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Cyclic Hardening of Metallic Glasses under Hertzian Contacts:
Experiments and STZ Dynamics Simulations

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A combined program of experiments and simulations is used to study the problem of cyclic indentation loading on metallic glasses. The experiments use a spherical nanoindenter tip to study shear band formation in three glasses (two based on Pd and one on Fe), after subjecting the glass to cycles of load in the nominal elastic range. In all three glasses, such elastic cycles lead to significant increases in the load required to subsequently trigger the first shear band. This cyclic hardening occurs progressively over several cycles, but eventually saturates. The effect requires cycles of a sufficient amplitude to achieve, and is not induced by sustained loading alone. The simulations employed a new shear transformation zone (STZ) Dynamics code to reveal the local STZ operations that occur beneath an indenter during cycling. These results reveal a plausible mechanism for the observed cyclic hardening: local regions of confined microplasticity can develop progressively over several cycles, without being detectable in the global load-displacement response. It is inferred that significant structural change must attend such microplasticity, leading to hardening of the glass.

Keywords: metallic glass, cyclic deformation, fatigue, nanoindentation

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1. Introduction

Performance under cyclic loading is critical in applications such as springs, actuators, and some sensors, which have been identified as potential markets for metallic glasses owing to their high elastic limits and resilience [1, 2]. Recent interest in metallic glass components with critical dimensions below the plastic zone size (to limit brittle failure) has driven integration of these materials into micro-electromechanical systems [1, 3, 4]; however in these systems, it is not uncommon to require lifetimes up to $10^{12}$ cycles or more [5], making fatigue a key issue. Fatigue damage can occur in some metallic glasses even at stresses as low as 10% of the yield stress [6], limiting their use in structural applications. It has become apparent that fracture and fatigue studies on metallic glasses are quite sensitive to testing geometry, loading state, and casting quality [6-12]. Furthermore, analysis of experimental fatigue results can be complicated by crack tip branching or crack initiation at a distance from the notch [8, 9, 13].

Despite progress in testing and analysis of the mechanical properties of metallic glasses, the structural features and mechanisms that control the behavior of metallic glasses under cyclic loading are still not entirely understood. In particular, the source of kinematic irreversibility, i.e., the mechanism of structural change near a stress concentrator under cyclic loading, in metallic glasses is unclear [14]; although it is surmised that shear transformation zones (STZs) have a role in the process, the ability of metallic glasses to undergo stable crack extension in the absence of a known strengthening mechanism remains to be satisfactorily explained. Conventional macroscopic cyclic loading tests have made some progress in mapping out behavior variation with different atmospheric conditions [10, 15-17], temperatures [18], and degrees of structural relaxation [19, 20], but the resolution of these tests is not sufficient to pinpoint the evolution of structural damage (or local property changes) in the vicinity of a stress concentration under cyclic loading. Instead of these bulk tests, high resolution testing of small volumes of material presents an interesting alternative approach that may yield more insight into the microscale material response to concentrated stress. For example, low load spherical nanoindentation techniques have successfully detected sub-nanometer perturbations associated with plastic
deformation in a variety of materials including metallic glasses [21-25], and are conducted at a scale commensurate with physically-motivated simulation techniques as well.

Previous results of low-load indentation in metallic glasses have revealed that stresses beneath the point of contact significantly exceed the material yield stress well before the first shear band forms [26-28]. Packard and Schuh [27] have rationalized this result by suggesting that high stresses at a local point beneath the contact are insufficient to trigger yield, but rather that the material flow law must also be satisfied in order to develop a shear band; the yield stress must be exceeded over an entire viable shear band path that connects to the free surface before the material will deform through shear banding. A consequence of this situation is that at local points beneath the contact, the yield stress can be locally exceeded in regions of material that are geometrically confined and which do not participate directly in the shear banding event. By extension, local “microplastic” atomic rearrangements are possible in the contact zone at stresses below the experimentally observed yield point. The proposal of microplastic events under cyclic loading is also consistent with reports of other authors studying changes in the properties of glasses under high static stress levels [29, 30].

