Amorphous Metallic Plastic

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We report cerium-based bulk metallic glasses with an exceptionally low glass transition temperature T_g, similar to or lower than that of many polymers. We demonstrate that, in near-boiling water, these materials can be repeatedly shaped, and can thus be regarded as metallic plastics. Their resistance to crystallization permits extended forming times above T_g and ensures an adequate lifetime at room temperature. Such materials, combining polymerlike thermoplastic behavior with the distinctive properties of metallic glasses, are highly unusual for metallic alloys and have great potential in applications and can also facilitate studies of the supercooled liquid state.

Polymeric glasses have a very wide range of applicability because they exhibit higher glass-forming ability (GFA), lower glass transition temperature T_g, and a more stable supercooled liquid region than those of metallic glasses [1–3]. The thermoplastic nature of common glassy polymers is exploited in molding and imprinting [1–3]. For metallic glasses, however, engineering application fields have been limited because of the limitation of alloy size and the lack of workability and machinability. While many metallic glasses are now available in bulk form [4–7], similar exploitation of their viscous flow is impeded by higher T_g and lower resistance to crystallization. Yet the mechanical and electrical properties of metallic glasses are, for some applications, far superior to those of polymers. In this Letter, we present a new Ce-based bulk metallic glass (BMG) showing superior GFA, high resistance to crystallization over a wide temperature range, and a remarkable combination of thermoplastic and metallic behaviors at temperatures close to room temperature (RT). This unique combination of properties makes the BMG rather similar to polymers in their formability and manufacturability, yet clearly its physical properties are very different from those of polymers: electrical conductivity and much greater stiffness. Such materials with the unique properties, which are not expected in crystalline alloys, have potential in applications and can facilitate studies of the supercooled liquid state.

Ingots with nominal compositions of $Ce_{70}Al_{10}Cu_{20}$ and $Ce_{68}Al_{10}Cu_{20}Nb_2$ (at. %) were prepared by arc melting commercial-purity Ce (99.5 wt. %) with high-purity Al (99.99%), Cu (99.99%), and Nb (99.9%) under a purified argon atmosphere. The ingots were remelted and suction cast into a Cu mold to obtain bulk form. The structure of the as-cast and processed samples was examined by x-ray diffraction (XRD) using a MAC M03 XHF diffractometer with $Cu - K_\alpha$ radiation at 40 kV. The microstructure of the as-cast sample was examined by high-resolution transmission electron microscopy (HREM) using a TECNAI-F20 instrument operated at 200 kV. Thin foils were prepared for microscopy by mechanical thinning and chemical polish-ing. Differential scanning calorimetry (DSC) was performed under a purified argon atmosphere in a Perkin-Elmer DSC-7, calibrated for temperature and energy with high-purity indium and zinc. Both isothermal and continuous heating (at a rate of 10 K min^{-1}) were used.

Mechanical properties (yield strength and elastic strain) were measured at RT and at 90 °C with a material test system (MTS) servohydraulic testing machine using a MTS 880 system (MTS System Corporation, USA). The cylindrical samples with length of 5 mm were cut by diamond cutter and the ends of the specimens were mechanically polished. Strain gauges were attached to the surface of the specimens to obtain one-dimensional local strain. Tests were in compression at a strain rate of 1×10^{-3} s^{-1}. Acoustic velocities were measured at RT using a pulse echo overlap method [8,9]. Quartz transducers (bonded to the specimen using honey) with harmonic frequency 10 MHz provided the excitation and detection of the ultrasonic pulses. The travel time of ultrasonic waves (carrying frequency is 10 MHz) propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns (Matec Instrument Inc. USA) [8,9]. The sample rods were cut to a length of about 7 mm, and their ends were carefully polished flat and normal to the longitudinal axis. Young's modulus E, bulk modulus B, Poisson ratio ν, and shear modulus μ were derived from the acoustic velocities [8,9]]. Vickers hardness was measured by a Vickers diamond pyramidal microhardness tester at RT using a Polyvar Met microhardness tester (Inspiratech 2000 Ltd., UK). The specimen surfaces were polished so that the indentation face is flat. A load 1.96 N and loading time 10 s was used to measure the diagonals of indentation. An average of 30 readings at different locations of the specimen surfaces were taken for each specimen, and the mean arithmetic values of the measured two diagonals were used for the calculation of the hardness. The electrical resistance of the $Ce_{70}Al_{10}Cu_{20}$ BMG at RT was measured on a physical property measurement system (PPMS) using a

standard four-probe technique by a PPMS 6000 (Quantum Design Inc. USA) instrument.

