## Short-range-order effects on intrinsic plasticity of metallic glasses

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Online publication date: 30 March 2010

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# Short-range-order effects on intrinsic plasticity of metallic glasses

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Through a systematical analysis of the elastic moduli for 137 metallic glasses (MGs) and 56 polycrystalline metals, we use a simple model developed by Knuyt et al. [J. Phys. F: Met. Phys. 16 (1986) p.1989; Phil. Mag. B 64 (1991) p.299] based on a Gaussian distribution for the first-neighbor distance to reveal the short-range-order (SRO) structural conditions for plasticity of MGs. It is found that the SRO structure with dense atomic packing, large packing dispersion and a significant anharmonicity of atomic interaction within an MG is favorable for its global plasticity. Although these conditions seem paradoxical, their perfect matching is believed to be a key for designing large plastic bulk MGs not only in compression but also in tension.

**Keywords:** plasticity; metallic glass; short-range-order; elastic modulus

## 1. Introduction

Intrinsic plasticity of bulk metallic glasses (BMGs) has received much attention due to their potential engineering applications [1–6]. Most BMGs show limited room-temperature ductility in compression and near-zero ductility in tension [7–12]. However, by the modification of alloy compositions or careful control of the fabrication process, several BMGs (e.g. Pt-, Cu-, Zr- and Fe-) have been found to exhibit pronounced global compressive [13–17] and even tensile plasticity [18,19]. Their plasticity is attributed to a unique structure correlated with atomic-scale inhomogeneity or free volume, leading to an inherent capability to form multiple shear bands analogous to slip systems seen in their crystalline counterparts. Recently, Wang et al. [20] have found that smaller molar volume or higher packing density should also be beneficial for plasticity in MGs. It is well known that the plasticity of polycrystalline metals decreases sequentially with the lattice type of their grains: face-centered cubic (fcc), body-centered cubic (bcc) and hexagonal close-packed (hcp) [21]. This implies that the more slip systems, directions and the higher atomic packing density favor plasticity of crystalline materials. It seems that plastic BMGs and crystalline metals could share similar atomic structures, at least over the short-range-order (SRO) scale. Previous studies [22–26] have identified solute-centered clusters as the SRO or the fundamental building blocks. As we know,

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the SRO atomic structure can determine the elastic moduli of materials, and the contributions of the atomic configuration farther than the SRO – that is, out of the range of the interatomic potential – are slight and can be ignored [27–30]. Actually, Poisson's ratio criterion for plasticity has been widely validated in both MGs [1,2,5,6] and crystalline metals [31,32]. It is therefore anticipated that the elastic moduli would build a bridge between intrinsic plasticity of BMGs and their SRO structures, which has not been analytically discussed.

In this work, based on systematical statistics of elastic moduli of 137 MGs and 56 polycrystalline metals, we use a simple model developed by Knuyt et al. [27,28] to elucidate how the SRO structure quantitatively affects the intrinsic plasticity of BMGs in terms of the bulk-shear modulus ratio $K/G$. The implications for searching plastic BMGs are discussed briefly.

## 2. Experimental observations

Benefiting from the advent of more and larger MGs, sufficient experimental data of elastic moduli have been obtained. Figure 1a shows shear modulus $G$ versus Young's modulus $E$ for 137 MGs (Pd-, Cu-, Ni-, Zr-, rare earth (RE)-, Fe- and Mg-based) [1,2,5,6,33–43]. For comparison, 56 polycrystalline metals [44] (14 fcc, 15 bcc and 27 hcp lattice) are also included. One can see that their $G$ and $E$ exhibit a universal scaling relationship, i.e. $G/E = 0.39$, implying that the shear deformation is absolutely dominant and universal for both amorphous and crystalline metals [45–48]. However, their elastic moduli $K$ and $G$ do not show a clear linear relation (Figure 1b), and the data are rather scattered. This means that the bulk deformation is highly material dependent for the present metals [46,47]. It is interesting to note that the distribution of $(K, G)$ for ductile BMG systems (including Cu-, Pd-, Ni-, Zr- and few plastic Fe-based) is consistent with that for plastic fcc polycrystalline metals. Their data just reside in the region above the critical line of $K/G = 2.5$ (black line in Figure 1b) dividing plasticity from brittleness of various MGs proposed by Lewandowski et al. [1]. Since elastic moduli provide information about atomic structure of solids, such comparison should give us some clues for plasticity of MGs. In fact, the essential difference between crystalline and amorphous solids is that the latter lack long-range order, while both of them have almost the same SRO structure [49]. As mentioned above, the plastic fcc polycrystalline metals have the building block with the highest atomic packing density and the most slip systems [21]. Thus, it can be speculated upon that the plastic BMGs maybe having similar SRO of atomic bonding.

