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Flow units perspective on elastic recovery under sharp contact loading in metallic glasses

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The obscure nature of glass physics has led to develop various correlations between different parameters and properties of metallic glasses. Despite these correlations, the clear picture of plastic deformation is still lacking. We have measured elastic recovery in metallic glasses by indentation, and found the elastic recovery correlate with different properties and parameters of metallic glasses. All these observations can be quite well explained with flow unit model which could provide clearer picture on the plastic deformations and nature of the metallic glasses. *Published by AIP Publishing.*
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I. INTRODUCTION

Indentation testing is an attractive probe to study plastic deformation in materials due to ease of operation, free sample size, and localized deformation.[1–3] Indentation technique also offers good opportunity to study plastic behavior even in brittle metallic glasses (MGs) as shear failure cannot occur in its constrained geometry.[4] Indentation results can be directly compared with compression or tensile tests.[1] Therefore, depth sensing techniques, such as micro- and nano-indentation technique, is a powerful tool to study and understand the mechanism of plasticity in metallic glasses, in addition to hardness measurement.[1–3] The property of hardness of a material is resistant to deformation which is an indicator of plastic deformation, and the hardness of a material depends on the bonding strength of constituent elements and microstructural heterogeneity. Hardness is found to increase with local heterogeneity[5] and decrease with residual stress[6] in MGs. The sharp contact loading leaves a permanent indent with a certain depth in the material. Some polymeric materials show almost complete depth recovery; on the contrary, some soft metals show negligible amount of depth recovery of indents, whereas bulk metallic glasses occupy the middle place among them.[3,7] The indentation stresses are mainly concentrated around the indent but these stresses can extend far into the elastic matrix.[7] Thus, hardness is an elastic-plastic parameter due to elastic and plastic flows of material.[3,7,8] Therefore, it is important to measure not only the plastic part but also the elastic component. These components can be correlated with mechanical properties and can help to understand their mechanisms in MGs.

Featureless microstructure of the metallic glass is different from that of crystalline materials which have grain boundaries, dislocations, stacking faults, and so on.[9] However, local heterogeneities have been reported in MGs with simulations and experiments.[10,11] Recently, various interpretations have been proposed to describe these local heterogeneities in terms of plasticity and relaxation in MGs as weakly bonded regions and strongly bonded regions, n-type and p-type regions, liquid like and solid like regions, core-shell model, and elastic matrix and flow units model.[13–17] In the elastic matrix and flow unit model, the flow units are flow defects of 1–2 nm in size which evolve from liquid like regions.[18–20] These flow units have lower atomic packing density, lower elastic moduli, higher mobility, higher energy dissipation, and higher energy states in energy landscape, as compared to the elastic matrix.[11,12,20–22] Stress or temperature can activate and percolate these flow units to yield global plasticity and relaxation in MGs.[20,23–25] Recently, different properties of MGs are found to correlate with concentration of flow units,[11,12,20,22,26,27] and a universal correlation, $P(t) = P_\infty/1 + c$, where P(t) is a measured property of MG and c is the concentration of flow units, is proposed to describe the behavior of different properties in MGs.[10]

The obscure nature of glass physics has led to establish various correlations between different glass properties and parameters.[28–30] One of the most important parameters for the design of bulk MGs for structural applications is Poisson's ratio ν. Previously, different correlations have been established between ν and other properties of glasses.[21,28,31–33] These correlations are useful to develop new MGs with better properties,[34] despite the deep understanding on the correlations still lacking.[17,19] In this work, we have systematically measured the elastic recovery in different bulk MGs and we have observed that elastic recovery in MG depends upon flow units. The elastic recovery is found to correlate with other parameters and properties of MGs, and the flow unit model is applied to understand the plastic behavior and relaxation in MGs.