In an earlier study of an iron-based metallic glass [31], some of the present authors demonstrated that cyclic loading using a spherical contact at very low loads, below the level needed to initiate a shear band, results in apparent strengthening of the glass. Although cyclic loading involved no obvious hysteresis, it led to a significant shift in the strength distribution of the glass, apparently due to an accumulation of structural change beneath the contact during cycling. This result was interpreted as being consistent with the notion of microplastic events occurring beneath the contact at sub-yield loads, and at least in the case of cyclic loading, suggests that these microplastic events favor a stronger (e.g., higher density, higher structural order, etc.) glass structure.

In this paper, we expand significantly upon the preliminary results in Ref. [31]. First, we report new corroborating results from two additional glasses, illustrating the generality of cyclic strengthening in this class of materials. Second, we verify through experiments that the strengthening trend in these experiments in fact requires the application of cyclic loads, and not
simply sustained loads. Third, we report two new features of cyclic strengthening: an apparent threshold in cyclic loading amplitude below which no strengthening occurs, and a saturation level of strengthening beyond which further cycling is ineffectual. Finally, we use the newly-developed “STZ dynamics” simulation method [32] to demonstrate the possibility of sub-yield STZ activity in the contact zone during cyclic loading of a model glass, without measurable hysteresis. These simulations provide an important qualitative validation of the cyclic strengthening mechanism proposed in Ref. [31].

2. Experimental technique

The three metallic glasses used in this article, Pd_{40}Ni_{40}P_{20}, Pd_{40}Cu_{30}Ni_{10}P_{20}, and Fe_{41}Co_{7}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2}, are prepared by casting into cooled molds under an inert atmosphere and confirmed amorphous as described in Refs. [33], [34], and [35], respectively. The glasses are sectioned, mounted, and mechanically polished to a surface roughness better than 5 nm according to standard metallographic techniques, to provide a smooth surface for indentation. The nanoindenter we use is a Hysitron, Inc. (Minneapolis, MN) instrument with force and depth resolution of 0.1 μN and 0.2 nm, respectively, outfitted with a spherical diamond tip of 1.1 μm radius.

As established in Refs. [26-28], for indentations on isotropic metallic glasses the load-displacement (P-h) curve initially follows the Hertzian prediction for elastic contact of a sphere on a flat plate [36, 37], given by

\[ P = \frac{4}{3} E_r R^{4/3} h^{3/2}, \]  

where P is the applied load, h is the displacement, R is the radius of the tip, and E_r is the reduced elastic modulus,

\[ \frac{1}{E'} = \frac{1}{E_{\text{sample}}} + \frac{1}{E_{\text{indenter}}} - \nu_{\text{sample}} \]  

with E the Young’s modulus and ν the Poisson’s ratio of the subscripted material. The nominal transition from elastic to plastic deflection is also clearly discernible in metallic glasses as the
point at which the first shear band forms [38, 39]. In nanoindentation experiments, this point appears as a discrete event that is detected as a sudden depth excursion at constant load (for a load-controlled machine), as well as a simultaneous velocity spike [27]. Figure 1a shows a typical example of a P-h curve for the Fe-based glass, where the location of the yield point is identified by the displacement burst as well as the departure from Eq. (1); the velocity spike is not visible here, but is used as described in Refs. [27, 31] to verify the location of the yield point. By focusing exclusively on the first shear band event, complications of shear bands from previous stages of deformation are avoided, and the stress field beneath the contact prior to shear localization is reasonably approximated by the Hertzian stress fields [27, 37, 40].

Throughout this paper, we present data for the yield point in such experiments using a statistical approach. Using identical test conditions, more than 100 yield events are recorded and the yield loads are plotted in a cumulative fashion. Baseline data for each of the three glasses in this study are presented in Figure 1b for conditions of monotonic loading, where each data point corresponds to a single nanoindentation test. These data show that the load at which the plastic yield event occurs is significantly distributed. This spread is not an artifact of experimental measurement; the resolution of yield point identification is substantially finer than the spread of the data in Figure 1b. Rather, the broad measured distributions of yield load in Figure 1b are a true reflection of the distribution of glass states that are sampled when conducting a large number of small-volume experiments. We find that plotting the data cumulatively reveals subtle changes to the distribution that might be obscured by limited sampling or by recording only statistical compilations (e.g., sample mean and standard deviation).

