Low Cycle Fatigue of Metallic Glass Nanowires

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Abstract

Low cycle fatigue fracture of metallic glass nanowires was investigated using molecular dynamics simulations. The nanowires exhibit work hardening or softening, depending on the applied load. The structural origin of the hardening/softening response is identified as the decrease/increase of the tetrahedral clusters, as a result of the non-hardsphere nature of the glass model. The fatigue fracture is caused by shear banding initiated from the surface. The plastic-strain-controlled fatigue tests show that the fatigue life follows the Coffin-Manson relation. Such power-law form originates from plastic-strain-dependent microscopic damage accumulation. Lastly, the effect of notch on low cycle fatigue of nanowires in terms of failure mode and fatigue life was also discussed.

Keywords: metallic glasses; nanowires; low cycle fatigue; fracture; work hardening.

1. Introduction

Nanometer-scaled metallic glasses have emerged as a scientifically interesting and technologically useful structural material^{1,2}. They possess an unusual suite of properties, such as excellent formability³, high elastic limit⁴⁻⁶, high strength^{4,7} and high ductility^{4,7,8}. Therefore, metallic glasses have great advantages for applications in the fields of microelectromechanical⁹, nanoelectromechanical systems¹⁰, micromachines¹ and biomedical applications¹¹. To utilize the extraordinary properties of nanometer-scaled metallic glasses, bulk metallic glass composites with nanometer-scaled microstructure^{12,13}, or bulk metallic glass foams¹⁴ with ligaments of nanometer-sized cross sections have been developed, which significantly enhanced the application prospects of metallic glasses. In the context of the above real-world applications, the fatigue behavior of nanometer-scaled metallic glasses, however, receives much less attention. Such omission is significant, since fatigue failure accounts for more than 90% of all mechanical failures¹⁵.

The fatigue limit of the submicron-sized metallic glasses was found to be as high as the yield stress¹⁶. Bulk metallic glass composites with micron-sized microstructures also exhibit enhanced fatigue endurance limit¹⁷. In the few experiments devoted to the cyclic deformation of nanometer-scaled metallic glasses, work-hardening was observed under cyclic tension^{4,5} or in nano-indentation test¹⁸. However, the exact fatigue fracture mechanism and the quantitative description of the fatigue life of nanometer-scaled metallic glasses are largely unknown.

Molecular dynamics (MD) simulations can provide important atomistic insights on the fatigue failure. In existing MD simulations on the fatigue behavior of metallic glasses, directional localization of free volume¹⁹ and defects²⁰ were suggested to be important for the fatigue damage initiation. Cyclic loading induced hardening²¹ and crystallization²² have also been observed in recent atomic simulations. However, it is challenging to directly simulate fatigue fracture in MD simulations. The foremost challenge arises from the deficiency of the available atomic force fields²³, which usually lead to model metallic glasses that are significantly more ductile than experimental metallic glass systems. For instance, the amorphous nanowire modeled by the widely used Lennard-Jones force field²⁴ exhibits little damage, let alone fracture, even after extensive push-pull cyclic loading with a strain amplitude as high as 36% in our preliminary result. Moreover, it has been shown that the sample preparation can significantly affect the deformation mode of the nanoscale metallic glass samples.²⁵ Specifically, nanoscale metallic glass samples made from the traditional cutting method (vitrify a bulk liquid to bulk glass, then cut to a nanowire) have unrelaxed surfaces, which will in turn suppress the shear band formation and likely fatigue fracture. As a result, to our best knowledge, no direct fatigue fracture process of metallic glass nanowires has been observed in MD simulations.

In this study, we conducted cyclic compression tension tests with a large strain range to directly examine the low cycle fatigue fracture behavior of metallic glass nanowires with atomic details. During the cyclic loading, the nanowire hardens under low strain amplitude and softens under higher strain amplitude. The final fracture of

the nanowires is caused by rapid shear band formation, true for the entire range of strain amplitudes explored in this study. In the plastic strain controlled fatigue tests, the fatigue life of the nanowire follows the Coffin-Manson relation. This power-law form can be rationalized from the microscopic deformation damage accumulation, which depends on the macroscopic plastic strain amplitude.