The $Ce_{70}Al_{10}Cu_{20}$ alloy when cast as rods is fully glassy for diameters up to 2 mm. The GFA of the ternary alloy is greatly improved by a minor addition of 2% Nb. This critical diameter is increased to at least 8 mm for the composition of $Ce_{68}Al_{10}Cu_{20}Nb_2$. Figure 1(a) shows that samples can be cast in rod and in sheet form with lustrous surfaces. As expected for casting of glassy alloys, when solidification does not involve crystallization, there is very little volume shrinkage, with consequent good castability. Earlier work on BMGs based on rare earth metals, for example, on neodymium [7], has shown that it can be difficult to obtain fully glassy structures; often there is a significant proportion of nanocrystals in the glassy matrix. For this reason particular care was taken to establish the structures of the cast alloys in the present work. Basic verification of amorphicity throughout the thickness of
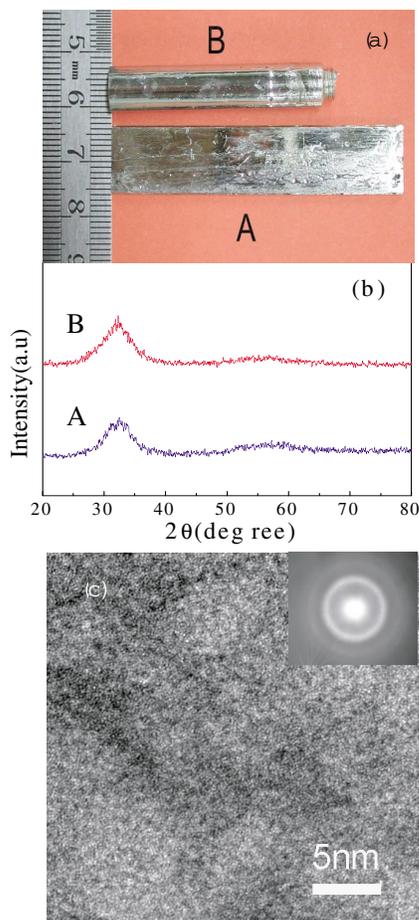
the samples was by XRD as shown in Fig. 1(b). In samples below the critical diameters already given, the XRD patterns show only the two broad maxima associated with an amorphous phase and no detectable Bragg peaks corresponding to crystalline phases. HREM [Fig. 1(c)] is more sensitive than XRD to minor volume fractions of dispersed crystals, but still shows only the uniform contrast expected for a single glassy phase.

If the grain size is in the nanometer range, polycrystalline structures can be misinterpreted as glassy [10]. According to Chen and Spaepen [10], true glassy structures can be distinguished from ultra-fine-grained polycrystals by isothermal calorimetry. For as-cast $Ce_{70}Al_{10}Cu_{20}$, the clear exothermic peak in the DSC trace (Fig. 2) indicates its glassy nature, in contrast to the decaying exothermic signal expected for coarsening of a polycrystalline structure. The glassy nature of the samples is also indicated by the distinct glass transition [10] (at T_g) and sharp crystallization exotherm (onset at T_x) visible on continuous heating in DSC. The $Ce_{70}Al_{10}Cu_{20}$ sample shows a T_g of 68 °C, lower than any previous BMGs [4,5], and a large supercooled liquid region ($\Delta T = T_x - T_g = 60$ K). With addition of 2% Nb, T_g is not obviously changed but ΔT is significantly increased to 81 K, indicating that for this alloy the supercooled liquid state is remarkably stable. The GFA of alloys correlates with their reduced glass (rg) transition temperature ($T_{rg} = T_g/T_1$) [11] and with the parameter $\gamma (= T_x/((T_g + T_1))$ [12], where T_1 is the liquidus temperature. Good GFA consistent with forming BMGs is associated with $T_{rg} \geq 0.6$ and $\gamma \geq 0.35$ [4,11,12]. The
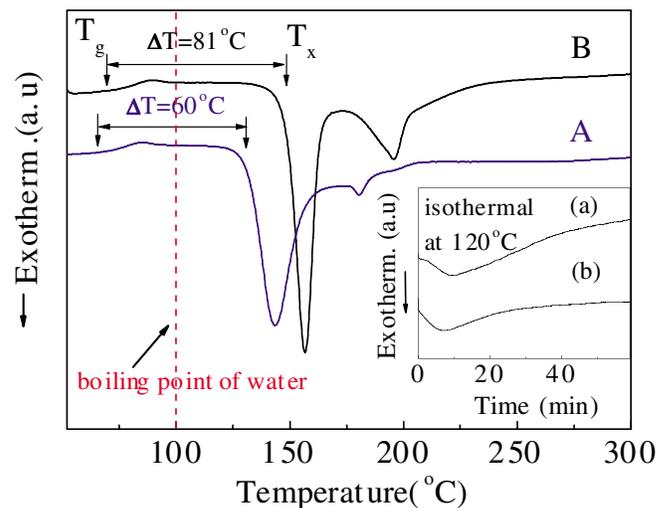

