Correlations between elastic moduli and molar volume in metallic glasses

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We report clear correlations between bulk modulus (K) and average molar volume V_m, and between Poisson's ratio ν and V_m for various bulk metallic glasses. The origin for the correlations between elastic moduli and V_m are discussed. The established correlation, associated with Poisson's ratio ν, and since the ν correlates with plasticity of metallic glasses, indicates that the average molar volume is important factor to be considered for plastic metallic glasses searching. The found correlations also suggest a close relation between the mechanical properties and the short-range atomic bonding, and assist in understanding deformation behavior in metallic glasses. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3106110]

Metallic glasses show remarkable physical or mechanical properties,[1] such as good glass-forming ability,[2,3] low glass transition temperature,[4–6] high strength,[7] good plasticity,[8] and excellent magnetic properties.[9,10] However, due to the disordered structural characteristic of metallic glasses, there is so far no exact model and theory on their microscopic structure in spite of great efforts, and understanding the relationship between the properties and microstructure of metallic glasses is still a challenge. It is still rather vague how the structure affects the mechanical and physical properties. Nevertheless, the correlations between their features and properties are helpful for understanding the nature of glasses and smartly searching bulk metallic glasses (BMGs).[3–8] Some correlations among the thermodynamic, kinetic, elastic, and physical properties of metallic glasses indeed have been found during the past decade.[4–8,11–18] While with the development of more metallic glass systems with unique physical and mechanical properties, more and more data have been collected, which may permit more correlations to be found. Recently, it is found that density or molar volume has close relation with glass-forming ability, plasticity, and other properties for some BMGs.[17–21] Density or molar volume of an alloy can reflect the information of the microstructure, and the survey of elastic moduli versus density has ever been widely applied to various materials.[22] Therefore, it is interesting and intriguing to see if there are some correlations between density or molar volume and features or properties in BMGs. In this letter, based on systematical statistics of more than 50 typical BMGs, we find that the bulk modulus and even the ductility of BMGs correlate with their average molar atomic volume. The physical insight of the correlations is discussed. These correlations are useful for understanding the deformation mechanics in metallic glasses and searching plastic BMGs.

Rare earth (RE) elements are a typical group in periodic table with similar physical and chemical properties. The BMGs based on RE elements are also found to have some common characteristics in formation and properties.[7] The statistical survey of elastic moduli versus density is applied to RE-based BMGs.[4,6,7] Figure 1(a) shows bulk modulus (K) versus density (ρ) for 18 different kinds of RE-based BMGs. One can see that the data are quite dispersed, and K and ρ do not exhibit a clear correlation. However, when the abscissa is changed into average molar volume, V_m (V_m=molar mass/density), as shown in Fig. 1(b), the K and V_m show clear exponential correlation. To further verify the correlation, the survey is applied to much more different kinds of BMGs whose K and V_m data are available (including 54 kinds of Ca-, Mg-, RE-, Zr-, Cu-, Ni-, Fe-, Pt-, Pd-, and Au-based BMGs with markedly different mechanical and physical properties).[4–7,23] Figure 2 shows the relationships of K versus ρ [Fig. 2(a)] and K versus V_m [Fig. 2(b)]. Similarly, the K versus ρ is quite scattered, while their K and V_m show clear correlation for these markedly different BMG systems.

To understand the correlation, a physical analysis was performed on bulk modulus. The bulk modulus for a solid can be expressed as follows:[24] $K=\Omega_0(\partial^2 U/\partial\Omega^2)_{\Omega_0}$, where U

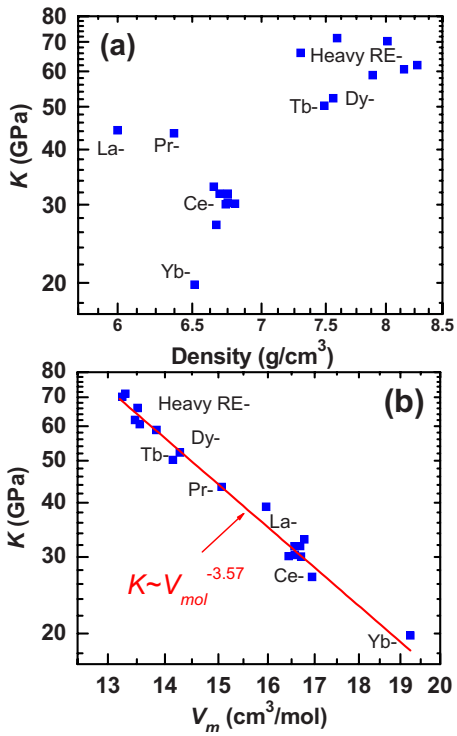

FIG. 1. (Color online) (a) Bulk modulus K of 18 kinds of RE-based BMGs (see Refs. 4 and 7) vs density. (b) The K vs V_m shown in logarithmic coordinates. The red line is the linear fitting data.

