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A Modified Free Volume Model for Characterizing of Rate Effect in Bulk Metallic Glasses *

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We investigate the plastic deformation and constitutive behaviour of bulk metallic glasses (BMGs). A dimensionless Deborah number $De_{\rm ID} = t_r/t_i$ is proposed to characterize the rate effect in BMGs, where t_r is the structural relaxing characteristic time of BMGs under shear load, t_i is the macroscopic imposed characteristic time of applied stress or the characteristic time of macroscopic deformation. The results demonstrate that the modified free volume model can characterize the strain rate effect in BMGs effectively.

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Recently, due to the development of bulk metallic glasses (BMGs), great efforts have been focused on the preparation and mechanical deformation behaviour of BMGs because of their potential applications in basic research and engineering.[1−3] The plastic deformation of bulk metallic glasses (BMGs) is fundamentally different from that in crystalline solids, because lack of long-range order in the atomic structure. For example, BMGs loaded under unconstrained conditions usually fail catastrophically with little global plasticity and ductility. This deformation behaviour has limited the application of BMGs as engineering material so far.[4] Therefore, understanding and characterizing the plastic deformation mechanism of BMGs are very important for applications of this class of materials to a variety of engineering problems.

So far, various micromechanical theories have been advanced to account for the mechanical behaviour of metallic glasses. It has been shown[5] that the plastic deformation in metallic glasses is strongly inhomogeneous at low temperatures (e.g. room temperature) and high stress, and that the highly localized deformation in shear bands is due to a local decrease in viscosity. Spaepen[6] argued that this decrease is due to the formation of free volume and that the attendant inhomogeneous flow is controlled by the competition between the stress-driven creation and diffusional annihilation of free volume. This hypothesis was later verified experimentally by Argon.[7] Subsequently, Steif *et al.*[8] extended Spaepen's model by considering an infinite body containing an initial band of slightly weaker material, and deriving an expression for the maximum stress at which catastrophic softening occurs due to the creation of free volume. Based on a similar idea of Argon and Spaepen, Langer and his co-workers proposed a shear-transformation-zone (STZ) theory of deformation in metallic glass that includes a set of dynamical state variables beyond stress and strain recently.[9,10] The transition between one state and the other constitutes an elementary increment of shear strain and controls the mechanical properties in BMGs.[9,10] However, the dynamical state variables and the evolvement of free volume related to the transition does not be clearly clarified either.

Otherwise, several authors have attempted to explain plasticity in metallic glasses by means of modifying classical plastic deformation theories or dislocation model.[11−14] Based on the hypothesis of stress-induced structural relaxation and the concepts of fictive stress, Chen *et al.*[11] proposed a fictive stress model to characterize the nonlinear viscoelastic behaviour in BMGs. Similar to soil mechanical methods, Anand and Su[12] assumed that the plastic dilation is related to its deformation slip system on BMGs and developed a finite-deformation, Coulomb–Mohr-type constitutive theory for the elastic–viscoplastic response of pressure-sensitive and plastically-dilatant isotropic materials. These models reproduced parts of the experimental results fairly well, while there is little information related to the microstructure of metal glasses. In addition, Gilman[13] and Li[14] attempted to describe the plastic deformation of metallic glasses in terms of dislocation models. However, the definition of dislocation in metallic glass was unacceptable. In particular, interactions between 'dislocations' and microstructure do not determine the mechanical properties of amorphous alloys in the manner common to crystalline solids. An obvious example is that metallic

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glasses do not strain harden. With lack of the corresponding material physical image, associated explanations on the plasticity in metallic glasses based on these models were unbelievable.

To date, many studies have demonstrated that free volume and its evolution in metallic glass plays a very important role in the mechanical behaviour of metallic glass. In experiments researchers also observed the evolution of free volume in deformed BMGs, and the results could be effectively interpreted qualitatively with free volume model.[6−8] Thus, the free volume models established by Spaepen *et al.*[6] are accepted by most researchers. However, there still exist some difficulties in the description of elastic–plastic deformation of metallic glasses in the free volume model at room temperature, especially the effect of strain rates. In this Letter, a dimensionless Deborah number $De_{\rm ID} = t_r/t_i$ is proposed to modify the free volume model to characterize the strain rate effect.

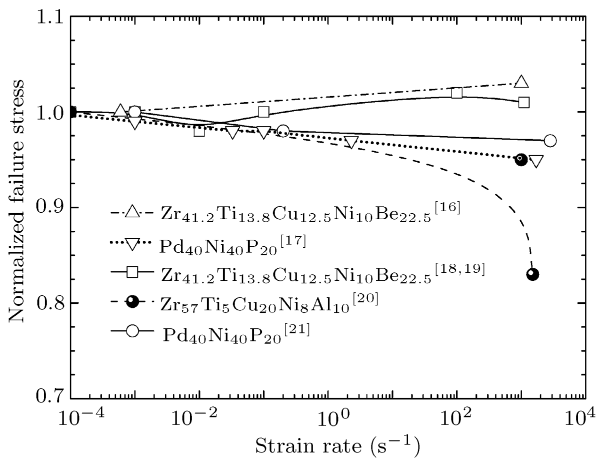

Fig. 1. Dependence of failure stress (normalized by the failure stress under quasi-static loading) on the strain rate for BMGs.

