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Strengthening behavior due to cyclic elastic loading in Pd-based metallic glass

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ABSTRACT

Nanoindentation technique was utilized to unravel the strengthening behavior of Pd-based metallic glass under elastic cyclic loading. This was conducted to ultimately evaluate fatigue behavior which is thought to be a major concern for the structural performance of bulk metallic glasses. The event of shear band formation is considered after subjecting the alloy to loading cycles in the nominal elastic regime, followed by a monotonic deep indent. In all experiments, substantial shift in the load needed to initiate a shear band (indicative of plasticity) was noted. Following prolonged cycling, a fatigue limit was observed evident by the saturation in hardening effect. By varying the amplitude of elastic loading, it appears that a critical loading is needed to initiate strengthening in the bulk metallic glass (BMG); i.e. a specific threshold need to be exceeded for the hardening effect to trigger. This was concluded following successive experiments with increasing number of cycles which proves the effect over multiple cycling. Moreover, the effect of higher loading rates becomes more significant as the successive number of cycles increases. For further assessment, comparative experiments were carried out between holding and cycling in the elastic region. These experiments suggested the necessity of cycling to achieve hardening in the alloy, as no hardening effect was observed following holding experiments. In general, strengthening effect was attributed to the possible development of regions of microplasticity due to the actuating force, without being able to detect these regions in the global load–displacement response. Additional tests were conducted to unravel the irreversibility of these cycling/hardening effects. It was found that slight recovery is possible when no resting time was introduced before the deep indent. This suggests that part of the cycling effects can be reversed which can be linked to the instability of the shear transformation zones (STZs).

1. Introduction

There has been great interest in recent years in the relatively and newly developed bulk metallic glasses (BMGs). They represent novel structures which are promising, in many occasions, to deliver novel properties, or combination of properties. However, they still need time to reach a commercialization stage and be able to substitute well-established and well-studied materials [1]. The current interest in these alloys is stemming from their remarkable combination of properties of high strengths and relatively low elastic moduli [2]. These metallic glasses have been the subject of interest for many researchers; nevertheless, the specific topic of fatigue-life has not been adequately addressed to date. It is well documented that metallic glasses are susceptible to early failure when subjected to fatigue loading conditions [2]. The performance of these glasses under cyclic conditions is of vital importance for multiple applications such as, actuators, sensors and others. Furthermore, the structural characteristics and mechanisms that control the behavior of metallic glasses subjected to fatigue loading are not very well-clarified. The ambiguity is persistent in their deformation mechanisms as they are free of crystalline defects (dislocations, grain boundaries, etc.). It is important to address these issues for BMGs as they are critical for failure analyses and life prediction attempts.

The previous work aiming at unraveling the underlying physics of shear band formation, structural changes due to cyclic loading and factors affecting fatigue behavior was relying on conventional macroscopic cycling tests [3,4]. Furthermore, others were attempting to map the variation of fracture mechanisms with different temperatures [5] and atmospheres [6,7] using conventional tests. Nevertheless, the success was quite limited due to the limitations in the resolution of these tests to identify the localized changes in the areas of stress concentrations under cyclic loading. These constraints have encouraged the use of techniques offering higher resolutions that facilitate studying smaller volumes to map the structural responses to dynamic loadings. One of the commonly used techniques nowadays is nanoindentation which depends on instrumented contacts of a tip, penetrating a specific material,

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and continuously recording the load–displacement response. These high-resolution data can unravel many discrete events such as shear band formation, dislocation source activation, phase transformations, and others [8].

On the other hand, some studies [9,10] have focused on the crystallization behavior of BMGs and nanoindentation was primarily used to study the effect of crystallization on the obtained mechanical properties and to give more insights on the operating deformation mechanisms. Moreover, the different mechanisms of fatigue-crack behavior in bulk amorphous alloys in air and an aqueous chloride solution were investigated elsewhere [11]. There has also been some work devoted for the modeling and prediction of the fatigue characteristics of BMGs [12]. However, only little work was performed on looking into the experimental validation of the developed models.