Our main purpose in this paper is to study the effects of cyclic loading below the yield point. Cyclic loading tests are performed by applying a loading function of the general form shown in Figure 2a. Sub-critical loads of 1.25 mN for Fe_{41}Co_{7}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2}, 0.2 mN for Pd_{40}Ni_{40}P_{20}, and 0.6 mN for Pd_{40}Cu_{30}Ni_{10}P_{20} are applied for a number of cycles (usually 1, 5, 10, or 20), prior to final loading to a peak load of 5, 1.5 and 2.5 mN, respectively. The sub-critical and peak loads are set based on monotonic loading results, with the peak load high enough to capture strengthening and cyclic loads as high as possible without causing observable shear banding. In
these tests, the rates for all loading and unloading segments are kept constant at 2.5 mN/s for Fe$_{41}$Co$_{7}$Cr$_{15}$Mo$_{14}$C$_{15}$B$_{6}$Y$_2$, 0.2 mN/s for Pd$_{40}$Ni$_{40}$P$_{20}$, and 1.5 mN/s for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$.

Some additional targeted experiments are conducted to assess the role of time-at-load and the amplitude of the loading cycles. For example, in the Fe-based and four-component Pd-based glasses we conduct experiments with hold segments but no cycling, following load functions of the general form shown in Figure 2b. 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 five cycles. For the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ glass we also perform experiments combining both the hold segment and five load cycles. The effect of cycling amplitude is also addressed in the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ glass, by considering a series of different sub-critical cyclic loads between 0.3-0.6 mN.

3. Cyclic Hardening

Figure 3 presents typical raw data for sub-critical cycling tests on each of the three glasses, where five sub-critical cycles precede final loading beyond the nominal yield load. Inspecting the P-h curves for these tests, we find that the range over which cycling occurs is barely discernible except for the higher density of data points in this region, because the data quite closely trace the elastic curve up and down. There is no obvious hysteresis or other deviation from the elastic prediction to within the resolution of the test (which is accurately captured by the size of the data points in Figure 3). However, this cycling does have an eventual impact on the load required to observe the first shear band event.

In Figure 4, the cumulative yield load measurements for all three glasses are presented for experiments involving cyclic loading, in comparison with the baseline monotonic loading data (reproduced from Figure 1b). In all cases, we see that cycling shifts the distribution to higher loads—higher by 20-30% in the extreme cases. What is more, this hardening appears to generally accumulate with increasing number of cycles, although the nature of the accumulation is different among the three glasses. In the Fe-based glass a single cycle leads to a shape change
in the distribution, but does very little in terms of shifting the median yield load. On the other hand, in the Pd-based glasses the first cycle leads to substantial strengthening without a large change in the distribution shape. And where the Pd$_{40}$Ni$_{40}$P$_{20}$ glass accumulates relatively little additional strength beyond the first cycle, the other two glasses do exhibit gradual strengthening over additional cycles.

The results from the two Pd-based glasses in Figures 4b and 4c corroborate the first report of cyclic hardening in the Fe-based glass in Ref. [31] (which presented the data from Figure 4a up to ten cycles). Although the details differ among these specimens, the data in Figure 4 suggest that the phenomenon may be general among all metallic glasses. The data in Figure 4 also provide new details not revealed in the prior work from Ref. [31]. In particular, we observe in these data that the cyclic hardening eventually saturates (i.e., the yield load distribution stops evolving significantly) after some number of cycles. This is highlighted in the data compiled in Figure 5, which plots the relative change in the distributions with the number of applied cycles. Again, the details of the saturation are different among these specimens, with Pd$_{40}$Ni$_{40}$P$_{20}$ saturated in five or fewer cycles, Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ saturating in the vicinity of seven, and the Fe-based glass exhibiting strengthening through at least ten cycles, but only little change (or even a subtle weakening) after twenty.

Cycling of the applied load is apparently critical to the strengthening effect observed in Figures 4 and 5. This is established in Figure 6, which illustrates the effect of sustained sub-yield loads (rather than cycling) on Fe$_{41}$Co$_{7}$Cr$_{15}$Mo$_{14}$C$_{15}$B$_{5}$Y$_{2}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$. In both cases, the results obtained with a holding period are quite similar to the baseline data obtained using a monotonic loading function; sub-critical sustained loading does not cause strengthening where cycling for the same amount of time does. Moreover, in Figure 6b the four-component Pd-based glass was subjected to both five cycles plus an equivalent hold; the results conform exactly to those obtained using only 5 cycles with no hold period. Thus, with or without added cycling, we find that sustained sub-critical loads do not influence the strength distribution of these glasses.

