Thulium-based bulk metallic glass

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We report the formation and properties of a thulium-based bulk metallic glass (BMG). Compared with other known rare-earth (RE) based BMGs, Tm-based BMGs show features of excellent glass formation ability, considerable higher elastic modulus, smaller Poisson's ratio, high mechanical strength, and intrinsic brittleness. The reasons for the different properties between the Tm-based and other RE-based BMGs are discussed. It is expected that the Tm-based glasses with the unique properties are appropriate candidates for studying some important issues in BMGs. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2908047]

Bulk metallic glasses (BMGs) have attracted attention because of their scientific significance and potential applications as engineering and/or functional materials.[1] Among them, Zr-, Ti-, Fe-, and Cu-based BMGs[1–5] are rendered as promising engineering materials as they show excellent mechanical properties. Rare-earth (RE) based BMGs are notable for their various interesting physical properties and potential functional applications.[6–12] For instance, the polymerlike Ce-based BMGs have good manufacture ability in macro-, micro- and nanometer scales,[9] and they also show heavy-fermion behavior[13] and abnormal pressure and temperature dependence of elastic and mechanical properties.[14] In a LaCe-based BMG, a second-order amorphous-to-amorphous phase transition is reported.[15] The Gd-, Ho-, Er-, and Dy-based BMGs have been found to have high refrigerant efficiency, which makes them attractive candidates for magnetic refrigerants in a wide temperature range.[16] However, up until now, no work has been reported on the glassy formation of Tm-based alloys in the RE family. The RE elements has profuse magnetic structures, chemical comparability, and a "continuous" range of elastic constants, melting temperature, and glass transition temperature A novel RE-based BMG could have unique different properties because different RE elements have different magnetic and electrical structures, and, in turn, permit more possibilities for the applications of the glasses. With the development of more RE-based BMGs, one can use these BMG systems to verify the known correlations between elastic constants and properties of BMGs.[6]

In this letter, the formation of RE thulium-based BMGs showing excellent glass-forming ability (GFA), high thermal stability, and wide glass-forming composition range, and their high strength, high elastic moduli, and considerable low Poisson's ratio, are reported. The glass transition temperature T_g, Vogel–Fulcher temperature T_0, and fragility parameter m, which are often used to characterize vitrification and properties of a supercooled liquid or a glass, are determined for the Tm-based BMG. The ideal brittle behavior approaching oxide glasses of the BMG makes it a model system to study the intrinsic fracture behaviors of glasses. The reasons for the different properties between the Tm-based and other RE-based BMGs are discussed. The results also further confirm the elastic moduli correlations among BMGs.

The Tm–Al–Co–Y alloys with nominal compositions listed in Table I were prepared by arc melting pure Al(99.99%), Co(99.99%), and Y(99.99%) with Tm (99.9%) in a Ti-gettered argon atmosphere. The amorphous nature was ascertained by x-ray diffraction (XRD) using a MAC Mo3 XHF diffractometer with Cu $K\alpha$ radiation. Thermal analysis was carried out in a PerkinElmer DSC-7 differential scanning calorimeter (DSC) and DTA-7 differential thermal analyzer (DTA). Acoustic velocities were measured in a pulse echo overlap method by a MATEC 6600 model ultrasonic system with a measurement sensitivity of 0.5 ns and a carrying frequency of 10 MHz. The density was measured using the Archimedean technique and the accuracy is within 0.1%. Young's modulus E, shear modulus G, bulk modulus K, Debye temperature θ_D, and Poisson's ratio ν were derived from the acoustic velocities.[17,18] A uniaxial compression was performed on a small-angle neutron scattering type universal tester with an initial strain rate of 5×10^{-4} s^{-1}. The fractography was observed using a Philips XL 30 scanning electron microscope (SEM).

