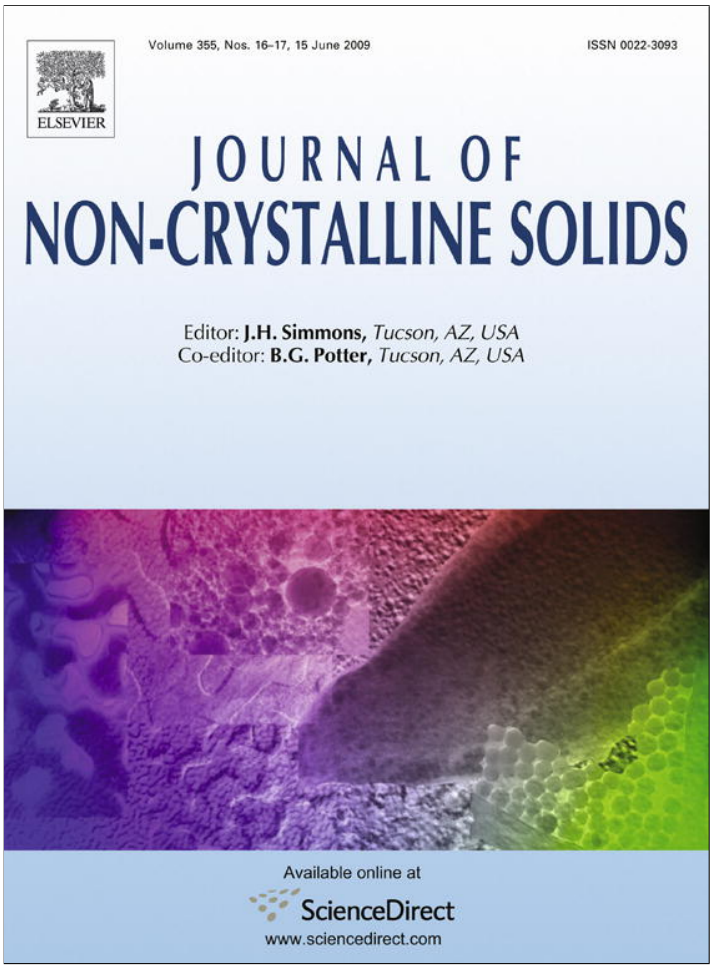

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Bulk metallic glasses based on binary rare earth elements

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ABSTRACT

Bulk metallic glasses (BMGs) are usually based on single element such as Zr, Cu, and Fe. In this work, we report the formation of a series of BMGs based on arbitrarily selected binary rare earth elements. Compared with single-base BMGs, the binary-base BMGs have unique characteristics of excellent glass-forming ability, tunable physical, chemical and mechanical properties. The binary-base BMGs might be of significance in scientific studies and have potential applications, and the approach for formation of metallic glasses has implications in the search for new BMG systems.

1. Introduction

Bulk metallic glasses (BMGs) have received considerable attention from both scientific and technological perspectives in the past decades due to their excellent glass-forming ability (GFA) and many superior physical and mechanical properties compared with their crystalline counterparts [1–7]. Recently, more and more multi-component BMGs such as Fe-, Mg-, Zr-, Pd-, Cu-, and Ln (Ln = La, Ce, Pr, Nd, Tb, Gd, Dy, Er, Ho, Tm)-based alloys have been fabricated [3–7]. It is noted that almost all these systems are based on a single element such as Zr, Cu, Ce and Fe. Actually, the general strategy for developing BMGs is to select one element as a base, and then, match the base element with other elements to obtain a good GFA. If a BMG based on two or more elements with different properties, and the composition of the base elements can be modulated in large composition range without deteriorating the GFA, some new attractive features and tunable properties could be expected for the BMG. The multi-base BMGs could also be a model system for investigating some long-standing issues in glass field. The approach also has implications for searching for novel BMGs and could increase the number of BMG compositions, and in turn pave a way for potential applications.