Very recently, there have been some reports on the possible strengthening of BMGs due to cyclic loadings in the elastic regime. The studies were carried out using nanoindentation technique and they demonstrated that a higher force is needed to induce permanent deformation in BMGs when it is cycled elastically at forces well below those needed to initiate plastic deformation [13]. Moreover, a mechanism for strengthening has been suggested by coupling experimentation with STZ dynamics simulations [14].

This paper represents an expansion on our recent findings by which the effect of the amplitude of elastic loading and loading rates are being highlighted. Additionally, the irreversible behavior of strengthening of the tested glassy alloy is being evaluated through resting-time experiment.

2. Experimental procedure

In this work a Pd-based bulk metallic glass with a nominal composition of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ was used. This alloy was prepared by casting into cooled molds under an inert atmosphere and confirmed amorphous using XRD and as described elsewhere [15]. To be able to carry on with nanoindentation, a smooth surface should be obtained and for that reason a standard metallographic procedure was followed; the glasses were sectioned, mounted, and mechanically polished to a surface roughness better than 5 nm. The nanoindentation was applied using a Hysitron instrument (Hysitron Inc., Minneapolis MN) with force and depth resolutions of 0.1 μN and 0.2 nm, respectively. A spherical diamond tip of 1.1 μm radius was used in the indentation for all experiments.

For the analysis of the load–displacement (*P*–*h*) curve, it has been previously [16,17] established that indentations on isotropic metallic glasses initially follows the Hertzian prediction for elastic contact of a sphere on a flat plate [18,19] and is given by

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

where *P* is the applied load, E_r is the reduced elastic modulus, *R* is the radius of the tip, and *h* is the displacement. The values of *E* can then be obtained by employing the following equation that relates E_r to *E* (Young's modulus) of both sample and indenter,

$$\frac{1}{E_r} = \frac{1-\nu^2_{\text{sample}}}{E_{\text{sample}}} + \frac{1-\nu^2_{\text{indenter}}}{E_{\text{indenter}}} \tag{2}$$

with ν being Poisson's ratio of the subscripted material. At each test the point at which plastic deformation begins is identified since the transition from elastic to plastic is apparent in metallic glasses as the point at which the first shear band forms [20]. This transition point appears as a discrete event that is detected as a sudden depth excursion (burst) at constant load (for a load-controlled machine) [14]. By focusing entirely on the first shear band formation, complications of shear bands from earlier stages of deformation are avoided, and the stress field beneath the contact prior to shear localization is reasonably approximated by the Hertzian stress fields [21,22]. Due to the nature of the shear band event and the sensitivity of the test a statistical approach is being utilized throughout this work. For each produced curve, more than 100 yield events are being recorded and the yield loads are plotted in a cumulative way. Before carrying on the cyclic testing, baseline data using monotonic loading conditions are being generated for the Pd-based glass. As the test involves indenting on a large number of small-volumes, the results of the observed yielding events at specific load points is largely distributed. Therefore, it was thought that plotting the data cumulatively reveals slight changes to the distribution that might be obscured by limited sampling or by recording only statistical compilations (e.g., sample mean and standard deviation).

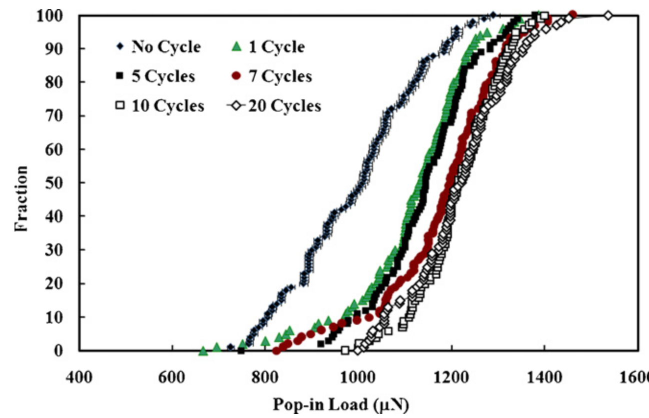

Fig. 1. The cumulative distribution of measured yield points, and its evolution with different number of sub-critical cyclic loadings. In all lines, each data point represents the yield load from a single test. The conditions used in this experiment were set to 600 μN as a cyclic elastic load, 1500 μN/s as a loading rate, and 2500 μN as maximum load. These data first appeared in [14].

