RAPID COMMUNICATIONS

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Bulk scandium-based metallic glasses

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The novel rare-earth scandium-based bulk metallic glasses (BMGs) are obtained by the copper mold casting method. Compared with other rare-earth BMGs reported so far, the Sc-based BMGs exhibit the highest elastic moduli (e.g., Young's modulus, E = 85 GPa; bulk modulus, B = 77.5 GPa), glass transition temperature (T_g = 662 K), and crystallization temperature (T_x = 760 K) combined with a large region of supercooled liquid (ΔT = 98 K). A good correlation between glass transition temperature and elastic moduli is found in a variety of rare-earth-based BMGs.

Intensive interest has been focused on investigating the metallic rare-earth (RE)-based bulk metallic glasses (BMGs) because of their technological and fundamental significance.[1–7] Recently, we reported that the Pr(Nd)–(Ni,Cu)–Al[3] and Ce–Al–(Ni,Cu)–(Nb,Co,Fe)[6] BMGs with high glass-forming ability (GFA) and ultralow glass-transition temperature (T_g) close to room temperature can be readily cast in bulk forms by the copper mold casting method (the GFA is usually defined as the critical cooling rate needed for the glass formation during solidification[1]). The GFA of these alloys is high enough to produce BMGs with critical thicknesses on the order of centimeters.[3–7] However, structural relaxation occurs in these low T_g glassy alloys even at ambient temperature and pressure, which would limit some applications. Previous studies have shown that there is a tendency for T_g to increase with increasing bulk modulus of the base element in the alloy.[8,9] To produce RE-based metallic glasses with higher glass transition temperature and crystallization temperature, in other words, to improve thermal stability, we tried to produce scandium-based BMGs. In the rare-earth family, Sc has a higher bulk modulus (B = 57 GPa)[10] and melting temperature (T_m = 1814 K),[10] the lowest density (2.702 g/cm^3),[10] the smallest atomic size (0.162 nm),[10] and a relatively low chemical activity. If the glassy structure can be formed, the Sc-based BMGs could have high T_g and unique elastic and mechanical properties. Furthermore, Sc–TM (TM = Fe, Co, Ni) glassy films were found to have excellent magnetic transportation cooling effects, which is the change in temperature of a material as a result of the alignment of its magnetic spins that occurs on exposure to an external magnetic field, and the effect forms the basis for magnetic refrigeration.[11,12] Therefore, the Sc-based BMGs might be attractive for scientific studies and application as functional materials.

The formation of Sc–Co and Sc–Fe binary metallic glassy ribbons with poor GFA was reported in 1990s.[11–13] Based on the results, in this work, we applied the addition method to improve the GFA of the alloys (yttrium and some transition metals have been found to be very effective for improving the GFA of the BMG-forming alloys).[14,15] With the addition of Al and Y elements, we find that the GFA of the Sc–Co alloy can be greatly improved and fabricated in bulk form. The GFA, thermal stability, and elastic properties of the novel BMGs are investigated and compared with that of various other BMGs.

The ScAlCoY alloys with the nominal compositions listed in Table I were prepared by arc melting of high-purity Sc, Y, Al, and Co metals 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 K_α radiation (MAC Inc., Japan). The microstructure of the as-cast sample was examined by transmission electron microscopy using a TECNAI-F20 (TECNAI Inc., Japan) instrument operated at an accelerating voltage of 200 kV. Thermal properties were investigated in a PerkinElmer differential scanning calorimeter (DSC)

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TABLE I. Thermodynamic parameters of the Sc-based BMGs and other BMGs. Heating rate: 20 K/min.