Previous works have shown some unique features in the formation of rare earth based BMGs: (1) nearly all the rare earth elements alloyed with other elements can be quenched into glass in bulky form with excellent GFA and large composition range. Even the alloys with similar compositions such as the series of $RE_{55}Al_{25}Co_{20}$ (RE = rare earth element in lanthanum family) can be made into fully glassy rods at millimeter scales [8]; (2) some BMGs are based on binary rare earth elements, for instance, a series of BMGs based on Ce and La elements, in which the composition of Ce and La can be gradually changed from 0 to 100 at.% without deteriorating the GFA, can be formed with tunable properties [9–11]. Other BMGs based on binary Sc and Y [12], Gd and Y [13], Gd and Dy [14], and even misch rare earth elements [15] have been reported. BMGs based on other binary CuZr or TiCu were also obtained [16–18]. However, it is not clear whether this strategy of the glass formation based on two or more elements is in general representative of most RE-based BMGs.

In this paper, we study the formation of BMGs by randomly choosing RE elements as the binary base to investigate their GFA. We find that it is general for the formation of BMGs based on arbitrarily chosen binary RE elements. Due to the similarity of the RE elements which are soluble in each other, the composition of binary RE elements can be gradually changed over a large composition range without deteriorating the GFA. These BMGs based on binary RE elements can be formed with tunable properties by modification of the composition of two base elements. We have discussed the reasons for the formation characteristics.

2. Experimental

All ingots of alloys with the composition of (RE1RE2)AlCo listed in Tables 1–3 were prepared by arc melting of high purity of rare earth elements with Co and Al in a Ti-gettered argon atmosphere.

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Table 1
The binary based BMGs with the composition $Tb_{36}RE_{20}Al_{24}Co_{20}$ and their thermodynamic parameters. The values of T_g, T_x, and T_l were determined from the thermal analysis traces with the accuracy of ±2 K.

Alloy system	T_g (K)	T_x (K)	ΔT (K)	T_l (K)	T_{rg}	γ	Maximum diameter
$Tb_{36}Ce_{20}Al_{24}Co_{20}$	549	614	55	930	0.590	0.415	2
$Tb_{36}Pr_{20}Al_{24}Co_{20}$	556	627	71	930	0.598	0.422	2
$Tb_{36}Nd_{20}Al_{24}Co_{20}$	567	636	69	960	0.591	0.417	2
$Tb_{36}Sm_{20}Al_{24}Co_{20}$	582	656	74	982	0.593	0.419	2
$Tb_{36}Gd_{20}Al_{24}Co_{20}$	594	653	59	1011	0.588	0.407	1
$Tb_{36}Dy_{20}Al_{24}Co_{20}$	608	662	54	1036	0.587	0.403	2
$Tb_{36}Ho_{20}Al_{24}Co_{20}$	617	672	55	1049	0.588	0.403	2
$Tb_{36}Er_{20}Al_{24}Co_{20}$	622	677	55	1050	0.592	0.405	2

Table 2
The binary based BMGs with the composition $(RE_xY_{1-x})_{56}Al_{24}Co_{20}$ and their thermodynamic parameters. The values of T_g, T_x, and T_l were determined from the thermal analysis traces with the accuracy of ±2 K.

Alloy system	T_g (K)	T_x (K)	ΔT (K)	T_l (K)	T_{rg}	γ	Maximum diameter
$Ce_{36}Y_{20}Al_{24}Co_{20}$	510	596	86	850	0.60	0.438	2
$Pr_{36}Y_{20}Al_{24}Co_{20}$	540	617	77	886	0.61	0.433	2
$Nd_{36}Y_{20}Al_{24}Co_{20}$	554	628	74	922	0.60	0.425	2
$Sm_{36}Y_{20}Al_{24}Co_{20}$	578	649	71	961	0.60	0.422	2
$Gd_{36}Y_{20}Al_{24}Co_{20}$	606	666	60	1048	0.60	0.403	2
$Tb_{36}Y_{20}Al_{24}Co_{20}$	619	686	67	1021	0.62	0.418	5
$Dy_{46}Y_{10}Al_{24}Co_{20}$	635	685	50	1025	0.63	0.413	5
$Ho_{35}Y_{21}Al_{24}Co_{20}$	644	696	52	1024	0.63	0.405	5
$Er_{36}Y_{20}Al_{24}Co_{20}$	661	719	58	1039	0.62	0.415	10
$Sc_{36}Y_{20}Al_{24}Co_{20}$	662	760	98	1048	0.63	0.444	3

The ingots were remelted and then suction cast into a copper mold to obtain cylindrical rods. The copper molds have internal cylindrical cavities with diameters of 1–5 mm. 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 NETZSCH differential scanning calorimeter DSC-404C under a continuous argon flow. The values of T_g, T_x, and T_l were determined from the thermal analysis traces with the accuracy of ±2 K.

