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Estimation of the shear transformation zone size in a bulk metallic glass through statistical analysis of the first pop-in stresses during spherical nanoindentation

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The size of the shear transformation zone (STZ) that initiates the elastic to plastic transition in a Zr-based bulk metallic glass was estimated by conducting a statistical analysis of the first pop-in event during spherical nanoindentation. A series of experiments led us to a successful description of the distribution of shear strength for the transition and its dependence on the loading rate. From the activation volume determined by statistical analysis the STZ size was estimated based on a cooperative shearing model.

Keywords: Bulk amorphous materials; Nanoindentation; Yield phenomena; Shear transformation zone

It is widely accepted that the fundamental carriers of plasticity in amorphous alloys are the shear transformation zones (STZs), which are atomic clusters that undergo inelastic shear straining under the influence of an applied stress [1–3]. STZs in metallic glasses are the analogs of mobile dislocations in crystalline solids. While dislocations can be imaged using a variety of techniques, direct observation of STZs is nigh impossible because of their transient nature. While it is generally understood that the activation of STZs occurs preferentially in those regions of the material where the atomic packing efficiency is relatively smaller (higher free volume content), the volume (or size) of an STZ is still an actively debated point. This is particularly so because of the difficulty associated with direct experimental assessment of it. This led to the study of STZ size either through molecular dynamics (MD) simulations or indirect experiments. For example, Pan et al. [4,5] utilized the rate dependence of hardness to estimate the volume of STZs. For this they modified the cooperative shear model (CSM) of Johnson and Samwer [6], which was developed on the basis of the potential-energy landscape. However, hardness is an indicator of the resistance to plastic flow rather than its initiation (yielding). Since plastic flow in metallic glasses occurs through localization (shear bands), negative rate sensitivity ensues. In such a scenario one cannot simply obtain the underlying kinetics of STZs.

One of the most popular methods to study small-scale yielding of materials is nanoindentation. During nanoindentation with a spherical or round indenter the load–displacement (*P*–*h*) curves often exhibit either a sudden burst of displacement when the test is performed under load control or a sharp load drop if the test is conducted under displacement control. This phenomenon is often referred to as “pop-in”. Since the pioneering work by Page et al. [7] the study of pop-ins, especially the first pop-in, has gathered wide interest because it indicates to elastic-to-plastic transition in crystalline and amorphous materials [8–14]. Recently Wang et al. [15] attempted to determine the size and activation energy of STZs in an Au–Ag–Pd–Cu–Si bulk metallic glass (BMG) by analyzing the high temperature nanoindentation pop-in data according to Argon’s classical constitutive equations [1]. Although a good first attempt, this study did not consider the wide variability in the pop-in data, which points to the stochastic nature of STZ

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activation and, hence, warrants a model that is intrinsically statistical in nature. We attempt such in this paper, with the objective of estimating the STZ size by statistical analysis of the pop-in data within the premise of the CSM model. From a series of nanoindentation experiments on a Zr-based BMG with a spherical indenter we have obtained the maximum shear stress at the elastic to plastic transition and its dependence on the loading rate. This data is utilized to ascertain the STZ size.

An ~7 mm diameter and ~70 mm long rod of Zr-based BMG, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (commercial designation Vit 105) was examined. No crystalline peak was detected in the X-ray diffraction (XRD) spectra of the specimen [16]. Experiments were conducted at room temperature using a Nanoindenter-XP (formerly MTS-now Agilent, Oak Ridge, TN) instrument equipped with a spherical tip. Hertzian contact analysis [17] of indentations made on fused quartz was utilized to estimate the tip radius R as 31.5 μm based on the assumption that the sample surface, which was polished to a mirror finish prior to testing, is flat. It is notable that R in the original Hertz analysis is the "relative" radius of the sphere-to-sphere contact and thus determined as $1/R = 1/R_i + 1/R_s$, where R_i and R_s are the radius of the indenter and sample, respectively. For a flat surface $1/R_s = 0$. Tests were conducted in load control mode at loading rates of 0.5, 1, 5, 10, and 20 mN s^{-1}. More than 120 tests were conducted at each rate so as to obtain statistically significant data sets. Thermal drift was maintained below 0.05 nm s^{-1} in all experiments.

