LETTER TO THE EDITOR

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Letter to the Editor

Elastic moduli and behaviors of metallic glasses

W.H. Wang *

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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Abstract

We report apparent correlations among the elastic moduli, fracture strength, Vicker's hardness and glass transition temperature for various and available metallic glasses with marked different elastic and mechanical properties. In particular, an attempt is made to link the observed correlations with glass transition, relaxation and glass-forming ability. The clear correlations imply that the physical properties of glasses would be better controlled by selection of elements with suitable elastic moduli as constituents.

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The nature and behaviors of glasses as well as the glass formation are central issues in condensed matter physics and material science. Substantial progress has been made in understanding the glasses, yet many key questions remain [1]. Elastic moduli are apparently important parameters for the general understanding of the structural characteristics, mechanical properties and glass transition in metallic glasses [2–6].

Theoretically, the Young's modulus E correlates with fracture tensile strength, σ of a material as [1]: $\sigma = \left(\frac{E\gamma}{d}\right)^{1/2}$, where γ is the surface energy per unit area, and d is the spacing of parallel atomic planes. For normal solids, σ is estimated to be about $E/5$–$E/10$ [1]. However, the practical fracture strength, σ for crystalline metallic materials are much lower than the theoretical values. The factors determining fracture strength have no simple link with interatomic potentials, yet there is a rough correlation between E and σ: $E/\sigma =$ 500–10000. The correlation provides evidences for the existence of defects such as dislocations in crystalline alloys and assists in understanding the relation between microstructure and mechanical properties.

By careful selection of composition some alloys now can be cast into *bulk metallic glasses* (BMGs) with a minimum dimension of $\geqslant 1$ mm at low cooling rates ($<10\ \mathrm{K\,s^{-1}}$) [4–6]. The availability of various BMGs has permitted better characterization of their mechanical and elastic properties, and significant data have been collected on the mechanical properties (e.g. fracture strength and toughness, Vicker's hardness, H_v), glass formation and elastic constants for various metallic glasses [4–6]. It would be intriguing to see if there exists a similar relation between mechanical behaviors and elastic properties in glassy alloys.

Primary analysis based on limited data from metallic glasses show that the strength normalized with respect to E [5,7]. However, a clear insight into the reasons for such a correlation was not presented. At present there is very active development of new compositions for forming BMGs [6]. For example, the Ce-based BMGs have low E value (~30 GPa, is comparable to those of polymers) [8] and Co-based glassy alloy exhibits ultrahigh fracture strength (5185 MPa) and high E (268 GPa) [9]. Sufficient data on elastic moduli,

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* Fax: +86 10 82640223.
E-mail address: whw@aphy.iphy.ac.cn

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mechanical properties and glass transition are now available to permit a better assessment for metallic glasses by establishing links among mechanical behaviors, glass formation, and elastic moduli.

In this letter, we tried to collect available relevant data on metallic glasses to show that there are remarkably good correlations among mechanical behavior, elastic modulus and glass transition temperature. We have tempted to exploit the significance and the fundamental origins of these correlations observed.

BMGs exhibit isotropic elastic constants that can be determined from the longitudinal and transverse sound velocities [6,10]. The elastic constants for metallic glasses were obtained via ultrasonic measurements (or obtained directly from literature sources). The experimental accuracy is better than 5% for the elastic constants. Values of fracture strength, H_v and glass transition temperature T_g were directly taken from literature sources. The scatter in strength data for identical tests on nominally identical materials is typically less than 10% [5].

