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Corrosion resistant Cr-based bulk metallic glasses with high strength and hardness

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A B S T R A C T

Novel Cr-based $Cr_{30}Fe_{26}Co_7Mo_{14}C_{15}B_6Y_2$ and $Cr_{45}Fe_{11}Co_7Mo_{14}C_{15}B_6Y_2$ BMGs with a critical diameter up to 8 mm were developed by copper mold casting. For the $Cr_xFe_{56-x}Co_7Mo_{14}C_{15}B_6Y_2$ (x = 15, 30 and 45 at.%) BMGs, chromium is effective on enhancing the corrosion resistance, mechanical properties and elastic moduli, though it decreases the glass forming ability. The Cr-based BMGs exhibit high glass transition temperature of 909–971 K, excellent corrosion resistance in aggressive hydrochloric solution, superior compressive fracture strength up to 4.35 GPa, high Vickers microhardness of 13.87 GPa, and high ratio of hardness to Young's modulus about 0.06, which are advantageous for engineering applications as novel corrosion/wear resistant materials.

1. Introduction

Bulk metallic glasses (BMGs) possess unique properties such as excellent corrosion resistance, high mechanical strength, high hardness and wear resistance due to the amorphous structure, and have attracted considerable attention in the fields of basic science and engineering applications [1–12]. Although a large number of BMGs have been developed in various alloy systems, further efforts on the development of new BMGs with combined high glass-forming ability (GFA), excellent corrosion resistance and good mechanical properties are expected to be made for extending their practical applications, e. g. as coating materials for earth-excavating, drilling and tunnel-boring machines, and promoting the theoretical researches. It is known that the corrosion behavior of metallic glasses is primarily determined by the characters of alloy elements, though the structural and chemical homogeneity leads to the formation of a uniform passive film and hence facilitates an excellent corrosion resistance. When the metallic glasses contain sufficient amount of passivating elements, they exhibit high corrosion resistance. Previous studies have shown that some Cr-containing BMGs exhibited high corrosion resistance, mechanical strength, hardness and wear resistance [13–16], and Cr has been found effective in improving corrosion resistance and mechanical properties of BMGs [17–22]. In addition, Cr possesses high hardness and elastic moduli as well as high melting point. If a Cr-based bulk metallic glass (BMG) is synthesized, excellent corrosion resistance and mechanical properties can be expected. However, no Cr-based BMG has been found so far. In this work, we investigate the GFA, thermal properties, corrosion behaviors, mechanical properties and elastic moduli of Cr–Fe–Co–Mo–C–B–Y BMGs with different Cr and Fe contents. It is found that Cr-based $Cr_{30}Fe_{26}Co_7Mo_{14}C_{15}B_6Y_2$ and $Cr_{45}Fe_{11}Co_7Mo_{14}C_{15}B_6Y_2$ (at.%) BMGs with diameters of 8 mm and 2.5 mm, respectively, can be obtained by copper mold casting. These BMGs exhibit a combination of excellent corrosion resistance and extremely high strength and hardness, which are essential to the applications as coatings and corrosion/wear resistant materials. The mechanisms for the formation and properties of the Cr-based BMGs are also discussed.

2. Experimental procedures

Alloy ingots with nominal compositions of $Cr_xFe_{56-x}Co_7Mo_{14}C_{15}B_6Y_2$ (x = 15, 30 and 45 at.%, denoted as Cr15, Cr30 and Cr45, respectively, for convenience in the following text) were prepared by arc melting mixtures of pure Cr, Fe, Co, Mo and C and FeB alloy (B: 20.85, Si: 0.34, C: 0.079, P: 0.023, Al: 0.054, Fe: balance, mass%) under a Ti gettered argon atmosphere. From the master alloys, cylindrical rods with diameters no more than 5 mm were fabricated by injection copper mold casting. For fabricating larger specimens, the ingots were remelted by induction and then poured into copper mold under a highly pure argon atmosphere. Ribbon samples were also prepared by melt spinning. Structure of the specimens was examined by X-ray diffraction (XRD) on Dmax2200PC Rigaku X-ray diffractometer with Cu $K\alpha$ radiation and JEM-2100F high-resolution transmission electron microscopy (HRTEM). Thermal properties of the specimens were evaluated by a NETZSCH DSC 404 C differential scanning calorimeter (DSC) at a heating rate of $0.33\ K\cdot s^{-1}$ in a flowing purified argon atmosphere within the error of ± 2 K.