Figure 1 shows a representative P–h curve exhibiting pop-ins. Figure 1 also shows the P–h curve obtained at low load (before the first pop-in), with the loading part of the curve retraced by the unloading curve, indicating that deformation is solely elastic before the first pop-in. This elastic behavior of the material during spherical indentation can be described by Hertzian contact theory [17]:

$$P = \frac{4}{3} E_r \sqrt{R} \cdot h^{\frac{3}{2}} \tag{1a}$$

and

$$\frac{E_s}{1 - \nu_s^2} = \left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i} \right)^{-1} \tag{1b}$$

where E and ν are the elastic modulus and Poisson ratio, with the subscripts s and i indicating the sample and the indenter. The reduced modulus E_r accounts for the fact that elastic deformations occur in both the indenter and the sample. Since a diamond tip is used ($E_i = 1141$ GPa, $\nu_i = 0.07$) [18]. By fitting the loading part of the P–h curve to Eq. (1a) the indentation modulus of the samples $E_s/(1 - \nu_s^2)$ was estimated to be ~100 GPa, which is in agreement with the reported value in the literature (~103 GPa based on $E_s = 89$ GPa, $\nu_s = 0.37$) [19].

The maximum shear stress at the first pop-in τ_{max} represents the critical shear strength for the onset of plasticity in the indented material. In spherical indentation τ_{max} occurs at a distance approximately half the contact radius directly below the rotational axis of the contact and is given as [17]:

$$\tau_{max} = 0.31 p_0 = 0.31 \left(\frac{3}{2} p_m \right) = 0.31 \left(\frac{6 E_r^2}{\pi^3 R^2} P \right)^{\frac{1}{3}} \tag{2}$$

where p_0 and p_m are the maximum and mean pressures of the contact, respectively. Even for indentations conducted under identical testing conditions τ_{max} estimated from the first pop-in load is distributed over a wide range of ~1.2–3.4 GPa, as seen in Figure 2. An important feature in Figure 2 is that τ_{max} is rate dependent; a higher loading rate generally results in a higher τ_{max}. These results are in contrast to some of the published literature. Ng et al. [20], who have examined the serrated flow (i.e. a series of pop-ins) behavior of a (Cu–Mg–Y)–Be BMG at room temperature using a sharp indenter, concluded that the flow is insensitive to strain rate. We wish to point that they used a sharp indenter, which means that the strains imposed are large and, hence, plastic flow is dominated by shear band kinetics [20]. In contrast, we used a spherical indenter and, hence, the plastic strains at the first pop-in event are rather small and capture the elastic-to-plastic transition. Recently Packard et al. [15] reported that in a Pd- and a Fe-based BMG the first pop-in stresses are rate- and temperature-independent. This observation led them to suggest that the distribution of the first pop-in stress predominantly originates from scattering in the local atomic structure rather than thermal fluctuations. However, at least in the Zr-based BMG examined here, detectable rate dependency of the pop-in stress exists, indicating that, with the inherent inhomogeneity of the atomic configuration in the amorphous state, thermal fluctuation could still have a role to play in the pop-in event. Therefore, it is likely that the rate dependency of the first pop-in event depends on the BMG composition (and thus

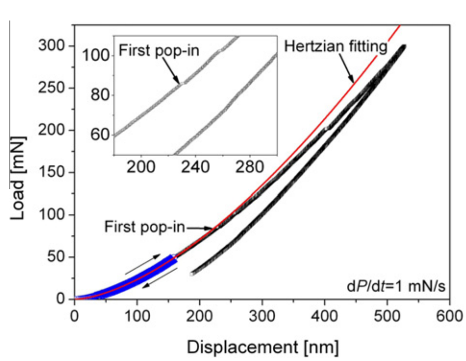

Figure 1. A representative P–h curve showing pop-ins and a Hertzian curve. (Inset) The loading part near the first pop-in.

