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# On the critical thickness for non-localized to localized plastic flow transition in metallic glasses: A molecular dynamics study



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#### ABSTRACT

Molecular dynamics simulations were employed to investigate the specimen thickness-dependent tensile behavior of a series of  $Cu_x Zr_{100-x}$  (x = 20, 40, 50, 64 and 80 at.%) metallic glass (MG) films, with a particular focus on the critical thickness,  $t_c$ , below which non-localized plastic flow takes place. The simulation results reveal that while the transition occurs in all the alloys examined,  $t_c$  is sensitive to the composition. We rationalize  $t_c$  by postulating that the strain energy stored in the sample at the onset of plastic deformation has to be sufficient for the formation of shear bands. The composition-dependence of  $t_c$  was found to correlate with the average activation energy of the atomic level plastic deformation events.

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Size-dependence of plastic deformation behavior of materials is a topic of current research within the materials engineering discipline [1–18]. Within it, "how the mechanical behavior of metallic glasses (MGs) changes as the size of the specimens is reduced?" and "what are the mechanics/mechanisms responsible?" are questions for which answers are being sought actively by the MG community. At macroscopic scale, and at sufficiently low temperatures, plastic flow in MGs, if and when it occurs, manifests as localized flow into narrow regions that are often referred to as shear bands. Preceding the shear band formation, flow occurs through the activation of shear transformation zones (STZs) [19], which are clusters of atoms undergoing collective shear in order to relax the imposed stress. Prior studies, especially those performed on micro/nanopillars in compression, have shown that a transition from localized flow to continued non-localized deformation occurs when the specimen size is sufficiently small. A number of explanations are offered in literature for the observed transition, most of which are similar -conceptually-to the Griffith's criterion for fracture [9–18]. Essentially, they argue that the change in the deformation mode occurs only when the reduction in the elastic strain energy that occurs with the shear band propagation is larger than the effective surface energy increase due to the formation of a shear band. Since elastic strain energy stored in a stressed solid is proportional to the size of the sample itself, larger than a certain critical sized samples will necessarily undergo a deformation mode transition. However, a shear band is a three-dimensional volume within the specimen that undergoes plastic deformation rather than a two-dimensional crack with well defined surfaces. Thus, question on the appropriateness of using the Griffithlike criterion arises, which we seek to address in this paper. Since precise fabrication of extremely small sized specimens, with systematic variation of specimen size while keeping the thermal history invariant, is rather difficult if not impossible, we resort to atomistic simulations to study the size-dependent tensile deformation behavior of MGs, and then critically examine the deformation mode transition in them.

MD simulations of  $Cu_{20}Zr_{80}$ ,  $Cu_{40}Zr_{60}$ ,  $Cu_{50}Zr_{50}$ ,  $Cu_{64}Zr_{36}$  and  $Cu_{80}Zr_{20}$  MGs were performed utilizing LAMMPS [20], employing the embedded-atom method potentials developed by Mendelev et al. [21], with the following sequential steps: (1) one big sample with a size of 28.2 nm (x) × 56.4 nm (y) × 5.6 nm (z) and ~500,000 atoms is generated. The detailed procedure of "melt–quench–duplicate" is similar to the procedures described in the literature [22,23]: after a cubic cell with five different compositions melted at 2000 K and zero pressure for two ns to ensure homogeneity, during which periodic boundary conditions (PBCs) were applied to all three dimensions, the cell was quenched from 2000 to 50 K over 19.5 ns at a cooling rate of  $10^{11}$  K/s. The final

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Fig. 1. Stress-strain curves and deformation maps for Cu-Zr MG films at three different thicknesses. (a) Cu<sub>20</sub>Zr<sub>80</sub> MG, (b) Cu<sub>40</sub>Zr<sub>60</sub> MG, (c) Cu<sub>64</sub>Zr<sub>36</sub> MG, and (d) Cu<sub>80</sub>Zr<sub>20</sub> MG.