2. Simulation Methodology

MD simulations were carried out with LAMMPS²⁶ (Large-scale Atomic/Molecular Massively Parallel Simulator) package (<http://lammps.sandia.gov>) with a modified binary Lennard-Jones (mBLJ) potential upon the Wahnstrom system.²³ The alloy consists of two equimolar species, which will be referred to as S and L for small and large atoms, interacting via a Lennard-Jones (LJ) potential of the form:

$$\phi_{mBLJ}(r) = \begin{cases} 4\varepsilon_{\alpha\beta} \left(\frac{\sigma_{\alpha\beta}^{12}}{r^{12}} - \frac{\sigma_{\alpha\beta}^6}{r^6} \right) - \varepsilon_{cutoff}, & r < r_{\alpha\beta}^s \\ 4\varepsilon_{\alpha\beta} \left(\frac{\sigma_{\alpha\beta}^{12}}{r^{12}} - \frac{\sigma_{\alpha\beta}^6}{r^6} \right) - \varepsilon_{cutoff} + \varepsilon_B \varepsilon_{LL} \cdot \sin^2 \left(\pi \frac{r_{\alpha\beta}^c - r}{r_{\alpha\beta}^c - r_{\alpha\beta}^s} \right), & r \geq r_{\alpha\beta}^s \\ 0, & r \geq r_{\alpha\beta}^c \end{cases} \quad (1)$$

Thus, the mBLJ potential has a traditional shifted LJ form and a shifted LJ form with a “bump” energy penalty, separated by $r_{\alpha\beta}^s \cdot \varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ (α, β denotes species of S or L) provide the energy and length scales, respectively. $r_{\alpha\beta}^s$ is taken as $1.5\sigma_{\alpha\beta}$, which is outside the first neighbor shell. The cutoff values $r_{\alpha\beta}^c$ were chosen to be species dependent, such that all pair interactions are precisely $0.0163 \varepsilon_{LL}$ at the cutoffs of

$r_{LL}^c = 2.5\sigma_{LL}, r_{LS}^c = 2.2917\sigma_{LL}, r_{SS}^c = 2.0833\sigma_{LL}$. The SS and LL bond energies are equal to that of the SL bond energy: $\varepsilon_{SS} = \varepsilon_{SL} = \varepsilon_{LL}$. The SS and LL length scales are related to the SL length scale by,

$$\sigma_{SS} = \frac{5}{6}\sigma_{LL}, \sigma_{SL} = \frac{11}{12}\sigma_{LL} \quad (2)$$

The two types of atoms have different masses: $m_L = 2m_0, m_s = m_0$, where m_0 is the mass unit. The reference time scale is $t_0 = \sigma_{LL} \sqrt{m_0 / \varepsilon_{LL}}$. All physical quantities will therefore be expressed in SI units following the conversion in a previous report.²⁷

$$\sigma_{LL} \approx 2.7 \text{ \AA}; m_0 \approx 46 \text{ amu}; \varepsilon_{LL} \approx 0.151 \text{ eV}; t_0 \approx 0.5 \text{ ps}.$$

This force field is inspired by the Dzugutov potential²⁸, which features an energy bump to mimic the Friedel's oscillations^{29–32} and to control the bonding covalency, thus can reduce the excessive ductility commonly presents in model metallic glasses. In this study, the bump height parameter ε_B used is 0.3. The corresponding model glassy nanowire fractures via shear banding (loses half of the tensile stress at around 20% strain) in an uniaxial tensile test²³. A standard velocity Verlet integrator with a time-step of 5 fs was used. Temperature control and stress control used in the MD simulations follow the standard Nose-Hoover formulation^{33,34}. Similar to a previous study²³, glassy nanowires with the length of 24.3 nm and diameter of 11.3 nm (about 0.13 million atoms) were chosen. Due to the high loading cycles required in fatigue tests, a study with an even larger sample size is very demanding at this moment. The nanowires were melted and equilibrated at a high pressure (9.4 GPa) and high temperature (2000 K) in a cylindrical container and quenched into a metallic glass

nanowire with zero pressure and at 60 K, with a cooling rate of $8.7 \times 10^{11} \text{ K/s}$. The quenching process mimics the experimental casting²⁵. Thus, the as-quenched glassy nanowires have relaxed surfaces²⁵. Periodic boundary condition applies only in the axial direction. During fatigue tests, the nanowire was uniaxially loaded by rescaling the simulation box with a strain rate of 0.4 ns^{-1} . The temperature was maintained at 60 K (20% of the glass transition temperature T_g) during the fatigue tests.

