Modelling and physical analysis of the high-temperature rheological behavior of a metallic glass

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Abstract: The high-temperature rheological behavior around the glass transition temperature of a metallic glass was investigated by strain rate jump experiments. The results suggest that plastic deformation behavior and apparent viscosity strongly depend on temperature and strain rate. The microscopic mechanisms of high temperature rheology of metallic glasses can be interpreted within the framework of the free volume model. The relative defect concentration deduced from the free volume model depends on temperature and strain rate and it explains the evolution of apparent viscosity with testing condition, which is inversely correlated with the defect concentration. The stress overshoot is found to be a characteristic of high-temperature rheological behavior. The physical origin of the stress overshoot is analyzed based on the physical expressions of the parameters in the free volume model. The results demonstrate that the strength of the stress overshoot is determined by the time of change from non-equilibrium to equilibrium defect concentrations.

Keywords: Metallic glass; High-temperature deformation; Free volume theory; Rheological behavior

1. Introduction

How to describe the correlation between mechanical behavior and microstructure of metallic glasses (MGs) is a challenging issue (Das et al., 2005). Benefitting from their disordered structure, metallic glasses have unique mechanical properties such as large elastic strain, high strength and high fracture toughness (Demetriou et al., 2011; Wang, 2012; Zhang et al., 2005). Unfortunately, they lack ductility at ambient temperature, impeding their use in many engineering applications. Many strategies, based on microalloying (Qiao et al., 2016b), phase separation (Kim et al., 2013), amorphous metal foams (Sarac et al., 2012) and metallic glass composites (Hofmann et al., 2008; Qiao et al., 2016a) have been conducted to improve ductility at ambient temperature. Due to the absence of conventional crystalline defects (i.e. vacancies, interstitials and dislocations), how to establish the correlation between the microstructure and the mechanical properties of metallic glasses is an important, still unsolved issue. As a

member of the big family of amorphous materials, metallic glasses exhibit mechanical behaviors similar to other disordered materials (Gauthier et al., 1997). In essence, the plastic deformation of metallic glasses is closely related to temperature and stress. In general, the deformation of MGs is driven by inhomogeneous flow at low temperatures or high strain rates, and homogeneous flow around the glass transition temperature T_g and low strain rates (Schuh et al., 2007; Spaepen, 1977). A deformation map with these two basic plastic deformation modes, homogeneous and inhomogeneous flow, was firstly constructed by Spaepen (Spaepen, 1977). In the case of homogeneous flow, each volume element of the alloy contributes to the plastic deformation leading to temporal and spatial homogeneity. For inhomogeneous flow, the strain is localized into a few narrow shear bands resulting in a catastrophic failure and limited plastic strain (Jiang et al., 2008; Pan et al., 2011; Spaepen, 1977). Recently, the deformation map has been extended. A second region of homogeneous flow (Homogeneous II), which lies in a higher strain rate and lower temperature region, was proposed by Schuh et.al (Schuh et al., 2004). In addition, a new deformation map divided the homogeneous regime into Newtonian and non-Newtonian flow (Li et al., 2013b; Schuh et al., 2007). The strain rate sensitivity m defined as $-d \log \sigma / d \log \dot{\epsilon}$ is used to divide the deformation map into Newtonian and non-Newtonian flow regions, $m = 1$ for Newtonian flow and $m < 1$ in the non-Newtonian region (Mei et al., 2011). It has been reported that Newtonian flow facilitates thermoplastic forming, a process that tends to be difficult in the non-Newtonian flow region (Li et al., 2013b). Understanding the physical mechanism of the deformation behavior of metallic glasses is then very important for engineering applications (Furukawa and Tanaka, 2009).

The macroscopic deformation mode depends on the viscoelastic behavior of MGs, the contribution of viscosity becomes predominant in the homogeneous flow region. In the framework of the dynamic mechanical analysis experiments, the viscoelastic behavior of MGs is sensitive to temperature and driving frequency (Lyu et al., 2018; Qiao et al., 2019). The mechanical relaxation spectra generally present two relaxation process: (I) the main relaxation process (α relaxation) is observed at high temperatures and low frequencies, and it is linked with the decrease of viscosity. The α relaxation is

a universal feature of MGs, which is related to large-scale atomic movements corresponding to the glass transition phenomenon (Wang, 2011); (II) the secondary relaxation (β relaxation) is related to localized atomic movements at lower temperatures or higher frequencies, and it is observed for instance in La-based MGs (Qiao and Pelletier, 2012). The β relaxation is strongly dependent on the initial state of the alloy system, the strength of β relaxation decreases by isothermal annealing and increases after plastic deformation (Qiao et al., 2014; Qiao et al., 2015). The evolution of defects in the glassy alloy is strongly linked with its mechanical properties, such as plasticity and strain softening (Dubach et al., 2009; Qiao et al., 2016b). It has been demonstrated that plasticity of MGs is enhanced by increasing the defect concentration, and defect concentration can be modified by adjusting the chemical composition or the processing protocol (Huang et al., 2007; Qiao et al., 2016b). Strain softening, or stress overshoot, is considered a transient state where the system is set in a new testing condition (Dubach et al., 2009).

