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Bulk metallic glasses based on heavy rare earth dysprosium

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Abstract

DyYAlCo bulk metallic glasses (BMGs) with high thermal stability have been obtained. The origin of the high thermal stability of these new BMGs is discussed, and it is apparent that the high bulk modulus of the base component is predominantly responsible for this feature.

Keywords: Dy-based bulk metallic glasses; Elastic moduli; Thermal stability

1. Introduction

The rare earth (RE)-transition metal metallic glasses are known for their high glass-forming ability (GFA) and promising magnetic properties [1,2]. They can be useful as magnetic functional materials particularly when they are available in bulk form [1–6]. Nevertheless, the known RE-based bulk metallic glasses (BMGs) commonly have low glass transition temperatures T_g and crystallization temperatures T_x which limit their practical application range, and thus new RE-based BMGs with high thermal stability and exceptional magnetic properties have attracted increasing interest. Previous studies have shown that the T_g and T_x would be enhanced by a higher elastic modulus of the base element [7]. Interestingly, the elastic constants of metallic glasses show a good correlation with a weighted average of the elastic constants for the constituent elements: $M^{-1} = \sum f_i M_i^{-1}$, where M is the elastic constant and f_i the atomic percentage of the component [6,8,9]. So consideration of elastic moduli can assist in selecting alloying components for controlling the elastic moduli and then thermal stability of the BMG-forming alloys. With this strategy, dysprosium is selected as the base element because of its relatively high bulk and high Young's modulus amongst the lanthanide family. In addition, dysprosium has a large magnetostrictive effect in low temperature. So the Dy-based BMGs could exhibit high thermal stability and large magnetostrictive property, which are attractive for potential application as functional materials.

In this work, we report for the first time a new family of Dy–Y–Al–Co metallic alloys, which can be readily cast into full glassy rods up to 5 mm in diameter. Unlike other RE-based BMGs, they exhibit high thermal stability corresponding to the highest T_g, T_x and activation energies in known RE-based BMGs. It is apparent that, in addition to the strong chemical interaction among the components, the high bulk modulus of the base component in the BMGs is predominantly responsible for the high thermal stability. The thermal stability is closely correlated with the elastic constants in the rare earth-based BMGs. The result might be significant for designing new glass-forming alloys with high thermal stability and in understanding the universal features of structural and physical properties of metallic glassy alloys.

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Table 1
Thermodynamic parameters of the Dy-based BMGs and other typical RE-based BMGs

BMG	T_g (K)	T_x (K)	T_m (K)	T_l (K)	T_{rg}	γ
$Dy_{40}Y_{16}Al_{24}Co_{20}$	633	682	1011	1031	0.626	0.410
$Dy_{46}Y_{10}Al_{24}Co_{20}$	631	675	1004	1025	0.628	0.408
$Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$	627	677	991	1023	0.633	0.410
$Dy_{46}Y_{10}Al_{23}Co_{20}Nb_1$	622	671	1001	1044	0.621	0.403
$Gd_{40}Y_{16}Al_{24}Co_{20}$	598	653	972	995	0.62	0.410
$Nd_{60}Cu_{20}Ni_{10}Al_{10}$	438	478	728	755	0.60	0.401
$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	417	469	708	810	0.59	0.372
$Ce_{70}Cu_{10}Ni_{10}Al_{10}$	359	377	639	714	0.56	0.351
$La_{60}Cu_{20}Ni_{10}Al_{10}$	387	447	694	–	0.56	–

The data of other RE-based BMGs were obtained from Refs. [3,5,6,8,17].