## 3. Short-range-order conditions for plasticity

To understand quantitatively the correlation between the SRO and the plasticity (here indicative of $K/G$) of MGs, we consider a simple model developed by Knuyt et al. [23,24] based on a Gaussian radial distribution function, RDF($r$), for the nearest-neighbor distance in an ideal unicomponent MG. The RDF is defined by a mean position $r_1$ and a width $\sigma_1$ for the atoms in the first shell around a central atom: RDF$(r) = (r/\sqrt{2\pi})[N_1/(r_1\sigma_1)] \exp[-(r - r_1)^2/(2\sigma_1^2)]$, where $N_1$ is the number of
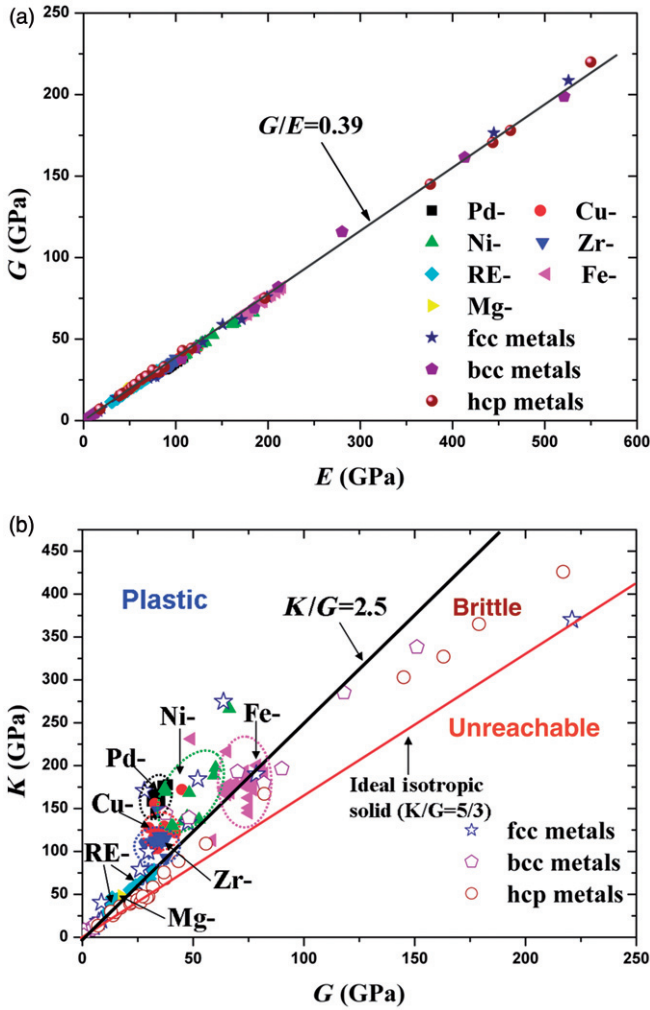
Figure 1. (Color online). (a) Shear modulus $G$ versus Young's modulus $E$ for 137 MGs and 56 polycrystalline metals and (b) their elastic moduli $K$ versus G. The black line is $K/G = 2.5$ dividing plasticity from brittle behavior of various MGs. The red line ($K/G = 5/3$) corresponds to ideal isotropic solids.