Stress overshoot phenomenon, namely, a maximum stress observed before the steady-state value, is a common characteristic during plastic deformation of amorphous materials. The microstructural origin of stress overshoot phenomenon was discussed in published reports (Gauthier et al., 1997; Quinson et al., 1996). The deformation of polymers can be divided into elastic, anelastic and plastic components (Quinson et al., 1996). The anelastic strain is associated with the expansion of shear micro-domains (SMD), which is necessary to create plastic deformation (David et al., 1997; Quinson et al., 1996). A similar concept was developed by Li et al. based on the free volume model and shear-transformation-zone (STZ) theory (Li et al., 2013a). A large volume fraction of STZs in the system is associated with plastic deformation, which has complex interactions. In contrast, a small volume fraction of STZs is isolated in tiny shear bands at small strain. The anelastic behavior is due to the reversion of STZs upon removal of external force (Lei and Atzmon, 2019). Similarly, the stress overshoot phenomenon is observed in the high-temperature deformation of MGs (Hasan and Boyce, 1995; Koumakis et al., 2012). Based on theories proposed for explaining the non-linear deformation of polymers, many theories were developed to describe the

high-temperature deformation behavior and explain its physical mechanism in MGs, such as stretched exponential behavior (Matsuoka, 1992), free volume theory (Bletry et al., 2006), quasi-point defects (QPD) theory (Pelletier et al., 2002), cooperative shear model (CSM) (Demetriou et al., 2006) and STZ theory (Langer, 2004). The stretched exponential is one of the most powerful expressions to describe many experimental results including rheological behavior, although the parameters in the function give little information about the physical origin of the mechanical behavior (Cheng et al., 2021; Wang et al., 2014; Zhang et al., 2017). Free volume theory has been widely used to understand structural relaxation, diffusion and rheological behavior (Bletry et al., 2007; Qiao et al., 2015; Spaepen, 1977). QPD theory is able to connect the macroscopic dynamic mechanical behavior with microstructural properties and describes the high-temperature rheological behavior (Pelletier et al., 2002). CSM, based on thermodynamics and cooperatively sheared flow zones, defines some parameters with physical significance (Demetriou et al., 2006). STZ theory combines the free volume model and the shear transformation (ST) theory, introducing an effective disorder temperature related with the STZ density (Langer, 2004). Additionally, free volume theory was developed to define the defect concentration with new expressions, which was efficient to simulate stress overshoot (Bletry et al., 2007). However, there is limited information about the evolution of defect concentration in high-temperature deformation. More importantly, the relation of defect concentration with stress overshoot is still unclear. In the current work, we will envision the microstructural origin of stress overshoot during the plastic deformation of MGs in the framework of the free volume theory.

2. Experimental procedure

In the current work, $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass was selected as the model alloy since it shows an excellent glass forming ability and thermal stability (Zhang et al., 2008). The ingot of $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass was prepared by arc-melting technique. In order to ensure compositional homogeneity, the pure elements were melted at least 4 times under purified Ar atmosphere. The plate samples were produced

by the water-cooled copper mold suction casting technique, with a size of 85 mm × 10 mm × 2 mm. The samples for mechanical spectroscopy, with a size of 30 mm × 2 mm × 1 mm, were prepared by water-cooling precision low-speed cutting machine. The temperature spectrum of Young modulus was detected by dynamic mechanical analysis (DMA Q800, TA, USA) (Lyu et al., 2018). The complex Young modulus E^* of MGs is expressed as $E^* = E' + iE''$, where E' is the storage modulus and E'' is the loss modulus. The ribbon samples for the tensile tests were prepared by single roller melt spinning. The tensile strain rate jump tests were conducted using the tension film configuration of the DMA device. It has been reported that the T_g of $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass is 679 K (Cheng et al., 2021). Experimental temperatures of tensile strain rate jump experiments were above $0.8T_g$ for achieving homogeneous deformation (693 K, 698 K and 703 K), and the applied strain rates were 1×10^{-4} , 2.5×10^{-4} , 5×10^{-4} , 1×10^{-3} and $2.5 \times 10^{-3} \text{ s}^{-1}$.