The cyclic loading tests were performed by applying a loading function that involves cycling in the elastic regime followed by deep indents (load functions are being described thoroughly in our previous work [14]). Sub-critical loads were varied from 300 μN up to 600 μN and applied for different number of cycles (1, 5, 7, 10, and 20), prior to final loading to a peak load of 2500 μN. The values of sub-critical and peak loads are chosen based on the monotonic loading results, with the peak load high enough to capture strengthening and cyclic loads that do not cause observable shear banding. Additionally, two loading rates of 1500 μN/s and 15,000 μN/s were used to assess any observable effect and the same loading rate was maintained during loading and unloading segments. Moreover, additional experiments were conducted to evaluate the importance of cycling action in the hardening process. For example, some experiments with hold segments equivalent to the time needed for cycling (but no actual cycling) were conducted. These experiments use the same amplitude as in cycling experiments, but explore the effect of a sustained load held for an equivalent duration as experienced during cycling, before a deep indent is employed. More experiments were performed combining both hold segment and loading cycles, to unravel the importance of cycling further. The effect of resting times is also being addressed by introducing some experiments that involving some resting time between the sub-critical cyclic loads and the deep indent.

3. Results and discussion

The main aim of this work is to study the effect of cyclic loading below the yield point on the observed strengthening. Fig. 1 shows the cumulative distribution of measured pop-in events for the metallic glass with different number of elastic cycles at a constant elastic load of 600 μN. These data were presented originally in our previous work [14] and being included here for clarity of the follow up tests that were performed on the same alloy. It should be mentioned that each data point represents the yield load from a single test. It can be seen that as the number of cycles increases the load needed to initiate yielding (shear band formation) increases in a cumulative manner. This is followed by saturation in the strengthening effect as the shape of cumulative yielding events of the 10 and 20 cycles coincided. Apparently, some structural changes occur beneath the indenter at a higher number of cycles which have negligible changes as the deformation cycles progresses. In these nanoindentation experiments, identical mechanical conditions are maintained in testing small volumes of the material. Therefore, the different structural inhomogeneities that may affect the process of shear banding, represents the only source of distribution in the pop-in loads as the resolution of yield point identification is considerably finer than the spread of the data [13].

The effect of different magnitudes of the elastic load in the overall strengthening behavior of the alloy is shown in Fig. 2. (Note that the data in Fig. 2a were presented originally in Ref. [14]; the data in Fig. 2b are new here.) By looking into the plots of 5 and 20 cycles a trend can be depicted which shows the presence of