first neighbors that is about 12 for amorphous metals [50]. Atoms interact via a potential with harmonic and anharmonic terms written as $U(r) = a(r - r_m)^2 + b(r - r_m)^3$, where $a > 0$, $b < 0$, and $r_m$ is the position of the potential energy minimum. Based on this structural information, Knuyt et al. [27,28] derived the expression for the bulk modulus as $K = K_{un} + K_{re}$, where the first 'Born term', resulting from strictly uniform deformation of a material, is written as $K_{un} = aN_1 r_m^2 / 9V_{at}[1 + \eta(2 + 3p) + 3\sigma^2(1 + 3p)]$, where $V_{at}$ is the mean atomic volume, the parameters $\eta = (r_1 - r_m)/r_m$, $\sigma = \sigma_1/r_m$ and $p = br_m/a$ account, respectively, for the mean atomic position derivation from $r_m$, the mean atomic dispersion and

a measure of the anharmonicity of the potential; the second term due to the negative contribution of atomic rearrangement is $K_{re} = -2a\sigma^2 r_m^2(1 + 2p + 3p^2)/V_{at}$. Analogously, the shear modulus also includes the 'Born term' and the rearrangement term, that is, $G = G_{un} + G_{re}$ with $G_{un} = aN_1 r_m^2/15V_{at}[1 + \eta(7 + 6p)/2 + 3\sigma^2(8 + 15p)/4]$ and $G_{re} = -2a\sigma^2 r_m^2(8 + 9p)/(5V_{at})$. Details of the mathematical derivation are found in Refs. [27–29].

Using the bulk and shear moduli expressions, their $K/G$ can be obtained in terms of the structural parameters: $\eta$, $\sigma$ and $p$. For an isotropic solid with the absence of defects ($\sigma = 0$, $\eta = 0$) and anharmonicity ($p = 0$), $K/G \approx 5/3$, as marked by the red (online) straight line in Figure 1b. It is found that brittle MG systems and polycrystalline metals (bcc and hcp) almost localize in the region between the critical line of $K/G = 2.5$ and the line of ideal isotropic solid. For real materials, the region below the red (online) line is never attainable. Figure 2a shows the variation of $K/G$ when varying $\eta$ and $\sigma$ with a typical $p = -1.75$ [29] for MGs. We find that either decreasing $\eta$ or increasing $\sigma$ leads to the increase of $K/G$ in favor of plasticity for BMGs. Decreasing $\eta$ means that atoms pack more densely. Recent studies [20,51] have indeed revealed that glasses with higher atomic packing density usually have larger Poisson's ratio, corresponding to better plasticity. Increasing $\sigma$ corresponds to a greater topological disorder or equivalently introduces large amount of free volume, which actually is the most popular mechanism of enhancing the plasticity of BMGs [13–17]. Although enhancing plasticity via modification of Poisson's ratio can be effective, it was also noted that composite approaches can also be effective in increasing the toughness [18,52]. Furthermore, we find that more significant anharmonicity ($p = -2.00$) of atomic interaction can result in an extension of plastic region ($K/G > 2.5$), as marked in Figure 2b. The result agrees well with the molecular dynamics simulations of the fracture in a model MG, during which a clear ductile-to-brittle transition was found due to a slight reduction in anharmonicity of interatomic potential [53]. Now, we can conclude that the SRO structural conditions for plasticity of BMGs are

(1) atomic packing is denser;
(2) such packing is more disordered; and
(3) atomic interaction is more anharmonic.

If the constitution atoms are fixed, i.e. the anharmonicity is identical, brittle BMG systems should have larger mean distance $r_1$ and less disorder $\sigma_1$ for the first shell as shown in Figure 3a. Rather, plastic BMGs have the SRO with smaller $r_1$ and larger $\sigma_1$ as shown in Figure 3b. It must be pointed out that these structural conditions derived from theoretical approach can be directly determined using real X-ray or neutron diffraction experiment (*vide post*). The first sharp diffraction peak carries significant information ($r_1$ and $\sigma_1$) about SRO in MGs. Thus, the present analysis provides a useful guidance to fabricate plastic BMGs.

