Thermodynamic Origins of Shear Band Formation and the Universal Scaling Law of Metallic Glass Strength

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We report a universal scaling law, $\tau_y = 3R(T_g\text{-RT})/V$, that uncovers an inherent relationship of the yield strength τ_y with the glass transition temperature T_g and molar volume V of metallic glasses. This equation is derived from fundamental thermodynamics and validated by various metallic glasses with well-defined yielding. The linearity between τ_y and T_g demonstrates the intrinsic correlation between yielding and glass-liquid transition, which contributes to the basic understanding of the strength and deformation of glassy alloys.

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One of the most attractive merits of glassy alloys is their ultrahigh strength relative to the crystalline counterparts [1–3]. Unlike dislocation slip in crystals, the room-temperature (RT) yielding and deformation of metallic glasses occur via the formation of nanosized shear bands [3–10]. A number of micromechanisms have been proposed to describe the spatially and temporally heterogeneous deformation. However, the physical process that governs the yielding and strength of glassy alloys still remains mysterious and has been the recent topic of intense discussion [3,6–9]. It was noticed a long time ago that the strength and Young's modulus of metallic glasses correlate with their glass transition temperatures, T_g [11–14]. By incorporating the term of molar volume V, the RT fracture strength of bulk metallic glasses (BMGs) has been found to have a linear relation with T_g [15]. A number of attempts have been made to explore the underlying physics of the linearity [15–17]. However, these works usually resort to a number of approximations and assumptions making their analysis untransparent. Consequently, the physical principle of the correlation between the strength and glass transition temperatures of BMGs remains to be known. In this report, we derive a universal scaling law from the fundamental thermodynamics and uncover the thermodynamic origin of shear band formation and BMG yielding.

Fifteen BMGs used in this study cover five typical alloy systems, including Zr-based, Cu-based, Ti-based, Ni-based, and Fe-based BMGs. All of them show pronounced plastic flow and thus the well-defined yield points can be determined from stress-strain curves. The glassy nature of the samples was ascertained by x-ray diffraction. Some of them were further inspected by transmission electron microscopy. Thermal analysis was performed by using a differential scanning calorimeter and differential thermal analyzer with a heating rate of 20 K/ min. Compressive specimens with an aspect ratio of 2:1 were cut from as-cast 2-mm-diameter rods. Since sample alignment as well as stress concentrations in compression testing can significantly affect yield stress and compressive plasticity [18], the two ends of the specimens used in this study were carefully polished to be flat parallel and normal to the axis of the rods. RT compression tests were carried out with a nominal strain rate of 1×10^{-4} or 5×10^{-4}/s.

Figure 1(a) shows the examples of stress-strain curves of three BMG samples. The other 12 BMG samples also have comparable or even larger plastic strains. The considerable plastic deformation of these samples allows us to precisely measure the yield points of the 15 alloys. As illustrated in Fig. 1(b), the yield strength that corresponds to the formation of a principal shear band is determined by the crossover point from elastic to plastic portions with a very small offset of 0.05%. Mechanical properties including yield strength σ_y and Young's modulus E along with thermal properties such as T_g and melting temperature T_m are summarized in Table I. The values of molar volumes V of the BMGs in the table are calculated according to the rule of mixtures [19]. To reveal the relationship between strength and T_g, we plot the yield shear stress, $\tau_y \approx \sigma_y/2$, as the function of $(T_g\text{-RT})/V$ and ignore the trivial normal stress dependence [10,20,21]. As shown in Fig. 2, the RT yield shear strengths of the 15 BMGs show a distinct dependence on $(T_g\text{-RT})/V$ in a linear manner.

In this study the well-defined yield strength spanning from ~1.7 to ~4.0 GPa is used for analysis. It is known that RT yielding of BMGs corresponds to the formation of a principal shear band when the critical shear stress that a material can sustain is reached [3,4]. According to recent experimental observations and computer simulations, the yield point of BMGs corresponds to the destabilized propagation by the percolation of a large number of local shearing events with a critical shear strain, γ_0 [5,8,9,15]. The transition from local shearing to macroscopic shear bands results from the dramatic increase of the atom mobility and softening along a shear plane motivated by the input of