FIG. 1 (color online). (a) An as-cast $Ce_{68}Al_{10}Cu_{20}Nb_2$ glassy rod 8 mm in diameter and a $Ce_{70}Al_{10}Cu_{20}$ glassy sheet $1.5 \times 12 \times 70$ mm³. (b) XRD patterns of the as-cast $Ce_{68}Al_{10}Cu_{20}Nb_2$ glassy rod and the $Ce_{70}Al_{10}Cu_{20}$ glassy sheet. (c) HREM image and selected-area electron diffraction pattern for the 1 mm diameter $Ce_{70}Al_{10}Cu_{20}$ as-cast sample, showing a single glassy phase with no evidence for nanocrystallization.

FIG. 2 (color online). DSC traces at a heating rate of 10 K min⁻¹ for $Ce_{70}Al_{10}Cu_{20}$ (A) and $Ce_{68}Al_{10}Cu_{20}Nb_2$ (B) glasses showing the unusually low T_g (~ 68 °C) and the large supercooled liquid region ΔT. The inset shows isothermal DSC traces for $Ce_{70}Al_{10}Cu_{20}$ glass held at 120 °C: (a) immediately after casting, and (b) after three months at room temperature (20–38 °C).

better glass former in the present work, $Ce_{68}Al_{10}Cu_{20}Nb_2$, has $T_{rg} = 0.53$, a value lower than expected for a BMG, but has $\gamma = 0.39$, exceeding the critical value.

The T_g value for $Ce_{70}Al_{10}Cu_{20}$ and $Ce_{68}Al_{10}Cu_{20}Nb_2$ is close to that of some common amorphous polymers such as nylon ($\sim 43\,^\circ$C), and even lower than that of polyvinylchloride ($75-105\,^\circ$C) [13]. It is nearly as low as the T_g of $\leq 40\,^\circ$C seen in the first reported metallic glasses, Au-Si ribbon [14]. The Au-Si glasses, as expected with T_g so close to RT and with vanishingly small ΔT, lacked stability. They started to crystallize after 3 h at RT and were fully crystalline in less than 24 h. The stability of the Ce-based BMGs is therefore of concern. However, isothermal DSC (Fig. 2, inset) shows that a sample stored at RT ($20-38\,^\circ$C) for three months is still glassy. The stability was further investigated over a range of temperature. Isothermal DSC was used to determine the time-temperature-transformation (TTT) diagram (Fig. 3). At $85\,^\circ$C, the lowest temperature at which the start and finish of crystallization can be reliably detected in the DSC, the time before crystallization is 9 h, similar to the lifetimes of the well studied Zr-based BMGs annealed at the same absolute fraction of their T_g [15]. As an empirical guide to stability, Fig. 3 gives an Arrhenius extrapolation with a predicted lifetime at $20\,^\circ$C of $\sim 10^{10}$ s (or 200 years). The activation energy is estimated to be 250 kJ mol^{-1}, which is similar to that of other BMGs [6].