II. EXPERIMENTAL

Ingots of different compositions were prepared in an electric arc furnace under Ti getter Ar gas atmosphere from high purity (minimum 99.9%) constituent elements. The various bulk MGs rods with 2 mm diameter were obtained using Cu mold suction casting technique by carefully controlling vacuum level, arc current, and time. The glassy structure of each rod was verified by the X-ray diffraction (XRD) using

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Cu-Kα radiations on a Bruker D8 AA25 diffractometer and by the thermal analyses using Perkine Elmer DSC 8000 in Ar atmosphere at a heating rate of 0.33 K/s. Elastic constants of the MGs, including Young's modulus E, shear moduli G and ν were measured using resonant ultrasound spectroscopy (RUS). Rectangle samples of volume about $2 \times 2.5 \times 4\,\mathrm{mm}^3$ with known masses were placed between the piezoelectric transducers, and the two independent elastic constants C_{11} and C_{44} for each alloy were obtained and used to calculate the elastic moduli. The elastic moduli of these MGs measured by resonant ultrasound spectroscopy are listed in Table I. Before indentation all the samples were polished on cloth to produce mirror like surface with Cr_2O_3 and Fe_2O_3 solutions in 1:3 ratio. Indentation was carried out with 100 g load for 5 s, 99 s, and 5 cycles each for 99 s (495 s in total) using Everone Vicker's hardness tester. Atomic force microscope (AFM) measurements of these indents were performed in a contact mode with the Asylum Research model MFP-3D-SA. In order to remove aging effects and compare the measured values of different MGs, all the samples were heated to their respective supercooled liquid region for 1 min before measurements. Each data point of elastic recovery calculation is the average of 2 to 5 indents, whereas RUS measurements are averaged over 3 samples of each bulk MG.

III. RESULTS AND DISCUSSION

The deformation under sharp contact loading in depth sensing techniques is a combination of elastic and plastic components.[8,35,36] Plastic deformation can be measured after unloading, whereas the elastic component can be theoretically calculated with the information of the geometry of the indenter, diameter, and depth of indentation. We have made few assumptions for elastic indentation depth calculation: the pressure distribution during indentation is such that the apex angle of indentation is replica of the semi angle of Vicker's indenter; the projected diameter is unaffected after unloading; the elastic recovery only alters the depth of indentions and diagonals remain nearly unchanged;[35,37] and the walls of indentations are straight. In fact, it is true for materials which show small elastic recovery, but not for those showing large amount of elastic recovery. Albeit the free surface either sinks or piles up around indentation but it does not seriously affect the elastic recovery analysis.[37] Therefore, total penetration of indentation just before unloading can be expressed as $h = d/2 \cot\Upsilon$, where d is the average length of both diagonals and Υ is the semi angle Vicker's indenter (in this case 74.05°). The relative elastic recovery or simply elastic recovery can be expressed as h_e/h and $h_e = h - h_p$, where h_e is the elastically recovered indentation depth and h_p is the permanent indentation depth after unloading as shown in Fig. 1. The d and h_p were measured using AFM.

TABLE I. Elastic moduli and T_g of different investigated MGs at room temperature. The elastic moduli values of $Zr_{46}Cu_{45}Al_7Ti_2$ and $Pd_{40}Ni_{30}Cu_{10}P_{20}$ are taken from Refs. 21 and 30, respectively.

	B (GPa)	E (GPa)	G (GPa)	N	T_g (K)
$Mg_{61}Cu_{28}Gd_{11}$	45.1	50.6	19.3	0.310	420
$La_{60}Al_{25}Ni_{15}$	39.4	39.7	14.9	0.347	468
$Cu_{46}Zr_{46}Al_8$	114.5	94.2	34.6	0.370	703
$Zr_{46}Cu_{45}Al_7Ti_2$	131.9	92.9	33.6	0.383	688
$Zr_{65}Cu_{15}Ni_{10}Al_{10}$	113.9	79.2	28.6	0.382	640
$Pd_{40}Ni_{30}Cu_{10}P_{20}$	172.6	99.8	35.5	0.404	559

The relative elastic recovery of different MGs is plotted with respect to ν in Fig. 2. The MGs exhibit a wide range of ν values as shown in Table I. There seems to be a clear correlation between elastic recovery and ν as shown in Fig. 2. $Pd_{40}Ni_{30}Cu_{10}P_{20}$ with highest Poisson's ratio value shows least elastic recovery, whereas $Mg_{61}Cu_{28}Gd_{11}$ having smallest ν exhibits largest amount of elastic recovery. This behavior can be explained on the basis of MG microstructure. It is generally accepted that microstructure of MG is composed of elastic matrix and liquid like regions or the flow units.[20–27] The MG with low ν contains lower fraction of flow units as compared with that of elastic matrix which results in higher elastic recovery, whereas MG with high ν having more flow units exhibits lower elastic recovery. Xue *et al.*[22] have estimated the concentration of flow units on the basis of density variation with annealing in $Pd_{40}Ni_{30}Cu_{10}P_{20}$ and $Cu_{46}Zr_{46}Al_8$ to be 0.895% and 0.643%, respectively. The reported values of flow unit concentration also support our results.