dimensions of the cubic cell were measured to be  $5.6 \times 5.6 \times 5.6$  nm<sup>3</sup>. It was then duplicated to a big sample with a size of 28.2 nm  $(x) \times 56.4$  nm  $(y) \times 5.6$  nm (z). (2) After 1 ns relaxation at 50 K of the big sample, films with various thicknesses, t, were cut from the central part of the big sample along x axis while the dimensions in y and z axes were not changed. (3) Subsequent to cutting, specimens were relaxed for 100 ps relaxation at 50 K. (4) All the films as well as the big specimen were tensile tested along y direction at a constant strain rate of  $1 \times 10^8 \text{ s}^{-1}$  to a total strain of 14% at 50 K. It is important to note here that all the studied films were subjected to the same processing history and strain rate. Thus, the only variable, other than composition, in this campaign is the film thickness. During deformation, PBCs were imposed on y and z directions, while the free surface condition was applied to the *x* direction, so that the deformed sample mimics a thin film. The time step for deformation was chosen as 1 fs. To visualize plastic shearing during deformation, the local shear invariant von Mises strain of each atom [24] in the sample was calculated using the equation:  $\eta^{\text{Mises}} = \sqrt{\frac{1}{2}} \text{Tr}(\eta - \eta_m I)^2$ , where  $\eta$  and  $\eta_m$  are the local Lagrangian and hydrostatic strains for that atom, respectively. Atoms with  $\eta_i^{\text{Mises}} \ge 0.2$  were termed as sheared atoms or "S-atoms" and were utilized to visualize the plastic deformation within the specimen. The region with a high density of "S-atoms" is identified as a shear band.

Fig. 1(a) shows stress–strain (SS) responses obtained on  $Cu_{20}Zr_{80}$  MG with three different t. While all the SS curves exhibit a peak stress followed by softening with the exception of the 28.2 nm-thick film that exhibits a sharp drop after a strain of ~9%, an apparent characteristic of localized deformation, similar to that reported in literature [22,23]. Localization of flow was also confirmed by the deformation map, displayed in the inset of Fig. 1(a), wherein the formation of a prominent shear band can be seen. The SS response of the film with t = 5.64 nm is similar, and necking of the sample was observed, which indicates that localization of flow is still prevalent. When *t* is further reduced to



**Fig. 2.** (a) Stress–strain curves of five 28.2 nm-thick and schematic illustration of the procedure utilized for estimating  $U_{SB}$ . (b) Stress–strain curves of  $Cu_{64}Zr_{36}$  MG with different thicknesses and schematic illustration of method utilized for computing  $U_n$ .

5.2 nm, however, the reduction in flow stress beyond the peak is gradual and the flow is non-localized (as can be seen from the deformation map obtained at a strain of 12% in the inset of Fig. 1(a)). A similar behavior is also detected for even thinner films. These results do indeed confirm that for the Cu<sub>20</sub>Zr<sub>80</sub> MG films, a transition in the deformation mode from shear band mediated (or localized) to non-localized flow indeed occurs, when *t* is reduced below a critical thickness, *t*<sub>c</sub>, of 5.42  $\pm$  0.22 nm (i.e. average of 5.64 and 5.2 nm, wherein the transition is noted).

The SS responses obtained on the other three MGs are displayed in Figs. 1(b)–(d). In these cases also, a deformation mode transition is noted at  $t_c = 6.78 \pm 0.28$ ,  $3.33 \pm 0.20$ , and  $2.98 \pm 0.16$  nm for Cu<sub>40</sub>Zr<sub>60</sub>, Cu<sub>64</sub>Zr<sub>36</sub>, and Cu<sub>80</sub>Zr<sub>20</sub>, respectively. These results, together with our previous work for Cu<sub>50</sub>Zr<sub>50</sub> MG films with  $t_c$  as 4.95  $\pm$  0.25 nm [17], further suggest that the thickness-induced deformation mode transition is a general feature in MGs. The non-localized deformation mode in small-size samples were further examined at strain of 20%, as shown in Fig. S1. We note that these  $t_c$  values are much smaller than the experimentally obtained ones (typically in the range of 50 to 300 nm) reported in literature. This discrepancy is due to the following possible reasons. (a) The effective strain rate,  $10^8/s$ , which is common for MD simulations, is much larger than the rates of  $10^{-2}$ – $10^{-4}/s$  used in many experiments. (b) The samples tested through MD simulations do not contain any external defects/flaws.