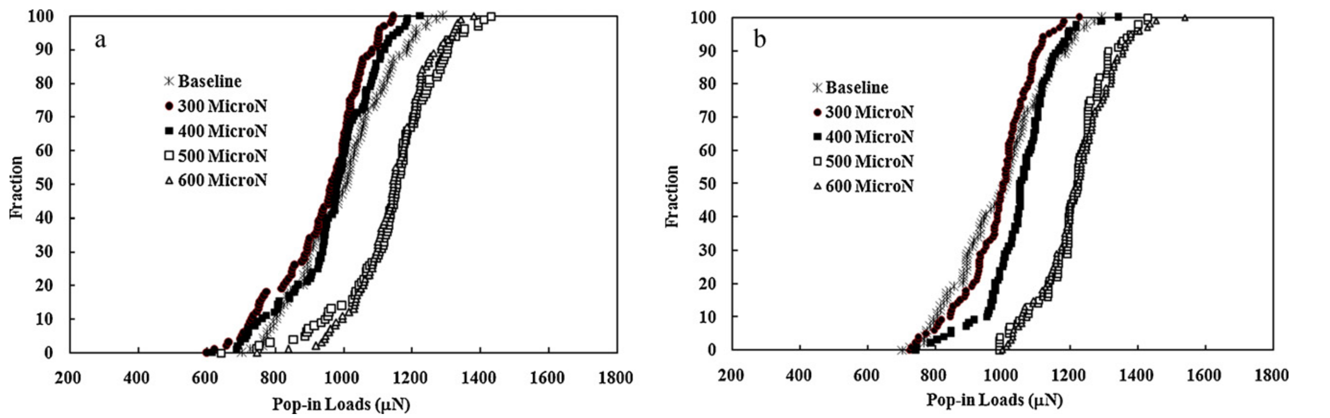

Fig. 2. The effect of different sub-critical cyclic loadings, for $Pd_{40}Cu_{30}Ni_{10}P_{20}$; (a) 5 cycles, (b) 20 cycles. In all lines, each data point represents the yield load from a single test. The Pd-based glass was tested at 1500 μN/s and 2500 μN of maximum load for variable loading cycles. Some of the data for the Pd-based glass in (a) first appeared in [14].

a threshold below which no strengthening can be triggered. At elastic loads of 300 and 400 μN no strengthening was observed at the presented number of cycles and the cumulative values of the yield points lie within the values of baseline (no cycling). Whilst, at higher loads of 500 and 600 μN a considerable strengthening was observed. Similar results were also seen with intermediate cycling at 7 and 10. Apparently, an endurance limit is identified for this glass composition below which no strengthening is observed. The noticeable strengthening in this glass is more likely a result of minute, isolated events, rather than gross plasticity which would likely result in a more apparent irreversibility. The fact that the volume beneath the indenter experiences extremely high local stresses suggests a mechanism of reversible atomic rearrangements that might be considered microplasticity which ultimately involves an accumulation of structural changes (e.g., changes in chemical or topological order, redistribution of free volume, etc.); without the formation of a shear band. Moreover, shear transformation zones "STZs" can be operated by the elastic stresses leading to an accumulation of small structural changes which produces local hardening in the volume of material that is subjected to the highest stress. In the microscopic level, the accumulation of STZ operations can then lead to shear band formation. It is important to mention that microplasticity involves reversible strain, but not reversible atomic configuration changes; although the strain recovers, the structure is different. This is why it is different than anelasticity, which involves recovery of the atomic configuration as well as the strain.

The effect of higher loading rates on the strengthening behavior is shown in Fig. 3 for different test conditions. It can be seen that when no elastic cycling is performed the value of yield points overlap for loading rates that are one order of magnitude different. As the number of cycles increases the effect of higher loading rates becomes more pronounced, as demonstrated by Fig. 3. Since the STZs operation processes that underlie the proposed microplasticity mechanism of hardening are thermally activated then they require some time for suitable thermal fluctuation to be trigger [14]. In the case of higher loading rates, the high imposed strain rates limit the available time for such fluctuations, which can delay yielding. This effect becomes more apparent as the number of cycles increases which can be compared by the delay in yielding caused by more cycling at 1500 μN/s. Interestingly, the accumulative damage caused by higher stain rates is higher than those for lower rates. This suggests that perhaps the local relaxation process beneath the indenter during cycling is enhanced by having more time to manifest itself and appear in the accumulative strength distribution.