Table 1 lists all available relevant data on typical metallic glasses we are able to find in the literatures (including almost all kinds of developed BMGs based on different elements with representative composition). Even though the original data are obtained from different groups with various testing conditions, the data on these metallic glasses, plotted in Fig. 1(a) and (b), show clear good correlations between fracture strength σ and E ($E/\sigma \approx 50$), and H_v and E ($E/H_v \approx 20$). Fig. 2 exhibits the relation between H_v with σ for these glasses. The H_v and σ, as expected, show a remarkable good correlation as: $H_v = 2.5\sigma$. There may be some composition-dependent spread in the correlation, but it is remarkable that the spread is so small and certainly much less than for that of the crystalline materials. As mentioned above, a similar linear relation is also evident for ordinary crystalline alloys. However, for these glasses, E/σ is 50, which approximately 10–200 times larger than those of their crystalline counterparts and is close to the theoretical strength (about $E/5$–$E/10$) [1]. This indi-

Table 1
Data of E, α, H_v, and T_g collected on representative metallic glasses (all compositions in at.%)

Glasses	σ (GPa)	H_v (GPa)	E (GPa)	T_g (K)	Refs.
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	1.8	5.233	101	620	[4,6]
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	1.83	6.1	100	623	[4,6]
$Zr_{65}Al_{10}Ni_{10}Cu_{15}$	1.45	5.6	83	652	[5,6]
$Zr_{52.25}Cu_{28.5}Ni_{4.75}Al_{9.5}Ta_5$	1.909	–	90	705	[20]
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	1.77	5.4	82	657	[21,6]
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	1.8		87.3	687	[22,6]
$Ti_{50}Cu_{23}Ni_{20}Sn_7$	1.3		85.3	681	[23]
$Ti_{50}Ni_{24}Cu_{20}B_1Si_2Sn_2$	2.1	6.1	110	726	[24]
$Cu_{60}Zr_{40}$	1.92		107	733	[25]
$Cu_{50}Zr_{45}Al_5$	1.89	5.35	102	701	[26]
$Cu_{55}Zr_{30}Ti_{10}Co_5$	2.31		130	714	[5]
$Cu_{60}Hf_{30}Ti_{10}$	2.16		124	725	[5]
$Cu_{60}Hf_{10}Zr_{20}Ti_{10}$	1.95	7	101	754	[12,6]
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	1.52	5.0	98	560	[5,6]
$Pd_{77.5}Si_{16.5}Cu_6$	1.55	4.5	96	630	[27,28]
$Pd_{40}Ni_{40}P_{20}$	1.7	5.3	108	583	[28–30]
$Pd_{80}Si_{20}$	1.34		70	607	[27–30]
$(Fe_{0.75}B_{0.2}Si_{0.05})_{96}Nb_4$	3.16	10.5	180	835	[31]
$[(Fe_{0.8}Co_{0.2})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4.17	12.0	205	830	[31]
$Fe_{61}Zr_8Y_2Co_6Mo_7Al_1B_{15}$		11.4	222	899	[32]
$Ni_{45}Ti_{20}Zr_{25}Al_{10}$	2.37	7.75	114	733	[33]
$Ni_{40}Cu_5Ti_{17}Zr_{28}Al_{10}$	2.3	8.45	133.9	762	[33]
$Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$	5.185		268	910	[9]
$W_{46}Ru_{37}B_{17}$		16.8	309	1151	[11]
$Mg_{65}Cu_{25}Gd_{10}$	0.834		56	417	[34]
$Mg_{65}Y_{10}Cu_{15}Ag_5Pd_5$	0.77		59	437	[35]
$Mg_{65}Cu_{20}Y_{15}$	0.82	2.6	69	420	[34]
$La_{55}Al_{15}Ni_{10}P_{20}$	~0.5	3	41		[5,6]
$Ce_{60}Al_{10}Ni_{10}Cu_{20}$	0.40	1.5	30	337	[8,12]
$Nd_{60}Al_{10}Fe_{20}Co_{10}$	0.45	2.2	51	493	[5,6]
$Pt_{60}Ni_{15}P_{25}$		4.1	96	485	[28]
$Pt_{60}Cu_{16}Co_2P_{22}$	1.1	4.02	~96	506	[37]
$Al_{88}Ni_9Ce_2Fe_1$	1.35		~70		[1]
$Ca_{65}Ag_{35}$		1.5	20	400	[36]
$Ca_{57}Mg_{19}Cu_{24}$	0.545		38	387	[36]