2. Experimental

The Dy–Y–Al–Co alloys with the nominal compositions listed in Table 1 were prepared by arc melting Dy, Y, Al, Co, Fe and Nb metals with a purity of 99.9% in Ti-gettered argon atmosphere. The ingots were remelted several times to ensure the homogeneity of the samples, and then were suck-cast into a copper mold to obtain cylindrical rods. The structure of the as-cast alloys was identified by X-ray diffraction (XRD) using a MAC M03 diffractometer with Cu-Kα radiation. Thermal properties were investigated in a Perkin–Elmer differential scanning calorimeter (DSC) DSC-7 and differential thermal analyzer (DTA) DTA-7 under a continuous argon flow. The acoustic velocities at ambient temperature measured by using a pulse echo overlap method and the travel time of ultrasonic waves propagating through the sample with a 10 MHz frequency were obtained using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns [10]. The density ρ was measured by the Archimedean principle with an error of 1%. The elastic constants (e.g., bulk modulus B, Young's modulus E, shear modulus G, and Poisson's ratio σ) were derived from the ultrasonic velocities and density [11].

3. Results and discussion

Fig. 1 shows the XRD patterns of the typical as-cast $Dy_{46}Y_{10}Al_{24}Co_{20}$ and $Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$ full glassy alloy rods. The broad diffused diffraction peaks and no appreciable diffraction peak corresponding to crystalline phase in the pattern indicate that the as-cast rod consists of fully amorphous phase within the detection limit of XRD. Fig. 2 presents the DSC curve of the $Dy_{46}Y_{10}Al_{24}Co_{20}$ BMG, which exhibits an obvious endothermic characteristic of the glass transition followed by two crystallization peaks. The inset is a DTA trace showing the melting process of this alloy. The single endothermal signal of the melting indicates that the multi-component alloy is in a eutectic composition point. The T_g, T_x, melting temperature T_m, and liquidus temperature T_l, are determined to be 631, 675, 1004 and 1025 K, respectively. The supercooled liquid region $\Delta T = T_x - T_g$, is 44 K. The reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_m$) [12] and the γ-value ($\gamma = T_x/(T_g + T_l)$) [13], which are very important parameters in evaluating

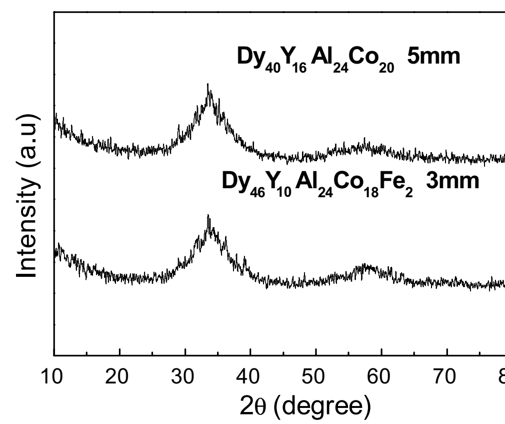

Fig. 1. XRD patterns of the as-cast $Dy_{46}Y_{10}Al_{24}Co_{20}$ and $Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$ alloys.

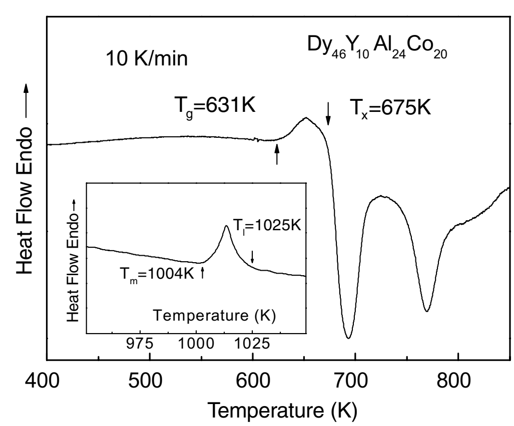

Fig. 2. DSC and DTA curves of the as-cast $Dy_{46}Y_{10}Al_{24}Co_{20}$ alloy showing the glass transition and crystallization as well as melting. The scanning rate is 10 K/min.

the GFA of an alloy, are 0.628 and 0.408, respectively. The distinctive glass transition and sharp crystallization events as well as large values of T_{rg} and γ further confirm the excellent GFA of the alloy. According to the formation criteria of the BMGs [2,14], the adequate atomic radius difference between Dy (0.177 nm), and Al (0.143 nm), and Co (0.125 nm), [15], the large negative heat of mixing between Dy and Co (−34 kJ/mol), [16] and the eutectic composition result in the excellent GFA of the alloys.