To understand the composition-dependence of  $t_c$  in Cu–Zr MGs, one should first answer the question: "why does the *t*-dependence of the deformation mode for a given composition occurs?" For this, we studied the energy needed for forming one mature shear band, as following, which is illustrated in Fig. 2(a) for Cu<sub>20</sub>Zr<sub>80</sub> MG. The S-atoms start appearing at the strain labeled "a", i.e. the maximum stress of the SS curve [25], i.e., notable plastic deformation starts at this strain. When the sample is strained to point marked "b", one mature shear band is



**Fig. 4.** (a) Variations of the number of S-atoms,  $N_{\rm s}$ , with strain during the shear band formation process in various Cu–Zr MG films. The film thickness in all cases is 28.2 nm. (b) The reciprocal of average energy required for forming one S-atom,  $U_{\rm S}^{-1}$ , together with critical thickness,  $t_{\rm cr}$  as a function of composition in Cu–Zr MG films.



Fig. 3. Variation of U<sub>p</sub> as a function of thickness for (a) Cu<sub>64</sub>Zr<sub>36</sub>, (b) Cu<sub>50</sub>Zr<sub>50</sub>, (c) Cu<sub>40</sub>Zr<sub>60</sub>, and (d) Cu<sub>20</sub>Zr<sub>80</sub> MGs. The dashed line represents the value of U<sub>58</sub> for each composition.

formed. Thus, it is reasonable to assume that the strain energy that is spent during deformation of the sample from point "a" to "b" is the energy required to localize plastic flow. The two solid straight lines are drawn parallel to the initial linear elastic part of SS curve at points "a" and "b". Before the formation of a mature shear band, the energy dissipated (area under the SS curve up to point b) can be partitioned into three parts labeled A, B, and C. The energy density in region A contributes to the local inelastic deformation and dissipates throughout the whole sample. The energy that is encompassed by region C corresponds to that recoverable by unloading from point "b", i.e., it is the elastic strain energy that remains in the sample even after a shear band has formed. Therefore, the energy that gets spent during the formation of a mature shear band is region B, defined as U<sub>SB</sub>. The SS curves of all five 28.2 nm-thickness Cu-Zr samples are shown in Fig. 2(a), the red arrows indicate the starting and the ending strains, i.e. points a and b in respective plots, which are utilized to estimate the values of  $U_{SB}$  for each composition and *t*.

We postulate that "localization of flow through the formation of shear bands occurs if and only if the total energy that is stored in the system at the onset of plastic deformation,  $U_p$ , is equal or larger than  $U_{SB}$ ". If  $U_p < U_{SB}$ , the stored energy is insufficient to cause localization, therefore the MG sample deforms in a non-localized manner. Values of  $U_p$ , which depend on t, are estimated as illustrated in Fig. 2(b) for Cu<sub>64</sub>Zr<sub>36</sub>MG samples. Fig. 3(a) shows the variations of  $U_p$  with t in Cu<sub>64</sub>Zr<sub>36</sub>MG, and the horizontal red dash line represents the value of  $U_{SB}$  estimated for that composition. Surprisingly, we found that at around  $t_c$ ,  $U_p$  is indeed close to  $U_{SB}$  in Cu<sub>64</sub>Zr<sub>36</sub> MG. Similar results were also obtained for Cu<sub>80</sub>Zr<sub>20</sub> (not shown), Cu<sub>50</sub>Zr<sub>50</sub>, Cu<sub>40</sub>Zr<sub>60</sub> and Cu<sub>20</sub>Zr<sub>80</sub> MGs, as shown in Figs. 3(b)–(d) respectively. These results confirm our postulate that it is the competition between  $U_p$  and  $U_{SB}$  that determines the deformation mode in the MG specimens.