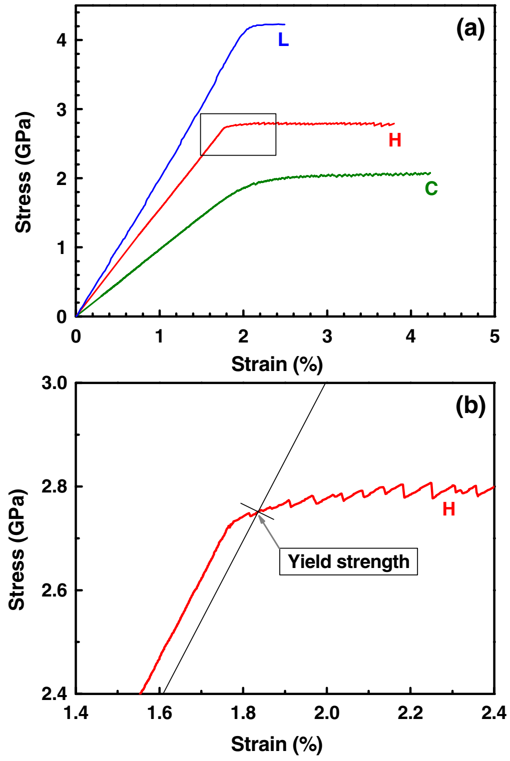

FIG. 1 (color online). (a) Three representative engineering stress-strain curves of the BMGs with obvious plastic deformation and evident yield points. (b) The enlarged portion of Curve *H* in (a) illustrating the determination of yield stress. The symbols (***C***, ***H***, and ***L***) in the figure correspond to the alloys given in Table I.

mechanical energy [22–24]. Thus, the transition is akin to a process of stress driven glass-to-liquid transition [17,22–25] and the yielding of BMGs can be rationally presumed as a critical point at which the accumulated internal energy by elastic deformation is high enough for the transition from a glass to a supercooled liquid. Starting from the fundamental laws of thermodynamics, we have $dU = dQ + dW$, where dU is the increase of the internal energy, dQ is the heat added to the system, and dW is the work done to the system. Because the formation of principal shear bands mainly depends on shear stresses, not pressure [20,21], it only leads to a sample shape change, not volume change. Thus, this process can be considered to be isochoric, i.e., $dW = V_s \gamma_0 d\tau$, in which V_s is the volume that undergoes the transition; τ is the shear stresses applied to the shear band, and γ_0 is the critical shear stain leading to the destabilization of local shearing events. The change of the internal energy in the isochoric system can be expressed by $dU = \rho V_s C_v dT$, where ρ the density, C_v is the mass specific heat, and dT is temperature increment. Since the time for the initiation of the shear band is extremely short, the yielding can be fairly viewed as an adiabatic process [26]. Moreover, the heat change caused by the pseudo-second-order glass transition is insignificant compared to the work done by applied force [27]. Thus, dQ can be ignored and the work is considered to completely transfer as the internal energy. Therefore, we have

$$V_s \gamma_0 \int_0^{\tau_y} d\tau = \rho V_s \int_{\mathrm{RT}}^{T_g} C_v dT. \tag{1}$$

Neglecting the weak temperature dependence of mass heat capacity from RT to T_g [27], by integrating the equation we can obtain

$$\tau_y = \rho C_v (T_g\text{-RT})/\gamma_0, \tag{2}$$

where $C_v = c_v/M$ with c_v the molar specific heat at a constant volume and M is the molar weight. Owing to the average molar volume of the BMGs $V = M/\rho$, we thus get

$$\tau_y = c_v (T_g\text{-RT})/(\gamma_0 V). \tag{3}$$

According to the Dulong-Petit law, the value of c_v at RT

TABLE I. Summary of yield strength σ_y, Young's modulus E, glass transition temperatures T_g, and calculated molar volume V of 15 BMGs from 5 alloy systems.

Label	BMG	σ_y (GPa)	E (GPa)	T_g (K)	T_m (K)	V (mm^3/mol
A	$Zr_{62}Cu_{15.4}Ni_{12.6}Al_{10}$	1.812	80	652	⋯	11 666
B	$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$	1.817	96	673	⋯	11 669
C	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	1.755	97	620	932	9949
D	$(Cu_{0.5}Zr_{0.5})_{95}Al_5$	1.824	90	693	⋯	10 570
E	$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	2.160	107	754	1128	9504
F	$(Ti_{0.5}Cu_{0.5})_{84}Ni_7Hf_5Zr_3Si_1$	2.254	105	687	⋯	9136
G	$Ni_{62.5}Zr_{20}Nb_{15}Pd_{2.5}$	2.808	150	867	1368	8792
H	$Ni_{60}Zr_{20}Nb_{15}Pd_5$	2.752	148	873	1353	8850
I	$Ni_{57.5}Zr_{20}Nb_{15}Pd_{7.5}$	2.717	146	870	1351	8907
J	$Ni_{55}Zr_{20}Nb_{15}Pd_{10}$	2.714	146	864	1349	8965
K	$Ni_{52.5}Zr_{20}Nb_{15}Pd_{12.5}$	2.705	145	861	1352	9023
L	$[(Fe_{0.8}Co_{0.1}Ni_{0.1})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4.177	208	818	⋯	6945
M	$[(Fe_{0.6}Ni_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4.014	203	770	⋯	6864
N	$Fe_{76}Si_{9.6}B_{8.4}P_6$	3.212	165	783	1271	7964
O	$(Fe_{0.76}Si_{0.096}B_{0.084}P_{0.06})_{99.9}Cu_{0.1}$	3.225	158	785	⋯	7956