Figure 1 shows XRD patterns of the as-cast $Tm_{55}Al_{25}Co_{20}$ and $Tm_{39}Al_{25}Co_{20}Y_{16}$ BMGs with diameters of 3 and 5 mm, respectively. The board diffraction peaks and no appreciable peaks corresponding to the crystalline phases can be seen within the resolution limit of the XRD for the samples, which indicate the full amorphous state of the alloys. The inset in Fig. 1(a) shows DSC curve of $Tm_{39}Al_{25}Co_{20}Y_{16}$ BMG, which exhibits an obvious endothermic characteristic of the glass transition followed by two sharp exothermic crystallization peaks. The melting process obtained via a DTA shows a single endothermal peak presented in Fig. 1(b), which indicates that the multicomponent alloy is close to the eutectic composition point. The T_g, crystallization temperature T_x, and liquidus temperature T_l, for $Tm_{39}Al_{25}Co_{20}Y_{16}$ were determined to be 664, 735, 1056, and 1090 K, respectively. The supercooled liquid region $\Delta T=T_x-T_g$, is 71 K, which is the largest one among the known RE-based systems. Meanwhile, the typical BMG also exhibits the highest T_g and T_x in all known RE-based BMGs.[6–8,19] The reduced glass transition temperature T_{rg} ($T_{rg}=T_g/T_l$) and the γ value [$\gamma=T_x/(T_g+T_l)$], which are effective parameters in evaluating the GFA of an alloy, are 0.609 and 0.419, respectively. The Tm-based alloy has a relatively wide glass-forming composition range as listed in Table I. The contents of Tm (at %) in the Tm–Y–Al–Co system can be varied from about 25% to 55% without obviously deteriorating the GFA.

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TABLE I. Thermodynamic parameter, fragility parameter, and elastic parameters of the Tm-based BMGs, and some typical RE-based BMGs.

Alloy systems	T_g (K)	T_x (K)	T_l (K)	m	ρ (g/cm^3)	E (GPa)	G (GPa)	K (GPa)	ν	θ_D (K)
$Tm_{39}Y_{16}Al_{25}Co_{20}$	664	735	1090	39	7.301	77.5	29.7	66.1	0.304	238
$Tm_{55}Al_{25}Co_{20}$	678	733	1180	36	8.274	72.2	27.6	62.0	0.306	216
$Tm_{45}Y_{10}Al_{25}Co_{20}$	672	734	1094	32	7.662	71.5	27.3	62.3	0.309	223
$Tm_{27.5}Y_{27.5}Al_{25}Co_{20}$	664	730	1078	30	6.476	68.0	25.8	61.9	0.317	234
$Tm_{40}Zr_{15}Al_{25}Co_{20}$	704	763	1126	35	7.695	73.8	28.0	68.1	0.319	228
$Tm_{40}Y_{15}Al_{25}Co_{10}Ni_{10}$	668	722	1079	34	8.032	79.4	30.4	68.7	0.307	236
$Al_{28}Tm_{25}Y_{25}Co_{22}$	675	730	1077	34	6.423	⋯	⋯	⋯	⋯	⋯
$Er_{50}Al_{24}Co_{20}Y_6$[a]	651	702	1079	⋯	⋯	71.1	27.0	65.1	0.318	218
$Ho_{39}Al_{25}Co_{20}Y_{16}$[a]	649	706	1171	49	⋯	69.1	26.2	63.6	0.319	⋯
$Ho_{55}Al_{25}Co_{20}$[a]	649	707	1055	25	7.888	66.6	25.4	58.8	0.311	210
$Dy_{46}Al_{24}Co_{18}Fe_2Y_{10}$[a]	627	677	1023	⋯	⋯	64.2	24.4	58.5	0.317	⋯
$Tb_{36}Y_{20}Al_{24}Co_{20}$[a]	619	686	1021	⋯	⋯	63.6	24.0	60.5	0.325	222
$Gd_{36}Y_{20}Al_{24}Co_{20}$[b]	603	658	1048	⋯	⋯	62.2	23.6	57.4	0.319	⋯
$Sm_{40}Y_{15}Al_{25}Co_{20}$[b]	590	657	950	⋯	⋯	57.1	21.5	54.7	0.326	213
$Nd_{60}Fe_{20}Co_{10}Al_{10}$[a]	485	615	815	⋯	⋯	54.1	20.7	54.1	0.317	⋯
$Pr_{60}Al_{10}Ni_{10}Cu_{20}$[a]	409	452	810	⋯	6.875	36.9	13.5	45.2	0.300	160
$La_{66}Al_{14}Cu_{10}Ni_{10}$[a]	395	449	731	⋯	⋯	35.7	13.4	34.9	0.330	⋯
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$[a]	359	377	639	⋯	6.670	30.3	11.5	27	0.313	144

[a]Reference 23.
[b]Reference 6.