BMG	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT (K)	T_{rg} (K)	γ	Ref.
$Sc_{36}Al_{24}Co_{20}Y_{20}$	662	760	970	1048	98	0.63	0.444	This work
$Sc_{40}Al_{20}Co_{20}Y_{20}$	657	725	⋯	⋯	68	⋯	⋯	This work
$Sc_{46}Al_{14}Co_{20}Y_{20}$	633	684	⋯	⋯	51	⋯	⋯	This work
*$Ce_{60}Cu_{20}Ni_{10}Al_{10}$	374	441	645	672	67	0.57	0.422	23
$Gd_{40}Al_{24}Co_{20}Y_{16}$	598	653	972	995	55	0.60	0.410	4
$Dy_{40}Al_{24}Co_{20}Y_{16}$	633	682	1011	1031	49	0.61	0.409	4
*$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	409	452	705	806	43	0.51	0.372	4,21
$Nd_{60}Cu_{s0}Ni_{10}Al_{10}$	438	478	728	755	40	0.58	0.401	21,22
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	623	672	932	996	49	0.625	0.415	21,25
$Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$	656	735	1108	1168	79	0.56	0.408	21
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	575	670	804	840	95	0.68	0.473	21

*DSC heating rate: 10 K/min.

DSC-7 (PerkinElmer Inc.,) and differential thermal analyzer (DTA) DTA-7 (PerkinElmer Inc.,) under a continuous argon flow. The values of T_g, crystallization temperature, T_x, and the liquidus temperature, T_l were determined from the thermal analysis traces with accuracy of ±1 K. The acoustic velocities at room temperature measured 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 (MATEC Inc.,).[16] The elastic constants (e.g., bulk modulus B, Young's modulus E, shear modulus G, Poisson's ratio ν, and Debye temperature θ_D were derived from the ultrasonic velocities and density.[17]

Figure 1 shows the XRD patterns of the as-cast $Sc_{60-x}Co_{20}Y_{20}Al_x$ (x = 14, 20, and 24) alloys with diameters of 1.0, 3.0, and 3.0 mm, respectively. All the alloys exhibit broad diffraction maxima characteristic of glass without obvious crystalline Bragg peaks within the detectable limitation of the XRD. The XRD results demonstrate the amorphous structure in bulk and high GFA of these alloys. The glassy structure has been confirmed by transmission electron microscope (Fig. 1, inset). The obvious crystalline diffraction peaks due to the precipitation of crystalline phases are observed for $Sc_{46}Y_{20}Co_{20}Al_{14}$ alloy cast in 3 mm (not shown), indicating a lower GFA for than $Sc_{46}Y_{20}Co_{20}Al_{14}$ than that of other two glass-forming alloys.

Figure 2 shows the DSC traces of the ScAlCoY BMGs with a heating rate of 20 K/min. All the DSC traces exhibit an obvious endothermic characteristic of the glass transition followed by several sharp crystallization peaks. Figure 3 is the DTA trace for typical $Sc_{36}Al_{24}Co_{20}Y_{20}$ BMG showing the melting process of this alloy with a heating rate of 10 K/min. The endothermal signal of the melting indicates that the multicomponent alloy is near eutectic composition point. T_g, T_x, melting temperature T_m, and T_l of $Sc_{36}Al_{24}Co_{20}Y_{20}$ BMG are determined to

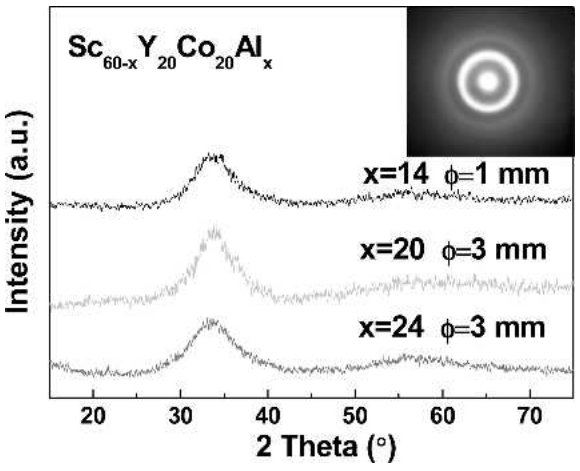

FIG. 1. XRD patterns of the as-cast rods 3 mm in diameter of the $Sc_{36}Al_{24}Co_{20}Y_{20}$, $Sc_{40}Al_{20}Co_{20}Y_{20}$, and $Sc_{46}Al_{14}Co_{20}Y_{20}$ glassy alloys. (Inset) Select area diffraction pattern of the $Sc_{36}Co_{20}Y_{20}Al_{24}$ BMG.

