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Correlations for predicting plasticity or brittleness of metallic glasses

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Abstract

An assessment is made of the extent to which the elastic properties of a metallic glass can be predicted from the properties of the constituent elements. The correlations established do permit estimation of the glass properties, and provide guidelines for the selection of compositions to promote plasticity rather than brittleness.

Keywords: Metallic glasses; Elasticity; Fracture; Plasticity

1. Introduction

All metallic glasses show near-zero ductility in tension, but while some are profoundly brittle, others show extensive plasticity, localized in shear bands. These latter materials, especially when available in bulk form, are interesting for structural applications because they combine ultra-high strength (elastic limit) with fracture toughness, K_c, greater than 20 MPa $m^{1/2}$, rising to 60 MPa $m^{1/2}$ in notched specimens. This toughness is associated with local plastic flow, the notch stimulating the operation of many shear bands [1]. The non-brittle metallic glasses show considerable plasticity in compression and in bending [2,3]. The degree of plastic deformation sustainable before failure differs widely from composition to composition, and some compositions embrittle on annealing.

For crystalline metals, there is a long-established approximate correlation between intrinsic plasticity or brittleness and elastic properties [4,5]: as the ratio of shear modulus μ to bulk modulus B increases, or equivalently as the Poisson ratio ν decreases, the material becomes more brittle. A recent compilation of data [6] shows a universal, sharp correlation for metallic glasses (Fig. 1): they are intrinsically brittle for $(\mu/B) > 0.41$–0.43, or equivalently for $\nu < 0.31$–0.32. These critical elastic parameters apply both for comparison of different metallic-glass compositions and for the property changes on annealing a given glass. A non-brittle metallic glass with μ/B or ν further from the critical value is less likely to embrittle on annealing.

In view of this correlation, prediction of the elastic constants of metallic glasses would permit development of materials less likely to be intrinsically brittle or to embrittle on annealing. We examine in particular bulk metallic glasses (BMGs) composed exclusively of metallic elements, and we explore the extent to which the elastic constants of the glass can be regarded as a weighted average of the moduli of the constituent crystalline elements. A basis for averaging may be found in the established correlations of μ with quadrupole polarizability and B with valence electron density [5].

2. Basis of the calculations

The calculations are based on the concept of the property of a glass being an average. We therefore restrict our consideration to systems in which the bonding is always metallic, specifically to BMGs in which all the constituent elements are metallic. We have tested predictions of elastic moduli based on a variety of averages of the moduli of the elements in crystalline form. This approach naturally excludes consideration of glasses including metalloids (B, C, P, for which the bond type changes on alloying) or gaseous elements (O, for which no elemental modulus is defined). The averages of the moduli can be weighted by atomic, weight or volume fraction. The last of these is the most successful, is the most likely form based on composite mechanics, and is the basis of the predictions tested in the present work. In a composite with the constituent phases aligned such that the strain

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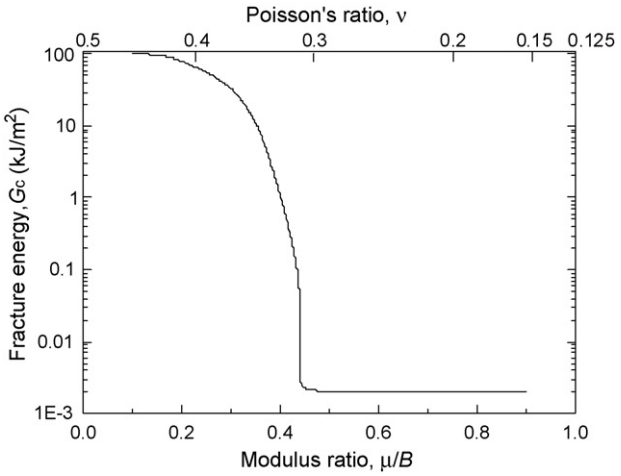

Fig. 1. Correlation of fracture energy G with modulus ratio μ/B (or ν) for metallic glasses (schematic, based on data in Ref. [6]).