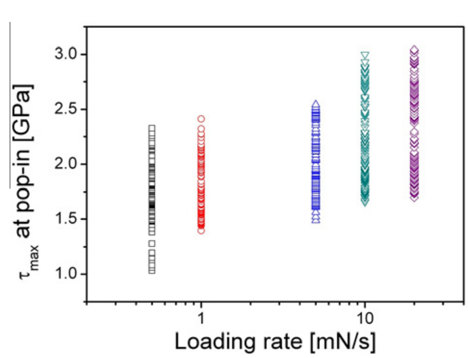

Figure 2. Variation in the maximum shear stress for the elastic to plastic transition τ_{max} with loading rate.

structural conditions such as the kinetics of structural relaxation), although detailed reasons for the difference are an unresolved issue at this point. From the pop-in data in Figure 2 the size of the STZ has been estimated using the following procedure.

The constitutive equation for stress-assisted, thermally activated yielding in amorphous alloys (regardless of the details of the mechanism involved) is given by a simple Boltzmann form:

$$\dot{\gamma} = \dot{\gamma}_0 \times \exp\left(-\frac{\Delta G^*}{kT}\right) = \dot{\gamma}_0 \times \exp\left(-\frac{\Delta F^* - \tau V^*}{kT}\right) \quad (3)$$

where $\dot{\gamma}$ is the inelastic shear strain rate (or the rate of a shear stress-induced event), ΔG^* is the Gibbs free energy of activation, kT is the thermal energy (k is the Boltzmann constant, T is the temperature), $\dot{\gamma}_0$ is the attempt frequency (i.e. the frequency of the fundamental mode vibration along the reaction pathway [9]), ΔF^* and V^* are the Helmholtz activation energy and volume of the event, respectively, and τ is the applied shear stress. According to Argon's classical model [1] V^* is equal to the product of the characteristic STZ volume Ω and the characteristic shear strain, i.e. $\Omega = V^*/\gamma_0$ [1,3,21].

In the CSM model of Johnson and Samwer [6] yielding is determined by the cooperative shear motion of STZs and, hence, intrinsically depends on V^*. They suggested an expression for activation energy:

$$\Delta G^* = 4C\mu\gamma_C^2\left(1 - \frac{\tau_{CT}}{\tau_{C0}}\right)^{\frac{3}{2}}\zeta\Omega \quad (4)$$

where μ is the shear modulus (32.5 GPa for the BMG under consideration here), τ_{CT} and τ_{C0} are the threshold shear strength at T and 0 K, respectively, γ_C is the shear strain ($=\tau_{CT}/\mu$), and the constants C and ζ are approximately equal to 1/4 and 3 [6], respectively. Note that μ has a weak temperature dependence under isoconfigurational conditions [6,22]. As Pan et al. [4,5] proposed, an expression for the activation volume V^* can be obtained by differentiation of the activation energy in Eq. (4):

$$V^* = -\left(\frac{\partial \Delta G^*}{\partial \tau_{CT}}\right) \quad (5)$$

From Eqs. (4) and (5) the volume of the STZ can be obtained as:

$$\Omega = \frac{\tau_{C0}}{6C\mu\gamma_C^2\zeta\left(1 - \frac{\tau_{CT}}{\tau_{C0}}\right)^{\frac{1}{2}}} V^* \quad (6)$$

With the data from 30 different metallic glasses Johnson and Samwer [6] arrived at a scaling law for their flow stress:

$$\gamma_C = \frac{\tau_{CT}}{\mu} = \gamma_{C0} - \gamma_{C1}\left(\frac{T}{T_g}\right)^M \quad (7)$$

where $\gamma_{C0} = 0.036 \pm 0.002$, $\gamma_{C1} = 0.016 \pm 0.002$, and $M = 0.62 \pm 0.2$. Therefore, for a given μ and T_g both τ_{CT} and τ_{C0} (i.e. $\gamma_{C0}\mu$ at $T = 0$ K) of a metallic glass can be estimated from this constitutive equation. Collectively, if V^* of the pop-in event can be estimated through nanoindentation tests the size of the STZ involved in yielding can be determined according to Eq. (6). It is worth noting that in Eq. (6) μ does not affect the calculated STZ volume because both τ_{CT} and τ_{C0} are linearly proportional to it.