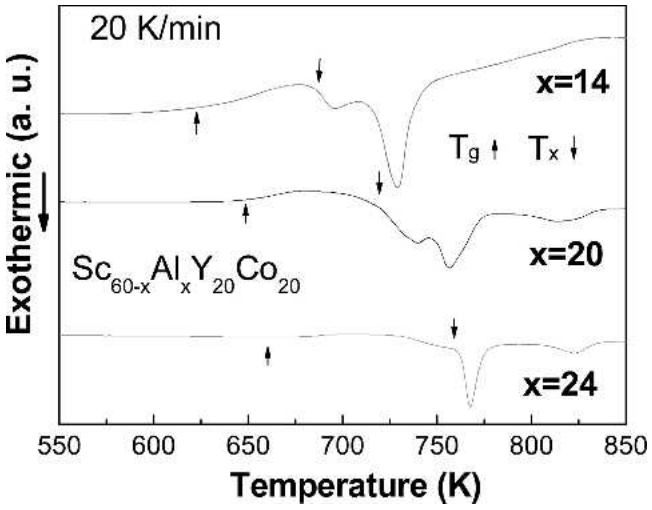

FIG. 2. DSC traces of the as-cast $Sc_{60-x}Al_xCo_{20}Y_{20}$ (x = 14, 20, and 24) alloys showing the distinct glass transition and sharp crystallization events.

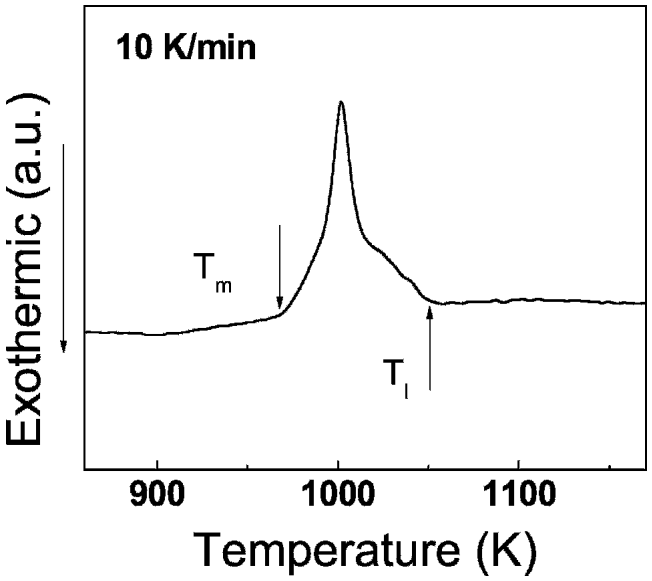

FIG. 3. DTA traces showing the melting behavior of the $Sc_{36}Al_{24}Co_{20}Y_{20}$ BMG.

be 662, 760, 970, and 1048 K, respectively. T_g, T_x, and the crystallization behavior are quite sensitive to the changes of Sc and Al contents, as shown in Fig. 2.

Compared with other rare-earth BMGs reported so far, the Sc-based BMGs exhibit the highest glass transition and crystallization temperatures. The supercooled liquid region $\Delta T = T_x - T_g$, is about 98 K. The reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_l$),[18] and the γ value ($\gamma = T_x/(T_g + T_l)$),[19] which are important parameters in evaluating the GFA of an alloy, are 0.63 and 0.444, respectively. The critical cooling rate for the $Sc_{36}Al_{24}Co_{20}Y_{20}$ alloy is estimated to be about 100 K/s.[20] The distinctive glass transition and the large values of ΔT, T_{rg}, and γ further confirm the excellent GFA of the alloy. The thermal parameters of the alloys and other BMGs are listed in Table I for comparison.