The fragility parameter m of $Tm_{39}Al_{25}Co_{20}Y_{16}$ BMG determined from kinetic nature of the glass transition is 39. The value can be classified to the intermediate strong liquids in the framework of fragility according to Angell's classification.[19–22] The Vogel–Fulcher temperature T_0 is 634 K. The crystallization activation energy is determined to be 2.91 eV. The density ρ, E, G, K, ν, and θ_D from the ultrasonic measurement for the BMGs are listed in Table I. Compared with other RE-based BMGs, the Tm-based BMGs have considerably large elastic moduli, especially E and G. The typical BMG $Tm_{39}Al_{25}Co_{20}Y_{16}$ has a considerably low Poisson's value of 0.304.[6–12,23] It is generally accepted that ν correlates with mechanical behavior; that is, small ν will yield brittleness and vice versa.[6,24,25] The compression test of $Tm_{39}Al_{25}Co_{20}Y_{16}$, presented in Fig. 2(a) shows no trail of plastic deformation since it breaks down when the stress reaches its strength limit of 1.96 GPa (about $E/38$). This is the highest fracture strength in the known RE-based BMGs [see Fig. 2(b)], which is even higher than that of high strength Zr-based BMGs.[1,2] For example, the fracture strength of La- and Ce-based BMGs is around 0.5 GPa, and most RE-based BMGs have fracture strength of less than 1 GPa.[6] Instead of shearing fracture in approximately 45° angle, which is the case in most BMGs, it shatters into many pieces, which rather resembles that of oxide glasses. Shear bands were hardly observed in the fracture Tm-based BMGs. Periodic strip patterns with a periodicity of 32 nm (shown in the inset of Fig. 2) can be clearly seen on the fracture surface of the BMG. The results indicate that the local softening mechanism in the fracture is an essential ingredient for con-

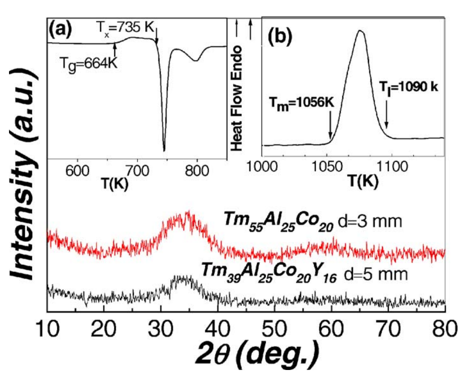

FIG. 1. (Color online) XRD patterns of the as-cast $Tm_{55}Al_{25}Co_{20}$ and $Tm_{39}Al_{25}Co_{20}Y_{16}$ alloy. DSC (inset a) and DTA (inset b) curves of the as-cast $Tm_{39}Al_{25}Co_{20}Y_{16}$ alloy. The scanning rate is 40 K/min for DSC and 10 K/min for DTA.