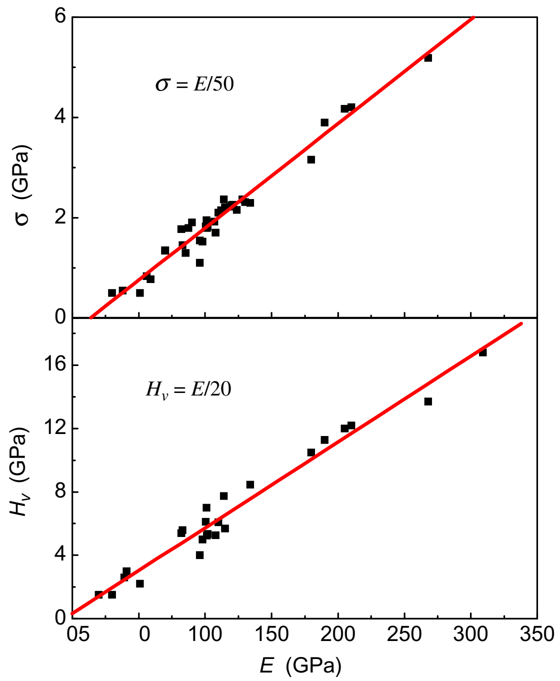

Fig. 1. The correlation of mechanical strength σ with elastic modulus E for all the metallic glasses for which relevant data are available.

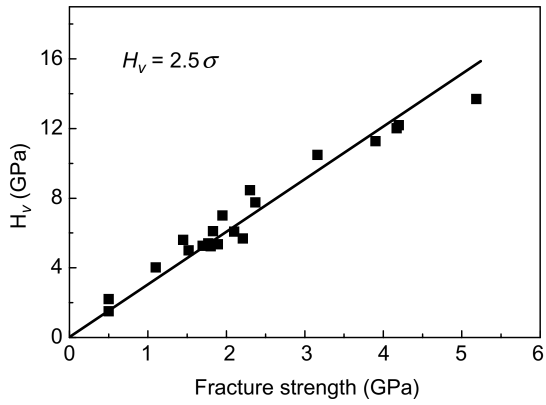

Fig. 2. The correlation of the elastic modulus E with mechanical strength σ for all the metallic glasses for which relevant data are available. The line is the guidance for eyes.

cates the fundamental mechanical properties of the metallic glassy materials are significantly different from those of crystalline alloys. The correlation is remarkably good as that found when comparing different glasses, as can be seen when all the data on various metallic glasses prepared by different methods with marked different properties are combined (Table 1). For example, with the lowest values of E, the glasses based on Ca, Pr and Ce, all have strength well below 500 MPa [6,8]. With high E the Co- and Fe-based BMGs have strength well in excess of 4000 MPa [9]. Recent reports of tungsten-based glasses [11] with extreme high E (=309 GPa) and exceptionally stronger mechanical properties than those of any metallic glasses so far reported fit well on the same correlation. The results suggest that the existence of the positive correlation does not depend on the chemical composition of the glasses but should be related to the intrinsic homogeneous glassy structure. Overall, it would appear that glassy alloys are more strength than their crystalline counterparts, and the high strength is intrinsic in glass and closely related to their elastic properties.

In parallel with this work, the fracture of metallic glasses, in relation to ratio of the bulk modulus B to the shear modulus μ (or Poisson's ratio v) has been studied [12]. The B/μ correlates with toughness, e.g. the intrinsic plasticity or brittleness of metallic glasses correlates with B/μ: high B/μ favors plasticity and vice versa. The good correlation between E and σ is regarded as to be a reflection of the similarity in the deformation and fracture mechanism between the various metallic glasses with marked differences in toughness. Furthermore, it is also shown a clear correlation between the fracture toughness and plastic process zone size for various glasses. Combining all above correlations, it might conclude that the metallic glasses precede a similar fracture mechanism even though they show marked different mechanical properties. At least, these correlations may assist in understanding the mechanisms of plastic flow and fracture in metallic glassy systems.