In general, the high liquid stability (near eutectic composition), the large supercooled liquid stability, and the large negative heat of mixing between Sc and Co(Al) (−32 kJ/mol) are responsible for the good GFA of the alloys.[1] Another important factor that influences the GFA is the complexity of the four-component alloy system. The atomic radius of Sc is 0.162 nm, that for Al is 0.143 nm, and that for Co is 0.125 nm, while that for yttrium is 0.182 nm. These differing sizes are expected to limit the solubilities of these elements in competing crystalline phases. The atomic-size differences in the multicomponent alloys also lead to efficient packing of atoms which lowers the ground-state energy difference between the amorphous and crystalline phases, and thereby suppressing nucleation in solidification.[1]

TABLE II. The elastic constants calculated from the acoustic data, and T_g for the Sc-BMG and other BMGs we developed recently. DSC heating is 10 K/min.

BMG	T_g (K)	E (GPa)	G (GPa)	B (GPa)	Ref.
*$Sc_{36}Al_{24}Co_{20}Y_{20}$	662	85.2	32.3	77.5	This work
$Dy_{46}Al_{24}Co_{18}Fe_2Y_{10}$	627	64.2	24.4	58.5	3
$Gd_{36}Al_{24}Co_{20}Y_{20}$	603	62.2	23.6	57.4	3
$Nd_{60}Fe_{20}Co_{10}Al_{10}$	485	54.1	20.7	54.1	20,21
$Pr_{60}Al_{10}Ni_{10}Cu_{20}$	417	37.2	13.6	45.2	3,20
$La_{66}Al_{14}Cu_{10}Ni_{10}$	405	35.7	13.4	34.9	3,20
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	359	30.3	11.5	27.0	22

*DSC heating rate: 20 K/min.

E, G, B, and θ_D of the as-cast $Sc_{36}Al_{24}Co_{20}Y_{20}$ BMG determined from acoustic measurement are 85.2 GPa, 32.3 GPa, and 77.5 GPa, and 337.1 K, respectively, which are distinctively larger than those of other RE-based BMGs (Table II). The density of the Sc-based BMG is 4.214 g/cm^3, and the specific modulus is $E/\rho = 85/4.2 = 20.2$ GPa·cm^3/g. For comparison, the specific modulus of the typical Zr-based $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG[21] is $E/\rho = 101/6.1 = 16.4$ GPa·cm^3/g. Therefore, the Sc-based BMGs can be considered as one of the highest specific modulus materials. The Poisson's ratio, ν, which more directly reflects the bonding forces of a material[17] than any other elastic constants, is 0.317. The result reveals that the BMG is still in metallic bonding.[21] It is known that ν of an isotropic solid for which the Cauchy relation $c_{12} = c_{44}$ holds is 0.25, independent of a specific material. The BMG as well as other BMGs, however, violates the requirement of the Cauchy relations. This is due to that the atoms in a metallic glass do not lie at centers of symmetry or only rarely so. The deviations from 0.25, thus provide a measure for the internal displacements or configurational entropy of the bulk glass-forming alloys. Previous studies have shown that the elastic constants (M) of a glass-forming alloy are correlated with the individual elastic constants (M_i) of the components of the alloy as[22,23]

$$M^{-1} = \sum f_i M_i^{-1} \quad , \tag{1}$$

where f_i is the atomic percentage of each component, respectively. From the correlation, one can see that the base element has the predominant contribution to M of a BMG. Sc metal has the higher elastic moduli (such as $E = 74$ GPa)[10] in the rare-earth family, which naturally explains why the Sc-based BMGs have such high elastic moduli. Furthermore, both elastic moduli and melting point represent the measure of the bonding forces. The larger the bonding force, the higher the melting point, and therefore the higher the elastic moduli. The Sc-based BMGs with high elastic moduli have the higher T_g and T_m, even higher than those of the most Zr-based BMGs. Based on a local topological instability model, the correlation between T_g and B was predicted[9]

$$T_g = 6.14 \times 10^{-3} \frac{\langle \Omega \rangle \langle B \rangle}{k_B} \quad ,$$

