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Elastic properties of Zr-based bulk metallic glasses studied by resonant ultrasound spectroscopy

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We report measurements of the elastic properties of Zr-based bulk metallic glasses, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, $Zr_{50}Cu_{30}Ni_{10}Al_{10}$, and $Zr_{50}Cu_{40}Al_{10}$ between 5 K and 300 K. Both the shear and longitudinal modulus have been measured as a function of temperature, allowing accurate determination of the Poisson's ratio and the related ratio of bulk modulus to shear modulus, *K/G*. These data make it possible to assess the influence of the alloy's composition on the mechanical properties and enable an evaluation of the correlation between the elastic moduli and the ductility of the alloys.

I. INTRODUCTION

Bulk metallic glasses (BMGs) with a unique combination of mechanical and physical properties are currently emerging as a new class of metallic materials for structural and functional use. The structural use of BMGs, however, encounters a technical difficulty in that most BMGs exhibit low ductility during plastic deformation under tension. To solve this material problem, considerable effort has been devoted to the alloy development of "ductile" BMGs. Whereas the brittleness of crystalline metals is known to be correlated to the ratio of the elastic shear modulus to the bulk modulus, *G/K*,[1] a similar assessment for metallic glasses was not available until recently, when Lewandowski and colleagues reported a universal correlation between the energy of fracture and the Poisson's ratio for bulk metallic glasses, with brittle glasses displaying a low Poisson's ratio.[2] This confirms earlier results from Schroers and coworkers who concluded that a large Poisson's ratio and a low glass transition temperature might be regarded as indicators of the ductile character of a bulk metallic glass and could therefore be used as a means of identifying ductile bulk metallic glasses.[3] The importance of the Poisson's ratio in the study of glasses was also pointed out by Novikov and Sokolov,[4] who showed that the ratio of instantaneous shear to bulk modulus *G/K* in glasses, or, alternatively, the Poisson's ratio ν, is linked to the fragility of the glass forming liquid, an important parameter used to evaluate the glass forming ability (GFA) of glasses. Even though the latter might not hold for BMGs,[5] these references suggest that a systematic study of the elastic properties and thus the Poisson's ratio of metallic glasses is expected to yield important information about their mechanical properties.

Zr-based alloys have received wide interest because of their superior GFA, high strength, and low Young's modulus (80–100 GPa), allowing these alloys to be used in a variety of applications.[6–9] Previously reported measurements of the mechanical properties of Zr-based alloys include tensile and compressive tests at room temperature,[10] quasi-static uniaxial compression tests,[11] tensile tests,[12] Charpy impact tests[9,13] as well as fatigue behavior measurements.[12,14,15] The present work reports measurements of the elastic moduli of Zr-based BMGs $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, $Zr_{50}Cu_{30}Ni_{10}Al_{10}$, and $Zr_{50}Cu_{40}Al_{10}$, using resonant ultrasound spectroscopy. Both the shear and longitudinal modulus have been measured as a function of temperature (5 K–300 K), allowing accurate determination of the Poisson's ratio and the related ratio of shear modulus to bulk modulus, *G/K*. These data make it possible to assess the influence of the alloy composition on the mechanical properties and enable an evaluation of the correlation between the elastic moduli and the ductility of the alloys.

II. EXPERIMENTAL DETAILS

Zr-based BMGs, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ and $Zr_{50}Cu_{40}Al_{10}$ were prepared by arc-melting pure Zr, Cu, Ni, and Al elements in argon atmosphere.[9,11,13] The glass transition temperature of

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these alloys is 686 K, 708 K, and 706 K, respectively. Samples of approximately 4 × 4 × 4 mm^3 were cut from the ingots and then polished into rectangular parallelepipeds. Each sample was flat-mounted between the two transducers of the resonant ultrasound spectroscopy (RUS) probe. RUS is a novel technique developed by Migliori and coworkers at Los Alamos National Laboratory for determining the complete elastic tensor of a solid by measuring its free-body resonances.[16] The mechanical resonances can be calculated for a sample with known dimensions, density, and elastic tensor. In a RUS experiment, the mechanical resonances of a freely vibrating solid of known shape are measured, and an iteration procedure is used to "match" the measured lines with the calculated spectrum. This allows determination of all elastic constants of the solid from a single frequency scan, which clearly indicates a main advantage of RUS: there is no need for separate measurements to probe different moduli, and multiple sample remounts and temperature sweeps are avoided. Another advantage lies in the ability of RUS to work with small samples: whereas conventional techniques can demand a sample size up to a centimeter, RUS measurements can be made on millimeter-sized samples.