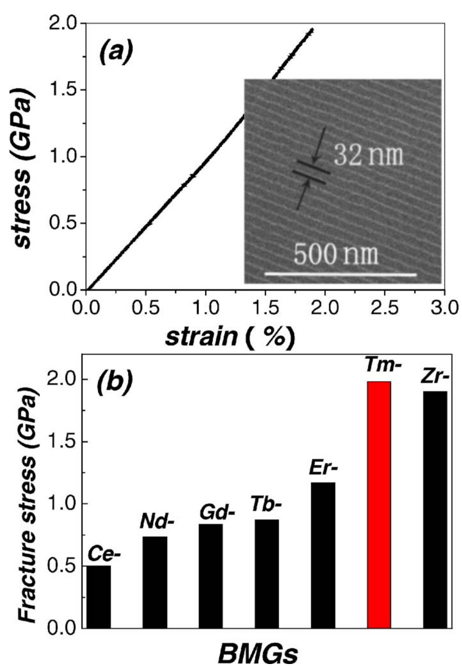

FIG. 2. (Color online) (a) Engineering stress-strain curves of the as-cast $Tm_{39}Al_{25}Co_{20}Y_{16}$ BMG (with a strain rate of 5×10^{-4} s^{-1} room temperature). The inset is the SEM fractography of the fracture surface of the as-cast $Tm_{39}Al_{25}Co_{20}Y_{16}$ BMG. (b) The comparison of the fracture strength between Tm-based BMG and other RE-based BMGs (Ref. 6) which shows that the Tm-based BMGs have much higher strength.

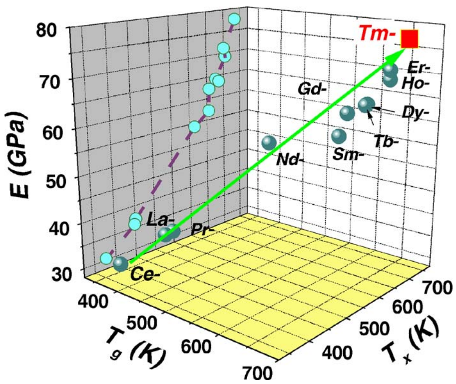

FIG. 3. (Color online) The dependence of E on T_g and T_x for typical RE-based BMGs.

trolling the fracture of the intrinsic brittle BMGs.[26] Although the RE elements in the lanthanum family have the same position in the periodic table, each RE has markedly different magnetic and electrical structures due to their different number and distribution of the $4f$ electrons. The profuse magnetic and electrical structures make these RE elements as well as the RE-based BMG possess different properties. We believe that the marked difference in properties between the Tm-based BMGs and others results result from the strong chemical interaction among the components in the Tm-based BMGs. The relatively larger negative enthalpy of mixing between Tm and other components of Al and Co and the larger elastic moduli of Tm compared to that of other RE elements are indicators of the strong chemical interaction among the components in the BMGs.[27] The stronger chemical interaction indicates the robust resistance to local structure change under deformation and high moduli and strength of the BMGs.

Many properties of metallic glasses are remarkably correlated with each other. A notable one is the elastic modulus of BMG, since it correlates with T_g, T_l, mechanical properties, and liquid fragility.[6] Recently, a cooperative shear model based on potential energy landscape state theory may shed some light on these correlations. It is argued that for a fixed glass configuration, the barrier height for shear flow is proportional to the isoconfigurational shear modulus G.[28] The RE elements have the same location in the Periodic Table of elements and have similar characteristics. Thus, they are a potential model system for studying and verifying these correlations. Figure 3 shows the comparison of E, T_g, and T_x of the BMGs based on the RE in lanthanide family (except for the main component, the other compositions are slightly different.[6,29]). It can be clearly seen that the Tm-based BMG have the largest elastic moduli, T_x and T_g among the RE-based BMGs and fit well to the correlations between T_g and the elastic moduli for BMGs. The result confirms that the BMG formation and properties could be tailorable by selecting of proper main component with suitable elastic constants.[6] A correlation between T_g and θ_D^2 in various BMGs has been reported;[6] that is, $T_g \propto \bar{M}\theta_D^2$, where $\bar{M}$ is the average atom weight. The correlation suggests that the glass transition of the BMG-forming alloys has the characteristic of melting.[6] For the Tm-based BMGs, their values of $\bar{M}\theta_D^2/10^4$ are in the range of 510–590 and fit the correlation well. The results further confirm that melting and glass transition in BMG-forming alloys share common characteristics.

In summary, we develop the Tm-based BMGs with excellent GFA, high thermal stability, large elastic modulus, low Poisson ratio, high strength, and intrinsic brittle properties. The elastic moduli and thermal properties of the Tm-based BMGs fit the known correlations. The found glass extends the family of the RE-based BMGs and provides model system to understand the glass transition and facture mechanism of the BMGs.

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