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Thermophysical and elastic properties of $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ bulk-metallic-glass-forming alloys

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By employing a containerless high-temperature high-vacuum electrostatic levitation technique, the thermophysical properties, including the ratio between the specific heat capacity and the hemispherical total emissivity, the specific volume, and the viscosity, of $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ bulk-metallic-glass (BMG)-forming liquids have been measured. Compared with $Cu_{50}Zr_{50}$, the improved glass-forming ability of $(Cu_{50}Zr_{50})_{95}Al_5$ can be attributed to its dense liquid structure and its high value of viscosity. Additionally, the relationship between the viscosity of various BMG forming liquids at the melting temperature and the elastic properties of the corresponding glasses at room temperature will be compared. *© 2006 American Institute of Physics.* [DOI: 10.1063/1.2408634]

The processing, the thermophysical, and mechanical properties of low-cost Cu-based bulk-metallic glasses (BMGs) have been intensively studied recently.[1–5] The Cu-based BMGs exhibit extraordinarily high strength and good compressive ductility, which are comparable with the Zr-based BMGs. In order to frustrate the crystal formation during the copper-mold casting process, previous studies indicate that BMG alloys should typically consist of at least three components, which have varying atomic sizes.[6] However, it was reported recently that binary Cu–Zr alloys can be cast into bulk amorphous structures with sample diameters up to 2 mm.[7–10] Subsequent studies reveal that small amounts of Al additions (several at. %) further increase its glass-forming ability (GFA) in the ternary Cu–Zr–Al alloys.[11] Das *et al.*[12] reported that both $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ BMGs exhibit good compressive ductility at room temperature. Most strikingly, the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ BMGs exhibit "strain hardening" effects during the compressive tests, which were not expected for the BMG alloys since there is no dislocation activities in the amorphous structure. Strain hardening is a desirable factor for the prevention of the strain localization. Nevertheless, the localized deformation within the shear bands was still primarily responsible for the observed plasticity in both $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ BMGs.[12] Therefore, the precise mechanisms responsible for the plastic deformation of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ BMGs require further investigations.[13,14]

Recently, it was reported that the ductility of BMGs was closely related to their Poisson's ratio.[15–17] For example, Pt-based BMG with high Poisson's ratio of about 0.41 shows an excellent compressive ductility.[15] Nivikov and Sokolov[18] reported that Poisson's ratio of a glass at room temperature correlates with the fragility of liquids at high temperature. This correlation was recently challenged by Yannopoulos and Johari[19] by compiling extensive experimental data covering various glass-forming systems. In this letter, in an effort to further understand the relationship between the fragility and the elastic properties of glass-forming alloys, we report the thermophysical properties, including the ratio between the specific heat capacity and the hemispherical total emissivity (c_p/ε_T), the specific volume (V), and the viscosity (η), of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ alloys in the molten liquid state. Moreover, the elastic properties, including Young's modulus (E), the shear modulus (G), the bulk modulus (B), and the Poisson's ratio (ν), of the corresponding glasses at room temperature will be measured.

The master $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ alloys were prepared by melting a mixture of the high-purity Cu (99.999%), Zr (99.9%), and Al (99.999%) in a mini arc melter under a Ti-gettered argon-gas atmosphere. To ensure the homogeneity, the samples were melted for at least five times. A sample of about 20 mg was levitated between a pair

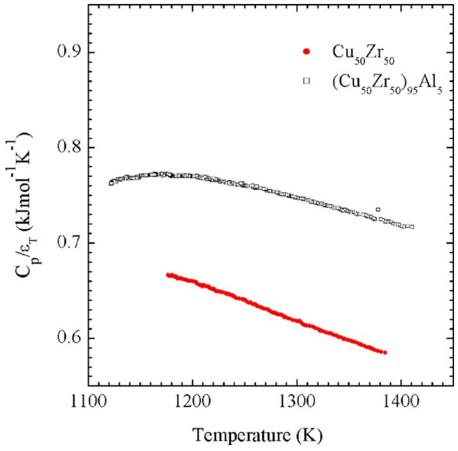

FIG. 1. Ratio between the specific heat capacity and the hemispherical total emissivity, c_p/ε_T, as a function of the temperature for the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ molten liquids during cooling.