## 4. Discussion

However, the structural conditions for plasticity of BMGs, that is, higher atomic packing density (smaller $r_1$ or $\eta$) and more significant atomic dispersion
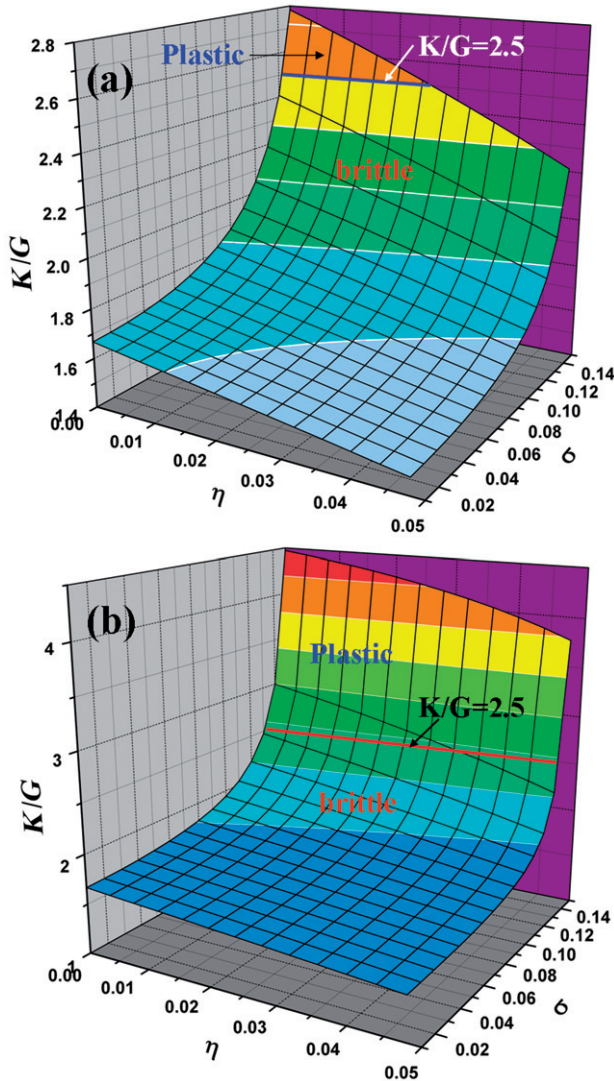
Figure 2. (Color online). The dependence of $K/G$ on mean position $\eta$ and atomic dispersion $\sigma$ of the first-neighbor shell with anharmonicity of interatomic potential, (a) $p = -1.75$ and (b) $p = -2.00$.

(larger $\sigma_1$ or $\sigma$), are difficult to satisfy simultaneously during the real experimental process. Higher density of atomic packing can be achieved by structural relaxation or by lowering cooling rate during glass formation, during which atomic disorder is reduced. Hence, a BMG becomes stiffer or harder. This is reflected in a change in the elastic constants and a decrease in Poisson's ratio and embrittlement as shown in Ref. [1]. However, the disordered packing of atoms implies that a BMG is soft. Often, we can obtain a soft BMG with disordered atomic packing by using higher cooling rate, during which more randomly distributed free volume is inherited from
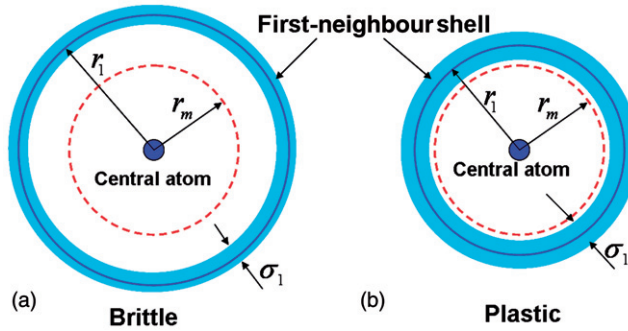
Figure 3. (Color online). Schematics of the first-neighbor shell in (a) brittle MGs with large mean position $r_1$ and little atomic dispersion $\sigma_1$ and (b) plastic MGs with small $r_1$ and large $\sigma_1$.
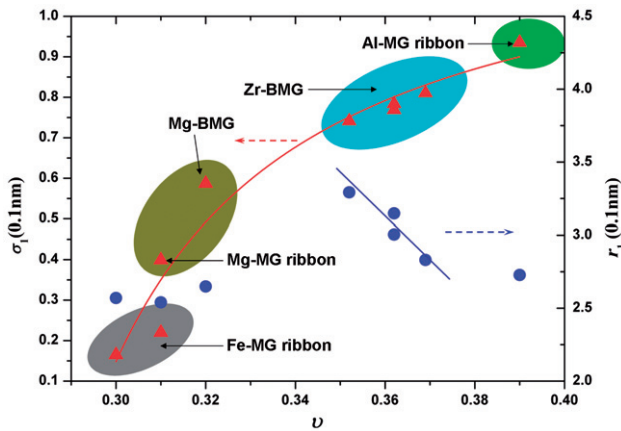