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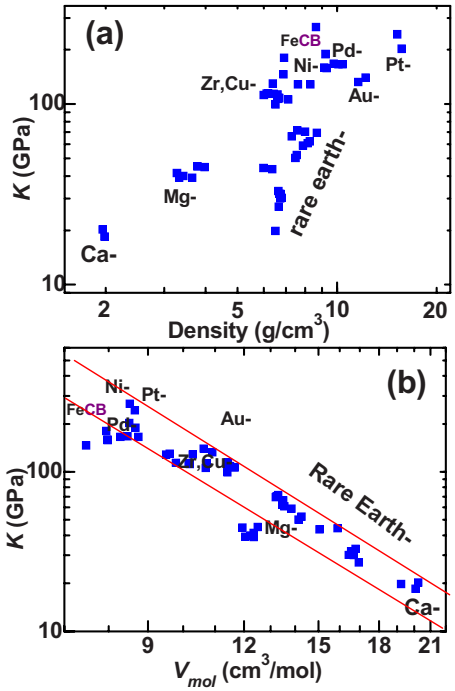

FIG. 2. (Color online) (a) K vs density for 54 kinds of various BMGs (including Ca-, Mg-, RE-, Zr-, Cu-, Ni-, Fe-, Pt-, Pd-, and Au-based BMGs) (Refs. 4–7 and 23). (b) The data of K vs V_m of the corresponding BMGs in logarithmic coordinates. The red line is the linear fitting data.

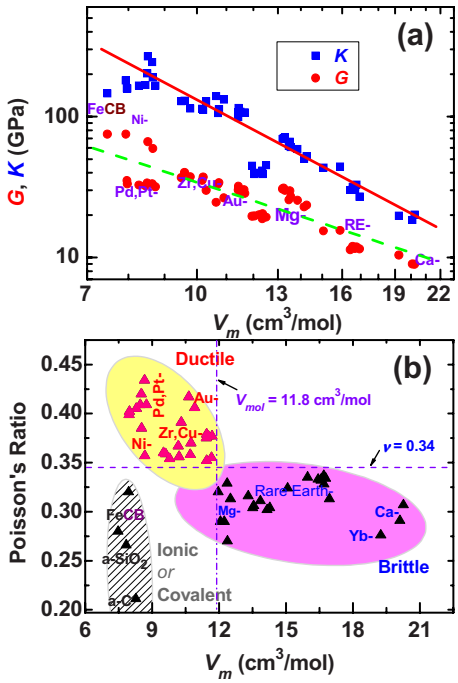

FIG. 3. (Color online) (a) A comparison for G vs V_m and K vs V_m for 54 kinds of BMGs. (b) The Poisson's ratio of various BMGs vs V_m. The critical values of ν=0.34 and V_m=11.8 cm^3/mol determine the toughness and brittleness in various BMGs.

is the potential energy, $U=(1/2)\Sigma z u_{ij}$; u_{ij} is the potential energy between two atoms of i and j, $u_{ij}=-Ar^{-n}+Br^{-m}=-A\Omega^{-n/3}+B\Omega^{-m/3}$, $\Omega=r^3$ is the atomic volume; Ω_0 is the equilibrium atomic volume, $V_m \sim N_A\Omega_0$, N_A is the Avogadro constant; A, B, m, and n are constants; and z is the number of near-neighbor atoms. The first term on the right-hand side of the u_{ij} equation represents the longer-range attractive energy and the second term represents the corresponding short-range repulsive energy. Minimum total potential energy is achieved when $\partial u_{ij}/\partial r|_{r=r_0}=0$. This induces $An/Bm=r_0^{-m+n}$. By substituting B with $B=An/mr_0^{-m+n}$, K can be expressed as $K=\Sigma_{ij}[An(m-n)/9]z\Omega_0^{-[(n+3)/3]}$, or $K \propto V_m^{-\alpha}$. From the data fit in Fig. 2(b), we get $\alpha \approx 2.6$ for these BMGs. Then, the exponent n $[\alpha=(n+3)/3]$ of the attractive part of the Lennard-Jones potential is estimated to be 4.8. This analysis confirms the correlation between K and V_m. Actually, the crystalline compounds with similar atomic structure and electronic physical properties share the same correlation in form of $K \sim \Omega_0^{-\alpha}$.[24] It is thought that the short-range order of BMGs is similar to the building block of crystals.[20] Then, the similar $K \sim V_m^{-\alpha}$ correlation existing in metallic glasses and crystals indicates that correlation derives from the short-range nature of atomic bonding.