For a glassy alloy, the thermal stability is commonly related to its T_g, T_x and the activation energy of the glass transition E_g and crystallization E_x. Usually, the thermal stable glassy alloys have the higher T_g, T_x, E_g, and E_x. For comparison, thermal parameters of the Dy-based and other typical RE-based BMGs [2,5,6,9,17] are listed in Table 1. It is seen that Dy-based BMGs have the highest T_g, T_x, and T_m among the known RE-based BMGs. The thermal stability of the BMG is distinctly improved with Dy base element. Kinetic analysis of the crystallization and glass transition of the Dy-based BMGs were performed using Kissinger's method [18]. Fig. 3(a) shows the DSC curves obtained from the $Dy_{46}Y_{10}Al_{24}Co_{20}$ BMG at different heating rates. The Kissinger's plots of T_g and T_x are shown in Fig. 3(b). The values of the effective activation energy for the glass transition, E_g and crystallization E_x are then determined to be 4.81 and 2.64 eV, respectively. The larger values of E_g and E_x indicate that the atoms of Dy-based BMGs need larger additional energy for the transition from glassy state to crystallization state.

The elastic constants of the typical Dy-based and other RE-based BMGs available are also listed in Table 2. The E, G, and B of the as-cast $Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$ BMG are 64.2 GPa, 24.4 GPa, and 58.5 GPa, respectively, which are relatively larger than those for other RE-based BMGs. Fig. 4 shows the relation between T_g of the BMGs and B (or E) of the RE-based BMGs. Even these RE-based BMGs have different components, fractions and solute alloying bases; the T_g values of the BMGs increase with B. It is noted that other BMG systems such as Zr-, Fe- and Cu-based BMGs also as well as glassy polymers satisfy the correlation [2]. The high bulk modulus can lead to high thermal stability for the BMGs. Egami [7] suggested that the bulk modulus

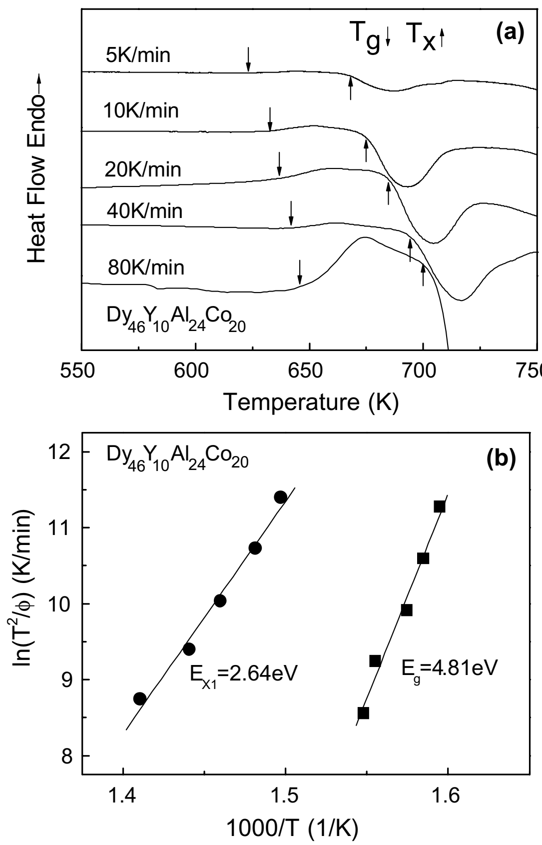

Fig. 3. (a) DSC traces of the as-cast $Dy_{46}Y_{10}Al_{24}Co_{20}$ BMG at the heating rates of 5, 10, 20, 40, and 80 K/min; (b) Kissinger plot of the glass transition temperature T_g and crystallization temperature T_x of the as-cast $Dy_{46}Y_{10}Al_{24}Co_{20}$ BMG.