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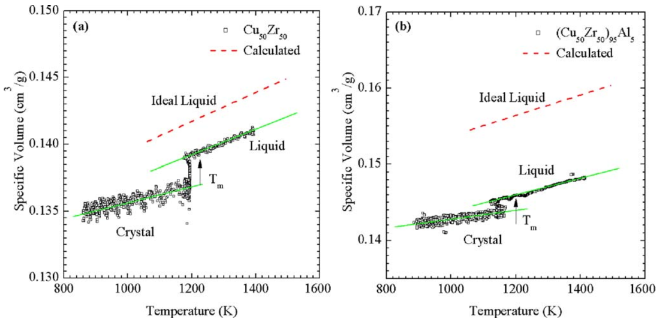

FIG. 2. Measured specific volume of the $Cu_{50}Zr_{50}$ (a) and $(Cu_{50}Zr_{50})_{95}Al_5$ (b) molten liquids and the corresponding crystal as a function of the temperature. The green solid lines in (a) and (b) are linear fits to the measured data using Eq. (2). The red dashed lines in (a) and (b) are calculated specific volumes for the ideal liquids.

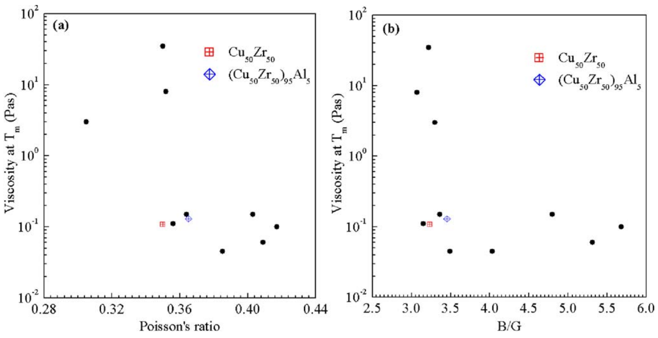

FIG. 3. Viscosity at T_m as a function of Poisson's ratio (a) and the viscosity at T_m as a function of the ratio of the bulk modulus and the shear modulus, B/G (b), for various bulk-metallic-glass-forming liquids, including $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$.

of electrodes in a containerless high-temperature high-vacuum electrostatic levitation (ESL) system, which was evacuated to 10^{-8} torr. The BMG sample was heated by a high-power cw Nd doped yttrium aluminum garnet laser and was cooled by turning off the laser power completely. The specific volumes of the liquid and crystal were measured by monitoring the sample-volume evolution using a charge-coupled device camera with a telescopic head. The viscosity of the molten drop was measured by inducing the resonant oscillation using an ac electric field. The detailed experimental procedures of the ESL experiments were described elsewhere.[20,21] The elastic properties of the BMGs at room temperature were measured by using a pulse-echo overlapping technique. The excitation and detection of the ultrasonic pulses were provided by X—or Y-cut (for longitudinal and transverse waves, respectively) quartz transducers. The frequency of the ultrasonic is 10 MHz.

The ratios between the specific heat capacity and the hemispherical total emissivity of the molten glass-forming liquids, c_p/ε_T, can be measured by ESL. Assuming that the cooling process in ESL is purely radiative, the c_p/ε_T can be calculated using Eq. (1),[22]

$$\frac{C_p}{\varepsilon_T} = -\frac{\sigma A}{m}(T^4 - T_0^4)\left(\frac{dT}{dt}\right)^{-1}, \qquad (1)$$

where σ is the Stefan-Boltzmann constant, A is the surface area, m is the mass, T is the temperature of the sample, T_0 is the environmental temperature, and dT/dt is the cooling rate, which can be obtained from the cooling curves of a sample in the ESL. Figure 1 shows the measured c_p/ε_T as a function of temperature for the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ molten liquids during cooling. The addition of 5 at.% Al significantly increases c_p/ε_T by about 15%–25% within the temperature range investigated.

