Thermal stability and glass-forming ability of Y-Ce-Co-Al bulk metallic glasses

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Materials

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Abstract: The thermal stability and glass-forming ability of $Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38, 41, 44) bulk metallic glasses with a diameter of 5 mm were investigated by differential scanning calorimetry and X-ray diffraction. The results show that the thermal stability of the alloys decreases with the addition of Ce. It has the best glass-forming ability when x=25, whose calculated values can reach about 30 mm in diameter. The effect of Ce element could be explained on the view of Miedema's theory and electronegativity difference of amorphous alloys.

Key words: bulk metallic glass; glass forming ability; thermal stability; Y-based alloys

1. Introduction

Bulk metallic glasses (BMGs) have many potential applications resulting from their unique properties, such as superior strength and hardness, excellent corrosion resistance, improved wear resistance, and superior soft magnetism property. At the same time, during the supercooled liquid region ($\Delta T_x = T_x - T_g^{onset}$), which implies high thermal stability of the supercooled liquid against crystallization, large viscous flowability of the supercooled liquid enables warm-working a metallic glass into bulk shapes. Therefore, BMGs have attracted much attention by materials scientific researchers increasingly, and have been prepared in Fe, Co, Zr, Ni, Mg, Pd, Ti, Cu, Nd and La based alloys one after another [1-6].

Guo [7] *et al.* have prepared $Y_{36}Sc_{20}Co_{20}Al_{24}$ BMG, which can form amorphous rods with diameters over 2 cm. However, Sc is manmade element, and very valuableness. At present, the price of Sc is about 50000-60000 RMB per kilogram. Cerium is the most abundant rare earth (RE) metal on the earth, which is also one of the most reactive RE metal and oxidizes very readily even at room temperature. Another intrinsic feature of cerium is its variable electronic structure and dual valency states, because of which only a small amount of energy is required to change the relative occupancy of the electronic levels [8]. So, the influence of Ce element on the glass forming ability and thermal stability of bulk metallic glasses in Y-Co-Al alloys was investigated in this paper.

2. Experimental procedure

$Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38, 41, 44) bulk metallic glasses with a diameter of 5 mm were prepared by rapidly quenching the master alloys that were made by arc melting into a water-cooled copper mold in an argon atmosphere. The amorphous structure was identified by a D/max-c X-ray diffractometry using Cu K_α radiation. The thermal stability was examined by differential scanning calorimetry (Perkin-Elmer DSC-7) at a heating rate of 0.33 K/s using 99.99% Ar.

3. Result and discussion

The X-ray diffraction patterns of $Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38, 41, 44) alloys with diameters of 5 mm are shown in Fig. 1. From Fig. 1, only a broad diffuse scattering peak occurs and no obvious crystalline peaks are seen in x=15, 20, 25, 28, 38, 41, which indicates that they are of amorphous structures. For x=44, there exits obviously sharp diffraction peaks at 2θ=32° that may correspond to crystalline phase. Fig. 2 shows DSC curves of above bulk metallic glasses at a scanning rate of 0.33 K/s. With an increase in Ce content, the onset temperature of the glass transition (T_g^{onset}), the crystallization temperature (T_x), and the melting temperature (T_m) decrease respectively. There are two crystalline phases for x=15, and the second crystallization peaks occur at the high temperature region with the addition of Ce. ΔT_x shows a large value

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of 83 K for *x*=25, which indicates a strong glass forming ability (GFA).
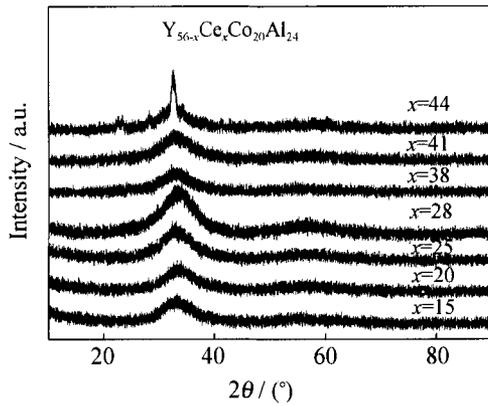