At RT the Ce-Al-Cu-(Nb) BMGs are brittle, even in compression [Fig. 4(a)] showing $\sim 1.5\%$ elastic strain followed by catastrophic failure. Brittleness is expected for metallic glasses with $\mu/B > 0.2$–0.3 [16], and Ce-based BMGs have $\mu/B = 0.42$ [16]. It is remarkable, though,

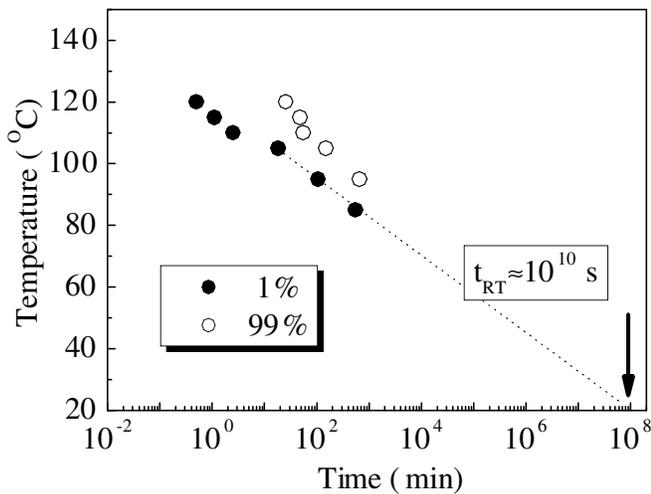that the brittleness is maintained so close to T_g. Raising the temperature to $90\,^\circ$C (in the supercooled liquid state) gives a complete change in behavior, to perfect superplasticity [Fig. 4(a)]. The sample can be compressed to 10% of its original height without cracking. Just as for a conventional polymeric thermoplastic, the material can be repeatedly compressed, stretched, bent, and formed into complicated shapes. The temperature required for this excellent deformability is approximately $100\,^\circ$C, which is normal for polymers but highly unusual for metallic alloys [17]. The ease of thermoplastic forming can be demonstrated using near-boiling water [Fig. 4(b) and 4(c),). It has been verified by XRD that samples remain fully amorphous after 10 min in near-boiling water, consistent with the TTT diagram (Fig. 3).
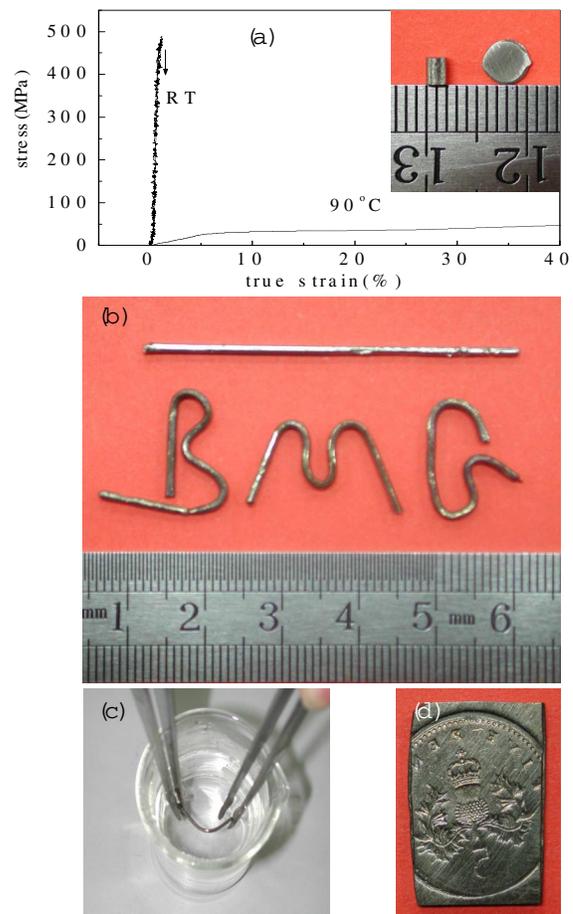

FIG. 4 (color online). (a) True stress-true strain curve of a 2 mm diameter $Ce_{70}Al_{10}Cu_{20}$ BMG rod tested under a compression at RT and at $90\,^\circ$C. The inset shows the starting sample, 2 mm in diameter and 3 mm in height, and the sample compressed at $90\,^\circ$C, 5 mm in diameter and 0.5 mm in height. (b) BMG rods formed into letters by simple manipulation in near-boiling water as shown in (c). (d) the impression of a United Kingdom five-pence coin made on the surface of a BMG sheet held in near-boiling water, demonstrating excellent imprintability and viscous deformability.