3. Results and discussion

3.1 Mechanical spectroscopy

In an amorphous material, the glass transition temperature T_g is regarded as the onset temperature of the structural evolution from an isoconfigurational glass state towards a metastable liquid state (Perez, 1998). Dynamic mechanical analysis provides a method to explore the structural relaxation processes of MGs. **Fig. 1** shows the temperature scans recorded from 300 K to 823 K at fixed driving frequency of 2 Hz and heating rate of 3 K/min. The temperature dependence of the normalized storage modulus E'/E_u and the normalized loss modulus E''/E_u of $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass resembles most of the other MGs, which can be divided into three distinctive regions denoted in **Fig. 1**: (I) E'/E_u is close to 1 for temperatures below 650 K, on the contrary, E''/E_u is practically equal to zero and can be neglected. It indicates that the mechanical behavior of MGs is mainly dominated by elasticity. (II) As heating continues, a decrease of E'/E_u and an increase of E''/E_u occur, which are related to drastic decline of viscosity. The maximum of E''/E_u corresponds to the α relaxation and it is connected with the dynamic glass transition phenomenon. (III) The

temperature dependence of E'/E_u and E''/E_u in the high temperature region ($T > 770$ K) is linked to the crystallization events. In the temperature range (II), viscosity is reduced radically while ductility is enhanced with increase of temperature. It is consistent with the experimental results obtained by capillary flow method and three-point beam bending (Demetriou et al., 2006; Tsang et al., 1991). The temperatures of the tensile strain rate jump tests are marked in **Fig. 1** with green dots, they are selected around T_g to ensure homogeneous deformation of the ribbon samples.

Fig. 1. Evolution of the normalized storage modulus E'/E_u and loss modulus E''/E_u of $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass with temperature. The arrow denotes the glass transition temperature T_g . The positions of the green balls are the temperatures of the tensile strain rate jump tests in the current work.

3.2. Characteristics of high-temperature deformation

The tensile, strain rate jump tests for $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass were conducted at different temperatures (**Fig. 2**). As expected, tensile deformation of metallic glasses is sensitive to strain rate and testing temperature. Namely, the lower the temperatures or the higher the strain rates, the greater the steady-state flow stresses σ_{flow} and the more pronounced stress overshoots (Langer, 2008). Stress overshoot is defined as the phenomenon of strain softening after a peak stress σ_{peak} . The σ_{flow} after a series of strain-rate jumps is consistent with the one in constant strain rate

compression test (Bletry et al., 2004). Moreover, the σ_{flow} remains unchanged during stress-relaxation cycles (Kawamura et al., 1997). The results illustrate that the σ_{flow} (i.e. the stress plateau) is strongly thermally activated for fully amorphous materials and the value is independent of the strain-rate path (Bletry et al., 2004; Kawamura et al., 1997). Additionally, the magnitude of stress overshoot detected after stress-relaxation cycles is unaffected by the number of cycles in the steady state (Qiao et al., 2015). Basically, the value of σ_{peak} is related to the fraction of the stress relaxation achieved in each cycle (Bletry et al., 2004; Kawamura et al., 1997; Qiao et al., 2015). Stress overshoot is associated with the evolution of defect concentration in the framework of the free volume theory. The σ_{peak} is reduced progressively with decreasing initial stress, whereas it rises with increasing stress-relaxation time (Bletry et al., 2004; Qiao et al., 2015). Physical aging below the glass transition temperature leads metallic glasses to more stable states, while plastic deformation induces the glasses toward more disordered states (De Hey et al., 1998). It can be assumed that the obvious stress overshoot is linked to the decrease of defect concentration. Furthermore, stress undershoot is decreased by decreasing the strain rate (Dubach et al., 2009; Kawamura et al., 1997). The mechanisms of stress overshoot are related to the evolution of the structure of glassy materials, we will discuss this issue in the following section.

Fig. 2. Stress-strain curves for $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass obtained by tensile strain-rate jump tests between $\dot{\epsilon} = 5.0 \times 10^{-4} \text{ s}^{-1}$ and $\dot{\epsilon} = 1.0 \times 10^{-3} \text{ s}^{-1}$ at 693 K, 698 K and 703 K, respectively.

The apparent viscosity $\eta = \sigma/3\dot{\epsilon}$ can be inferred from the stress-strain curves. According to free volume theory, the general relation between tensile stress σ and plastic strain rate $\dot{\epsilon}_{\text{pl}}$ at fixed temperature T for plastic homogeneous flow is expressed as (Spaepen, 1977):

$$\dot{\epsilon}_{\text{pl}} = c_f 2\nu_D \exp\left(-\frac{\Delta G^{\text{m}}}{kT}\right) \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) \quad (1)$$

where c_f is the defect concentration, ν_D the Debye frequency related to the frequency of atomic vibration, ΔG^{m} is the activation energy for diffusion with no applied force, k is Boltzmann's constant, V is the atomic volume defined as the volume of matter participated in defect migration, σV is related to the difference of free energy per atom after jumping and the hyperbolic sine term represents the impact of external stress on the energy barrier. Taking the contribution of the elastic component into account, a simple form of total strain rate in homogeneous flow is reported as (Steif et al., 1982):