Fig. 1.   XRD patterns of $Y_{56-x}Ce_xCo_{20}Al_{24}$ (*x*=15, 20, 25, 28, 38, 41, 44) alloys.
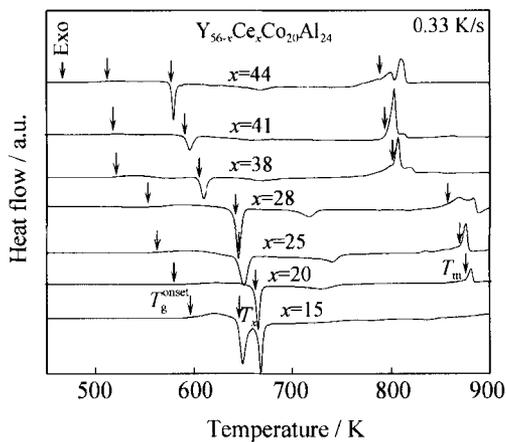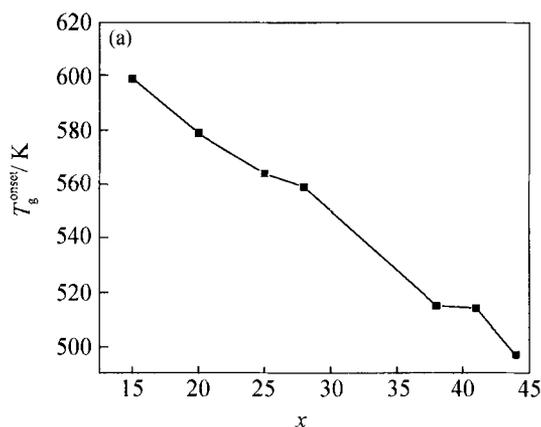

Fig. 2.   DSC curves of $Y_{56-x}Ce_xCo_{20}Al_{24}$ (*x*=15, 20, 25, 28, 38, 41, 44) alloys.

Fig. 3 shows the changes of the onset temperature of the glass transition (T_g^{onset}) and the onset crystallization temperature (T_x) in $Y_{56-x}Ce_xCo_{20}Al_{24}$ (*x*=15, 20, 25, 28, 38, 41, 44) alloys. From Fig. 3, the both parameters are all in a trend of decrease with the increase of Ce. It is obvious that the thermal stability

decreases with the addition of Ce. For comparison, γ and Z_c are also used to measure the GFA, which was defined in Ref. [9]:

$$\gamma = \frac{T_x}{T_g + T_l} \tag{1}$$

$$Z_c = 2.80 \times 10^{-7} \exp(41.70\gamma) \tag{2}$$

The values of γ are 0.4490, 0.4450, 0.4361, 0.4392, 0.4399 and 0.4360 for *x*=15, 20, 25, 28, 38, 41, and 44, respectively. The values of Z_c are 37.9, 32.07, 22.13, 25.18, 25.93 and 22.04 for *x*=20, 25, 28, 38, 41 and 44, respectively. The distinct glass transition and the sharp crystallization as well as large value of γ further confirm the high GFA of the alloys.

The results above show that the addition of Ce plays an important role in GFA and thermal stability of Y-Ce-Co-Al alloys. Thermodynamics and chemical enthalpy are useful to explain the nature of the glass forming ability. According to Miedema's theory, the formation enthalpy of amorphous alloys can be estimated as follows [10]:

$$\Delta H_{amor}^{form} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} C_i C_j \Delta H_{ij}^{chem} + (3.5\sum_{i=1}^{n} C_i T_m^i)/1000 \tag{3}$$