attributed predominantly to the base element of a metallic glass has a correlation with its thermal parameters. The relation between the T_g and B of glasses was described in terms of the atomic level stresses. This concept originates from the realization that in glasses most of the interatomic distances are non-ideal, being either stretched or compressed, resulting in the pressure between atoms. As the local atomic pressure is closely correlated with the local bulk modulus, depending on the interatomic potential, it is deduced that the T_g was positively related to B of metallic glasses, which fits well for a large number of conventional metallic glasses [19]. The rule also fits for various RE-based BMGs even

Table 2
The elastic constants, thermodynamics parameters, for the as-cast $Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$ BMG and other typical RE-based BMGs

Glass	T_g (K)	T_x (K)	E (GPa)	G (GPa)	B (GPa)	σ
$Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$	627	677	64.2	24.4	58.5	0.317
$Gd_{36}Y_{20}Al_{24}Co_{20}$	603	658	62.2	23.6	57.4	0.319
$Nd_{60}Al_{10}Ni_{10}Cu_{20}$	438	478	–	–	–	–
$Pr_{60}Al_{10}Ni_{10}Cu_{20}$	417	469	37.17	13.64	45.16	0.363
$La_{66}Al_{14}Cu_{10}Ni_{10}$	405	431	35.72	13.44	34.91	0.33
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	359	377	30.3	11.5	27.0	0.313

The data of other RE-based BMGs were obtained from Refs. [3,5,6,8,17].

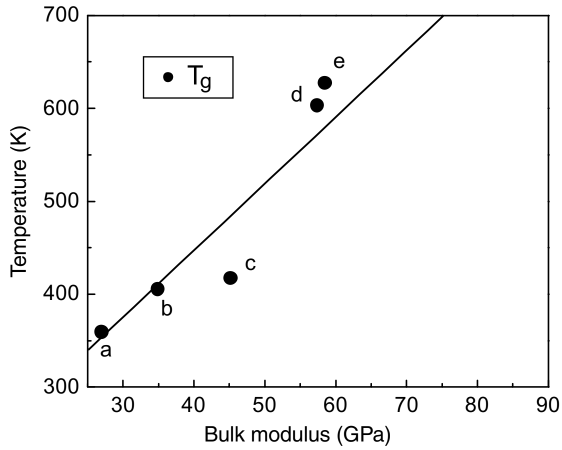

Fig. 4. The relationship between T_g and the bulk modulus of the base elements of the RE-based BMGs. a–e refer to $Ce_{70}Cu_{10}Ni_{10}Al_{10}$, $La_{66}Cu_{14}Ni_{10}Al_{10}$, $Pr_{60}Cu_{20}Ni_{10}Al_{10}$, $Gd_{36}Y_{20}Al_{24}Co_{20}$, and $Dy_{46}Y_{10}Al_{24}Co_{18}Fe_2$ BMGs, respectively.

though they have different components, fractions and solute alloying bases.

According to the relationship between the compressibility of solids and their moduli, the elastic constants of an alloy can be correlated with the individual elastic constants of its components as [6,8,9]: $M^{-1} = \sum f_i M_i^{-1}$, where M is any elastic constant and f_i is the atomic percentage of the component. From the correlation, one can see that the base element makes the predominant contribution to M of an alloy. Dy with a relatively higher bulk modulus (41 GPa) among RE metals, the higher T_g, T_x and large activation energies for the glass transition and crystallization result from the chemical interaction among the components. Thus, the high bulk modulus of the base component leads to high value of B of the BMG, and then can cause high thermal stability for the BMGs. The value of Poisson's ratio σ of the Dy-based BMGs is similar to that of other RE-based BMGs. σ is correlated with the atomic configuration in amorphous materials. The result reveals that the BMGs have highly dense random packed structure as for other BMGs [3].

4. Summary

In conclusion, the heavy RE-based Dy–Y–Al–Co BMGs with high GFA and thermal stability are obtained in fully bulk amorphous state by a conventional casting method. The high thermal stability is closely related to the high elastic constants of the base component of Dy in the BMG.

Acknowledgements

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