Figure 4. (Color online). Experimental atomic dispersion $\sigma_1$ and mean position $r_1$ of the first-neighbor shell for various MGs versus their Poisson's ratio $\nu$.

the liquid [13–17]. But such BMG systems have lower density of atomic packing, which is adverse to the plasticity. Fortunately, Figure 2 shows that $\sigma$ affects $K/G$ much more significantly than $\eta$, indicating that $\sigma$ or $\sigma_1$ is a dominant factor controlling the plasticity of BMGs. In order to validate this point, we plot $\sigma_1$ and $r_1$ obtained from experimental diffraction data versus Poisson's ratio $\nu$ on $Al_{87}Ni_7Nd_6$ MG ribbon [54], $Zr_{55}Cu_{35}Al_{10}$ BMG [55], $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ BMG [56], $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMG [57,58], $Mg_{60}Cu_{30}Y_{10}$ BMG [59], $Mg_{65}Cu_{35}$ MG ribbon [60], $Fe_{40}Ni_{40}P_{14}B_6$ MG ribbon [28] and $Fe_{80}B_{20}$ MG ribbon [28] in Figure 4 (only rough ranges are shown). It can be seen that there is an excellent correlation between $\nu$ and $\sigma_1$ (left $y$-axis), indicating that more plastic MGs with higher $\nu$ have larger disorder $\sigma_1$ of atomic packing. However, there seems no clear relation between $\nu$ and $r_1$ (right $y$-axis). For Zr-based BMGs with similar components [55–58], we note that, with increasing $\sigma_1$ facilitating plasticity, $r_1$ decreases (blue line (online) in Figure 4), which further improves intrinsic plasticity of BMGs. This is why the Zr-based BMGs show relatively good plasticity. Could we achieve the goal that a BMG holds the structure with small $r_1$ and large $\sigma_1$? So far, there have been two potential ways.

The first is by imposing high pressure on BMGs. In this case, the reduction in $r_1$ is dominant [51] and $\sigma_1$ almost does not change [29], resulting in an increase of the $K/G$ ratio (Figure 2). This is favorable for plasticity of BMGs, which is consistent with the experiments on pressure effects on MGs [8,12,61,62]. In the recent work of Caris and Lewandowski [12], tests without superimposed hydrostatic pressure exhibited zero compressive plasticity, while pressures in excess of 450 MPa produced significant compressive plasticity. The second feasible way is to separate BMGs into two parts: a hard region with high atomic packing density and a soft region with large atomic packing disorder. Recently, Liu et al. [16] synthesized a Zr-based BMG with extremely high compressive plasticity through the appropriate choice of composition under the direction of Poisson's ratio criterion [1]. Microstructural analysis indicates that the plastic BMGs are indeed composed of hard regions surrounded by soft regions. The hard and soft regions work cooperatively enabling BMGs to be plastic by forming multiple shear bands during loading. The soft–hard-region model for plasticity of BMGs has been validated by many experiments [63,64] and other analyses [5,65]. It is worth noting that the possibility of enhancing plasticity via larger scale composite approaches also exists, as shown elsewhere [18,52].

## 5. Conclusions

We suggest that plastic BMGs should meet the SRO structural characteristics: high atomic packing density, large disorder of packing and significant anharmonicity of interatomic potential. It is expected that a monolithic BMG may be very plastic not only in compression but also in *tension*, when a *perfect* balance among the above conditions is realized by careful selection of its compositions, controlling liquid–glass transition and temperature and/or mechanical treatments. Our findings may shed a quantitative insight into the atomic-scale mechanisms of macroscopic plasticity for BMGs. It must be pointed out that this work focuses on the SRO structural aspect of plasticity of BMGs. In fact, the bonding between SRO clusters, similar to grain boundaries in polycrystalline alloys, could also play a role in the plasticity of BMG, which deserves to be studied in future.

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