and above is approximately equal to a constant, i.e., $c_v = 3R = 24.94$ J/mol · K (R is gas constant) for metals regardless of their crystal structures. Additionally, the Dulong-Petit law has been found to persist in BMGs [27]. Therefore, the equation can be expressed as

$$\tau_y = 3R(T_g\text{-RT})/(\gamma_0 V). \tag{4}$$

In Fig. 2, we plot the relationship between τ_y and $(T_g\text{-RT})/V$ as the solid line. As one can see, Eq. (4) fits the experimental results well, verifying that there is an intrinsic correlation between the yield strength of BMGs and their glass transition temperatures. It is interesting to note that the fitting slope is just equal to the Dulong-Petit limit $3R$ while γ_0 is equal to 1. In comparison of Eq. (4) with the empirical relation found by Yang *et al.* [15], one can easily find that the slope of 50 in their study is actually the product of Dulong-Petit limit $3R$ and the Schmid factor 2, both of which are invariable for BMGs. It is important to mention that the scaling law has been derived based on the fundamental thermodynamics without the employment of any microscopic model. Thus, the current derivation does not involve all the assumptions and approximations concerning the microscale process [15–17].

On the basis of Eq. (4), we can deduce the correlation among Young's modulus E and T_g, which has been widely discussed in the literature [11–14]. Since $E = \sigma_y/\varepsilon_E = 2\tau_y/\varepsilon_E$ and the RT elastic limit (ε_E) of BMGs is approximately 2%, we can thus get

$$E = 3R(2/\varepsilon_E)(T_g\text{-RT})/V. \tag{5}$$

Figure 3 illustrates the relationship between E and T_g, in which the solid line is the plot of E vs $(T_g\text{-RT})/V$ with the slope of $3R(2/\varepsilon_E)$. Again, the experimental results remarkably follow the prediction, which further validates the scaling law by another macroscopic variable.

The yielding of BMGs by the formation of principal shear bands and subsequent strain softening has been attributed to dramatic temperature rise that is closely related to the magnitude of the shear offset [17,22]. Moreover, the unique fractographs of metallic glasses, i.e., vein patterns and liquid droplets, have led to the assumption that the shear band destabilization is associated with the melting of BMGs [28]. Through the scaling law, we can clarify whether the shear band formation is controlled by glass transition or by melting. On the basis of Eq. (4), if the yielding is controlled by melting, we can simply replace T_g by T_m and obtain the equation

$$\tau_y = 3R(T_m\text{-RT})/V. \tag{6}$$

This equation suggests a linear relation between τ_y and T_m/V with a slope of $3R$. Alternatively, it is well known that glass transition of bulk glass formers often takes place at a temperature of about $0.6T_m$ [29]. According to Eq. (4), the correlation between melting temperature T_m and BMG strength can be described by

$$\tau_y = 3R(0.6T_m\text{-RT})/V. \tag{7}$$

Apparently, the main difference between Eqs. (6) and (7) is the slopes of τ_y vs T_m/V plots. As shown in Fig. 4, Eq. (7) fits the experimental data very well with the slope of $1.8R$, not $3R$ suggested by the Eq. (6), unequivocally demonstrating that the yielding of BMGs is intrinsically associated with glass transition, not melting.

For dislocation-free crystals, the shear strength is solely determined by interatomic potentials for cooperative shearing of periodic crystal lattices and has been estimated to be $\sim G/5$ by Frankel [6]. Although metallic glasses are also dislocation-free materials, their shear strength is only $\sim G/30$ due to the existence of free volumes, where the constituent atoms have a low atomic coordination, produced by local geometrical frustrations in the disordered