$$\dot{\epsilon} = c_f 2\nu_D \exp\left(-\frac{\Delta G^{\text{m}}}{kT}\right) \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) + \frac{\dot{\sigma}}{E} \quad (2)$$

where E is the apparent elastic modulus and $\dot{\epsilon}$ is the sum of plastic and elastic strain rate. $\dot{\sigma}/E$ is equal to zero at the peak stress and the steady-state region. If a constant c_f under fixed temperature is assumed, Eq. (2) can be rewritten as (Spaepen, 1977):

$$\dot{\epsilon} = \dot{\epsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) \quad (3)$$

where c_f is supposed to be $c_{f,\text{eq}}$ in the glass transition range and the temperature dependent frequency factor is $\dot{\epsilon}_0 = 2c_{f,\text{eq}}\nu_D \exp\left(-\frac{\Delta G^{\text{m}}}{kT}\right)$. In such framework:

$$\eta = \frac{\sigma}{3\dot{\epsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right)} \quad (4)$$

indicating a negative correlation between η and c_f .

Parameters $\dot{\epsilon}_0$ and V can be obtained by fitting Eq. (3). It considers the maximum values of stress when an overshoot exists, as it is suggested by Demetriou et

al (Demetriou et al., 2006). It is worth noting that V deduced by Eq. (3) is based on a one-to-one relationship between stress and strain rate (for a given temperature), whereas the plateau state in the tensile experiments is not stable. Additionally, it has been demonstrated that V deduced from peak stress is effective to predict the plateau state (Demetriou et al., 2006). Therefore, the maximum stresses were used here to calculate $\dot{\epsilon}_0$ and V . **Fig. 3** shows that the strain rate $\dot{\epsilon}$ dependence of peak stress σ_{peak} follows a hyperbolic sine law for the three temperatures. The values of the fitting parameters V and $\dot{\epsilon}_0$ are listed in **Table 1**. It is difficult to compare the values of $\dot{\epsilon}_0$, as they show a large dispersion for different materials. The values of V obtained in the glass transition range are similar to those observed in other ZrCu-based and Mg-based MGs, such as $\text{Zr}_{46}\text{Cu}_{38}\text{Ag}_8\text{Al}_8$ (0.284~0.329 nm³) (Cui et al., 2014), $\text{Cu}_{46}\text{Zr}_{45}\text{Al}_7\text{Y}_2$ (0.276~0.456 nm³) (Cui et al., 2014), $\text{Zr}_{44}\text{Cu}_{40}\text{Ag}_8\text{Al}_8$ (0.237~0.372 nm³) (Liu et al., 2011) and $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ (0.268~0.331 nm³) (Gun et al., 2007) MGs. However, these values are lower than those calculated for La-based MGs, such as 0.439~1.240 nm³ for $\text{La}_{30}\text{Ce}_{30}\text{Al}_{15}\text{Co}_{25}$ MGs (Chen and Qiao, 2020) and 0.465~1.011 nm³ for $\text{La}_{60}\text{Ni}_{15}\text{Al}_5$ MGs (Qiao et al., 2013). In these previous investigations, the high value of the activation volume of La-based MGs was ascribed to the evident β relaxation of these systems (Qiao et al., 2013). In addition, V is influenced by c_f , a larger V is associated with a higher c_f (Qiao et al., 2013). Taking the mean atomic volume of the glass as $\Omega = 0.013 \text{ nm}^3$, the activated volume of the model alloy corresponds to the displacement of 20-30 atoms in the glass transition temperature range. This result illustrates that the jump of atoms is assisted with displacements of their neighbors during the high-temperature deformation.

Fig. 3. Evolution of peak stress σ_{peak} and strain rate $\dot{\epsilon}$ at different temperatures for $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass. Solid lines are fitted curves of Eq. (3).

Table 1. Activation volume V and frequency factor $\dot{\epsilon}_0$ of $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass at different temperatures.

Chemical composition	Temperature (K)	V (nm ³)	$\dot{\epsilon}_0$ ($10^{-4} \times \text{s}^{-1}$)
$\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$	693	0.296	0.715
	698	0.291	1.572
	703	0.317	1.763

shown in **Fig. 1**. In addition, the variation of η with the strain rate can be described by the Kohlrausch-Williams-Watts (KWW) equation (Matsuoka, 1992).