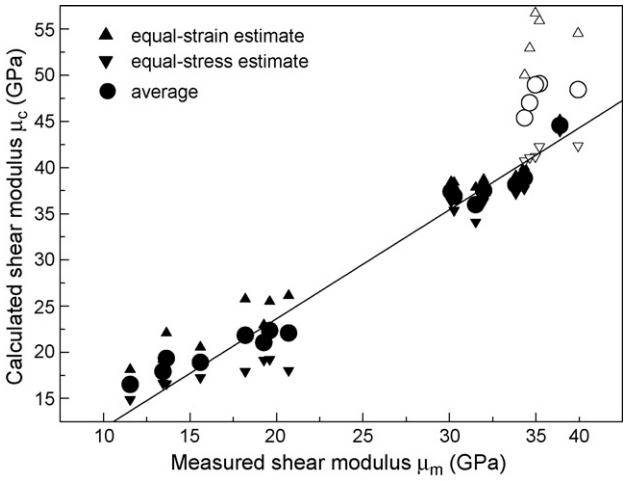

Fig. 2. Calculated vs. measured values of shear modulus for bulk metallic glasses (BMGs, compositions given in the caption to Fig. 5). Solid symbols are for compositions without Be; open symbols for those with Be. Three calculated values are shown: upper bound from equal-strain assumption (Eq. (1)), lower bound from equal-stress assumption (Eq. (2)), and the average of the two bounds. The straight line is a fit to the average of the bounds for compositions without Be.

is the same in each phase, the modulus of the composite is an average of the moduli of the constituent phases. Applying this uniform-strain model in the present case for the mixing of constituent elements, we calculate the shear modulus μ, and bulk modulus B of the alloy according to

$$\bar{X}_c = \sum_{i=1}^{n} \frac{X_i c_i V_i}{\bar{V}_m}, \tag{1}$$

where X_i, c_i and V_i are the modulus (μ or B), atomic fraction and volume per atom for the i-th constituent element; $\bar{V}_m$ and $\bar{X}_c$ 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. As is well known from composite mechanics, this calculation gives an upper bound on the predicted modulus. The lower bound is given by an assumption of uniform stress rather than strain (corresponding to an average of compliances):

$$\bar{X}_c = \left(\sum_{i=1}^{n} \frac{c_i V_i}{X_i \bar{V}_m} \right)^{-1}. \tag{2}$$

The values of V_i in Eqs. (1) and (2) are calculated from

$$V_i = \frac{M_i}{\rho_i N_A}, \tag{3}$$

where M_i, and ρ_i are the molar atomic weight and density of the i-th component element, and N_A is the Avogadro's number. Data on pure-metal properties are taken from Refs. [7,8]. For a metal with two or more polymorphs, the values used are those for the crystal structure of maximum density. The average atomic volume of the glass $\bar{V}_m$ is given by

$$\bar{V}_m = \frac{M}{\rho N_A}, \tag{4}$$

where M is the average molar mass of the glass, and ρ is its measured density.

3. Results and discussion

The availability of BMGs has facilitated the determination of elastic constants using standard ultrasonic methods. In the present work, values of μ or B for metallic glasses and their constituents were obtained directly from the literature or were calculated from the values of other moduli using standard relations [7,9]. Metallic glasses, ideally, are elastically isotropic and have only two independent elastic constants. The accuracy is ~1% for the acoustic velocity measurement and ~5% for the density measurement, giving an overall accuracy for modulus measurements of ~5%. Fig. 2 is a plot of μ, calculated from Eqs. (1) and (2), against the measured modulus for twenty BMGs based on Ce, Cu, La, Mg, Nd, Pr or Zr (compositions, in at.%, are given in the caption to Fig. 5). Also shown, and the focus of consideration, is a straight-line fit to the arithmetic mean of the upper- and lower-bound estimates of μ. When the data from Be-containing glasses are excluded, there is a clear correlation:

$$\mu_c = 1.18\mu_m. \tag{5}$$

Fig. 3 is a similar plot of B showing a good correlation between calculated (i.e. average of upper and lower bounds) and measured values. For consistency with the fitting in Eq. (5), data from Be-containing glasses are excluded to obtain:

$$B_c = 0.92B_m. \tag{6}$$

We consider briefly why the presence of beryllium leads to a significant deviation from the main correlation in Fig. 2. The elastic constants of beryllium are unusual: in contrast to almost all pure metals, its μ is greater (156 GPa) than its B (110 GPa), i.e. it has an abnormally low ν, of 0.03. Also, the atomic diameter of beryllium is so small that it may act more as an interstitial rather than a substitutional solute in the glass.

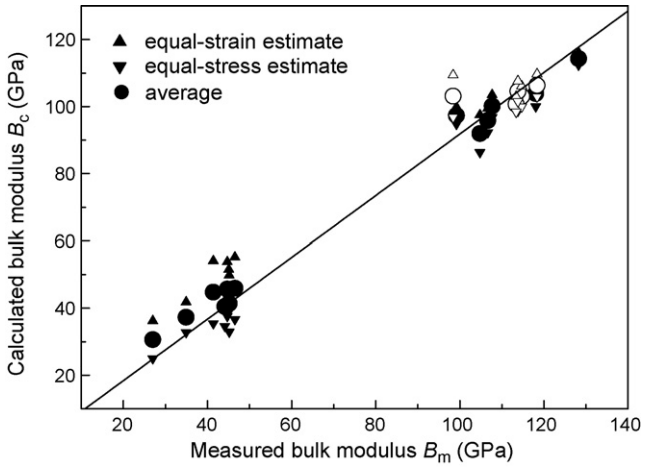

Fig. 3. Calculated vs. measured values of bulk modulus for BMGs. Solid symbols are for compositions without Be; open symbols for those with Be. Three calculated values are shown: upper bound from equal-strain assumption (Eq. (1)), lower bound from equal-stress assumption (Eq. (2)), and the average of the two bounds. The straight line is a fit to the average of the bounds for compositions without Be.

It has often been noted that the shear modulus of metallic glasses is lower than that of their crystalline counterparts. However the comparison is not straightforward: usually there is not a single crystalline phase of the same composition as the glass. Eq. (5) provides a quantitative correlation that the modulus of the glass is ~20% lower than would be predicted from the average of its crystalline components.

To interpret such effects, we note the volume changes accompanying glass formation. The measured average atomic volume of the glass (Eq. (4)) can be compared with the average, $\bar{V}_c$, of the atomic volumes of the constituent elements:

$$\bar{V}_c = \sum_{i=1}^{n} V_i c_i. \tag{7}$$

Fig. 4 shows a straight-line fit:

$$\bar{V}_c = 1.01\bar{V}_m. \tag{8}$$

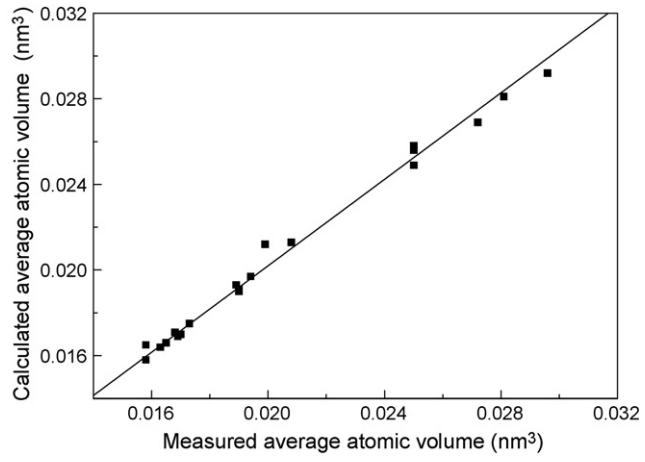

Fig. 4. Calculated (Eq. (7)) vs. measured average atomic volumes of metallic glasses.