Measurements as a function of temperature were performed using a specially designed probe that fits in a physical property measurements system from Quantum Design (San Diego, CA). Because BMGs are isotropic, only two independent elastic constants, typically the longitudinal modulus L and the shear modulus G, must be determined, and the bulk modulus K, Young's modulus E, and Poisson's ratio ν can be calculated using the following equations

$$K = \frac{3L - 4G}{3} \quad , \tag{1}$$

$$E = \frac{G(3L - 4G)}{L - G} \quad , \tag{2}$$

$$\nu = \frac{L - 2G}{2(L - G)} = \frac{3K - 2G}{6K + 2G} \quad . \tag{3}$$

III. RESULTS AND DISCUSSIONS

The upper panel of Fig. 1 shows the temperature dependence of the shear modulus G for two different samples of the Zr-based alloy $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$, and illustrates how the modulus increases with decreasing temperature. The small difference between both samples is most likely due to a minor difference in density, the sample with the higher density (6.88 g/cm^3) having a slightly higher modulus compared with the sample with the lower density (6.86 g/cm^3). The temperature dependence of the shear modulus can be modeled quite well using the so-called Varshni function, $c_{ij}(T) = c_{ij}^0 - s/(e^{t/T} - 1)$, with T the temperature, c_{ij}^0 the elastic constant at 0 K, and s and t fitting parameters.[17] This function was shown by Varshni to describe the temperature dependence of the elastic constants of many simple substances and characterizes to some extent "normal" elastic behavior. A similar temperature dependence is observed in the other Zr-based glasses $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, illustrated in the bottom panel of Fig. 1. The figure clearly illustrates how all three alloys follow the "normal" Varshni-behavior, and at the same time shows how the elastic moduli of the alloys reflect changes in composition: whereas the shear moduli of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ and $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$ are very similar, the shear modulus of $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ is significantly lower over the temperature range from 5 K to 300 K. Longitudinal moduli (L), bulk moduli (K), and Young's moduli (E), summarized in Table I, show the same trend, which is in good agreement with the results obtained by tensile and compression tests at room temperature for alloys with comparable composition (i.e., 93 GPa for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$,[12] 89 GPa for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$,[12]

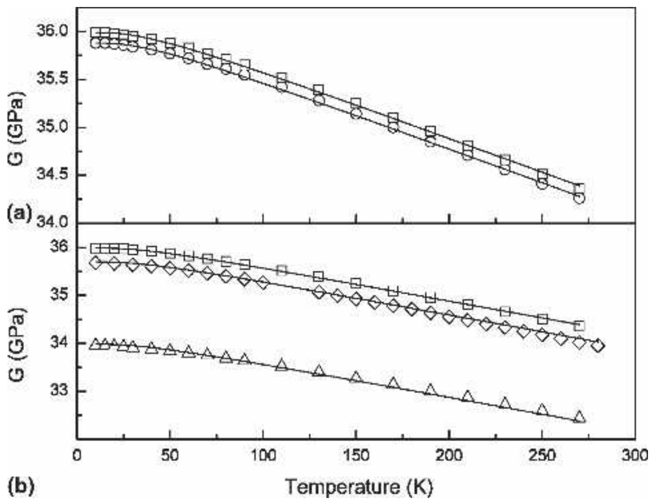

FIG. 1. (a) Shear modulus G as a function of temperature for two samples of $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$ and (b) shear modulus G as a function of temperature for $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$ (□), $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ (◊), and $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ (Δ). The solid lines represent a fit using the Varshni model, with parameters s = 0.7 GPa and t = 100 K. c^0 = 36.0 GPa and 35.9 GPa for $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$, c^0 = 35.7 GPa for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, and c^0 = 34.0 GPa for $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$.

TABLE I. Shear modulus (G), longitudinal modulus (L), bulk modulus (K), and Young's modulus (E) at room temperature for Zr-based alloys $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$, $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$, and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$.

	$\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$	$\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$	$\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$
G (GPa)	32.4	34.4	34.0
L (GPa)	160	167	166
K (GPa)	117	121	121
E (GPa)	89	94	93

TABLE II. Comparison of experimental density and elastic constants at room temperature with the calculated values based on the volume fraction of the constituent elements.