Figure 2 displays the specific volumes of the liquid and corresponding crystal of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ alloys during the cooling process in the ESL. The specific volume drops abruptly during the crystallization of the liquid. The specific volume $V(T)$ for both the liquid and crystal shows a linear relationship with the temperature T and can be described by[4,21]

$$V(T) = V_m[1 + \alpha(T - T_m)], \qquad (2)$$

where V_m is the specific volume at the melting temperature T_m. For $Cu_{50}Zr_{50}$, the best linear fit yields $V_m^L = 0.1394\ \mathrm{cm^3\ g^{-1}}$ and $\alpha^L = 6.537 \times 10^{-5}\ \mathrm{K^{-1}}$ for the liquid, and $V_m^C = 0.1369\ \mathrm{cm^3\ g^{-1}}$, and $\alpha^C = 3.935 \times 10^{-5}\ \mathrm{K^{-1}}$ for the crystal. For the $(Cu_{50}Zr_{50})_{95}Al_5$ alloy, $V_m^L = 0.1459\ \mathrm{cm^3\ g^{-1}}$, and $\alpha^L = 7.669 \times 10^{-5}\ \mathrm{K^{-1}}$, for the liquid, and $V_m^C = 0.1440\ \mathrm{cm^3\ g^{-1}}$ and $\alpha^C = 4.302 \times 10^{-5}\ \mathrm{K^{-1}}$ for the crystal. Included in Fig. 2 is the specific volume for an ideal liquid. The specific volume for an ideal liquid containing an i element with a specific volume of V_i can be calculated by $V = \Sigma x_i V_i$ with x_i the molar fraction of V_i. Due to the atomic interaction and the development of the short- and/or

TABLE I. Viscosity η at T_m for various BMG forming liquids, Young's modulus E, the shear modulus G, the bulk modulus B, Poisson's ratio ν, and the ratio between the bulk modulus and the shear modulus B/G for various BMG alloys at room temperature.

Alloy	η at T_m (Pa s)	E (GPa)	G (GPa)	B (GPa)	ν	B/G	Ref.
$Cu_{50}Zr_{50}$	0.108	84.0	31.3	101.2	0.35	3.23	This study
$(Cu_{50}Zr_{50})_{95}Al_5$	0.13	90.1	33.0	113.7	0.365	3.45	This study
$Cu_{42}Zr_{42}Al_7Y_5$	0.15	84.6	31	104.1	0.364	3.36	4 and 28
$Cu_{60}Zr_{30}Ti_{10}$	0.11				0.356	3.15	28 and 29
$Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$	8	95	34.1	114.1	0.352	3.07	28, 30, and 31
$Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$	35	95.7	35.2	113.4	0.35	3.22	31 and 32
$Pd_{40}Ni_{40}P_{20}$	0.15	93	33.2	158	0.403	4.80	31, 33, and 34
$Pd_{77.5}Cu_6Si_{16.5}$	0.06	89.7	31.8	166	0.409	5.31	33 and 34
$Mg_{60}Cu_{25}Y_{10}$	3				0.305	2.30	34 and 35
$Ni_{60}Nb_{35}Sn_5$	0.045	183.7	66.32	267	0.385	4.03	23 and 28
$Ni_{60}Nb_{40}$	0.045					3.49	23 and 28
$Au_{55}Cu_{25}Si_{20}$	0.1	69.8	24.6	139.8	0.417	5.68	33, 28, and 34

