Centimeter-scale-diameter Co-based bulk metallic glasses with fracture strength exceeding 5000 MPa

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Co48−xFexCr15Mo14C15B6Er2 (x = 2.5 and 5) bulk metallic glasses (BMGs) with critical size (dc) up to 15 mm in diameter were synthesized by copper mold casting. Co43Fe5Cr15Mo14C15B6Er2 BMG has a wide supercooled liquid region (84 K) and ultrahigh fracture strength exceeding 5000 MPa, which is the highest value for reported metallic glasses with dc exceeding 1 cm. Furthermore, the Poisson ratio, Young modulus, shear modulus and bulk modulus of this alloy were evaluated to be 0.31, 217 GPa, 82 GPa and 214 GPa, respectively. The ideal configurational entropy of Co48−xFexCr15Mo14C15B6Er2 (x = 0 and 5) has been calculated. The introduction of the similar element Fe in the Fe-free Co-Cr-Mo-C-B-Er alloy will be beneficial to increasing the ideal configurational entropy and depressing the critical cooling rate to achieve greater glass-forming ability. The combination of superior glass-forming ability and ultrahigh fracture strength makes the present Co48−xFexCr15Mo14C15B6Er2 (x = 2.5 and 5) BMGs promising candidates as advanced structural materials.

bulk metallic glass, glass forming ability, mechanical properties, Co alloys

The mechanical properties of metallic glasses have been widely studied in recent years. It has been reported that fracture strength is in the range of 1500–2000 MPa for Zr-based metallic glasses [1–4], 1800–2400 MPa for Ti-based metallic glasses [5,6], 2000–2500 MPa for Cu-based metallic glasses [7,8], 3000–4000 MPa for Fe-based metallic glasses [9–11], and 4000–6000 MPa for Co-based metallic glasses [12–14]. In contrast with conventional crystalline alloys, monolithic metallic glasses have exceptionally high fracture strengths. It is therefore expected that those metallic glasses can be used as structural materials.

Currently, one obstacle that restricts the industrial application of metallic glasses as structural materials is their limited glass-forming ability (GFA). It is believed that there is a large atomic size difference and negative heats of mixing among the main constituent elements, which can be defined as dissimilar elements, in good glass-forming alloys [15].

During the last decade, bulk metallic glasses (BMGs) with critical diameter mainly of the millimeter scale and occasionally of the centimeter scale, which satisfy this compositional criterion have been discovered [2,4,5,7,9]. Recently, we found that the GFA of some glassy alloys consisting of dissimilar elements can be improved when elements with atomic sizes and chemical properties similar to those of the components are added [16–20]. Using this new concept of the coexistence of similar and dissimilar elements, we have synthesized many BMGs with superior GFA; e.g. the critical diameter of La-Ce-Al-Co-Cu BMGs reaches 32 mm [18].

The aim of this research is to develop BMGs with high fracture strength exceeding 5000 MPa and high GFA with critical diameter exceeding 1 cm. Despite there being an increasing number of research papers on the mechanical properties of BMGs, only Co-based BMGs have been reported to exhibit ultrahigh strengths up to 5–6 GPa in a compression test [12,14]. Recently, our group reported that
Co_{48}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} BMGs with superior GFA can be produced in bulk form with critical thickness of 10 mm [21,22]. Therefore, Co_{48}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} alloy was chosen as the starting composition and Fe was introduced as a similar element to partially substitute Co. The GFA of Co_{48-x}Fe_{x}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} (x = 2.5 and 5) alloys can be improved by the substitution of Fe for Co. Moreover, the present BMGs exhibit ultrahigh fracture strength exceeding 5000 MPa.