We examined if any correlation exists between t<sub>c</sub> and surface energy  $\gamma$ , glass transition temperature T<sub>g</sub>, Poisson's ratio, strength, and Young's modulus. As shown in S3 and S4, no correlation can be found. Then, 'is the tendency for flow localization within a MG related to the ease with which plastic deformation in it can be triggered?' To answer this question, we focus on the evolution of S-atoms with strain next. In Fig. 4(a), we have plotted the variation of the number of S-atoms,  $N_s$ , between the strains of 8 and 12%. A comparison of this plot with that displayed in Fig. 2(a) indicates that  $N_s$ , increases nearly-synchronously with the decrease in post-peak stress in all the studied Cu-Zr MGs. Since S-atoms cause stress relaxation through local strain accommodation, an increase in  $N_s$  during the formation of the shear bands can be considered as the reason for the strain softening observed in Fig. 2(a). This, in turn, implies that activation of S-atoms and strain localization may be intimately linked. To examine this, the average activation energy for forming one S-atom,  $U_{\rm S}$ , was first estimated by dividing  $U_{\rm SB}$  with the number of S-atoms formed in the same strain range shown in Fig. 2(a). This implicitly assumes that all of  $U_{SB}$  is transferred into the formation of S-atoms in the whole sample. In Fig. 4(b), the reciprocal of  $U_{\rm S}$  together with critical thickness,  $t_{\rm c}$  is plotted as a function of composition, which shows that lower  $U_{\rm S}$  results in higher  $t_{\rm c}$ . We would like to emphasize here that local short-range structures in the five Cu–Zr MGs analyzed by Voronoi tessellation are different, which further affect the values of  $U_{\rm S}$ . Consequently, one expects that  $t_{\rm c}$  should depend on the composition in Cu-Zr MGs, as observed in Fig. 4(b). Note that conceptually both "S-atom" and STZ involve large local atomic displacements. However, the former concerns itself with specific atoms, simply because it is relatively easier to track the strain associated with each atom, than clusters of them as in the case of STZs. Thus, it may appear that they are conceptually different. However, it is reasonable to view STZs as S-atoms combined with their nearest neighbors, for large displacements of individual atoms have to be necessarily involve displacements of nearest neighbors [25]. Thus, the energy to activate S-atoms or STZ might be strongly correlated to each other. For the correlation between local atomic packing with the average energy required for forming one S-atom in the five Cu–Zr MGs, more studies are required. We also recognize that the value of  $t_c$  will also depend on the structural state of the alloy, which depends on a number of things including the cooling rate employed. To examine this, we have estimated the values of  $t_c$  for Cu<sub>64</sub>Zr<sub>36</sub> MG samples that were synthesized with the additional cooling rates of 10<sup>10</sup> and 10<sup>12</sup> K/s. A comparison of the SS responses and the deformation maps is made in Fig. S5. The results clearly show that at a lower cooling rate results in a reduction of  $t_c$ . This result highlights the importance of processing history of MG samples on deformation transition. Finally, we note that the time scales involved in MD simulations are significantly different from those of experiments. Thus, one needs to be careful while comparing the results of simulations and experiments.

In summary, the composition-dependence of tensile behaviors of  $Cu_xZr_{100-x}$  (x = 20, 40, 50, 64 and 80 at.%) MG films were investigated by MD simulations. The results reveal that with decreasing *t*, the deformation mode transits from the localized to non-localized deformation modes. The critical thickness for this transition, which was found to vary with the composition, was rationalized by recourse to energetics. It was postulated and then validated that the elastic strain energy stored in the system just at the onset of plastic deformation has to be necessarily sufficient for the formation of shear band; if not, non-localized flow will prevail. Further, the critical thickness is found to be closely related to the average energy required for forming S-atoms (or shear transformation zones). Higher the energy required for STZ activation, lower will be the critical thickness. Our research is expected to trigger further investigations for the size-dependent deformation behavior of MGs.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.scriptamat.2015.12.012.

