting high-purity elements (> 99.9% purity) in an Ar atmosphere (99.999%). The ingots were re-melted at least 6 times to guarantee chemical homogeneity. As-cast specimens were prepared by arc-suction casting into a cylindrical water-cooled Cu mold with a diameter of 2 mm and a length of 50 mm. Phase identification was carried out by X-ray diffraction (XRD, Shimadzu XRD-6100) with Cu Kα_1 radiation (λ = 1.5406 Å). The microstructure of the as-cast alloys was investigated using scanning electron microscopy (SEM, JEOL JSM-6390). The thermal properties such as the glass transition temperature (T_g) and the onset temperature of crystallization (T_x) were measured by a differential scanning calorimeter (DSC, Perkin-Elmer DSC-8500) under a constant heating rate of 40 K/min. In order to execute compression tests, cylindrical specimens with a 2:1 aspect ratio were prepared by mechanical polishing and the mechanical properties of the specimens were examined by uniaxial compression testing at an initial strain rate of $10^{-3}\,s^{-1}$ at room temperature. In addition, the 3–6 samples were tested for each composition to ensure the reliability of the mechanical properties.

3. Results and discussion

In order to investigate the effect of metalloid elements (C and B) on the GFA, thermal stability, and mechanical properties of Co-based BMGs, compositions of $Co_{52}Cr_{10.4}Mo_{17.6}C_{20}$ (C20), $Co_{52}Cr_{10.4}Mo_{17.6}C_{15}B_5$ (CB31), $Co_{52}Cr_{10.4}Mo_{17.6}C_{13.3}B_{6.7}$ (CB21), $Co_{52}Cr_{10.4}Mo_{17.6}C_{12}B_8$ (CB32), $Co_{52}Cr_{10.4}Mo_{17.6}C_{10}B_{10}$ (CB11), and $Co_{52}Cr_{10.4}Mo_{17.6}B_{20}$ (B20) were selected for the investigations. Fig. 1 shows the XRD patterns of the as-cast alloy rods with 2 mm diameter. As depicted in Fig. 1, the XRD pattern (a) of the C20 alloy (initial alloy) shows crystalline peaks corresponding to cubic Co_2Mo_4C (*Fd3/m*, a = 1.125 nm) and cubic Co_6Mo_6C (*Fd/3m*, a = 1.090 nm) together with a broad diffuse diffraction maxima around 43°. With additional 5 at.% of B, sharp diffraction peaks of $Co_{11}B_2C$ (*Fm3m*, a = 1.147 nm) appear together with other Co-Mo-C intermetallic compounds such as the Co_2Mo_4C and Co_6Mo_6C for the CB31 alloy (b). These findings are in good accordance with previous findings for similar compositions as the present alloy [17,28]. With further increase of the B ratio, i.e. for the CB21 (c) and CB32 (d) alloys, the samples show an almost identical broad diffraction maxima around 43°, which is the typical characteristic of an amorphous structure. Although some weak crystalline peaks appear in the XRD pattern of CB32, their intensity is not conspicuous. On the other hand, sharp crystalline peaks are superimposed on the diffuse diffraction maxima in the XRD pattern of the CB11 alloy (e) revealing that this alloy is only partially amorphous. The B20 alloy (f) exhibits only sharp crystalline peaks without a broad diffraction maxima, indicating a fully crystalline microstructure.