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Corrosion behaviors of the glassy rods with a diameter of 2 mm and the SUS316 stainless steel counterpart were tested by immersion tests and electrochemical measurements in 1 M HCl solutions. Prior to the corrosion tests, the specimens were mechanically polished in cyclohexane with silicon carbide paper up to no. 2000, degreased in acetone, washed in distilled water, dried in air and further exposed to air for about 24 h for good reproducibility. The average corrosion rates were estimated from the weight loss of at least three samples of each composition after immersion in the HCl solution open to air at 298 K for 168 h, for which an analytical balance with a precision of 1×10^{-5} g was used. The electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and a saturated calomel reference electrode (SCE). Anodic polarization curves were measured at least three times of each composition to confirm reproducibility at a potential sweep rate of 0.833 $mV \cdot s^{-1}$ after open circuit immersion for 1 h when the open circuit potential became almost steady.

Uniaxial compressive test on the glassy rod specimens with a diameter of 2 mm and a length of 4 mm was conducted using a Instron-5565 mechanical testing machine at a strain rate of 2.1×10^{-4} s^{-1}. Fracture morphologies were observed by CamScan 3400 scanning electron microscopy (SEM). Vickers microhardness (H_v) was measured on the glassy rods with a diameter of 2 mm using a FM-800 Vickers microhardness tester under a load of 1000 g and a loading time of 15 s. The density (ρ) of the BMGs was measured by the Archimedes technique. Elastic properties were examined on the glassy specimens with a diameter of 2 mm and an aspect ratio of 2:1 by a pulse-echo ultrasonic echography technique using an Olympus Panametrics-NDT 5703PR. Using the measured data of longitudinal and transverse sound velocities, the elastic moduli i.e., Young's modulus (E), shear modulus (G), bulk modulus (K), and Poisson's ratio (ν), were calculated, for which the error bands were below 5%. All the tests of uniaxial compression, Vickers microhardness, density and elastic moduli were conducted for at least three samples of each composition.

3. Results

3.1. Glass formation and thermal properties of $Cr_xFe_{56-x}Co_7Mo_{14}C_{15}B_6Y_2$ alloys

Fig. 1 shows the XRD patterns of the as-cast $Cr_xFe_{56-x}Co_7Mo_{14}C_{15}B_6Y_2$ (x = 15, 30 and 45 at.%) rods with their critical diameters for glass formation (d_c). Only a broad diffuse halo without any appreciable crystalline peaks can be seen for these cast rods, demonstrating the formation of amorphous structure. The d_c is 14 mm, 8 mm and 2.5 mm for the Cr15, Cr30 and Cr45 alloys, respectively. This indicates that Cr-based BMGs with high glass-forming ability are formed at x = 30 and 45 at.%, although the d_c of the present alloy system decreases with the increase in Cr content. The maximum diameter of the Cr15 BMG prepared in this work is slightly smaller than that reported in Ref. [23], which may be due to the different experimental conditions, such as we use a commercial grade FeB alloy instead of pure Fe and B. Fig. 1b presents the HRTEM image and selected-area electron diffraction (SAED) pattern (the inset image of Fig. 1b) of the as-cast Cr45 rod with a diameter of 2.5 mm. The HRTEM image exhibits a homogeneous contrast and the corresponding SAED pattern shows a broad halo ring, which further confirm the amorphous structure of the present BMG.