$$\eta = \eta_N \left\{ 1 - \exp \left[- \left(\frac{\sigma_{tc}}{\dot{\epsilon} \eta_N} \right)^{\beta_{kww}} \right] \right\} \quad (5)$$

where σ_{tc} is associated with the transition point of characteristic stress, the Kohlrausch exponent β_{kww} ranges from 0 and 1 and η_N is obtained by free volume theory. The fitting results of the KWW equation are plotted in **Fig. 4**. Non-Newtonian flow is observed at higher strain rates, while η remains constant for Newtonian flow at lower strain rates. The temperature behavior of η_N can be described by the Vogel-Fulcher-Tammann law (Fulcher, 1925), the Cohen-Grest model (Grest and Cohen, 2007) as well as the cooperative shear model (Demetriou et al., 2006). As shown in **Fig. 4**, the values of η_N obtained from the free volume theory are validated by the KWW equation. The apparent energy barrier for shear flow increases with the decreasing temperature, resulting in the increasing of η_N . According to Eq. (5), σ_{tc} and β_{kww} are listed in **Table 2**. The parameter β_{kww} describes the degree of deviation from Newtonian flow, and is related to the slope of the solid line in the non-Newtonian flow region (as shown in **Fig. 4**). The parameter β_{kww} increases as temperature decreases, which implies a larger degree of deviation from Newtonian flow.

Fig. 4. Strain rate dependence of the apparent viscosity η at various temperatures for the $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass. Dashed lines are deduced from Eq. (4) and solid lines are fitted by Eq. (5).

Table 2. KWW fitting parameter σ_{tc} and β_{kww} of $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass at various temperatures.

Chemical composition	T (K)	σ_{tc} (MPa)	β_{kww}
$\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$	703	104.61	0.89
	698	112.56	0.87
	693	106.16	0.82

A master curve can be extracted to analyze the characteristics of viscosity, which is derived by shifting the curves of the normalized viscosity η/η_N . The master curve can be related to both the KWW equation and the free volume theory. For the KWW equation is expressed as following (Matsuoka, 1992):

$$\frac{\eta}{\eta_N} = 1 - \exp \left[- \left(\frac{\sigma_{tc}}{\dot{\epsilon} \eta_N} \right)^{\beta_{kww}} \right] \quad (6)$$

In addition, η/η_N can be expressed according to free volume theory (Hao et al., 2020) as:

$$\frac{\eta}{\eta_N} = \frac{\operatorname{arcsinh} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right)}{\frac{\dot{\epsilon}}{\dot{\epsilon}_0}} = \frac{\operatorname{arcsinh}(x)}{x} \quad (7)$$

Fig. 5 (a) and (b) present the master curves of normalized viscosity η/η_N versus $\dot{\epsilon}\eta_N$ and $x = \frac{\dot{\epsilon}}{\dot{\epsilon}_0}$ for the $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass, respectively. The solid lines certify the efficiency of these methods to describe the variations of viscosity. The fitting results β_{kww} and σ_{tc} in this work and other typical metallic glasses are listed in **Table 3**. Values of β_{kww} and σ_{tc} of La-based metallic glass are much smaller, which is probably related to higher defect concentration in those alloy systems. Although there are many similarities in the high-temperature deformation of glasses, the physical mechanism of the transition from non-Newtonian to Newtonian rheology needs further research (Lu et al., 2003; Wang et al., 2005).

Table 3. KWW fitting parameters σ_{tc} and β_{kww} of typical metallic glasses

Chemical composition	σ_{tc} (MPa)	β_{kww}	Reference
$\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$	114	0.89	-
$\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$	118	0.78	(Zhang et al., 2017)
$\text{La}_{30}\text{Ce}_{30}\text{Al}_{15}\text{Co}_{25}$	32.6	0.70	(Chen and Qiao, 2020)

Fig. 5. The master curves of normalized apparent viscosity η/η_N vs. (a) $\dot{\epsilon}\eta_N$ and (b) $x = \frac{\dot{\epsilon}}{\dot{\epsilon}_0}$ for $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass. The solid lines are obtained by Eq. (6) and Eq. (7), respectively.

3.3. Determination of the kinetic parameters based on the steady-state region

In the free volume theory proposed by Spaepen (Spaepen, 1977), the homogeneous deformation is resulting from individual atom jumping in nearby holes, with a size larger than the critical atomic volume v^* . The probability of atomic jumping is defined as $\Delta f \exp(-\gamma v^*/v_f)$, where the factor Δf is associated with the fraction of volume available for jumping, γ is an overlap factor ($0.5 \leq \gamma \leq 1$) and v_f is the mean excess volume per atom. The excess free volume is defined as $x = v_f/\gamma v^*$ (Cohen and Turnbull, 1959). For homogeneous flow, $\Delta f = 1$, the concentration of flow defects c_f is therefore given by

$$c_f = \exp(-1/x) \quad (8)$$

Indicating that c_f is very sensitive to a slight variation of x . It has been found that c_f moves towards an equilibrium defect concentration during isothermal annealing at temperatures near T_g . The change of c_f can be described by $\dot{c}_f = -k_r c_f (c_f - c_{f,eq})$ (Duine et al., 1992), where k_r is a rate constant of defect annihilation and is expressed by $k_r = v_r \exp(-Q_r/kT)$ with Q_r an activation energy and v_r a pre-exponential factor. The $c_{f,eq}$ is the metastable equilibrium defect concentration at a given temperature. However, in practice, it is difficult to determine the value of $c_{f,eq}$ (Daniel