Experimentally, the effects of strain rate in BMGs are dependent on the loading conditions and chemical components of the material itself. BMGs under different applied loading conditions usually show different strain-rate-dependent behaviours. At high temperatures ($> 0.70T_g$, where T_g is the glass transition temperature), the strength or fracture stress of BMGs usually exhibits significant strain rate effect.[15] In contrast to the plastic deformation at high temperature, the strength or fracture stress of BMGs at low temperature often shows little strain rate effect. This is especially true at room temperature. As illustrated in Fig. 1, Bruck *et al.*[16] reported that the compressive strength of a Zr-based BMG is independent of the strain rate. Mukai *et al.*[17] demonstrated that tensile fracture stress of a $Pd_{40}Ni_{40}P_{20}$ BMG is essentially independent of strain rate. Liu *et al.*[18,19] reported that the shear strength of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG is independent of the strain rates in their 'plate-shear' and shear punch tests. Hufnagel *et al.*[20] and Mukai *et al.*[21] observed that the uniaxial compression failure stress slightly decreases with the increasing strain rate. Apparently, the strain rate dependence of deformation behaviours in BMGs varies with loading procedures.

Theoretically, based on the free volume theory, Cohen and Turnbull,[22] Turnbull and Cohen,[23,24] and Spaepen[6] developed a general constitutive equation to characterize plastic flow of metallic glasses. According to this model, the shear strain rate can be written as

$$\dot{\gamma} = \frac{\dot{\tau}}{\mu} + 2f \exp\Big(-\frac{a}{\xi}\Big)\exp\Big(-\frac{\Delta G^m}{k_B\theta}\Big)\sinh\Big(\frac{\tau\Omega}{2k_B\theta}\Big), \tag{1}$$

where τ is the applied shear stress, $\dot{\gamma}$ is the shear strain rate, $\xi = v_f/v^*$ is the concentration of the free volume, α is a geometrical factor of order unity, f is the frequency of atomic vibration, ΔG^m is the activation energy, Ω is the atomic volume, k_B is Boltzmann's constant, μ is the shear modulus, and θ is the absolute temperature. Equation (1) shows that the concentration of the free volume ξ plays a key role in the deformation of metallic glasses. An as-prepared metallic glass is thermodynamically unstable and has a non-equilibrium amount of free volume. During the deformation under the shear stress, the concentration of the free volume is continuously created by an applied shear stress and annihilated by structure relaxation due to atom rearrangement. In the model of Spaepen,[6] the free volume is created by an applied shear stress τ and annihilated by a series of atomic jumps, and the net rate of the change of concentration of free volume is

$$\frac{\partial\xi}{\partial t} = f\exp\Big(-\frac{\alpha}{\xi}\Big)\exp\Big(-\frac{\Delta G^m}{k_B\theta}\Big) \cdot\Big\{\frac{\alpha}{\beta\bar{\mu}\xi}\times\Big[\cosh\Big(\frac{\tau\Omega}{2k_B\theta}\Big)-1\Big]-\frac{1}{n_D}\Big\}, \tag{2}$$

where n_D is the number of atomic jumps required to annihilate a free volume equal to the atomic (hard sphere) volume v^*, and $\beta = \dfrac{2}{3}\dfrac{1+\nu}{1-\nu}\dfrac{v^*}{\Omega}$, $\bar{\mu} = \dfrac{\mu\Omega}{2k_B\theta}$ with ν being Poisson's ratio. By numerically solving Eqs. (1) and (2), the shear stress-strain and evolution of the concentration of free volume can be obtained. In the calculation, we take $\alpha = 0.15$, $f = 1\times10^{13}\,{\rm s}^{-1}$, $\Delta G^m = 1\times10^{-19}\,{\rm J}$, $\Omega = 26.1\times10^{-30}\,{\rm m}^3$, $k_B = 1.381\times10^{-23}\,{\rm J/K}$, $\mu = 35.3\,{\rm GPa}$, $v^* = 0.8\,\Omega$, $\nu = 0.36$, $\theta = 300\,{\rm K}$, $n_D = 3$ (Huang *et al.*[25]). The shear stress and the concentration of free volume are assumed to zero and 0.008 respectively in the initial configuration. The calculated steady value of the dimensionless shear stress-shear strain curves at different strain rates are presented in Fig. 2. It can be seen from the figure that the dimensionless shear stress and failure strain (corresponding to the maximum stress) are strongly sensitive to the shear strain rate, i.e. the dimensionless shear stress and failure strain markedly increase with increasing shear strain rate. However, the existed experimental results[16−19] demonstrated that the failure stress and failure strain of many BMGs are independent of strain rates, and even some have negative strain rate effect at room temperature. Furthermore, $\alpha = 0.15$ is inconsistent with the free volume model and the calculated results for $0.5 < \alpha \leq 1$ are worse.[6] Evidently, the existed free volume model could not catch the effect of strain rate in metallic glasses at room temperature. Much more information on the plastic flow behaviours of BMGs should be involved in the model.