#### References

- [1] G. Kumar, A. Desai, J. Schroers, Adv. Mater. 23 (2011) 461-476.
- [2] H. Guo, P.F. Yan, Y.B. Wang, J. Tan, Z.F. Zhang, M.L. Sui, E. Ma, Nat. Mater. 6 (2007) 735–739.
- [3] D.C. Jang, J.R. Greer, Nat. Mater. 9 (2010) 215–219.
- [4] Q.K. Li, M. Li, Intermetallics 14 (2006) 1005–1010.
- [5] L. Tian, Z.W. Shan, E. Ma, Acta Mater. 73 (2013) 4823-4830.
- [6] A. Dubach, R. Raghavan, J.F. Loffler, J. Michler, U. Ramamurty, Scr. Mater. 60 (2009) 567–570.
- [7] J.R. Greer, J.T.M. De Hosson, Prog. Mater. Sci. 56 (2011) 654-724.
- [8] D.T.A. Matthews, V. Ocelik, P.M. Bronsveld, J.T.M. De Hosson, Acta Mater. 56 (2008) 1762-1770.
- [9] C.Q. Chen, Y.T. Pei, J.T.M. De Hosson, Acta Mater. 58 (2010) 189–200.
- [10] C.Q. Chen, Y.T. Pei, O. Kuzmin, Z.F. Zhang, E. Ma, J.T.M. De Hosson, Phys. Rev. B 83 (2011) 180201.
- [11] C.Q. Chen, Y.T. Pei, J.T.M. De Hosson, Scr. Mater. 67 (2012) 947-950.
- [12] O.V. Kuzmin, Y.T. Pei, J.T.M. De Hosson, Scr. Mater. 67 (2012) 344–347.
- [13] O.V. Kuzmin, Y.T. Pei, C.Q. Chen, J.T.M. De Hosson, Acta Mater. 60 (2012) 889-898.
- Y. Ma, Q.P. Cao, S.X. Qu, X.D. Wang, J.Z. Jiang, Acta Mater. 60 (2012) 3667–3676.
   Y. Ma, Q.P. Cao, S.X. Qu, X.D. Wang, D.X. Zhang, J.Z. Jiang, Acta Mater. 60 (2012) 4136–4143.
- [16] Q.P. Cao, C. Wang, K.J. Bu, S.Y. Liu, X.D. Wang, D.X. Zhang, J.Z. Jiang, Scr. Mater. 77 (2014) 64–67.
- [17] C. Zhong, H. Zhang, Q.P. Cao, X.D. Wang, D.X. Zhang, J.Z. Jiang, Scr. Mater. 101 (2015) 48–51.

- [18] C.C. Wang, J. Ding, Y.Q. Cheng, J.C. Wan, L. Tian, J. Sun, Z.W. Shan, J. Li, E. Ma, Acta Mater. 60 (2012) 5370–5379.
  [19] A.S. Argon, Acta Metall. 27 (1979) 47–58.
  [20] S. Plimpton, J. Comput. Phys. 117 (1995) 1–42.
  [21] M.I. Mendelev, D.J. Sordelet, M.J. Kramer, J. Appl. Phys. 102 (2007) 043501.
  [22] A.J. Cao, Y.Q. Cheng, E. Ma, Acta Mater. 57 (2009) 5146–5155.

- [23] H.F. Zhou, C. Zhong, Q.P. Cao, S.X. Qu, X.D. Wang, W. Yang, J.Z. Jiang, Acta Mater. 68 (2014) 32–41.
- [2014] 32–41.
  [24] F. Shimizu, S. Ogata, J. Li, Mater. Trans. 48 (2007) 2923–2927.
  [25] C. Zhong, H. Zhang, Q. P. Cao, X. D. Wang, D. X. Zhang, U. Ramamurty, J. Z. Jiang, in preparation.