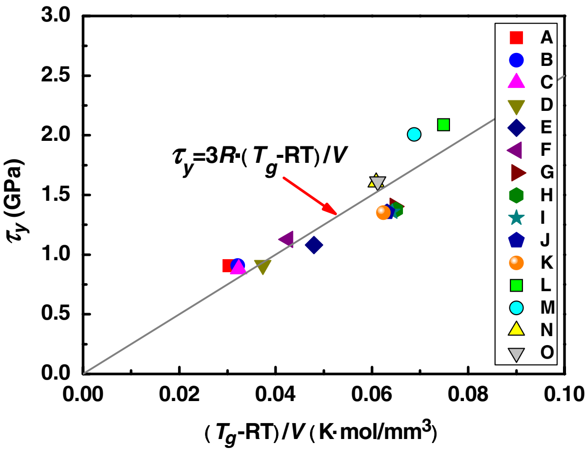

FIG. 2 (color online). The relationship between yield shear stress τ_y and glass transition temperature T_g. The solid line is the plot of Eq. (4), $\tau_y = 3R(T_g\text{-RT})/V$, in which R is the gas constant.

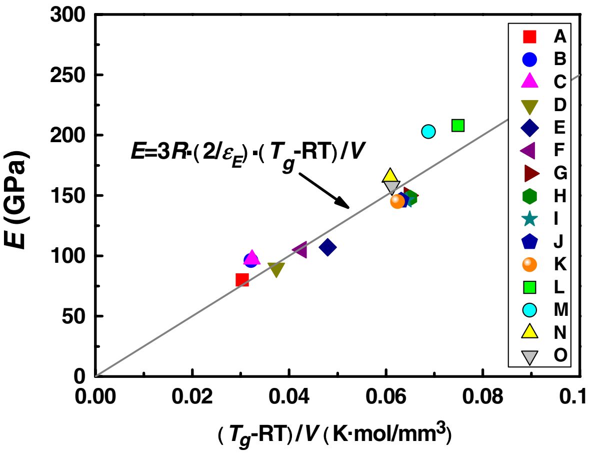

FIG. 3 (color online). The relationship among Young's modulus E and glass transition temperture T_g. The solid line is the plot of equation $E = 3R(2/\varepsilon_E)(T_g\text{-RT})/V$, in which R is the gas constant and ε_E is the elastic limit in uniaxial compression.

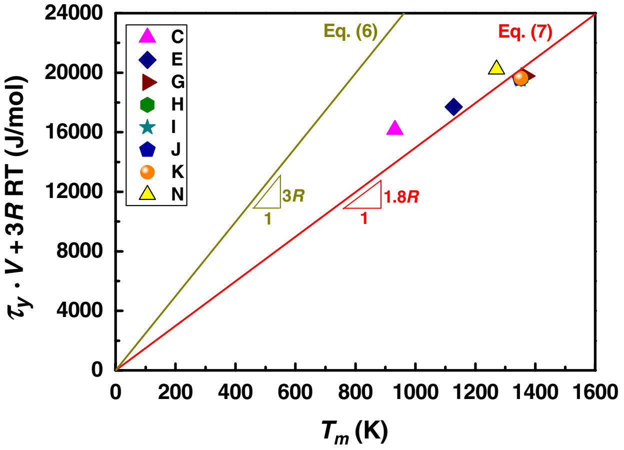

FIG. 4 (color online). The plot of ($\tau_y \cdot V + 3R \cdot \mathrm{RT}$) vs T_m for 8 BMGs. The slope of the left solid line is $3R$ according to equation $\tau_y = 3R(T_m\text{-RT})/V$, while that of the right line is $1.8R$ based on equation $\tau_y = 3R(0.6T_m\text{-RT})/V$.

solids [3–5]. In the free-volume regions, where mechanical coupling to the surrounding is weak, inelastic relaxation becomes possible by local atom rearrangements, without affecting the surroundings significantly. Thus, these sites are the preferred regions to initiate the destabilization of glassy structure caused by either temperature (glass transition) or applied shear stresses (local shearing). The linear correlation between τ_y and T_g evidently demonstrates that the strength of BMGs is controlled by a process of shear transformation, equivalent to glass transition, and thus the strength of BMGs is determined by the free volume or loose atomic packing regions. This is, in principle, consistent with all the microscopic models [4–6] on the heterogeneous plasticity of metallic glasses.

In summary, we have successfully derived a universal scaling law based on the fundamental thermodynamics and validated by various ductile BMGs. The linearity between yield strength and glass transition temperature unambiguously demonstrates that the elastic destabilization of metallic glasses driven by external forces is equivalent to the glass transition induced by mechanical energy, and that the strength of BMGs is governed by local geometrical frustrations and defects in the disordered solids. This universal strength equation has important implications in understanding the deformation mechanisms of disordered and nonequilibrium solids and in designing new glassy alloys with improved strength.

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