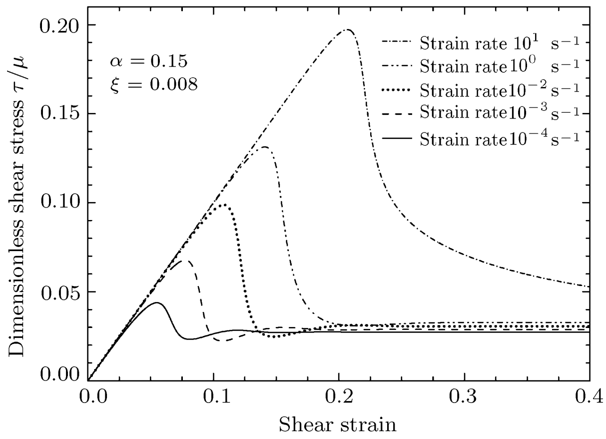

Fig. 2. Calculated shear stress strain curves based on the original free volume model.

Firstly, as mentioned above, the free volume concentration ξ plays a key role in the deformation of metallic glasses. The coalescence of free volume in BMGs is controlled by the competition between the stress-driven creation process and the annihilation process due to structural relaxation. Analogies with dislocations in crystalline alloys, free volumes are the defects in metallic glasses. Free volume and its evolution represent the damage and damage evolution of BMGs under applied loadings. Since metallic glasses are in metastable equilibrium, they will shift to low energy configuration and annihilate free volumes when they are relaxed. At the same time, free volumes could be created under high loadings. Thus, mechanical properties of metallic glasses were controlled by the competition between the annihilation and creation of free volumes. Among these processes, the stress-driven creation is tightly related to the macroscopic deformation response to applied loading, and the structural relaxation annihilation processes is due to atomic jumps in metallic glasses. Both the annihilation and creation of free volume are time dependent. Thus a dimensionless Deborah number, namely the ratio of the structural relaxation characteristic time to the macroscopic deformation response characteristic time can be introduced to characterize the competition between the annihilation and creation of free volumes in BMGs. The Deborah number was initially introduced by Reiner[26] to characterize what 'fluid' a material is. Recently, Bai *et al.*[27,28] have demonstrated that this dimensionless number is a key parameter for characterizing damage evolution and damage localization of materials. In the present case, the dimensionless Deborah number can be defined as

$$De_{\rm ID} = t_r/t_i, \quad (3)$$

where $t_r = 1/R$ is the structural relaxing characteristic time of BMGs under shear load, $t_i = 1/\dot{\gamma}$ is the macroscopic imposed characteristic time of applied stress or the characteristic time of macroscopic deformation; $R = f\exp\Big(-\dfrac{\Delta G^m}{k_B\theta}\Big)$ is the frequency of atomic jumps to annihilate free volume, and $\dot{\gamma}$ is the imposed shear strain rate by the applied loading. According to Eq. (3), one can find that the larger the Deborah number $De_{\rm ID}$ is, the slower the structural relaxation annihilation process of free volume is. Thus, a relatively larger Deborah number $De_{\rm ID}$ will lead to a relatively higher remaining free volume concentration in BMGs and a weak capacity of load. The existed experimental observations[18,19] that the number of shear bands initiated at high strain rate is larger than that at low strain rate could be mainly attributed to this reason. Obviously, the Deborah number $De_{\rm ID}$ could characterize these effects of loading rates: failure stress is rate independent and shear bands are rate dependent. However, the existed models do not include any information about this kind of competition.

Secondly, to achieve a simple equation on the net rate of the change of the free volume concentration in metallic glasses, Spaepen[6] assumed that the volume v of a spherical hole that an atom can be squeezed into is equal to the hard-sphere volume v^* of the atom. In fact, under a large applied loading, the volume v of a spherical hole could be much smaller than the atom volume v^*. Thus a larger number of fractions of potential jump sites are introduced. This assumption underestimates the creation of free volume and leads to a fancied carrying capacity of metallic glasses that the model characterizes. This is especially serious under a highest applied loading.