Figure 7 reveals another interesting feature of cyclic hardening in the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ metallic glass, namely that there is an apparent threshold in the cycle amplitude in order to observe
hardening. Here the sub-critical cycling load is varied between 0.3 and 0.6 mN (results at 0.6 mN are the same as in Figure 4c), and all the data shown employ five sub-critical cycles. In comparison to the monotonic loading results (marked ‘uncycled’ in the figure), sub-critical loads of 0.5 and 0.6 mN produce consistently higher yield loads; however, lower sub-critical loads have an essentially negligible effect.

The data in Figures 4-7 not only show that cyclic loading in the elastic range hardens metallic glasses, but that this hardening manifests progressively over several cycles, requires reciprocating load, and is significant only at sufficiently high loading amplitudes. It is of special significance that these data are all collected in glass containing no prior shear bands or cracks; whereas conventional macroscopic cyclic loading tests and fatigue tests involve pre-existing defects or prior deformation (as at a crack tip), the present nanoindentation tests reflect the properties of virgin glass. This is important because deformation through shear banding and/or cracking is widely understood to lead to dramatic structural changes in metallic glass, including free-volume accumulation [41, 42], nanocrystallization [41], and nanovoid formation [43, 44]. In the present case, our observations of hardening must be rooted in some structural change beneath the contact, but not by virtue of “conventional” glass plasticity via shear band formation. The universal absence of hysteresis in our P-h curves in the cycling range indicates that there are no substantial differences between the way the contact area and modulus evolve upon loading and recover upon unloading; we conclude that any structural changes in the glass induced by cyclic loading are very subtle, or are confined to a small fraction of the probed volume of glass.

As already outlined in the Introduction, in prior work of some of the present authors [31], a possible origin for cyclic hardening in metallic glasses was proposed. The explanation lies in the idea that shear bands do not form at the position of maximum stress around a stress concentration, but rather form on the most highly stressed slip lines that can accommodate flow. Consequently, there are points beneath the contact that experience high stresses—even exceeding the macroscopic yield stress of the glass—before the first shear band forms [27]. Thus, during cyclic loading in the nominal elastic range, below the point where the first shear band forms, some parts of the material are actually cycled to stresses locally exceeding the bulk yield strength. In these regions, it is plausible that local atomic rearrangements occur because of the
very high stress levels. Such microplastic events are likely to-and-fro STZ activations that are net forward on loading and net backward on unloading, but which are hysteretic; the forward and backward events apparently average out over a complete cycle, but do not cancel out strictly at every point within the material. In Ref. [31], this process is envisioned to lead to an accumulation of small, permanent structural changes (e.g., redistribution of free volume, changes in chemical or topological order, etc.) producing a locally hardened region beneath the contact.

The data in this work generally align with the mechanism described above. Hardening is indeed caused by cycling, and accumulates gradually, which is in line with local to-and-fro STZ activation that is kinematically irreversible. Assuming a natural bias for STZ activation at the weakest sites in the stressed volume, a back-and-forth cycle would be expected to ratchet local regions of material into lower energy states, so cyclic loading can lead to exhaustion of fertile sites for microplasticity. The saturation of hardening can then be interpreted as the system gradually shaking down to an “ideal glass” configuration of higher structural order than the as-cast material. This may or may not be similar to the configurational state of lower free volume and higher chemical order achieved in well-annealed glasses. It is possible that cycling may cause the glass to reach configurational states inaccessible by thermal relaxation alone (including, possibly, nanocrystallization) and may include anisotropic changes in the local resistance to plastic flow, delaying shear band formation along the slip lines required by the indenter geometry. Finally, the observation of an apparent threshold cycling amplitude is intuitively reasonable, since sufficiently low applied loads would be unable to trigger STZ activity at all, or at least unable to restructure the glass in the vicinity of the eventual yield shear band.