Figure 3 shows the elastic recovery of various MGs as a function of loading time. As the loading time is increased, either more flow units are activated or their size is increased and this leads to reduction in elastic recovery. Recently, it is shown that increasing the time of applied stress on MGs, flow units with higher activation energy are also activated.[8,25] According to the elastic model,[38] flow units behave like solid if probed at very short time scale. Previous investigations have shown that flow units exhibit wide range of activation energy due to local heterogeneity in MGs.[24,25] Flow units are not activated spontaneously; rather, these require sufficient time to be activated under the applied load. When the load is initially applied, flow units with low activation energy are activated. Further increasing time more and more, flow units with higher activation energy are activated, and weakly bonded regions around the flow unit gradually coalesce with it, thereby increasing the size of flow unit.[20,24] If the loading time is continued for sufficient time, these flow units percolate to yield the global plasticity.[11,23,24] The

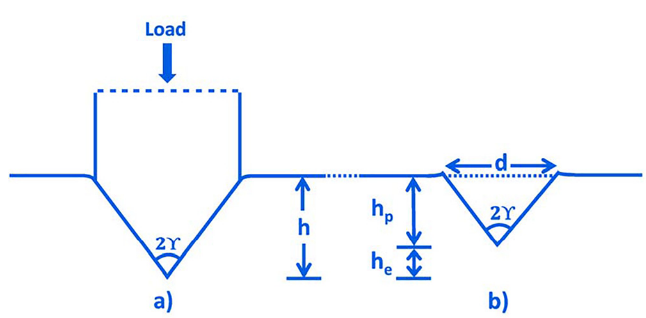

FIG. 1. The schematic illustration of Vicker's indentation at two different stages: (a) just before unloading and (b) after unloading.

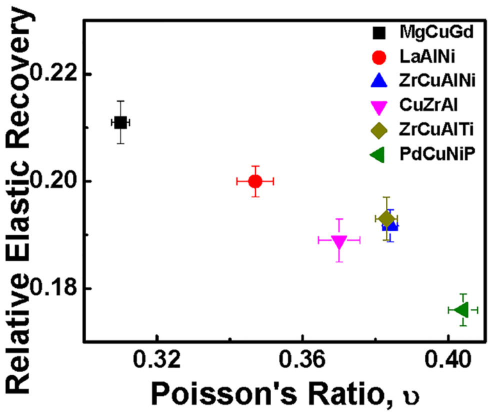

FIG. 2. The relation between Poisson's ratio and relative elastic recovery of different bulk MGs.

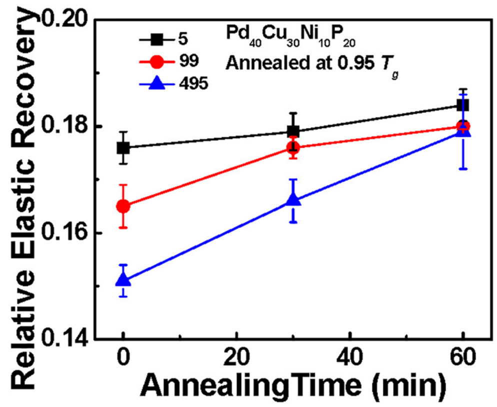

FIG. 4. A comparison of relative elastic recovery of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ with annealing time at 0.95Tg for 3 different loading times 5 s, 99 s, and 495 s.