There are two ways in which V^* can be estimated using the first pop-in data in Figure 2. The first and simple way is through the rate dependence of τ_{max}. For this Eq. (3) can be rewritten as:

$$V^* = kT\left(\frac{\partial \ln\dot{\gamma}}{\partial \tau_{max}}\right) \quad (8)$$

and thus V^* can be deterministically obtained from the slope of the fit of $\ln\dot{\gamma}$ and τ_{max}. In this analysis the strain rate of a spherical indentation can be approximated as $A^{-1}(\mathrm{d}A/\mathrm{d}t)$ at the pop-in load (where A is the contact area), instead of $h^{-1}(\mathrm{d}h/\mathrm{d}t)$, which is typically used in sharp indentation. Although V^* obtained through this approach has a proper physical meaning (by virtue of Eq. (8)), the influence of the variability in τ_{max} is ignored in such an analysis. Further, estimation of the effective strain rate is only approximate, at best. Hence, we have not utilized this approach in the present study. Instead, we have adopted the second, statistical approach, which is described below.

The cumulative distribution of τ_{max} is illustrated in Figure 3. Schuh and Lund [9] suggested that thermally assisted and stress-biased yielding always exhibits a spread in yield strength. This is because the thermal noise sometimes favors yielding and sometimes works against it. On this basis, the cumulative distribution function of pop-in events (i.e. the cumulative probability in Fig. 3) can be described as a function of the instantaneous shear stress beneath the indenter τ [9]:

$$f = 1 - \exp\left[-\frac{kT\dot{\gamma}_0}{V^*(\mathrm{d}\tau/\mathrm{d}t)}\exp\left(-\frac{\Delta F^*}{kT}\right)\exp\left(\frac{\tau V^*}{kT}\right)\right] \quad (9)$$

Note that $(\mathrm{d}\tau/\mathrm{d}t)$ is a constant for nanoindentation tests conducted with a constant loading rate $\mathrm{d}P/\mathrm{d}t$. Eq. (9) can be rewritten as:

$$\ln[\ln(1-f)^{-1}] = \left\{\frac{\Delta F^*}{kT} + \ln\left[\frac{kT}{V^*(\mathrm{d}\,\tau/\mathrm{d}t)}\right]\right\} + \left(\frac{V^*}{kT}\right)\tau \quad (10)$$

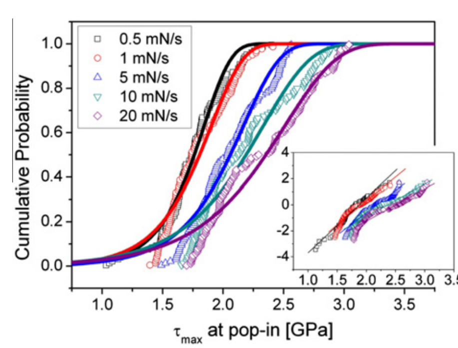

Figure 3. The cumulative probability distributions of the maximum shear strengths τ_{max} at various loading rates. (Inset) The linear fit to the $\ln[\ln(1-f)^{-1}]$ vs. τ_{max} data.

Table 1. The activation volume and STZ size calculated based on the statistical analysis of the first pop-in data.

Loading rate (mN s^{-1})	Activation volume V^* (nm^3)	STZ size	
		STZ volume Ω (nm^3)	Number of atoms in STZ N
0.5	0.0173	0.387	29
1	0.0151	0.337	25
5	0.0141	0.314	23
10	0.0103	0.229	17
20	0.0102	0.226	17

Therefore, considering $\tau = \tau_{max}$, V^* can be estimated from the slope of a $\ln[\ln(1-f)^{-1}]$ vs. τ_{max} plot, as shown in the inset in Figure 3, where the tails of the distribution are excluded. The correlation factor (R^2) for every case of linear fit in the inset is higher than 0.95. Values of V^* obtained at different loading rates are listed in Table 1. By combining these with τ_{CT} and τ_{C0} (determined using Eq. (7)) Ω can be estimated from Eq. (6), which are also listed in Table 1. The values of Ω range between 0.23 and 0.39 nm^3. In turn, the number of atoms in the STZ (N) can be estimated on the basis of a dense-packing, hard-sphere model of metallic glasses with an average atomic radius $R = \left(\sum_i^n A_i r_i^3\right)^{\frac{1}{3}}$. Here A_i and r_i are the atomic fraction and the atomic radius of each element, respectively [4]. The estimated N is also provided in Table 1. This gives an STZ size of approximately 20–30 atoms, in good agreement with the literature [1–3,15,21,23]. Computer simulations also reveal local shear events on the same size scale [3]. Estimates made by Pan et al. [4] are higher at ~200–300 atoms for the STZ in Zr-based BMGs. However, as noted earlier, their analysis was made with rate-dependent hardness data, whereas we use the elastic–plastic transition in our analysis.