	$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$		$Zr_{50}Cu_{30}Ni_{10}Al_{10}$		$Zr_{50}Cu_{40}Al_{10}$	
	Experiment	Calculated	Experiment	Calculated	Experiment	Calculated
ρ (g/cm^3)	6.63	6.56	6.88	6.78	6.86	6.79
G (GPa)	32.4	38.3	34.4	37.9	34.0	36.3
K (GPa)	117	105	121	105	121	103
E (GPa)	89	89	94	88	93	84
ν	0.373	0.336	0.370	0.339	0.371	0.341

and 86 GPa for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$).[11] Recent attempts to "predict" the elastic moduli of novel BMGs have explored to what extent the elastic constants of the glasses can be regarded as a weighted average of the moduli of the constituent crystalline elements. These calculations are based on the concept of the property of a glass being an average, restricting consideration to systems in which all the constituent elements are metallic. The averages of the moduli can be weighted by atomic weight[18–20] or volume fraction,[21] with the latter being more successful. It needs, however, to be pointed out that both averaging techniques must be used with caution, as it has been shown that they sometimes fail to provide an accurate estimate for BMGs.[22] Table II shows quite good agreement between the experimental values of the elastic moduli and the calculated moduli using $X_c = \Sigma X_i c_i V_i / V_m$ where X_i, c_i and V_i are the modulus, atomic fraction, and volume per atom for the i-th constituent element,[23] V_m and X_c are the measured average atomic volume and the calculated modulus of the metallic glass, and the summation is over all n elements of which the glass is composed.

TABLE III. Room temperature elastic moduli and Poisson's ratio for various Zr-based metallic glasses.

	G (GPa)	K (GPa)	E (GPa)	K/G	ν
$Zr_{50}Cu_{40}Al_{10}$	23.0	121	93	3.56	0.372
$Zr_{50}Cu_{30}Ni_{10}Al_{10}$	34.4	121	94	3.52	0.370
$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$	32.4	117	89	3.61	0.373
[a]$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	37.4	114.8	101.3	3.06	0.353
[a]$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	35.2	113.4	95.7	3.22	0.359
[a]$Zr_{53}Ti_5Cu_{20}Ni_{12}Al_{10}$	32.1	106.8	87.6	3.32	0.363
[a]$Zr_{48}Nb_8Cu_{12}Be_{24}Fe_8$	35.2	113.4	95.7	3.22	0.359
[a]$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	32.0	107.7	87.3	3.37	0.365
[a]$Zr_{65}Cu_{15}Ni_{10}Al_{10}$	31.0	106.7	83.0	3.52	0.367

[a] Data from Ref. 20.

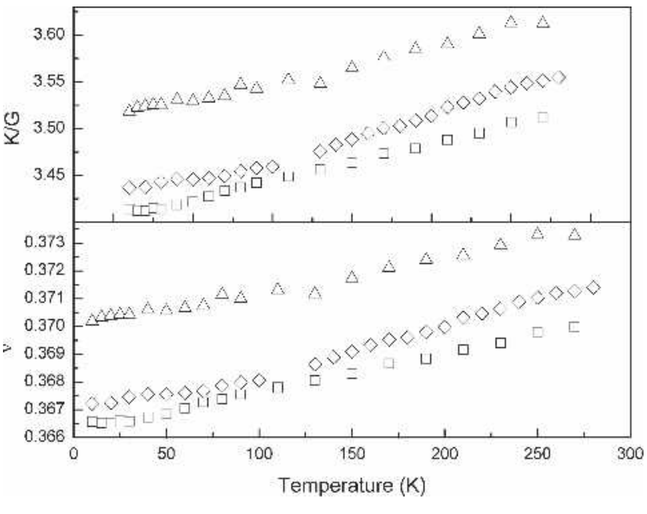

FIG. 2. (a) The ratio of bulk modulus to shear modulus K/G and (b) the Poisson's ratio ν as a function of temperature for $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ (□), $Zr_{50}Cu_{40}Al_{10}$ (◊), and $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (Δ).

The elastic moduli for our Zr-based glasses follow the trend of previously reported data for Zr-based alloys with slightly different compositions,[20,24] summarized in Table III. It is worth pointing out that, among the Zr-based glasses, the alloys used in the present study have the largest reported K/G values. This is reflected in a relatively high Poisson's ratio for all three alloys, reaching 0.373 in $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ at room temperature. Figure 2 shows the temperature dependence of the Poisson's ratio ν as well as the ratio of bulk modulus to shear modulus K/G. The high Poisson's ratios (and K/G values) correlate with the enhanced ductility observed in these alloys,[9,13] confirming the suggested link between the elastic moduli and the ductility of the alloys.

IV. SUMMARY

The elastic moduli of three Zr-based bulk metallic glasses, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, $Zr_{50}Cu_{30}Ni_{10}Al_{10}$, and $Zr_{50}Cu_{40}Al_{10}$ were measured between 5 K and 300 K using resonant ultrasound spectroscopy. The temperature dependence of the moduli follow normal "Varshni" behavior, and the values at room temperature follow the trend of other Zr-based alloys with slightly different compositions. The enhanced ductility of the present alloys is reflected by their larger Poisson's ratio, confirming the suggested relationship between ductility and elastic moduli of metallic glasses.

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