Competing effects contribute to the difference between $\bar{V}_c$ and $\bar{V}_m$. For a given atomic species a random packing is less dense than a close-packed crystalline packing. On the other hand, when different atomic species are mixed, there is a volume change associated with non-ideality of the solution. For metallic glass-forming systems, the enthalpy of mixing of the elements is negative, correlated with a negative volume change [10]. Eq. (8) suggests that the effect of chemical mixing outweighs that of the crystal-amorphous structure change. That the actual volume is less than expected (Eq. (8)) correlates well with the actual B being greater than predicted (Eq. (6)).

As noted in Section 1, the ratio μ/B is of interest in predicting whether a metallic glass is plastic or brittle. The best estimate from the modulus values for the elements, is a scaled, calculated ratio $(\mu/B)_{sc}$, based on Eqs. (5) and (6):

$$\left(\frac{\mu}{B}\right)_{sc} = \frac{0.92\mu_c}{1.18B_c} = \frac{0.78\mu_c}{B_c}. \tag{9}$$

As seen in Fig. 5, there is considerable scatter about the line showing the expected 1:1 scaling with the measured ratio μ_m/B_m. This arises from combining the scatter in Figs. 2 and 3, and from the limited range of μ/B. Also shown on each axis is the critical range, $(\mu/B) > 0.41$–0.43, for metallic glasses to be intrinsically brittle [6]. The calculated and measured values of the modulus ratio are correlated: glasses with low μ_m/B_m, known to be plastic, are unambiguously predicted to be plastic on the basis of $(\mu/B)_{sc}$. On the other hand, glasses with high μ_m/B_m known to be brittle are not clearly predicted to be brittle.

Notwithstanding the scatter in Fig. 5, the correlation between the calculated and measured modulus ratios is good enough to direct the selection of elements for metallic glasses. Elements

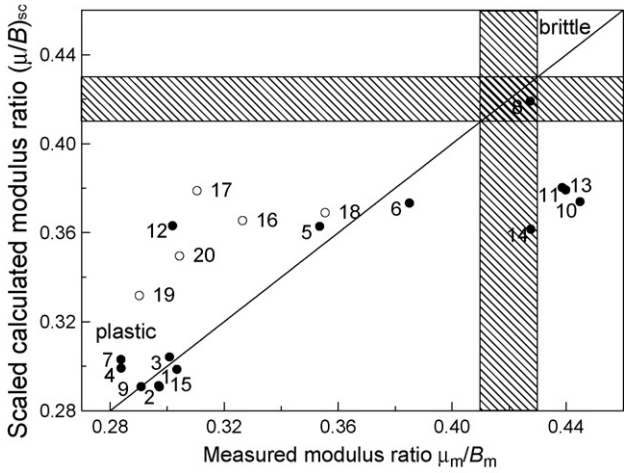

Fig. 5. Scaled, calculated (Eq. (9)) vs. measured values of modulus ratio for the metallic glasses (compositions in at.%): (1) $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$; (2) $Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$; (3) $(Zr_{55}Al_{15}Ni_{10}Cu_{20})_{96}Y_4$; (4) $Zr_{65}Al_{10}Ni_{10}Cu_{15}$, (5) $La_{55}Al_{25}Cu_{10}Ni_5Co_5$; (6) $La_{66}Al_{14}Cu_{10}Ni_{10}$; (7) $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$; (8) $Cu_{50}Zr_{42.5}Ti_{2.5}Al_5$; (9) $Cu_{47}Zr_{47}Al_6$; (10) $Mg_{65}Cu_{25}Tb_{10}$; (11) $Mg_{65}Cu_{25}Gd_{10}$; (12) $Pr_{55}Al_{12}Fe_{30}Cu_3$; (13) $Pr_{60}Al_{10}Ni_{10}Cu_{20}$; (14) $Ce_{70}Al_{10}Ni_{10}Cu_{10}$; (15) $Nd_{60}Al_{10}Fe_{20}Co_{10}$; (16) $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$; (17) $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$; (18) $Zr_{41}Ti_{14}Cu_{12.5}Ni_2Be_{22.5}$; (19) $Zr_{48}Nb_8Cu_{14}Ni_{12}Be_{18}$; (20) $Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$. The straight line is the 1:1 correlation. The critical range for plastic/brittle behaviour (from Fig. 1, $(\mu/B)_{crit} = 0.41$–0.43) is also shown.