et al., 2002). According to Eq. (8), $c_{f,eq} = \exp(-1/x_{eq})$ with $x_{eq} = (T - T_0)/B$, where T_0 and B are material dependent constants. Several sets of parameters T_0 and B are able to describe experimental results, resulting in a large uncertainty of the values of $c_{f,eq}$ (almost six orders of magnitude for a given temperature). Nevertheless, the variation of $c_{f,eq}$ with temperature is clear: the higher the temperature, the higher the value of $c_{f,eq}$.

Furthermore, plastic deformation leads to the creation of free volume, leading to the increasing of c_f . The rate of growth for c_f was proposed to be $a_x \dot{\epsilon} c_f \ln^2(c_f)$, where a_x is a proportionality factor dependent on temperature (De Hey et al., 1998). Taking annihilation and creation of free volume into account, the expression of $\dot{c}_f$ is expressed as follows (De Hey et al., 1998):

$$\dot{c}_f = -k_r c_f (c_f - c_{f,eq}) + a_x \dot{\epsilon} c_f \ln^2(c_f) \quad (9)$$

which includes the effects of both structural relaxation and plastic deformation.

Considering Eq. (2) and Eq. (9), Bletry et al. proposed a useful model to analyze the high-temperature deformation of glasses (Bletry et al., 2006). In the framework of free volume theory, c_f reaches a stationary value in the steady-state flow and then $\dot{c}_f = 0$. In this region, a balance between the annihilation and the creation of free volume is established. The concentration of steady-state defects c_f^* is then given by the following expression (De Hey et al., 1998):

$$c_f^* = c_{f,eq} + \frac{a_x}{k_r} \dot{\epsilon} \ln^2(c_f^*) \quad (10)$$

accordingly, Eq. (2) can be rewritten as:

$$\dot{\epsilon} = c_f^* \dot{\epsilon}_{0,c} \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) \quad (11-1)$$

with

$$\dot{\epsilon}_{0,c} = 2v_D \exp\left(-\frac{\Delta G^m}{kT}\right) \quad (11-2)$$

where $\dot{\epsilon}_{0,c}$ is constant at fixed temperature. The set of parameters ($c_{f,eq}$, a_x/k_r , $\dot{\epsilon}_{0,c}$) can be inferred according to Eqs. (10) and (11) by using two sets of data ($\dot{\epsilon}_i, \sigma_i$) in the

stationary regime (Bletry et al., 2006). $c_{f,eq}$ is uncertain by mechanical testing, whereas the correlation of the relative defect concentration $(c_f^* - c_{f,eq})/c_{f,eq}$ with strain rate is unique at a given temperature. Based on the set of parameters ($c_{f,eq}$, a_x/k_r , $\dot{\epsilon}_{0,c}$) determined above, stress-strain curves of homogeneous flow can be simulated by Eqs. (2) and (9).

Table 4 shows the set of parameters ($\dot{\epsilon}_{0,c}$, $c_{f,eq}$, a_x/k_r) obtained at elevated temperatures for the $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass. It has been reported that a_x/k_r and $\dot{\epsilon}_{0,c}$ are positively and negatively related with $c_{f,eq}$, respectively, indicating that it is not possible to obtain the defect concentration directly, but only its relative variations (Bletry et al., 2006). $c_{f,eq}$ is assumed to be 2×10^{-13} in this work. **Fig. 5** illustrates the evolution of $(c_f^* - c_{f,eq})/c_{f,eq}$ with strain rate at different temperatures. $(c_f^* - c_{f,eq})/c_{f,eq}$ is proportional to strain rate, which is in agreement with other reported results (Bletry et al., 2006). Moreover, higher values of $(c_f^* - c_{f,eq})/c_{f,eq}$ are observed at higher temperatures, corresponding with the decrease of flow stress and apparent viscosity at elevated temperatures.

Table 4. Parameters of constant $\dot{\epsilon}_{0,c}$, metastable equilibrium defect concentration $c_{f,eq}$ and ratio a_x/k_r at different temperatures for the $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass

Chemical composition	Temperature(K)	$\dot{\epsilon}_{0,c}$ ($10^8 \times s^{-1}$)	$c_{f,eq}(10^{-13})$	$a_x/k_r(10^{-13})$
$Zr_{48}Cu_{34}Ag_8Al_8Pd_2$	693	3.3	2.00	1.2298
	698	6.5	2.00	2.5154
	703	6.5	2.00	2.4498

Fig. 5 The evolution of relative defect concentration $(c_f^* - c_{f,eq})/c_{f,eq}$ with strain rate $\dot{\epsilon}$ for $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass at different temperatures