activation of flow units is time dependent; fast at the beginning, gradually slows down and approaches saturation.[20] Therefore, we observed reduction in elastic recovery with loading time which is sharp at first and saturates over time. In addition to the decrease in elastic recovery at 99 s, we have also observed same trend after 5 loading cycles of each 99 s, in turn total 495 s. However, the reduction in elastic recovery is less pronounced at 495 s, as compared to elastic recovery at 99 s. Under cyclic loading, material should deform elastically as long as the load is not increased.[8] Previously, plastic deformation has been reported for different MGs even in elastic regime under quasi-static cyclic loading.[16,17,39] However, this phenomenon is attributed to the strain rate. At lower strain rate, MG undergoes plastic deformation, whereas at higher strain rate MG deforms elastically under cyclic loading.[11,39] At higher strain rate, time is not sufficient to activate significant fraction of flow units and MG behaves elastically.[23] Therefore, we infer that Vicker's indenter produce relatively low strain rate which activates flow units even in elastic regime and $Pd_{40}Ni_{30}Cu_{10}P_{20}$ plastically deforms in static cyclic loading. Hence, we observed further reduction in elastic recovery in $Pd_{40}Ni_{30}Cu_{10}P_{20}$ at 495 s.

In order to see the effect of annealing on elastic recovery, we annealed $Pd_{40}Ni_{30}Cu_{10}P_{20}$ at $0.95T_g$ for different times and results are plotted in Fig. 4. The elastic recovery of the MG was found to increase with annealing time for the different loading conditions. It is well established that density of flow units of the MG is decreased with annealing.[11,12,22,24,25] Therefore, the increased elastic recovery with annealing is due to the annihilation of the flow units induced by isothermal annealing. These results further confirm the dependence of elastic recovery on flow units.

Figure 5 displays elastic recovery and hardness. MG with low hardness shows more elastic recovery, whereas high hardness exhibits lesser elastic recovery. Hardness is proportional to Young's modulus E.[8] It can be seen from Table I that $La_{60}Al_{25}Ni_{15}$ and $Mg_{61}Cu_{28}Gd_{11}$ MGs exhibiting largest elastic recovery have lower elastic moduli. On the other hand, $Pd_{40}Ni_{30}Cu_{10}P_{20}$ having highest E exhibits least amount of elastic recovery. In Fig. 6, the elastic recovery of MGs is plotted with their respective T_g. In this plot, a saddle point can be seen at $Pd_{40}Ni_{30}Cu_{10}P_{20}$ composition. First, elastic recovery decreases with increasing T_g and crossover at $Pd_{40}Ni_{30}Cu_{10}P_{20}$. Previously, it is reported that activation energy of flow units among MGs is found to scale with T_g.[12,22] The flow units in MGs with high T_g have higher activation energy than flow units with low T_g MGs. However, Lu *et al.*[11] have found a considerable difference of activated flow units in $La_{68}Al_{20}Cu_{10}Co_2$ and $La_{75}Ni_{7.5}Al_{16}Co_{1.5}$ MGs with similar T_g.[12] Therefore, activation energy of flow units could not be solely related to T_g of MG. Our results also

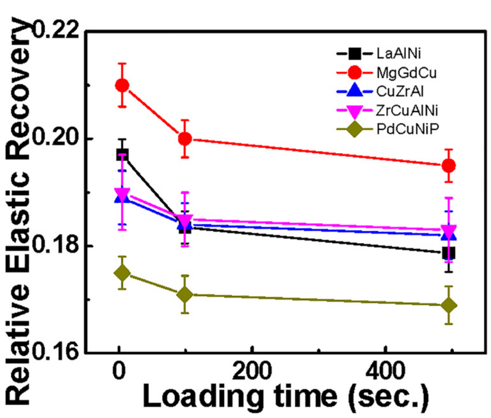

FIG. 3. The behavior of relative elastic recovery of different bulk MGs as function of loading time at room temperature.

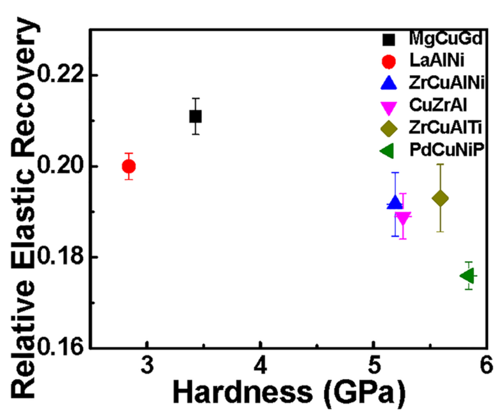

FIG. 5. The relation of hardness and relative elastic recovery of various bulk MGs which shows these properties have inverse correlation.