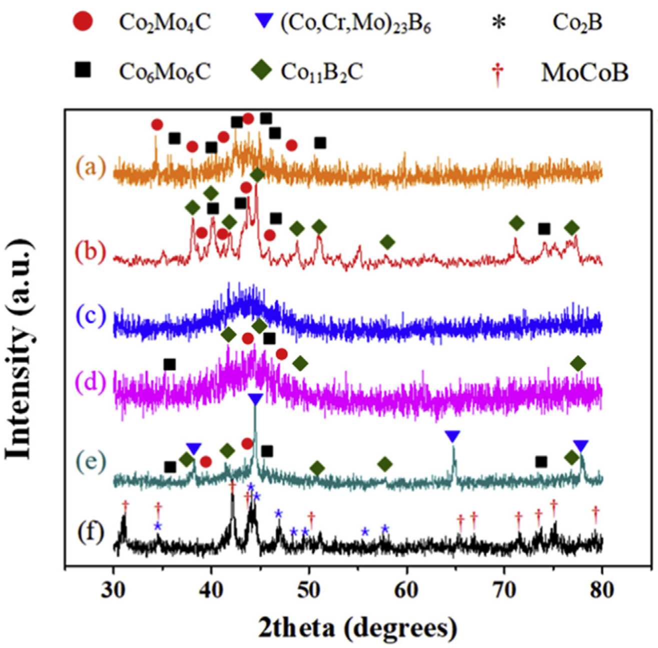

Fig. 1. X-ray diffraction patterns of the as-cast (a) $Co_{52}Cr_{10.4}Mo_{17.6}C_{20}$ (C20), (b) $Co_{52}Cr_{10.4}Mo_{17.6}C_{15}B_5$ (CB31), (c) $Co_{52}Cr_{10.4}Mo_{17.6}C_{13.3}B_{6.7}$ (CB21), (d) $Co_{52}Cr_{10.4}Mo_{17.6}C_{12}B_8$ (CB32), (e) $Co_{52}Cr_{10.4}Mo_{17.6}C_{10}B_{10}$ (CB11), and (f) $Co_{52}Cr_{10.4}Mo_{17.6}B_{20}$ (B20) alloys.

Fig. 2 shows cross-sectional SEM backscattered electron (BSE) images of the present alloys together with images taken at low magnification as inset for each alloy. The BSE image of the C20 alloy in Fig. 2a displays 3 different types of contrast, indicating the formation of a bulk metallic glass composite. Combining the SEM contrast variations and the XRD results, it can be demonstrated that the region A corresponds to the amorphous phase because no contrast can be observed, while regions B and C are crystalline phases. The bright phase is the Co_2Mo_4C phase, and the dark phase is Co_6Mo_6C. The Co_2Mo_4C phase shows bright contrast due to the higher amount of Mo in this phase. The BSE image of the CB31 alloy in Fig. 2b reveals an almost fully crystalline microstructure and the dark $Co_{11}B_2C$ phase is formed through the B addition, as can be deduced from the XRD results and the contrast variation in the BSE images [17]. With further addition of B (CB21), the volume fraction of crystalline phases decreases significantly. Especially, the CB21 alloy displays a homogenous contrast, indicating a monolithic amorphous microstructure (Fig. 2c). The CB32 alloy (Fig. 2d) reveals crystals in the amorphous matrix. It is very difficult to identify the crystalline phase due to the low intensity of the XRD pattern, but it is conceivable that the crystals are some intermetallic compound(s) containing metalloids [17,28]. As the B content increases further (CB11 and B20), the volume fraction of crystalline phases increases and the B20 alloy shows a fully crystalline microstructure with Co_2B and MoCoB phases, as shown in Fig. 2 e and f. These microstructural features such as crystalline phases and contrast variation were very similar to the characteristic of the analogous BMG systems reported by many authors [17,18,28,39], thus it is believed that the description of the microstructural features mentioned above is quite reasonable and acceptable.

Fig. 3 displays the DSC curves of the as-cast alloys. As shown in Fig. 3a, all alloys except B20 exhibit a glass transition and a wide supercooled liquid region (SCLR) followed by crystallization peaks. This distinct glass transition and exothermic events indicate the presence of an amorphous phase, in agreement with the XRD and SEM results. Fig. 3b shows the DSC curves at larger magnification revealing the SCLR. The C20 alloy has a relatively low T_g (787.1 ± 3.8 K) and primary T_x (835.4 ± 4.2 K) and a narrow SCLR ($\Delta T_x = T_x - T_g$ = 48.3 K) followed by two crystalline peaks with low exothermic enthalpy of crystallization (ΔH_x) of 20.9 ± 0.5 J/g and 21.4 ± 0.3 J/g, respectively. This features indicate that the C20 alloy contains a low volume