Thus, all of the experimental observations in the present work at least qualitatively conform to the proposed mechanism of cyclic microplasticity. However, the above arguments are strictly qualitative. It remains to be established that, in the complex stress field beneath the contact:

(i) Microplasticity, i.e., confined STZ activity (which would tend to redistribute stresses), is energetically plausible,

(ii) Such local STZ activity can occur in a significant volume of material without being globally perceptible in the P-h curve,
(iii) The low-temperature kinetics of STZ activation are commensurate with the timescales of cycling experiments (which span several seconds), and

(iv) To-and-fro STZ activity can lead to hardening.

Resolving these issues requires a model that captures both the complex stress field created by the test geometry (which evolves when local STZ activity accommodates strain and restructures the stress field), and the corresponding global load-displacement response of the indenter tip. To establish the kinetic plausibility of the mechanism requires a model incorporating stress-biased thermal activation of STZs. In the following section, we present an STZ Dynamics simulation of indentation in metallic glasses, and apply it specifically to the case of cyclic loading. Although we cannot make direct predictions pertaining to point (iv), we verify points (i)-(iii) above.

4. STZ Dynamics Simulations

We use the STZ Dynamics simulation method recently proposed by Homer and Schuh [32], which we adapt here to the case of indentation loading. This is a coarse-grained method that treats the STZ as the basic unit process for shape change. A simulated volume of glass is partitioned into an ensemble of potential STZs which are mapped onto a finite-element mesh. A kinetic Monte Carlo (KMC) algorithm controls the rate of activation of STZs within the ensemble, and STZ activation is effected by a forced shear shape change of several elements in the mesh. The finite element method is used to continuously recalculate the stress distribution as STZs are activated. The great benefit of this method vis-à-vis atomistic simulation is that it permits study over large time scales, and can thus be matched quite closely to the kinetic conditions of our experiments. Further details on the method are available in Ref. [32].

The simulated nanoindentation problem addressed here is carried out on a two-dimensional simulation cell comprised of plane-strain elements, with approximate width and height of 100 and 35 nm, along the x- and y-axes respectively. The indenter is modeled as a rigid surface with a tip radius of 40 nm and in all cases the indentation displacement rate is set at 1 nm/s along the
The bottom edge of the cell (along x) is fixed, rendering the geometry equivalent to that of a film atop a substrate of infinite stiffness. Periodic boundary conditions are applied at the lateral edges (along y). The top surface (along x) is free, but subject to the constraint of frictionless hard contact with the indenter. Similar boundary conditions and test geometries have been employed for simulated nanoindentation by molecular dynamics [40].

The material and geometric STZ properties employed for these simulations are those of a model metallic glass, as taken from Ref. [32]. The shear modulus of the glass is 35.8 GPa, its Poisson’s ratio is 0.352, the Debye temperature is 327 K, and the STZ volume is 0.8 nm$^3$. These material parameters have been shown to accurately capture the kinetics of glass flow over many orders of magnitude in strain rate, and at many temperatures [32].

The KMC algorithm of Ref. [32] has been slightly adapted to more efficiently simulate nanoindentation, during which the stress state (and thus the STZ activation rate) varies quite dramatically. Specifically, we enforce here a maximum elapsed time per KMC step of 5 ms. If during that time the KMC algorithm predicts a transition, it is allowed; otherwise the STZ activation is suppressed and the system evolves by 5 ms. In either case the indenter tip is moved by an appropriate distance to effect a constant displacement rate.

For purposes of comparison with experiment, it is important to note that the indentation rate used here (1 nm/s) is closely matched to that in the experiments (~5-40 nm/s), and many orders of magnitude slower than typically used in atomistic simulations of indentation (~5.4×10$^8$ nm/s [40]). In terms of micromechanics and kinetics of STZ activity, we can therefore expect to make reasonable qualitative comparisons with the experiments. However, we emphasize that a quantitative comparison between model and experiment is not possible or appropriate. The simulations employ a model glass, geometry, and test conditions that are somewhat different from the experiments (e.g. properties, plane strain vs. axisymmetric, displacement- vs. load-controlled). More importantly, the present STZ Dynamics model does not specifically incorporate a structural state variable (such as free volume or an order parameter). As such, the

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1 The effect of system size and tip radius are found to have a negligible effect on the overall nature of deformation by running a monotonic loading test using an indenter radius of 100 nm and a system size of 250 by 100 nm (data not shown).
model cannot explore the complex reaction pathways that lead to intrinsic structural hardening or softening, such as those apparently sampled in the experiments. Thus, the model is not capable of directly modeling cyclic hardening, but it may be used to validate the concept of microplasticity upon cyclic loading. We limit our attention in what follows to focus on the latter aspects of the problem (surrounding the potential for microplasticity) that are accessible with the present model.