Fig. 3 shows there is empirical correlation between E of the metallic glasses and T_g ($T_g \propto 2.5E$). The similar correlation has also been reported in silica and other glasses [13,14]. Thus, the correlation between strength and E can also be expressed in terms of T_g. Higher value of T_g gives higher strength. In fact, there is a clear tendency for σ to increase with increasing T_g. Recent reports of tungsten-based metallic glasses [11] with exceptionally high strength and high T_g (1174 K) and

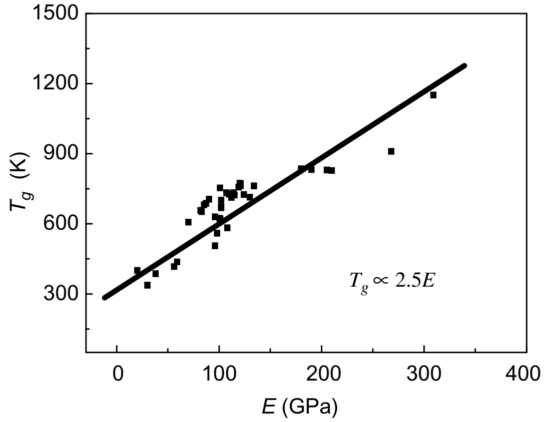

Fig. 3. The correlation of the elastic modulus E with glass transition temperature T_g for all the metallic glasses for which relevant data are available. The line is the guidance for eyes.

soft Ce-based BMG [8] with exceptionally low T_g (337 K) and σ fit well on the tendency. It is generally known that the T_g is dominated by the bonding force among the constituents, Consequently, the high mechanical strength of the metallic glasses is due to the stronger bonding force among the constituent elements. It is known that shear modulus μ which depends on the interatomic distance and especially the repulsive branch of the interatomic potential, is closely related to the melting temperature, T_l [15]. A good rule of thumb, associated with the ratio of T_g and T_l, has for many years been proposed for evolution of glass-forming ability by Turnbull [16]: that is, good metallic glass formers require T_g/T_l to be higher than 0.67. It is successful empirical rule for finding new metallic glass system [4–6]. The T_g and T_m themselves are correlated with E and μ respectively. That indicates the glass-forming ability is in connection with the elastic property in glass-forming system. Experimental results show that elastic property indeed correlates with glass-forming ability [10]. The vitrification of a metallic liquid is often characterized by the thermodynamic and kinetic criterions, so the correlation would provide a new route for metallic glasses design.

More intriguingly, we note that the very basic elastic property: the relative strength of shear and bulk moduli B/μ or alternatively Poisson's ratio ν, can be a measure of fragility, m of a glass-forming liquid. Analysis of experimental data reveals correlation of B/μ to m as in equation [17]: $m = 29(B/\mu - 0.41)$. The correlation found emphasizes a simple rule: the better the glass can resist deformation, the stronger the behavior that is exhibited during its structural relaxation. The correlation implies that the degree of the non-Arrhenius liquid viscosity is determined by its elastic properties. Therefore, the correlation found would lead to the factors that determine m of a metallic glass-forming system in its solid state. Because the B/μ correlates with toughness as indicated above, the fragility can be correlated with toughness. This phenomenon implies that the properties and structure of a metallic glass are essentially those of a frozen liquid.

Thus above results imply that the microscope elastic constants in metallic glasses appear to be important parameter that monitor or control the fracture, relaxation, glass-forming ability and even fragility of glass-forming liquid. Interestingly, on the other hand, the elastic constants of metallic glasses show a good correlation with a weighted average of the elastic constants for the constituent elements as: $M^{-1} = \sum f_i M_i^{-1}$, where M is elastic constants and f_i the atomic percentage of component [8,18,19]. So consideration of elastic moduli can assist in selecting alloying component for controlling the elastic moduli and then glass-forming ability, fragility, relaxation, and mechanical properties, all are the key concerns for metallic glasses. This can guide future alloy development. At present, the development of new BMGs has always been 'hit or miss' whether the resulting glass has excellent glass-forming ability or would turn out to be excellent in mechanical properties, while the search for glass-forming compositions follows well established guidelines [4,5]. The established clear correlations, associated with elastic moduli and since the moduli of glasses scale with those of their elemental components, may provide useful guidelines for the development of new BMGs and control their physical properties by selection of elements with suitable elastic moduli as constituents.

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