The issue of whether there is a vital need for cycling to induce strengthening or perhaps applying a sustained sub-critical load might produce the same strengthening effect becomes pertinent. Additional experiments were performed to unravel the importance of cycling action in the strengthening phenomena in BMGs. Holding of the indenter at certain loads for defined periods – equivalent to cycling actions – reveals the need of cycling to induce strengthening. This is apparent in Fig. 4, where in part (a) cycling was not observed when holding only was applied. When cycling was combined with holding the graph coincided perfectly with the cycling curve indicating the importance of cycling action. However, when only holding was conducted for different periods (equivalent to different cycles) some strengthening was observed for periods equivalent to high number of cycles, such as, 10 and 20. This indicates that a specific time scale and a force are needed to initiate strengthening in BMGs. In sub-critical holding experiments, the material is placed in a high stress state for a defined period of time to allow sufficient time for different processes to experience a favorable thermal fluctuation. The results in here suggest that simply holding for a long period at elevated stresses does not introduce appreciable structural changes, which lead to strengthening. Principally, a sustained load must give more time for successful STZ flips at high stresses. On the contrary, Fig. 4 demonstrated that holding at a load of 600 μN for 12 s (equivalent to the total cycling

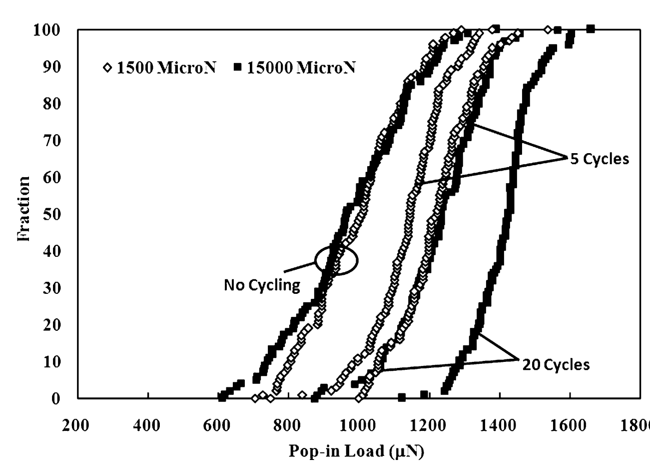

Fig. 3. The effect of loading rate as the number of sub-yielding cycles is increasing; (a) No cycles, (b) 5 cycles, (c) 20 cycles. All experiments were conducted at 600 μN as elastic- and at 2500 μN as maximum-loading.

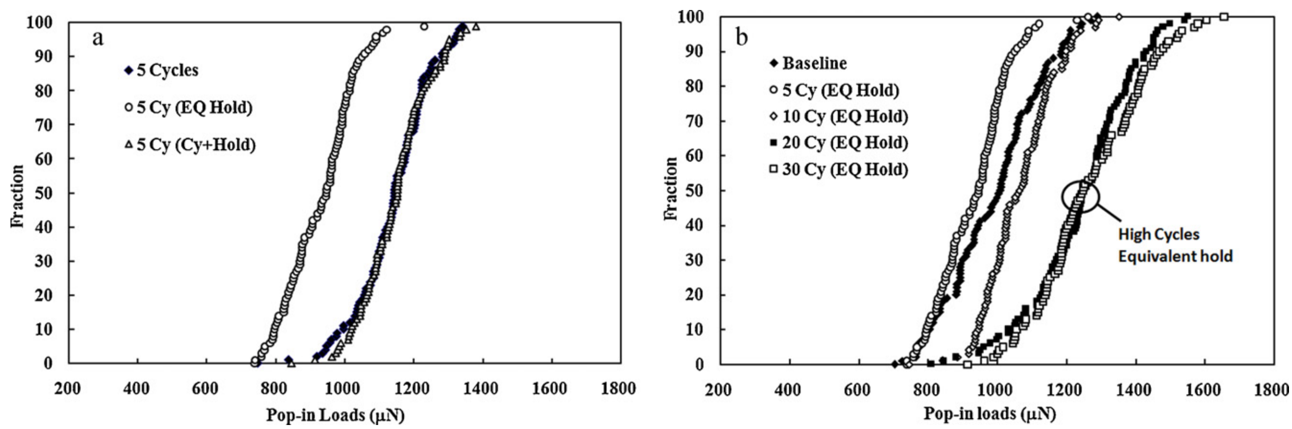

Fig. 4. The effect of holding time against cycling; (a) comparison between holding and cycling for 5 cycles, (b) equivalent holding for prolonged cycles. All experiments were conducted at 600 μN as elastic- and at 2500 μN as maximum-loading. Holding time was set to 12 s (equivalent to the needed time to perform 5 cycles).

time for the 5 cycles) prior to loading to the yield point does not result in strengthening. This shows that cycling is important to trigger strengthening rather than simply exposing the material to high stresses.