The glass transition, crystallization and melting behavior of the Cr15, Cr30 and Cr45 rods are shown in Fig. 2(a) and (b). Upon heating, the alloys exhibit distinct glass transition and subsequent supercooled liquid region prior to crystallization. With the Cr content increasing from 15 to 45 at.%, the glass transition temperature (T_g) and the onset temperature of crystallization (T_x) increase from 853 K to 971 K and from 906 K to 1009 K, respectively, leading to the decrease in supercooled liquid region ($\Delta T_x = T_x - T_g$) from 53 K to 38 K. Meanwhile, there is no distinct difference in the values of T_g and T_x and the heat of the main crystallization reaction between the rod and ribbon samples of the same

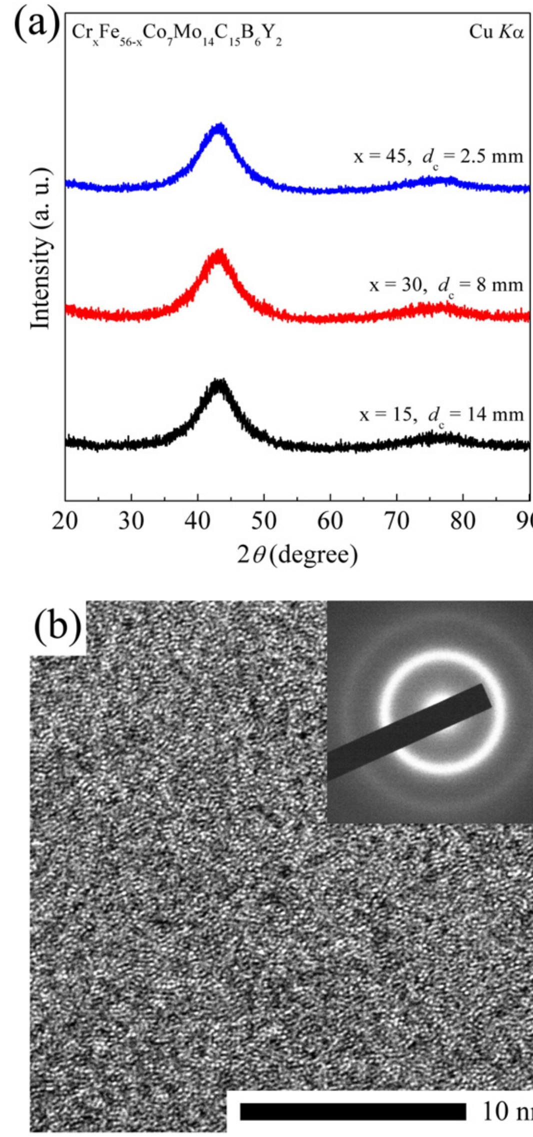

Fig. 1. (a) XRD patterns of as-cast $Cr_xFe_{56-x}Co_7Mo_{14}C_{15}B_6Y_2$ rods with their critical diameters for glass formation (d_c) and (b) is the HRTEM image and SAED pattern (the inset image) of the as-cast Cr45 rod with a diameter of 2.5 mm.

compositions, further confirming the glassy structure of the cast rods with their critical diameters. The melting temperatures (T_m) of the Cr15, Cr30 and Cr45 alloys were measured to be 1388 K, 1404 K and 1484 K, respectively. Accordingly, the reduced glass transition temperatures T_{rg} ($= T_g / T_m$) were calculated. The values of the thermal parameters and d_c for the Cr–Fe–Co–Mo–C–B–Y glassy alloy system are summarized in Table 1.

3.2. Corrosion behavior of $Cr_xFe_{56-x}Co_7Mo_{14}C_{15}B_6Y_2$ alloys

Changes in open-circuit potentials with immersion time for the Cr15, Cr30 and Cr45 BMGs and SUS316 in 1 M HCl solution open to air at 298 K are shown in Fig. 3(a). It is observed that the potential of SUS316 gradually increases in the initial time period and then reaches a constant value about - 0.315 ± 0.005 V. In comparison, the potentials of the Cr15, Cr30 and Cr45 BMGs initially rise steeply and then slow down until it reaches the constant values, implying that the stability of surface films is enhanced during the immersion. The corrosion potentials of the Cr15, Cr30 and Cr45 BMGs are 0.048 ± 0.004 V, 0.066 ± 0.004 V and 0.074 ± 0.005 V, respectively, indicating that the stability of the surface films increases with the increment of Cr content, and