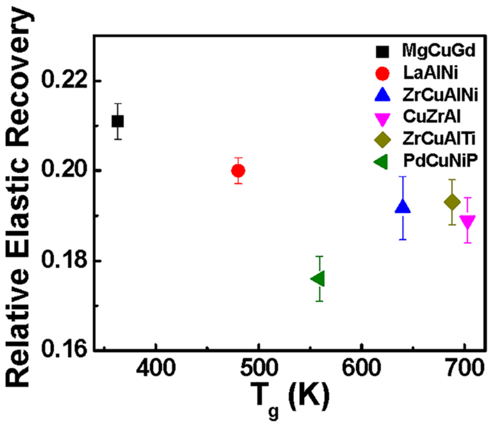

FIG. 6. Relative elastic recovery as a function of glass transition temperature of different bulk MGs.

show that the activation energy of flow units in $Mg_{61}Cu_{28}Gd_{11}$ and $La_{60}Ni_{15}Al_{25}$ does not depend on T_g. The behavior of fragility with relative elastic recovery is displayed in Fig. 7. MG with higher fragility values shows lower amount of relative elastic recovery and vice versa. More fragile liquids are known to possess larger amount of flow units and higher ν, which in turn leads to lesser elastic recovery.[30,33,40–42] Less fragile liquids have lower amount of free volume and lower ν values, and therefore, these MGs show larger elastic recovery.

Elastic recovery depends on the local heterogeneity in MGs. MGs with more inhomogeneous microstructure have more flow units which can bear more plastic deformation under the application of load for certain time thereby revealing less elastic recovery. MGs with high ν can undergo large amount of plastic deformation and elastic recovery decreases as ν increases. MGs having higher values of elastic moduli show high ν and hardness. Therefore, MGs with lower hardness show higher elastic recovery and vice versa. MGs forming liquids with high fragility retain more flow units on cooling below T_g and exhibit low elastic recovery. Hence, MGs showing less amount of elastic recovery possess more number of flow units, high Poisson's ratio, high hardness, and high fragility. Activation of these flow units is a time dependent process, and with the increase of loading time more flow units are activated and reach saturation at longer loading times. Therefore, we initially observe sharp and at a later stage less pronounced decrease in elastic recovery. Low strain rate produced in Vicker's indentation provides enough time to activate considerable amount of flow units so that MG deforms plastically in cyclic loading.

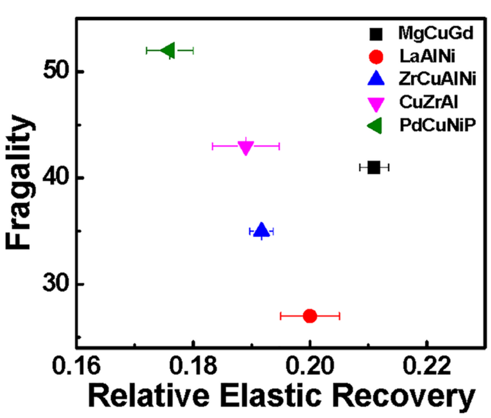

FIG. 7. Relation between relative elastic recovery and fragility of different bulk MGs. Fragility values of these bulk MGs have been reported from Ref. 41.

IV. CONCLUSION

We have measured the elastic recovery by indentation in different bulk MGs. Elastic recovery is found to inversely correlate with Poisson's ratio and hardness. As the value of ν as well as hardness is increased, elastic recovery is decreased. Increasing the loading time reduces elastic recovery, whereas increasing the annealing time increases elastic recovery in $Pd_{40}Ni_{30}Cu_{10}P_{20}$. Elastic recovery shows a crossover as a function of glass transition temperature which suggests that activation energy of flow units does not entirely depend on T_g of MG. Finally, we show that bulk MGs with high elastic recovery are more fragile than bulk MGs with low elastic recovery. These observations clearly show that elastic recovery depends upon the flow units in MGs.

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