Table 1
Values of the ratio of shear modulus μ to bulk modulus B and of the Poisson ratio ν for isotropic polycrystalline pure metals

	μ/B	ν
Au	0.12	0.44
Nb	0.22	0.40
Pd	0.24	0.39
Pt	0.27	0.38
Hf	0.27	0.37
Al	0.35	0.34
Cu	0.35	0.34
Zr	0.39	0.33
Ti	0.42	0.32
Ni	0.43	0.31
Ca	0.44	0.31
Co	0.45	0.30
Fe	0.48	0.29
Mg	0.49	0.29
Nd	0.50	0.28
La	0.52	0.28
Pr	0.52	0.28
Y	0.54	0.26
Tb	0.57	0.26
Gd	0.58	0.26
Ce	0.61	0.25
Be	1.02	0.03

Data from Refs. [7,8].

with low μ/B, or equivalently high ν, are expected to favour plasticity rather than brittleness in the glass. Table 1 shows the large variation for common elements in BMGs: both μ/B and ν vary over roughly one order of magnitude. Among the elements considered, the noble metals are prominent among those favouring plasticity, Be clearly favours brittleness, while Ni, Fe and Mg are intermediate cases. The ability to predict μ/B for a metallic glass of given composition is potentially important for application of metallic glasses as engineering materials. In principle, compositions can be selected to have μ/B ratios so low as to ensure both plasticity and resistance to annealing-induced embrittlement.

4. Conclusions

For BMGs composed only of metallic elements, the shear modulus μ and bulk modulus B are found to scale linearly with an average of the moduli of the constituent elements in crystalline form. The correlation is especially good for averages based on volume fraction and when glasses containing Be are excluded. The predicted values of μ, B and average atomic volume are, respectively, 20% greater, 8% less and 1% greater than measured. Despite some scatter, the elastic properties of a metallic glass can be predicted sufficiently well to guide the selection of alloying elements (those with low μ/B or high Poisson ratio ν) to improve plasticity of the glass and enhance resistance to annealing-induced embrittlement.

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References

[1] P. Lowhaphandu, J.J. Lewandowski, Scripta Mater. 38 (1998) 1811–1817.
[2] J. Schroers, W.L. Johnson, Phys. Rev. Lett. 93 (2004), art. 255506.
[3] F. Guo, H.-J. Wang, S.J. Poon, G.J. Shiflet, Appl. Phys. Lett. 86 (2005), art. 091907.
[4] S.F. Pugh, Philos. Mag. 45 (1954) 823–843.
[5] J.J. Gilman, Electronic Basis of the Strength of Materials, CUP, Cambridge, 2003.
[6] J.J. Lewandowski, W.H. Wang, A.L. Greer, Philos. Mag. Lett. 85 (2005) 77–87.
[7] Smithells Metals Reference Book, Butterworth–Heinemann, Oxford, 1992.
[8] http://www.webelements.com.
[9] W.H. Wang, P. Wen, Y. Zhang, M.X. Pan, R. Wang, Appl. Phys. Lett. 79 (2001) 3947–3949.
[10] L. Battezzati, M. Baricco, J. Less-Common Metals 145 (1988) 31–37.