To begin, we consider conventional monotonic nanoindentation tests. As a baseline for our subsequent analysis, we first conduct an ideal elastic indentation, i.e., one in which the energy barrier for STZ activation was increased to infinity, and thus plasticity was suppressed. The P-h curve resulting from this simulation is shown in Figure 8, as a solid black line. This curve also matches the expectations of the Hertzian contact solution (which, for the plane-strain cylinder-on-plate geometry, does not have a closed analytical form [45]). When the same simulation is conducted with STZs allowed to activate, the result is shown in Figure 8 as the blue data points; the response initially follows the elastic curve exactly, but at a depth of about 2 nm begins to noticeably depart from the elastic curve as plastic flow sets in.

Snapshots showing a portion of the simulation cell during the indentation are provided in the bottom panel of Figure 8, corresponding to the marks ‘A’, ‘B’ and ‘C’ on the P-h curve. In each of these snapshots, a red solid line denotes the outer envelope of material in which the local deviatoric (von Mises) stress exceeds the nominal yield stress of the model glass (taken as 3.27 GPa from pure shear simulations at 10⁻³ s⁻¹ in Ref. [32]). Similarly, the load at which the yield stress is first reached at any point beneath the contact is marked by the solid horizontal red line on the P-h curve. It is interesting to observe that high deviatoric stress is not necessarily correlated to the activation of STZs, as there is a significant regime at loads where some portion of the material reaches the yield stress, but before the first STZ activity is observed. In this regime, the stress field still matches the elastic prediction exactly and therefore the yield envelope is symmetric as in panel ‘A’. It is only at a somewhat higher load that STZs activate, with local spatial correlations along slip lines (panel ‘B’). At this point, the stress and strain field is no longer simple, being perturbed and redistributed by virtue of the STZ activity, and the envelope in which the nominal yield stress is exceeded is asymmetric and irregular as a result.
An important point to note, however, is that at ‘B’, despite the activity of numerous STZs and the appreciable volume of material above the nominal yield stress, the global P-h curve is still in excellent agreement with the elastic curve. Significantly beyond point ‘B’, the departure of the response from the ideal elastic curve is unambiguous, and the extent of plastic deformation is large (panel ‘C’). In this regime the distribution of plastic strain beneath the point of contact is quite reminiscent of that expected from slip-line field theory, as also seen in experiments on metallic glasses [39, 46]. As an online supplement to this discussion, a movie of such a monotonic elastic-plastic indentation is provided; this movie illustrates in real time the STZ activity that occurs beneath the indenter, along with the P-h curve that results during one of these simulations.

We now turn our attention to cyclic indentation simulations, which were conducted at displacement amplitudes of 1.2, 1.6, 2.0, 2.4, and 2.8 nm. The P-h curves from these simulations are shown in Figure 9. As expected based on the above discussion, at low amplitudes of 1.2 and 1.6 nm, the stress levels achieved are below that necessary to trigger STZ activity on the time scales of the test, and the response is perfectly elastic. On the other hand, for the largest amplitude of 2.8 nm, copious STZ activity occurs below the indenter, and measurable dissipation occurs after the first cycle. Obvious plastic (residual) displacement is accumulated after the first cycle, with subsequent cycles appearing essentially perfectly elastic. At intermediate displacement amplitudes of 2.0 and 2.4 nm, we see the interesting behavior of most direct relevance to this work: in this range we see significant STZ activity beneath the indenter, but relatively little permanent deflection in the P-h curves. If we assign a displacement resolution similar to that in nanoindentation (~0.2 nm, twice the width of the data points in Fig. 9), these simulations appear in the P-h curves as essentially perfectly elastic. In fact, for the 2.0 nm displacement amplitude, with a resolution (and data point size) of 0.1 nm, we can detect no hysteresis or dissipation in the P-h curve in Figure 9. However, despite the appearance of elastic conditions, Figure 10 shows that in these two cases, there is significant STZ activity beneath the indenter.