Based on the above-mentioned considerations, we modify Spaepen's model to include the effect of applied loading and its rates. First, we replace v^* with v and assume that v is as functions of applied loading and material. The function of v can be expressed as

$$v = v^* f(\tau, A),$$

where A is a parameter of the applied loading rate and given by $f_A = (De_{\rm ID}) = a - b \times \log(De_{\rm ID})$; a and b are determined by the properties of materials. Then, Eqs. (1) and (2) can be rewritten as

$$\dot{\gamma} = \frac{\dot{\tau}}{\mu} + 2f \exp\Big(-\frac{\alpha\bar{v}}{\xi}\Big) \exp\Big(-\frac{\Delta G^m}{k_B\theta}\Big) \cdot \sinh\Big(\frac{\tau\Omega}{2k_B\theta}\Big), \quad (4)$$

$$\frac{\partial\xi}{\partial t} = \bar{v} \cdot f \cdot \exp\Big(-\frac{\alpha\bar{v}}{\xi}\Big) \exp\Big(-\frac{\Delta G^m}{k_B\theta}\Big) \cdot \Big\{\frac{\alpha}{\beta\bar{\mu}\xi} \times \Big[\cosh\Big(\frac{\tau\Omega}{2k_B\theta}\Big) - 1\Big] - \frac{1}{n_D}\Big\}, \quad (5)$$

where $\bar{v} = v/v^*$, $f(\tau, A) = 1 - f_A(De_{\rm ID})\frac{\tau}{\tau_f}$. For $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG, its failure stress is independent of strain rate. Based on the modified model, the recalculated results are presented in Fig. 3, where $a = 0.85$, $b = 0.019$, $\tau_f \cong 0.031\mu$, $\alpha = 0.75$, and $\xi_0 = 0.006$. From Fig. 3, one can find that the recalculated stress strain curves are independent of strain rates. The results demonstrate that the modified model can describe the strain rate effect of the Zr-based BMGs very well. The values of α and ξ_0 are more reasonable and matched the free volume model better than the unmodified model. Because a and b are related to the material itself and strain rate effects are material-dependent, different values of a and b can characterize varying strain rate effects in BMGs.

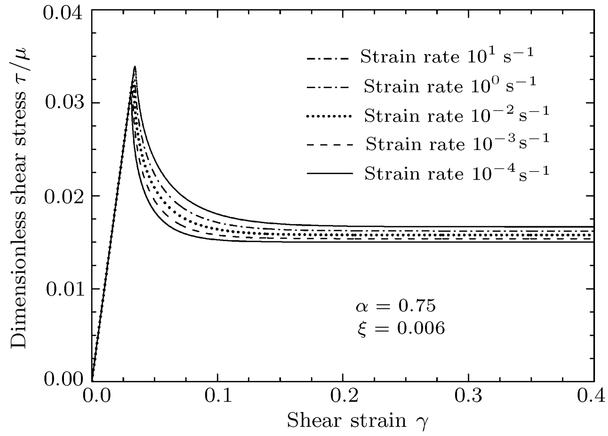

Fig. 3. Calculated shear stress strain curves based on the modified free volume model.

It is noted that other material parameters do not be modified in the present model to characterize the rate effect except for free volume. Thus a question naturally arises: does the rate effect exert any influence on these factors? Actually, the rate effect influences these factors. For example, adiabatic heating induced temperature rise and softened the crystalline materials under high strain rate. But the reports[6−10,18,19,29,30] demonstrate that free volume creation-softening plays a dominant role in the mechanical properties of BMGs, and adiabatic heating softening exerts a secondary influence at high strain rates. However, the temperature rise $\Delta\theta$ was also estimated by $\Delta\theta = K\tau\gamma/(\rho c_p)$ in our early calculation on BMGs. To our surprise, the temperature rise has little effect on the modification of the significant strain rate effect of the constitutive behaviours. The reason is that the temperature rise accelerates the annihilation processes of free volume. Therefore, the thermal-softening effect of the BMGs was almost eliminated by the annihilation processes of free volume. Secondly, although the temperature rise and increased load could influence the activation energy ΔG^m to some extent. The effect of the activation energy on the deformation is similar to that of temperature effect and has little impact on the calculated results. Lastly, within the scope of reasonable variation of the other parameters (Ω, k_B and μ) under different strain rates, the calculated dimensionless stress-strain curves still have significant strain rate effect based on Eqs. (1) and (2). Thus, the free volume concentration ξ controls the mechanical properties of BMGs under different strain rates and can be modified to characterize the rate effect in BMGs effectively.

In summary, a Deborah number $De_{\rm ID} = t_r/t_i$ and a materials related function $f_A(De_{\rm ID}) = a - b \times \log(De_{\rm ID})$ are introduced into the free volume model to characterize the time-dependent rate effect in BMGs. The results demonstrate that the modified free volume model may be a potential method to characterize the plasticity of BMGs at present.

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