where $\langle \Omega \rangle$ is the average local volume and k_B is Boltzmann constant. Figure 4 shows the relation between T_g and B, E, and G moduli of the various rare earth BMGs we developed recently. It demonstrates that T_g does smoothly increase with increasing elastic moduli of these RE-based BMGs. Similar observations have also been found between T_g and elastic moduli in other metallic glasses and even in glassy polymers. In addition, unlike conventional polycrystalline materials, amorphous materials usually exhibit the same elastic-perfectly plastic yield behavior that has been observed in the $Pd_{78}Cu_6Si_{16}$[24] and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMGs,[25] they have anomalous large elastic strain (~2–3%) below T_g. The elastic characteristic is also found in these new BMGs. The comparison of the present results with that high elasticity reported for other BMGs[21] confirms that the elastic response reflects the common property of the glassy alloys.

Therefore, consideration of the elastic moduli can assist in selecting alloying components for controlling the elastic moduli and thermal stability which are the key concerns for the resulting metallic glasses. At present, the development of new BMGs has always been "hit or miss" whether the resulting glass would turn out to be excellent in properties.[1,21,25] The clear correlation may provide useful guidelines for the development of new BMGs with controllable properties by selection of elements with suitable elastic moduli as constituents.

In summary, the new Sc-based ScAlCoY BMGs with high elastic modulus and high thermal stability are obtained. The glass transition temperature (T_g = 662 K) is higher than that of other rare earth based BMGs, even higher than that of the Zr- and Pd-based BMGs. The relative high GFA and high T_g in the RE-based BMGs open up wide temperature and time window for study the glass transition and the nature of supercooled liquid. It is also found that these BMGs have much higher elastic moduli (such as E = 85 GPa) compared with that of other known RE-based BMGs. Furthermore, a good correlation between the glass transition temperature and the elastic moduli are found in various glassy alloy systems. The finding is useful for the BMG-forming alloys design.

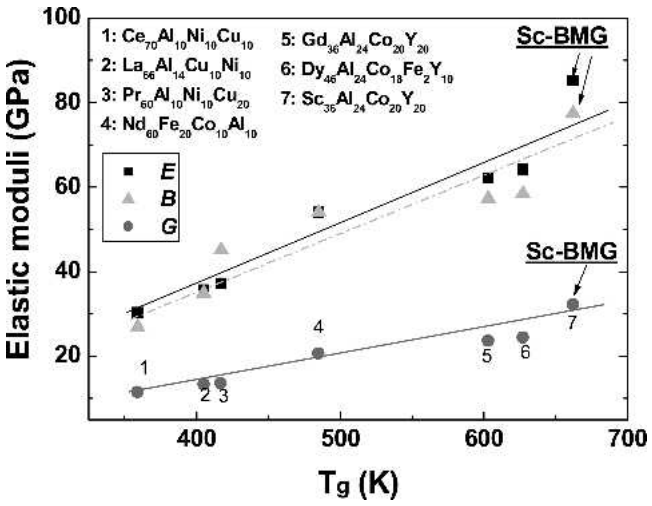

FIG. 4. Relationship between the T_g and the E (square marks), B (closed circles), and G (triangle symbols) of various RE-based BMGs: $Sc_{36}Al_{24}Co_{20}Y_{20}$ (this work), $Dy_{46}Al_{24}Co_{18}Fe_2Y_{10}$ (Refs. 3, and 4), $Gd_{36}Al_{24}Co_{20}Y_{20}$ (Refs. 3, and 4), $Nd_{60}Fe_{20}Co_{10}Al_{10}$ (Refs. 21 and 22), $Pr_{60}Al_{10}Ni_{10}Cu_{20}$ (Refs. 3, 4 and 21), $La_{66}Al_{14}Cu_{10}Ni_{10}$ (Refs. 3, 4 and 21), and $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ (Ref. 23). The Sc-based BMG shows the highest elastic moduli among the RE-based BMGs. The lines provide guidance for the eyes.

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