As comparison, the relation between shear modulus G and V_m is also investigated and shown in Fig. 3(a). We can see that G also shows roughly correlation upon V_m for all the investigated BMGs systems, while K shows much stronger increase in tendency with decreasing of V_m. For the systems with smaller V_m, such as Pd-, Pt-, Zr-, Ni-, Cu-, and Au-based BMGs, the G is relatively smaller than that of the RE- and Ca-based BMG. The Poisson's ratio ν, which is equivalent to the ratio of K/G, has a clear correlation with plasticity of a BMG, and the correlation is a guidance for exploring tough BMGs.[14] The different changing tendency of K and G stimulates us to survey the relationship between Poisson's ratio ν and V_m among various BMGs. Figure 3(b) shows the data of ν versus V_m for various BMGs and some metalloid glassy materials. Remarkably, there is a clear trend that the BMGs with smaller V_m possess bigger ν. In the plasticity and ν correlation, there exists a critical value of ν=0.34 dividing plasticity from brittleness of various BMGs.[14] Below 0.34 or values for K/G less than approximately 2.5, the BMGs exhibit brittle behavior or low toughness, and higher values of ν give higher toughness and better plasticity. Surprisingly, a similar critical value of V_m (11.8 cm^3/mol) exists to determine the toughness and brittleness in various BMGs, which is in rather good consistence with that of the plasticity and Poisson's ratio correlation.[7,14] One can see from Fig. 3(b) that the cyan zone (including Mg-, RE-, and Ca-based BMGs) shows the brittle behavior characterized with smaller ν (<0.34) and bigger V_m (>11.8 cm^3/mol). The magenta-colored zone (including Pd-, Pt-, Zr-, Ni-, Cu-, and Au-based BMGs) contains the ductile systems that are characterized with bigger ν (>0.34) and smaller V_m (<11.8 cm^3/mol). The cyan-colored zone (including typical brittle glasses of amorphous-SiO_2, amorphous-carbon, and carbon or boron alloyed $Fe_{61}Mn_{10}Cr_4Mo_6Er_1C_{15}B_6$ and $Fe_{53}Cr_{15}Mo_{14}Er_1C_{15}B_6$ BMGs)[25] containing the covalent/ionic bonding amorphous materials is characterized with smaller V_m (V_m <11.8 cm^3/mol) but smaller ν (ν<0.34). The result indicates that the plasticity of BMGs could be related to V_m.

The plausible correlation between V_m and plasticity could be understood based on the elastic moduli of BMGs. The value of G is a key parameter that determines the flow in glasses,[15] while K represents the resistance to the change in volume. A low value of G implies weak resistance to plastic deformation in shear, while a high value of K implies strong resistance to the dilatation required for shear bands or mode I crack propagation. Also, this would make it more difficult

to attain the critical shear displacement and thus explain the increased toughness. Thus, the systems which have relatively smaller G and bigger K (corresponds to the Pd-, Pt-, Zr-, Ni-, Cu-, and Au-based BMGs with smaller V_m) will favor plasticity behavior, while the others that have relatively smaller K and bigger G (corresponds to brittle BMGs and metalloid glassy materials with bigger V_m) would be brittle. The correlation between ν and V_m suggests that there is a probability to get ductile BMGs with smaller V_m, and that the mechanical behavior depends mainly on the short-range atomic bonding rather than that of the medium range order.[26]

An issue of current interest is the toughening of metallic glasses at room temperature. The link between mechanical behavior and V_m indicates that volume should play an important role in the flow of metallic glasses. Recently, it is found that the density and packing density relate tightly with glass-forming ability and flow in BMG, and smaller packing density or density would be positive for plasticity in metallic glasses.[17–21] In "jamming" system, one of the means for fluidizing a solid is to decrease the volume fraction.[26] The link between mechanical behavior and V_m assists in guiding alloy design to alleviate brittleness in BMGs by considering volume factor, and in elucidating flow and fracture mechanisms in metallic glasses. The close links between V_m (or microstructure) and elastic moduli of BMGs can be used to sensitively reflect their structural change in BMGs induced by aging, crystallization, pressure and temperature, and mechanical treatments, which can assist in understanding of the microstructure features and nature of glasses.

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