Moreover, it was important to verify the persistence of these structural changes and if they are reversal as time elapses. Fig. 5 shows the results from resting-time experiment which are conducted to include retraction of the indenter from the sample surface for finite time after elastic cycling and before deep indentation is carried out. As can be seen from the graph, when a resting time of 24 s was introduced (equivalent to cycling time of 10 cycles) the strengthening effect was partially recovered. This highlights the plausible partial reversibility of the strengthening behavior, but ultimately the effect of strengthening prevails as more resting times did not introduce more reversibility in the observed strengthening. This underlines the instability of the STZ flips and the possible restoration of some STZs in defined configurations as they are identified at specific time and location. However, more exploration is needed to unravel the mechanisms of restoration and the reversibility of the strengthening behavior. Work is under way in attempting to model strengthening behavior and the inclusion of the possible reversibility to offer better understanding of the overall performance of BMGs under cyclic loadings. It is important to mention, however, that these contact experiments involve a largely compressive stress state, whereas most fatigue studies are conducted in tension, and the mechanical properties of glasses are significantly tension-compression asymmetric. Conventional fatigue studies essentially involve testing in geometries with prior deformation and damages. The use of nanoindentation technique allows fine-scale studies of cyclic deformation on fresh glass volumes, and should thus offer a more insightful view of the structural characteristics of kinematic irreversibility under dynamic loading.

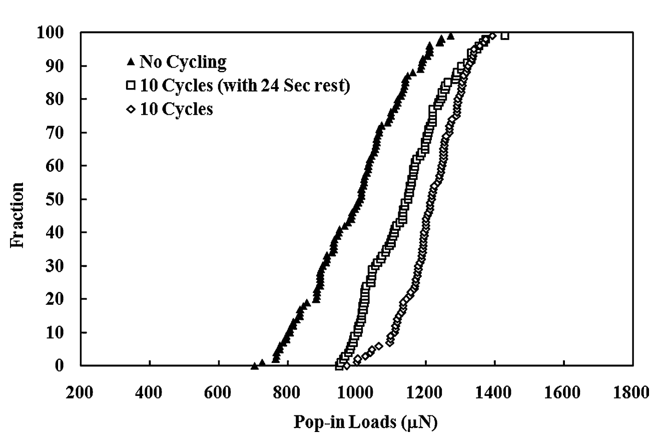

Fig. 5. The introduction of resting time before the deep indentation. All experiments were conducted at 600 μN as elastic- and at 2500 μN as maximum-loading. Holding time was set to 24 s (equivalent to the needed time to perform 10 cycles).

4. Conclusions

The effect of cyclic loading on the strengthening behavior of Pd-based bulk metallic glass was examined. The nanoindentation approach permits fine-scale studies of cyclic deformation on different areas of the glass, and can offer a clearer view of the structural aspects of kinematic irreversibility under cyclic elastic loading. The conclusions derived from the present work are listed below:

- Hardening is found to occur progressively over several cycles and increases as the number of cycles increase. However, the strengthening effect saturates after 10 cycles
- It appears that there is a threshold below which loads cannot initiate strengthening in BMGs
- Higher loading rates would cause higher resistance to penetration with increased number of elastic cycles
- Cycling is necessary to initiate strengthening in BMGs. However, longer holding times have an effect on strengthening
- By the introduction of resting time, the strengthening effect was partially reversed which highlights the instability of the structural changes beneath the nanoindenter.

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