1 Experimental

Co_{48-x}Fe_{x}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} (x = 2.5 and 5) alloy ingots were prepared by arc-melting the mixtures of pure Co, Fe, Cr, Mo, C, B, and Er (all with purity of 99.9 mass %) metals in a high-purity argon atmosphere. The ingots were remelted at least four times to ensure their chemical homogeneity. From the master alloys, cylindrical rods were fabricated by copper mold casting under a high-purity argon atmosphere. Cross sections of the as-cast rods were examined by X-ray diffractometer with Cu Kα radiation to study the structure. Co_{43}Fe_{5}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} glassy alloy with diameter of 15 mm was observed with a JEM-2100F transmission electron microscope at an operating voltage of 200 kV. The thermal stability was examined by NETZSCH DSC 404C differential scanning calorimetry (DSC) at a heating rate of 0.33 K/s. Fracture strength was measured by an Instron testing machine. The specimens were 1 mm in diameter and 2 mm in length, and the strain rate was 4.2 × 10^{-4} s^{-1}. Nanoindentation experiments were conducted at room temperature using an ENT-1100a nanoindenter. The density (ρ) was measured employing the Archimedes technique using a Mettler Toledo balance (readability: 0.1 µg). Elastic constants (Poisson’s ratio (ν), Young’s modulus E, shear modulus G and bulk modulus B) were determined from the density and velocities of the longitudinal wave (V_L) and transverse wave (V_T) in the material with an Olympus Panametrics-NDT 5900 PR ultrasonic testing device. The latter were measured employing a pulse-echo ultrasonic echography technique in infinite mode and in reflection mode via coupling gels. ν, E, G and B can be calculated from [23]:

\[ ν = \frac{1 - 2r^2}{2 - 2r^2}, \]
\[ E = \frac{V_T^2 \rho (1 + ν) (1 - 2ν)}{1 - ν}, \]
\[ G = \frac{E}{2(1 + ν)}, \]
\[ B = \frac{E}{3(1 - 2ν)}, \]

where \( r = V_T/V_L \). The error bands of the calculation elastic constants are below 5%.

2 Results and discussion

XRD patterns of as-cast Co_{48-x}Fe_{x}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} (x = 2.5 and 5) cylindrical samples with different diameters are shown in Figure 1. No appreciable peaks are detected for the samples of Co_{43}Fe_{5}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} with diameter of 12 mm and Co_{43}Fe_{5}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} with diameter of 15 mm within the resolution limit of the XRD, which indicates fully amorphous structure.

It has been pointed out that alloys with microcrystalline phase can also exhibit broad diffraction halos like those of metallic glass. During DSC scanning, however, metallic glasses exhibit exothermic peaks, while microcrystalline materials have monotonically decaying heat flow signals [7]. Hence, DSC scanning was performed in the present study. The DSC curves of a Co_{43}Fe_{5}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} ribbon sample and cylindrical sample with diameter of 15 mm are shown in Figure 2. Apparent exothermic peak characteristics of crystallization processes confirm the glassy structure of the samples. No obvious difference is detected between DSC traces of the ribbon and cylindrical samples, indicating similar glass states. In addition, the Co-based BMG has high-thermal-stability characteristics of a high glass transition temperature (T_g) of 844 K and wide supercooled liquid region (∆T_g), where T_g is the onset temperature of crystallization of 84 K, and it is thus useful in thermoplastic applications as a nano-molding material [24,25].

To further clarify the microstructure, a high-resolution transmission electron microscope (HRTEM) image with a selected-area electron diffraction (SAED) pattern (inset) of the as-cast Co_{43}Fe_{5}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} sample with diameter

![Image](url)

Figure 1 X-ray diffraction (XRD) patterns of as-cast Co_{48-x}Fe_{x}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} (x = 2.5 and 5) cylindrical samples in different diameters.
of 15 mm is shown in Figure 3. The SAED pattern exhibits only a halo ring, which is inherent to a glassy phase, and indicates no distinguishable crystals presenting in the sample. The HRTEM image confirms that there are no distinguishable crystals on the nanometer scale. Integrating the results of XRD, DSC and transmission electron microscopy, it is concluded that the critical diameter of Co_{43}Fe_{5}Cr_{15}Mo_{14}C_{15}B_{6}Er_{2} BMG can reach 15 mm.