3. Results and discussions

We choose Tb as one base element and matched this with a series of other RE elements to prepare the binary-base BMGs. Fig. 1 shows typical XRD patterns for the as-cast $Tb_{36}RE_{20}Al_{24}Co_{20}$ (RE = Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er) cylindrical rods with diameter of 2–3 mm. The broad diffraction peaks in the patterns without any clearly visible sharp diffraction peaks corresponding to crystalline phases indicate that the as-cast samples consist of fully amorphous phase within the detectable limit of the XRD (only the Tb–Gd alloy relatively poor glass-forming ability, and its XRD trace has minor sharp diffraction peak near second hallo pattern). Fig. 2 presents the DSC traces of the as-cast $Tb_{36}RE_{20}Al_{24}Co_{20}$ BMGs. It can be seen that an obvious endothermic characteristic of the glass transition followed by crystallization peaks is exhibited for all the BMGs. The distinctive glass transition and sharp crystallization event as well as large values of supercooled liquid region $\Delta T = T_x - T_g$, T_{rg} ($=T_g/T_l$) and γ confirm the good GFA of these BMGs. Table 1 lists their thermodynamic parameters.

We also selected Y as another base and combined it with other RE elements. As listed in Table 2, Y can cooperate with most RE elements in lanthanum family and form $(RE_xY_{1-x})_{56}Al_{24}Co_{20}$ (RE = Sc, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) BMGs with excellent GFA and different properties. All these alloys can be copper mold cast at least 2 mm in diameter. Some of them have a maximum diameter of 5 mm (RE = Tb, Dy, Ho) or even 10 mm (RE = Er). These BMGs have a gradual increase of T_g, elastic moduli, melting temperature, and similar ΔT, T_{rg} and γ.

To further confirm the strategy, the RE elements are arbitrarily chosen as the binary base and matched with other common BMG-forming elements such as Al, Cu, Co, Ni for searching binary-base BMGs. Fig. 3 shows XRD patterns of typical binary rare earth based BMGs. The cases for the binary RE-base BMGs in the form of $(RE1_x\,RE2_{1-x})$–TM–Al (TM stands for transition metal) are shown in Table 3. All these alloys with different composition and binary RE base can be cast into fully amorphous state in bulk cylinder form with diameter of several millimeters in size. The results further confirm that it is common for the bulk glass formation based on two or more RE elements.

The RE elements have similar atomic radii, and are soluble in each other. The formation of binary RE-base BMGs will not violate the empirical rules for metallic glass formation. The multiple rare earth base causes confusion in the system which is expected to cause an increase of melt viscosity in the supercooled liquid and increasing the barrier for the formation of stable nuclei in the melt, and in turn the growth of the kinetically favored crystalline phases are inhibited by the poor mobility of the constituents according to the confusion principle [24]. From the viewpoint of thermodynamics, the mixing among RE elements in BMGs is associated with

Table 3
The cases for the binary-base BMGs with the composition $RE1_xRE2_{1-x}$–TM–Al [10,12,14,19–23].