Stress overshoot is a unique phenomenon of the high-temperature rheological behavior of metallic glasses. Free volume theory associates stress overshoot with the necessary time of flow defects to reach a steady state. According to free volume theory, stress-strain curves can be simulated by Eqs. (2) and (9), as shown in **Fig. 6**. The values of parameter a_x are 3.0×10^{-3} , 1.0×10^{-2} , 1.2×10^{-2} for 693 K, 698 K and 703 K, respectively. The values of a_x used in this work are similar to the ones of $\text{Cu}_{40}\text{Zr}_{44}\text{Ag}_8\text{Al}_8$ metallic glass composites (0.035) and $\text{Zr}_{52.5}\text{Al}_{10}\text{Cu}_{27}\text{Ti}_{2.5}\text{Ni}_8$ metallic glass (0.02) (Bletry et al., 2007; Zhang et al., 2015). It can be observed that simulated curves deviate from experimental results at high strain rates. The reasons of such deviation may include three aspects: (I) Steady-state stresses are not accurate due to the uncertainty of the values of the kinetic parameters. (II) Size effects or microstructural variation during tensile testing, leading to an inaccurate estimation of the parameter V .

(III) Influence of V on the simulated results; V may change with c_f while V is defined as a constant in this work. The mechanism of stress overshoot can be explained by the STZ theory: a scarcity of free volume results in an inefficient creation of STZs, leading to a higher stress value before the strain softening. It was revealed that free volume directly effects the ST rates rather than the density of STZs (Jiang et al., 2015). In the framework of this study, strain is affected by defect concentration in a given temperature and strain rate, where the other parameters in Eq. (2) and (9) are constant. This will give a clear and simple physical origin of the stress overshoot phenomenon.

Fig. 6. The simulated results of stress-strain curves for $Zr_{48}Cu_{34}Ag_8Al_8Pd_2$ metallic glass at different temperatures.

3.4. Discussion of the kinetic parameters

Taking into account the physical explanation of the parameters in Eqs. (2) and (9), the aim of the numerical calculations in this section is to obtain information of the glass structural evolution during plastic deformation. The effect of the different parameters, including activation volume V , constant $\dot{\epsilon}_{0,c}$, ratio a_x/k_r , proportionality factor a_x , initial defect concentration $c_{f,0}$, and thermal equilibrium concentration of defects $c_{f,eq}$ will be discussed here. We will take a typical segment with visible stress overshoot in

Fig. 6 as the reference curve for numerical calculations. The initial system is deformed at $T = 698$ K and $\dot{\epsilon} = 2.5 \times 10^{-3} \text{ s}^{-1}$, with initial stress $\sigma_0 = 273$ MPa and $c_{f,0} = 2.9 \times 10^{-13}$.

In the present study, the activation volume V is found to be 0.291 nm^3 . A study of the influence of the value of parameter V for three different values (0.25 , 0.30 and 0.35 nm^3) is shown in **Fig. 7** (a). Clearly, steady-state flow stress presents a remarkable decrease with a slight increase in V . A further comparison of the stress overshoot with different values of V is shown in **Fig. 7** (b), where stress-strain curves have been shifted vertically to the same steady-state flow stress level, i.e. $\sigma_{\text{flow}} = 0$. Clearly, the strength of the stress overshoot, evaluated by the difference between σ_{peak} and σ_{flow} , is increased by decreasing V . Moreover, the higher the value of V , the shorter time the system needs to reach the steady state. This is due to the fact that a higher V gives rise to faster atomic movements, which decreases the height and width of the stress overshoot.

Fig. 7 (c) and (d) unveil the effect of $\dot{\epsilon}_{0,c}$ on the plastic deformation process, where $\dot{\epsilon}_{0,c}$ is related to thermally activated atomic jumps. Activation energy ΔG_m of the atomic jump is inversely proportional to $\dot{\epsilon}_{0,c}$, and lower σ_{flow} is related to higher values of $\dot{\epsilon}_{0,c}$. Shifted stress-strain curves, displayed in **Fig. 7** (d), illustrate that the strength of stress overshoot is independent of $\dot{\epsilon}_{0,c}$, whereas the strain corresponding to σ_{peak} shifts to higher values if decreasing $\dot{\epsilon}_{0,c}$. This reflects that higher strain is needed to activate the atomic movement if ΔG_m is increased. It has been documented that V and $\dot{\epsilon}_{0,c}$ are reduced after physical aging for a La-based metallic glass, which results in higher stress values and more significant stress overshoot at same testing conditions (Qiao et al., 2015).

Fig. 7. Influences of the activation volume V and the constant $\dot{\epsilon}_{0,c}$ on high-temperature deformation.