The behavior captured in Figures 9 and 10, for displacement amplitudes of ~2.0 nm, corresponds to the speculative “microplasticity” that is believed to occur during cyclic indentation
experiments, as originally proposed in Ref. [31]. These simulations confirm that under the mechanical load of an indenter, and at time scales relevant to the experiments, it is plausible that the applied stress field significantly exceeds the yield stress of the material in local regions beneath the indenter, and leads to local microplastic events sufficiently small and localized so as to be transparent to the global P-h measurement. What is more, these simulations reveal that this STZ activity can occur progressively over the course of several load cycles; close inspection of Figure 10 reveals that at 2.0 nm amplitude, new STZ activity occurs on cycles 1, 3, and 5, while at 2.4 nm amplitude there is evolution on each and every cycle. In addition, STZ activations are observed on both the downward indentation into the sample as well as during the retraction of the tip from the sample in response to the local and evolving stress landscape. As an online supplement to Figures 9 and 10, two movie files showing the cyclic indentation simulations at displacement amplitudes of 2.0 and 2.4 nm are provided. These show the evolution of STZ activity beneath the indenter and its effect on the global P-h response.

At least qualitatively, the observations from our simulations line up well with those from the experimental work, and most importantly, they validate the plausibility of microplastic structural rearrangements. Cycling can indeed cause undetected microplasticity, and structural change via STZ activation can occur progressively over the course of several load cycles. As already noted earlier, the present model does not include a mechanism for hardening in the region affected by microplasticity. However, we note that the amount of material deformed on cycling is fairly significant, and is located in the regions that experience high stresses. If this material has been locally “aged”, “annealed”, or otherwise restructured by virtue of local STZ activity, then this affected volume could be stiffer or stronger than the surrounding material. Upon further loading, it could preferentially bear load, shedding it from the virgin glass, or directly impede the formation of a shear band attempting to traverse it. While many details of this cyclic hardening phenomenon remain to be clarified, the present simulations support the notion of microplastic structural rearrangement as a root cause of it.

5. Conclusion
Through a combined program of experimental and simulation work, we report an exploration of cyclic contact loading in metallic glass. Experimentally, we use a nanoindenter with a spherical diamond tip, and reveal that two Pd-based and one Fe-based glass exhibit cyclic hardening. Specifically, load cycles in the nominal elastic range are found to lead to marked hardening of the glass against the formation of the first shear band. This hardening is found to occur progressively over several cycles, and saturate after some number of cycles. Hardening is not observed when holding at a constant subcritical load (rather than cycling), nor when cycling at sufficiently low load amplitudes.

The mechanism responsible for cyclic hardening has been proposed in a prior paper to be local microplastic events that occur beneath the indenter, but which are too small to detect as hysteresis in the load-displacement curves. In indentation, shear bands are known to form at load levels well beyond the point where some portion of the material exceeds the yield stress, and cycling over this range can lead to local shear transformation zone (STZ) activity. Locally confined plasticity of this kind could be undetectable using today’s experimental techniques, but still lead to structural changes. We address the plausibility of this mechanism using computer simulations of cyclic indentation.

Computationally, we use an STZ Dynamics model, which combines finite element and kinetic Monte Carlo techniques, to validate the potential for microplasticity under cyclic contact. The simulations reveal that, indeed, a small but significant amount of STZ activity can occur beneath a Hertzian contact without being perceptible in load-displacement curves, and that this activity occurs progressively over several cycles. An important aspect of this modeling approach is that the kinetics of STZs are captured over long time scales (several seconds), which permits a more reasonable (albeit qualitative) comparison with the experimental work.

Cyclic loading and fatigue stand as major concerns for the structural performance of metallic glasses in load-bearing or structural applications. The present results should offer complementary insight into these phenomena to those from more conventional macroscopic tests. Of course, our 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. On the other hand, conventional fatigue studies necessarily involve testing in geometries with prior deformation and damage, i.e., from crack growth and prior shear banding. The present approach permits fine-scale studies of cyclic deformation on virgin glass, and should thus offer a cleaner view of the structural aspects of kinematic irreversibility under cyclic loading. The use of STZ Dynamics simulation also opens new paths for the study of damage evolution in metallic glasses, on time scales more relevant for fatigue problems.