FIG. 3. Time-temperature-transformation diagram for crystallization of $Ce_{70}Al_{10}Cu_{20}$ glass. Isothermal DSC traces have been used to estimate the times to 1% and 99% crystallized at each temperature. The dashed line extrapolated to room temperature ($\sim 20\,^\circ$C) shows the onset time for crystallization at that temperature to be $\sim 10^{10}$ s (~ 200 y).

Although showing thermoplastic behavior like nylon or polyvinylchloride, the Ce-Al-Cu-(Nb) metallic thermoplastics show mechanical and physical properties which are very different from polymeric materials. Their density (6.738 Mg m^{-3}), Vickers hardness (1.50 GPa), fracture toughness (10.0 MPa m$^{1/2}$), $E = 31.0$ GPa, $B = 30.0$ GPa, $\mu = 12.0$ GPa, $\nu = 0.32$, and tensile strength (490 MPa) are all much higher than those of typical polymers [13]. The electrical resistivity of the BMG is ~ 119 $\mu\Omega$ cm; it is thus a metallic conductor, in contrast to the insulating properties of typical polymers. Although cerium metal oxidizes readily even at RT, the new Ce-Al-Cu-(Nb) alloys maintain a good surface finish, thus appearing to be oxidation- and corrosion-resistant.

As demonstrated by the simple experiment in Fig. 4(d), imprinting is possible for the Ce-based BMGs, as for BMGs in general which can show good micro- and even nanoimprintability [18,19]. The demonstration of thermomechanical data storage by forming nanoindentations through Joule heating of scanned nanotips uses a polymer as the storage medium [20]. For this application and for imprintability generally, there is an advantage in the increased precision possible when the medium has higher elastic moduli. Ce-based BMGs have, for example, Young's moduli 7–12 times those of typical polymers, while their low T_g means that no more energy is needed than for polymer imprinting. It may also be useful that this imprintability is combined with electrical conductivity.

One of intrinsic defects of metallic glassy materials is brittleness. The structural features limit the global plasticity of the BMGs in unconfined geometries to less than 1% at RT and severely restrict the use of the materials in structural applications. A lot of efforts have been made to overcome the problem but focused on the fabrication of BMG composites [4–6]. With increasing temperature, deformation becomes homogeneous and BMGs exhibit a large plasticity in the vicinity of T_g. This suggests that BMGs with low T_g close to RT, where mechanical properties are typically determined, are more likely to exhibit RT plasticity. This is supported by the low T_g value of Pt-based BMG [21]. Our work is suggestive for solving the problem and gives an implication that it is possible to get BMGs with low T_g close to RT, which are more likely to exhibit RT ductility and even superplasticity.

With one of the most stable metallic supercooled liquids near RT, Ce-based alloys make it possible to observe the intrinsic viscous behavior of the supercooled liquid near RT. These are ideal systems to investigate structural relaxation and supercooled liquid state in alloys. For example, the glass can be used to study the long-term (months to year) aging in metallic glasses by natural annealing at RT. Such long-term aging, which is not expected in other metallic glasses with high T_g, could assist in understanding some long-standing issues concerning slow relaxation kinetics in glasses.

The desirable properties combination of the Ce-based BMGs arises from the fortuitous value of T_g which results from the lower elastic moduli of the BMGs. Sufficient data on elastic moduli and T_g of various BMGs show that there is clear correlation [6,18]: The lower value of elastic modulus gives lower T_g. On the other hand, the elastic constants M of BMGs show a good correlation with a weighted average of the elastic constants M_i for the constituent elements as [18,22]: $M^{-1} = \Sigma f_i \cdot M_i^{-1}$, where f_i denotes the atomic percentage of the constituent. The results imply that the value of T_g of a BMG depends strongly on the M of its components. The established correlations, associated with elastic moduli, and since the moduli of glasses scale with those of their elemental components, provide useful guidelines for the development of the polymerlike BMGs by selection of components with suitable elastic moduli.

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