Figure 4 shows the mixing enthalpy of constituents in the (Co, Fe)-Cr-Mo-C-B-Er alloys. It is found that the mixing enthalpies are $-24$ kJ/mol for the Co–Er pair, $-19$ kJ/mol for the B–Mo pair, $-16$ kJ/mol for the Cr–B pair, $-11$ kJ/mol for the B–Fe pair and $-9$ kJ/mol for the Co–B pair. The large negative mixing enthalpies for constituent elements of
the present BMGs indicate strong cohesive forces, and lead to dense packing in the liquid state, which is favorable for glass formation during solidification [15].

The reason that the Fe-containing alloy has greater GFA than the Fe-free alloy (Co48Cr15Mo14C15B6Er2) is discussed on the basis of thermodynamics. It has been reported that the maximum thickness of a metallic glass (Dc) can be determined as [26]:

\[ R_c (K/s) = 10/D_c^2 \text{ (cm)}, \]

where \( R_c \) is the critical cooling rate. In accordance with classical crystallization theory, \( R_c \) for metallic glasses can be written as [27–29]:

\[ R_c = \frac{k_B T_m^3}{a \eta_{ZT}} \exp \left[ f_1 \left( \frac{\Delta H - T_m \Delta S_{\text{ideal}}}{300R} \right) - f_2 \left( \frac{T_m S_n}{300R} \right) \right], \]

where \( Z \) is a constant, taken as \( 2 \times 10^{\delta} \), \( k_B \) is Boltzmann’s constant, \( a \) is the average interatomic distance, \( \eta \) is the viscosity, \( \Delta H \) is the mixing enthalpy of the system, \( \Delta S_{\text{ideal}} \) is the ideal configurational entropy, \( S_n \) is the mismatch term of entropy and \( R \) is the gas constant. Employing the method of least squares, \( f_1 \) and \( f_2 \) were calculated to be 0.75 and 1.2, respectively [27–29].

According to the regular solution model, \( \Delta H \) and \( \Delta S_{\text{ideal}} \) are defined for multi-component systems with \( N \) elements [27–29]:

\[ \Delta H = \sum_{i=1}^{N} \Omega_i c_i c_j, \]

\[ \Delta S_{\text{ideal}} = -R \sum_{i=1}^{N} \ln c_i, \]

where \( R \) is the gas constant, \( c_i \) is the mole fraction of \( i \), and \( \Omega_i \) is the regular solution interaction parameter between elements \( i \) and \( j \). \( \Omega_{ij} \) can be calculated as:

\[ \Omega_{ij} = 4 \Delta H_{AB}^{\text{mix}}. \]

The relation follows from the definition in eq. (7) for the equal-atomic composition of a binary A-B system, and \( \Delta H_{AB}^{\text{mix}} \) is the mixing enthalpy of the binary A-B system. In our previous research, \( T_m \) and \( \Delta S_{\text{ideal}} \) were confirmed to be the primary factors resulting in the difference in \( R_c \) among alloys with similar elements coexisting. According to eq. (6), alloys with higher \( \Delta S_{\text{ideal}} \) always exhibit lower \( R_c \) and greater GFA. In the present study, the ideal configurational entropy of Fe-containing alloy calculated from eq. (8) is 13.34 J/(mol K), higher than that of Fe-free alloy (12.01 J/(mol K)). \( T_m \) of Fe-containing alloy is 1365 K, higher than that of Fe-free alloy (1350 K). Assuming the two alloys possess similar values for other factors, such as the average interatomic distance and viscosity, the ratio of \( R_c \) (Fe-containing alloy) to \( R_c \) (Fe-free alloy) can be calculated as:

\[ \frac{R_c \text{ (Fe-containing alloy)}}{R_c \text{ (Fe-free alloy)}} \approx \frac{1365^2}{1350^2} \exp \left[ \frac{0.75 \times 1350 \times 1.01 - 1365 \times 13.34}{300 \times 3.14} \right] = 0.56. \]

According to eq. (5), the ratio of \( D_c \) (Fe-containing alloy) to \( D_c \) (Fe-free alloy) can be calculated as:

\[ \frac{D_c \text{ (Fe-containing alloy)}}{D_c \text{ (Fe-free alloy)}} \approx \sqrt{\frac{R_c \text{ (Fe-containing alloy)}}{R_c \text{ (Fe-free alloy)}}} = 1.34. \]

This value is in good agreement with the experimental results (15/10=1.5) in the present work. Thus, the decrease in the critical cooling rate resulting from the configurational entropy can reasonably explain the obvious improvement in GFA of the Co-based alloy for this substitution.