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References
Figure 1  
(a) Example load-displacement (P-h) curve in monotonic loading, showing the first shear band event for the Fe-based glass. (b) Cumulative distribution of yield loads during monotonic loading into cumulative plot showing all three glasses.
Figure 2  Typical loading functions used in the nanoindentation experiments; those shown are for Fe_{41}Co_{7}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2}, including (a) an example with five sub-critical cycles at 1.25 mN prior to final loading to 5 mN, and (b) an example incorporating a 4 s sub-yield hold at 1.25 mN.
Figure 3  Example load-displacement curves for experiments involving 5 sub-critical cycles. In (a), Fe$_{41}$Co$_7$Cr$_{15}$Mo$_{14}$C$_{15}$B$_6$Y$_2$ is cycled to 1.25 mN before final loading to 5 mN. In (b), Pd$_{40}$Ni$_{40}$P$_{20}$ is cycled to 0.2 mN before final loading to 1.5 mN. In (c), Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ is cycled to 0.6 mN before final loading to 2.5 mN. In all tests, there is no obvious hysteresis during the cycling and the elastic prediction (solid curve) is followed up to the first shear band event, marked as a black point.
Figure 4  The cumulative distribution of measured yield points, and its evolution with sub-critical cyclic loading, for all three glass compositions, including Fe_{41}Co_{7}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} (a), Pd_{40}Ni_{40}P_{20} (b), and Pd_{40}Cu_{30}Ni_{10}P_{20} (c). In all graphs, each data point represents the yield load from a single test. Some of the data for the Fe-based glass in (a) first appeared in Ref. [31].
Figure 5: Time-evolution of the median measured yield load for various numbers of subcritical cycles. The bars denote the 25-75 percentile ranges of the full distributions from Figure 4. For each glass an apparent saturation of hardening is observed upon multiple cycling.
Figure 6  Results of experiments involving sub-critical load holding, showing the cumulative yield point measurements. (a) After holding Fe$_{41}$Co$_7$Cr$_{15}$Mo$_{14}$C$_{15}$B$_6$Y$_2$ at a sub-critical load of 1.25 mN for 4 seconds, differences from the uncycled data (monotonic loading) are negligible, whereas cycling leads to measurable change in the distribution. (b) Similar results are obtained with Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$. Additionally, the combination of cyclic loading plus an equivalent hold exhibits the strengthening level associated with 5 cycles alone.
Figure 7 Effect of applied cycling amplitude on the apparent hardening, as observed in the cumulative yield load distribution. These data are for sub-critical cycling for five cycles in Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, and suggest that there is an apparent threshold below which no strengthening occurs in the range of 0.4-0.5 mN.
Simulated nanoindentation results for monotonic loading. The graph shows the load-displacement curve for a single monotonic indentation test, in comparison with results for a purely elastic contact for comparison. Snapshots of the system during the simulation are provided below the graph as marked by ‘A’, ‘B’ and ‘C’. The red contour on the snapshots shows the region of material that has exceeded the yield stress, while the gray regions denote the operation of STZs.
Figure 9 Load-depth curves for the simulated cyclic nanoindentation where the limiting amplitude of the cycling depth is marked by each curve, ranging from 1.2 – 2.8 nm. The elastic reference is plotted with each cycling simulation for comparison. Cycling at depths where the load does not reach the minimum load for STZ activation, 1.2 and 1.6 nm, results in a perfectly elastic material response. Cycling above the minimum load for STZ activation leads to plasticity through STZ activity in all cases, 2.0 – 2.8 nm, although the hysteresis in the load-depth curve is not immediately apparent in all cases.
Figure 10  Snapshots of a portion of the 2.0 and 2.4 nm cycled systems after each of the five cycles, illustrating the progressive nature of the structural change. The gray regions show the local plastic strains accumulated by STZ activation. In addition, it can be seen that the sample surface remains relatively smooth in spite of the fact that significant plastic structural change has occurred below the surface.