where ΔH_{amor}^{form} is the amorphous formation enthalpy, ΔH_{ij}^{chem} the chemical enthalpy, C_i the atom fraction of element *i*, and T_m^i the melting point of element *i*. The glass forming ability of bulk metallic glass could be predicted by calculating the formation enthalpy of the alloys. In general, the bigger the formation enthalpy, the higher the glass forming ability. Fig. 4 shows the change of the formation enthalpy of $Y_{56-x}Ce_xCo_{20}Al_{24}$ (*x*=15, 20, 25, 28, 38, 41, 44) alloys. It has the maximum value, −51.62 kJ/mol, for *x*=25, so it maybe has the best glass forming ability in theory.
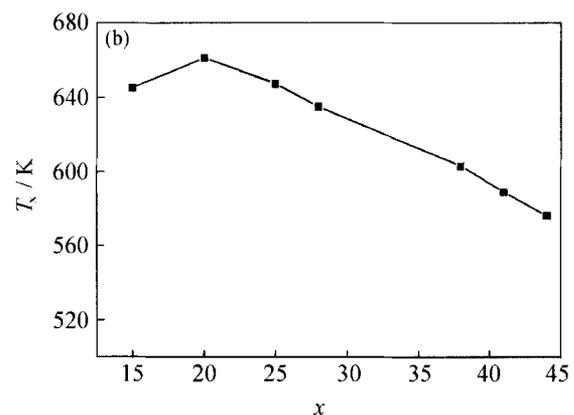

Fig. 3.   Changes of the onset temperature of glass transition (T_g^{onset}) (a) and the onset crystallization temperature (T_x) (b) in $Y_{56-x}Ce_xCo_{20}Al_{24}$ (*x*=15, 20, 25, 28, 38, 41, 44) alloys.
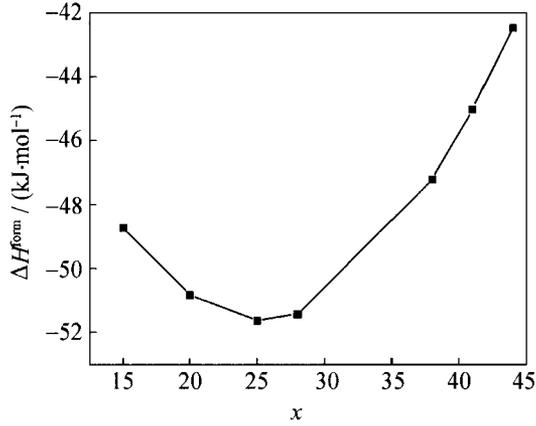
Fig. 4. Relationships between ΔH^{form} and Ce (content) of YCeCoAl alloys.

In accordance with structural chemistry view of glass formation, it is the chemical bond characteristic, the most important factor, that leads to the structure of the material. The role of the glass formation can be explained by chemical bond characteristic inside materials. As we know, the metal elements with same or similar eletronegativity are combined together to form alloys and metals. As extreme bond types, pure metallic bond, covalent bond and ionic bond hardly exist in a practical material. Generally, they exist in a series of mixture bonds in the material. It is important to form mixed bond for the glass formation. When the metal bond with high coordination number and less orientation transfers to the covalent bond, it tends to have orientation and saturation by the extreme polarization and are energetically beneficial to the forming of alloys with a low coordination number, and thus it is easy to form the glass. The electronegativities are quite different among these components of the $Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38, 41, 44) alloys. The computing method of the electronegativity difference Δx in multicomponent alloys is as follows [11]:

$$\Delta X = \sqrt{\sum_{i=1}^{n} C_i (X_i - \overline{X})^2} \qquad (4)$$

$$\overline{X} = \sum_{i=1}^{n} C_i X_i \qquad (5)$$

where C_i is the atom fraction of element i in the alloy, x_i the Pauling electronegativity, $\overline{X}$ the arithmetical mean value of electronegativity. In the formula above, the Pauling scale of electronegativity was used, in detail, Y=1.22, Ce=1.12, Co=1.88, Al=1.61. The values of Δx are 0.284, 0.289, 0.293, 0.296, 0.304, 0.306, and 0.308 for the $Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38,

41, 44) alloys, respectively. In general, the larger the electronegativity difference, the higher the bond force between atoms. So compound may be formed when the electronegativity difference increasing to a certain value, which may result in the appearance of crystallization phases for x=44 as shown in Fig. 1.

4. Conclusions

In $Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38, 41at%, 44) alloys, it can be prepared completely amorphous samples for x=15, 20, 25, 28, 38, and 41 with the diameter up to 5 mm. With the increase of Ce content, the thermal stability of $Y_{56-x}Ce_xCo_{20}Al_{24}$ (x=15, 20, 25, 28, 38, 41, and 44) alloys decreased gradually. The alloy with the best glass-forming ability was found with a large value of supercooled liquid region (ΔT_x=83 K) for x=25.

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