medium-range orders in the liquids, the measured specific volume of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ liquids is significantly smaller than the calculated values, in agreement with previous study.[23] This difference is more significant for $(Cu_{50}Zr_{50})_{95}Al_5$ (about 7%) than for $Cu_{50}Zr_{50}$ (about 2%), indicating that $(Cu_{50}Zr_{50})_{95}Al_5$ exhibits a more dense liquid structure than $Cu_{50}Zr_{50}$ when compared to their respective ideal liquids. The dense structure for $(Cu_{50}Zr_{50})_{95}Al_5$ liquid is further supported by a smaller percentage difference in the measured specific volume between the liquid and crystal at T_m, i.e., $(V_m^L - V_m^C)/V_m^C$ [1.8% for $Cu_{50}Zr_{50}$ and 1.3% for $(Cu_{50}Zr_{50})_{95}Al_5$]. These results indicate that 5 at. % Al help stabilize the Cu–Zr liquid, resulting in a smaller difference in the specific volume between the liquid and crystal and consequently an improved GFA.

The viscosity of a molten liquid is related to the diffusivity of the liquid atoms and therefore, to its GFA. Moreover, the viscosity of the molten liquid is associated with the liquid fragility, a concept introduced by Angell to differentiate liquids with various dynamic characteristics.[24] A strong liquid exhibits an Arrhenius-like temperature dependence of the viscosity, whereas the temperature dependence of the viscosity for a fragile liquid deviates from the Arrhenius behavior with a steep change in the viscosity at the glass-transition temperature T_g. Since the viscosity at T_g for various glass-forming liquids is 10^{12} Pa s, it follows that a fragile liquid has a lower value of viscosity in the molten liquid state than that for a strong liquid.[25–27] Therefore, the viscosity of the glass-forming liquids in the molten liquid state is an important kinetic parameter, which may influence their GFA as well as their fragility. The viscosity of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ molten liquids were measured over a wide temperature range by ESL. Particular attention will be paid to the viscosity of the liquids at the melting temperature T_m, which provides a direct comparison of the values of the viscosity among various BMG liquids, as illustrated in Table I. It is noted from Table I that the viscosity at T_m for the $(Cu_{50}Zr_{50})_{95}Al_5$ is higher than that for $Cu_{50}Zr_{50}$. In addition to the smaller difference in the specific volume between the liquid and crystal for $(Cu_{50}Zr_{50})_{95}Al_5$, the higher value of the viscosity may also help explain its good GFA, as compared with $Cu_{50}Zr_{50}$.

Whether there exists a correlation between the liquid fragility and glass Poisson's ratio ν or similarly between the liquid fragility and the ratios between the bulk modulus and the shear modulus of glasses (B/G) is still under debate.[18,19,34] The measured elastic properties, including E, G, B, and ν, of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ alloys at the room temperature were listed in Table I, including the data for other BMG alloys cited from the literature. Since the viscosity at T_m is associated with the fragility of glass-forming liquids, the plots of the viscosity at T_m vs ν and the viscosity at T_m vs B/G for the various BMG alloys were made, as shown in Fig. 3. It appears that the viscosity did not change much ($\sim$0.1 Pa s) when ν changes from 0.36 to 0.42 (or when B/G changes from 3.4 to 5.8). However, the viscosity increases abruptly when $\nu \leqslant 0.36$ (or when $B/G \leqslant 3.4$). In contrast to the expectation from the results reported by Nivikov and Sokolov,[18] the viscosity at T_m for different BMG alloys did not show a progressive increase with decreasing ν (or B/G).

In summary, the thermophysical properties of the $Cu_{50}Zr_{50}$ and $(Cu_{50}Zr_{50})_{95}Al_5$ glass-forming liquids have been measured using an ESL technique. Compared with the binary $Cu_{50}Zr_{50}$ alloy, the improved GFA of the ternary $(Cu_{50}Zr_{50})_{95}Al_5$ alloy is due to the more dense liquid structure, leading to a smaller difference in the specific volumes between the liquid and the corresponding crystal, as well as to a higher value of viscosity at T_m. The relationship between the viscosity of the molten metallic glass-forming liquids and their elastic properties (ν and (B/G) of the corresponding glasses at the room temperature has been compared.

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