Before closing, possible reasons for the observed rate dependence of τ_{max} (which in turn may conceivably reflect the rate dependence of V^* and N) are hypothesized. In Eq. (3) the Boltzmann factor, $\exp(-\Delta G^*/kT)$, is the probability of overcoming the barrier ΔG^* by thermal fluctuations in T (such that $\Delta G^* >> kT$). Therefore, one could anticipate that the probability increases if it takes longer to reach a certain critical stress [9,10]. Thus, as the loading rate is increased the probability becomes lower and a higher stress is required to produce a critical thermal fluctuation to overcome ΔG^*, resulting in an apparent higher yield strength. However, this is not fully understood in a quantitative manner, and further detailed investigations are essential for a better understanding of this rate effect.

In summary, the size of an STZ that instigates the initiation of plastic flow in metallic glasses was estimated by recourse to the study of the statistical behavior of the first pop-in stress during spherical nanoindentation. The distribution of the critical shear strength for the transition and the activation volume of the pop-in event were determined by analyzing the cumulative probability of the event. Finally, the STZ size was estimated from the activation volume based on the CSM.

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[1] A.S. Argon, Acta Metall. 27 (1979) 47.
[2] A.S. Argon, L.T. Shi, Acta Metall. 31 (1983) 499.
[3] C.A. Schuh, T.C. Hufnagel, U. Ramamurty, Acta Mater. 55 (2007) 4067.
[4] D. Pan, A. Inoue, T. Sakurai, M.W. Chen, Proc. Natl. Acad. Sci. USA 105 (2008) 14769.
[5] D. Pan, H. Guo, W. Zhang, A. Inoue, M.W. Chen, Appl. Phys. Lett. 99 (2011) 241907.
[6] W.L. Johnson, K. Samwer, Phys. Rev. Lett. 95 (2005) 195501.
[7] T.F. Page, W.C. Oliver, C.J. McHargue, J. Mater. Res. 7 (1992) 450.
[8] H. Bei, Z.P. Lu, E.P. George, Phys. Rev. Lett. 93 (2004) 125504.
[9] C.A. Schuh, A.C. Lund, J. Mater. Res. 19 (2004) 2152.
[10] C.A. Schuh, J.K. Mason, A.C. Lund, Nat. Mater. 4 (2005) 617.
[11] S. Shim, H. Bei, E.P. George, G.M. Pharr, Scripta Mater. 59 (2008) 1095.
[12] C.E. Packard, C.A. Schuh, Acta Mater. 55 (2007) 5348.
[13] H. Bei, Z.P. Lu, S. Shim, G. Chen, E.P. George, Metall. Mater. Trans. A 41 (2010) 1735.
[14] C.E. Packard, O. Franke, E.R. Homer, C.A. Schuh, J. Mater. Res. 25 (2010) 2251.
[15] L. Wang, Z.P. Lu, T.G. Nieh, Scripta Mater. 65 (2011) 759.
[16] B.-G. Yoo, K.-W. Park, J.-C. Lee, U. Ramamurty, J.-I. Jang, J. Mater. Res. 24 (2009) 1405.
[17] K.L. Johnson, Contact Mechanics, Cambridge University Press, Cambridge, 1985.
[18] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
[19] C.T. Liu, L. Heatherly, D.S. Easton, C.A. Carmichael, J.H. Schneibel, C.H. Chen, M.H. Yoo, J.A. Horton, A. Inoue, Metall. Mater. Trans. A 29 (1998) 1811.
[20] K.Y. Ng, L. Zuo, A.H.W. Ngan, Scripta Mater. 61 (2009) 955.
[21] M. Heggen, F. Spaepen, M. Feuerbacher, J. Appl. Phys. 97 (2005) 033506.
[22] M.L. Lind, G. Duan, W.L. Johnson, Phys. Rev. Lett. 97 (2006) 015501.
[23] M. Heilmaier, J. Eckert, Adv. Eng. Mater. 7 (2005) 833.