Element	Compositions
Y	$Y_{36}Sc_{20}Al_{24}Co_{20}$, $RE_{36}Y_{20}Al_{24}Co_{20}$ (RE = Ce, Pr, Nd, Sm, Gd, Tb, Er, Sc)
La	$La_{30}Ce_{30}Al_{20}Ni_5Cu_{15}$, $La_{40}Nd_{16}Al_{24}Co_{20}$
Ce	$Tb_{36}Ce_{20}Al_{24}Co_{20}$, $Ce_{34}La_{34}Al_{10}Cu_{20}Co_2$, $Ce_{30}Sm_{26}Al_{24}Co_{20}$
Pr	$Pr_{36}Y_{20}Al_{24}Co_{20}$, $Tb_{36}Pr_{20}Al_{24}Co_{20}$, $Pr_{36}La_{20}Al_{24}Co_{20}$, $Pr_{35}Gd_{21}Al_{24}Co_{20}$
Nd	$Nd_{36}Y_{20}Al_{24}Co_{20}$, $Gd_{36}Nd_{20}Al_{24}Co_{20}$, $Nd_{50}Dy_6Al_{24}Co_{20}$
Sm	$Sm_{36}Y_{20}Al_{24}Co_{20}$, $Sm_{40}Nd_{15}Al_{25}Co_{20}$, $Sm_{41}Pr_{15}Al_{24}Co_{20}$
Gd	$Gd_{36}Dy_{20}Al_{24}Co_{20}$, $Gd_{33}Er_{22}Al_{25}Co_{20}$, $Gd_{46}Ce_{10}Al_{24}Co_{20}$
Tb	$Tb_{36}RE_{20}Al_{24}Co_{20}$ (RE = Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er)
Dy	$Dy_{50}Gd_7Al_{23}Co_{20}$, $Dy_{46}Y_{10}Al_{24}Co_{20}$, $Dy_{30}Sm_{26}Al_{24}Co_{20}$
Ho	$Ho_{36}Dy_{20}Al_{24}Co_{20}$, $Ho_{35}Y_{21}Al_{24}Co_{20}$, $Ho_{28}Gd_{28}Al_{24}Co_{20}$
Er	$Er_{36}Ho_{20}Al_{24}Co_{20}$, $Er_{36}Tb_{20}Al_{24}Co_{20}$, $Er_{45}Dy_{11}Al_{24}Co_{20}$ $Er_{30}Gd_{26}Al_{24}Co_{20}$
Sc	$Sc_{36}Y_{20}Al_{24}Co_{20}$, $Sm_{40}Sc_{15}Al_{25}Co_{20}$

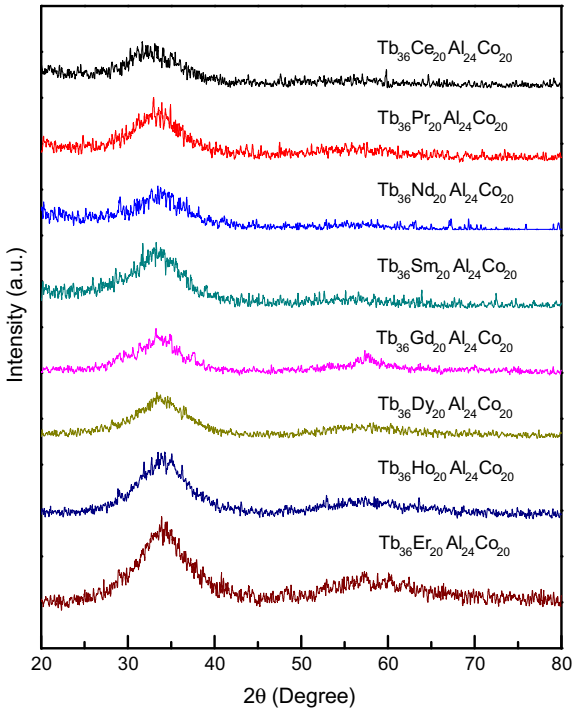

Fig. 1. XRD patterns of the as-cast $Tb_{36}RE_{20}Al_{24}Co_{20}$ (RE = Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er) alloy rods.