However, it is not possible to use V and $\dot{\epsilon}_{0,c}$ to reveal the evolution of defect concentration during the plastic deformation process. According to Eq. (9), a_x/k_r is directly related with the defect concentration. **Fig. 8** (a) and (b) exhibit the effect of a_x/k_r on the stress-strain curve and defect concentration, respectively. The results show that stress overshoot is linked to a remarkable variation of defect concentration: once defect concentration at a given testing condition reaches the steady state value, the stress also enters in a plateau. Additionally, strain softening is noticeable for higher values of a_x/k_r , due to the lower value of the defect concentration once the dynamical equilibrium is reached. It has been mentioned that a_x and k_r are related to free volume creation and annihilation, respectively. Therefore, with increasing value of a_x/k_r , the rate of free volume extinguishment is delayed as compared with the generation, resulting in more pronounced strain softening.

It is interesting to note that stress overshoot is indiscernible at very low a_x/k_r . As revealed in **Fig. 8** (a) and (b), the defect concentration drops rapidly for $a_x/k_r = 0.1 \times$

10^{-13} , forcing the stress to monotonously increase with no strain softening. These results imply that inhibiting the creation of free volume or promoting structural relaxation, i.e., decreasing strain rate or increasing temperature, is effective to decrease the stress overshoot. Similarly, it is illustrated in **Fig. 8** (c) and (d) that strain softening corresponds to the growth of defect concentration. In **Fig. 8** (c) and (d), a_x/k_r is equal to 1.515×10^{-13} in the simulated processes. The higher the value of a_x coincides with the faster growth of defect concentration during plastic deformation, giving rise to lower σ_{peak} and shorter time to attain σ_{flow} . It is worth noting that k_r is proportional to a_x in this numerical simulation, therefore, larger a_x is related to faster atomic movement. Strain softening vanishes if $a_x = 1.5$, which is caused by a faster rate of creation and annihilation of defects resulting in a dynamic equilibrium reached with shorter time. The great sensitivity of σ_{peak} with a_x is in agreement with previously reported results (Blettry et al., 2007). It is noteworthy that stress overshoot is covered at lower value of a_x , i.e., at $a_x = 1 \times 10^{-5}$. σ_{flow} raises significantly in this condition with no obvious adjustment of c_f remaining equal to $c_{f,0}$. The value of k_r is decreased with decreasing a_x as a_x/k_r is a constant. The phenomenon presented in **Fig. 8** (c) and (d) indicate that the creation and annihilation of defects are inhibited in the simulation time window when $a_x = 1 \times 10^{-5}$.

Fig. 8. Influences of parameters ratio a_x/k_r and proportionality factor a_x on high-temperature deformation

As discussed in the previous section, stress overshoot is closely related to the initial defect concentration $c_{f,0}$ parameter. **Fig. 9** displays the effect of initial defect concentration $c_{f,0}$ on the plastic deformation process. The values of σ_{flow} are independent of $c_{f,0}$ as seen in **Fig. 9** (a). Furthermore, the strength of stress overshoot is enhanced with the increase of $c_{f,0}/c_f^*$, i.e., stress overshoot is imperceptible if $c_{f,0}$ is equal to c_f^* . Therefore, the stress overshoot is clearly associated with the evolution of defect concentration from $c_{f,0}$ to c_f^* . As shown in **Fig. 9**: if $c_{f,0}/c_f^* > 1$, stress undershoot can be observed; whereas if $c_{f,0}/c_f^* < 1$, stress overshoot is detected. It has been demonstrated that stress undershoot is visible after a decrease of strain rate at low temperatures (Dubach et al., 2009). The reason is due to the relatively high value of $c_{f,h}^*$ achieved at higher strain rate and the resulting higher $c_{f,0}$ after changing to a lower strain rate, which prevents to reach rapidly the new dynamical equilibrium defect concentration $c_{f,l}^*$ corresponding to the lower strain rate. The stress overshoot can be then suppressed by reducing the disagreement between initial defect concentration and steady-state defect concentration or by improving the atomic mobility.

Fig. 9. Influences of the initial defect concentration $c_{f,0}$ parameter on high-temperature deformation of the model alloy.

4. Conclusions

During plastic deformation of metallic glasses, a stress overshoot can be observed increasing the strain rate or decreasing the temperature. In this work, the homogeneous deformation behavior of $\text{Zr}_{48}\text{Cu}_{34}\text{Ag}_8\text{Al}_8\text{Pd}_2$ metallic glass was investigated using the Kohlrausch-Williams-Watts equation and the free volume model. The free volume model is able to describe the main traits of the homogeneous deformation, revealing the physical origins of the observed experimental behavior. The steady-state flow stress is highly influenced by atomic mobility and the stress overshoot phenomenon is determined by the time needed to reach the equilibrium defect concentration. It has been found that reducing the disagreement between initial defect concentration and steady-state defect concentration suppresses the stress overshoot.

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