Figure 5 shows compressive stress-strain curves for the Co48–xFe-xCr15Mo14C15B6Er2 (x = 2.5 and 5) bulk metallic glasses with diameter of 1 mm. Both samples present elastic deformation with an increase in compressive stress, followed by final abrupt fracture, and as a result, the rods break into pieces. For reported BMGs with critical diameter exceeding 1 cm, such as Mg82Cu26.5Ag6Cd11, Pd8Cu50Ni10P20, Zr62Al15.5Ni10Cu17.5 and Fe42Co13Cr13Mo15B8Y2, the fracture strengths range from 1000 to 3400 MPa [2,10,30,31]. In the present study, the fracture strength of Co48Fe2Cr15Mo14C15B6Er2 BMG is 5200 MPa, which is the highest among amorphous alloys with critical diameter exceeding 1 cm so far.

To further investigate the fracture behavior of the Co48–xFe-xCr15Mo14C15B6Er2 BMG, nanoindentation experiments were carried out on 4 mm rods in a load-control mode. A typical load-displacement (P-h) curve obtained in a nanoindentation test is shown in Figure 6. There are several discontinuities in the curve (marked by arrows), the presence of which are known as the “pop-in” effect. During this
period, the displacement of the indenter increases with little or no change in the load, indicating microplastic deformation.

Ultrasonic measurements were carried out to determine the elastic constants of Co$_{43}$Fe$_{5}$Cr$_{15}$Mo$_{14}$C$_{15}$B$_{6}$Er$_{2}$ BMG with density $\rho = 8.36$ g cm$^{-3}$. The Poisson ratio, Young modulus, shear modulus and bulk modulus were calculated to be 0.331, 217 GPa, 82 GPa and 214 GPa, respectively. Figure 7 shows good correlation between the fracture strength and Young’s modulus for typical metallic glasses and the present BMGs. The Co-based BMGs have high fracture strength and Young’s modulus among the present metallic glasses. It has been pointed out by Inoue et al. that electrons of the metalloid elements can transfer from the original element to the $d$ shell of transition metal elements to form $s$-$d$ hybrid bonds [13]. In the present study, there is strong interaction between metalloid atoms (B) and the metal (Co and Fe) through $s$-$d$ hybrid bonding, which results in the high strength of the Co$_{8x}$Fe$_{x}$Cr$_{15}$Mo$_{14}$C$_{15}$B$_{6}$Er$_{2}$ ($x = 2.5$ and 5) BMG.

3 Conclusions

Co$_{8x}$Fe$_{x}$Cr$_{15}$Mo$_{14}$C$_{15}$B$_{6}$Er$_{2}$ ($x = 2.5$ and 5) BMGs with ultrahigh strength exceeding 5000 MPa and high thermal stability can be formed with diameters exceeding 1 cm by copper mold casting. The Poisson ratio, Young modulus, shear modulus and bulk modulus of the alloy with $x = 5$ were determined to be 0.331, 217 GPa, 82 GPa and 214 GPa, respectively. The high GFA and ultrahigh strength of the Co$_{8x}$Fe$_{x}$Cr$_{15}$Mo$_{14}$C$_{15}$B$_{6}$Er$_{2}$ ($x = 2.5$ and 5) BMGs can be attributed to the large negative mixing enthalpies among the constituent elements and strong chemical bonds between B and Co/Fe. These Co-based BMGs with combination of superior GFA and ultrahigh strength are promising for further applications as structural materials.

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