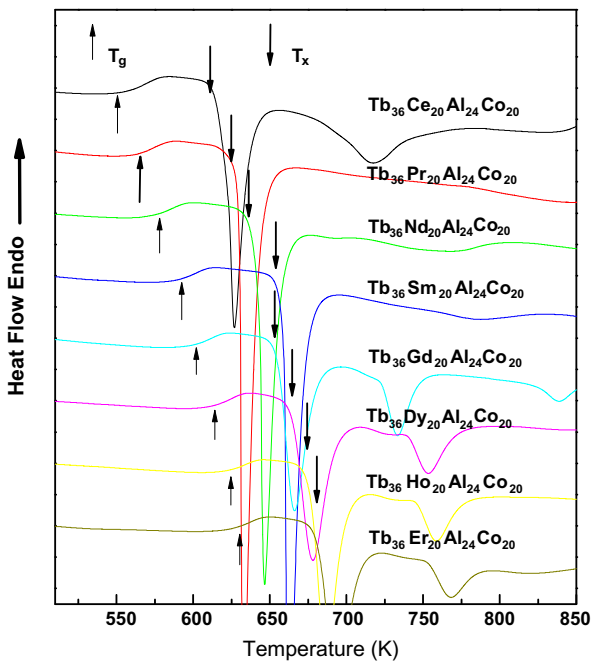

Fig. 2. DSC curves of the as-cast $Tb_{36}RE_{20}Al_{24}Co_{20}$ (RE = Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er) alloy rods.

larger entropy of fusion and consequently, smaller values of Gibbs free-energy difference between supercooled liquid and crystalline solid, which favor high GFA [3]. BMGs usually based on single element such as Zr, Cu, and Fe. Our approach could be extended to other BMG-forming alloy systems for exploring more BMGs.

Rare earth elements in lanthanum family have well-regulated changing atomic size, density and elastic constants. The BMGs based on different RE elements then have gradually changing properties and features such as the changing glass transition temperature, GFA, mechanical properties, elastic constant and fragility with different RE bases. For instance, the T_g of RE-based BMGs ranges from as low as 333 K for Ce-based BMGs [7]), to as high as 704 K for Tm-based BMGs [4]. The Young's modulus of these alloys ranges from 29.9 GPa for Ce-based BMGs to 79.4 GPa for Tm-based BMGs [25]. The binary RE-base BMGs can modulate these properties and features by gradually changing the composition of the binary RE base. These BMGs could also be model system to study some issues in BMG-forming alloys [25].

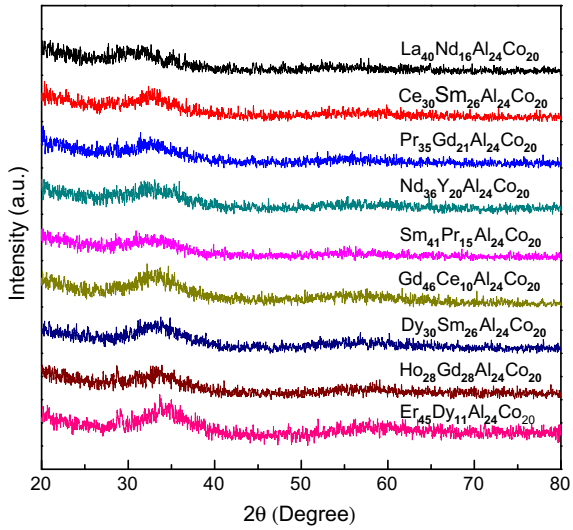

Fig. 3. XRD patterns of the as-cast binary rare earth base BMGs.

The RE-based BMGs present unique physical properties, such as superplasticity and polymer-like thermoplastic formability near room temperature [7] and heavy fermion behavior [26] in Ce-based BMGs, hard magnetic properties in Nd- and Pr-based BMGs [27], multiple spin glass behavior in Pr-based BMGs [28], and magnetocaloric effect in Gd-, Ho-, Dy-, and Er-based BMGs [21,22,29]. The binary or multiple RE-based BMGs could combine these unique physical properties by combining base RE elements. For example, heavy RE-based BMGs with the composition $(RE1_x RE2_{1-x})_{56}Al_{24}Co_{20}$ usually have large magnetocaloric effect at different temperatures. By modulating the RE elements and composition of the heavy RE base, a series of alloys with large magnetic entropy covering wider temperature range can be obtained in desirable working temperature scope between 2 and 150 K.

4. Conclusions

Various BMGs with binary RE base could be developed, and their formation is attributed to the similarity of the RE elements. By adjusting the composition of the base elements, more binary or multiple based rare earth BMGs could be obtained. The approach has implications in the search for new BMG system.

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