3. Total-strain-controlled fatigue tests

First, we applied total-strain-controlled symmetric compression-tension fatigue tests on the nanowires, in which the strain amplitude in tension or compression spans from 4% to 6% with the interval of 0.5%. Five independent samples were tested for each strain amplitude to investigate the statistics of the fatigue behaviors. Shown in Fig. 1(a), at the total strains of 4% and 4.5%, the stress exhibits a slightly cyclic-hardening behavior before fracture (upon which the stress drops significantly). However, at higher strain levels, there is generally a cyclic-softening behavior before the stress significantly drops. Such behavior is likely due to the competition between aging-induced hardening (possibly mechanically-assisted) and deformation-induced softening. At low loads, aging dominates; while at high load, deformation dominates. The fatigue life of the sample was identified as the first cycle in which the peak tensile stress reduces to half of the initial stress amplitude. The tensile stress was chosen here since the fractured sample might still be able to sustain a certain amount of compressive stress. The plastic strain ε_p of every cycle is

defined to be half of the strain difference between the two zero-stress points, as shown in Fig. 1(b). As shown in Fig. 1(c), the higher the applied total strain amplitude ε , the higher the plastic strain ε_p observed. Similar to the stress evolution, ε_p also exhibits either softening or hardening behavior, depending on the strain amplitude. For samples with total-strain amplitudes lower than 4.5%, ε_p decreases during the majority of the cyclic loading, before surges rapidly upon failure. Cyclic strain induced work hardening behavior was also observed in nano-indentation tests^{18,21} and in cyclic tensile tests on metallic glass nanowires^{4,5}. With the total-strain amplitude of 5%, the plastic strain, ε_p , maintains at a constant level until fracture. For samples with total-strain amplitudes higher than 5%, the plastic strain increases during the whole fatigue tests, indicating strain softening behavior.

The sudden increase in the plastic strain marks the onset of fracture in all of the total-strain-controlled fatigue tests. The atomic deformation morphology further reveals that the onset of fracture is caused by the rapid shear band formation and propagation process as shown in the side views of the nanowires of Fig. 2. The color coding follows the local atomic shear strain according to a previous study³⁵. The top views of the nanowires during fatigue tests evidently show that the shear band initiates at the surface and floods into the nanowire at the later stage of the fatigue test. While the cause of fatigue failure of macroscopic metallic glasses seems complex, with cracks or a mixture of crack and shear banding involved^{36,37}, we show here that shear banding is the major failure mechanism for nano-scale metallic glass samples in low cycle fatigue tests. Such shear banding behavior is somewhat similar

to the persistent slip bands, which is the major form of damage for crystalline materials under fatigue tests^{38–41}. In low cycle fatigue for nano-scale metallic glasses, as we show here, the majority of the fatigue life is spent in the shear band initiation. While in high cycle fatigue tests of macroscopic metallic glass samples, it was reported that the crack propagation process almost takes up the whole fatigue life⁴².

4. Plastic-strain-controlled fatigue tests

To better understand or predict the low cycle fatigue behavior of the amorphous nanowires, it is important to evaluate the quantitative relationship between the plastic strain and the fatigue life. In fact, the fatigue life has long been directly associated with the plastic strain in the well-known Coffin-Manson relation⁴³ in the form of $\varepsilon_p = \varepsilon_f \times N_f^c$, where N_f is the fatigue life, ε_f and c are two fitting parameters termed the fatigue ductility coefficient and the fatigue ductility exponent, respectively.

To directly quantify the effect of plastic strain, we conducted MD simulations of plastic-strain-controlled fatigue tests. Experimental plastic-strain-controlled fatigue tests have been conducted on crystalline materials^{38–41,44}, in which the estimation of the elastic strain amplitude was required to determine and tune the plastic strain amplitude in real time. However, the estimation of the elastic strain might not be accurate due to the complicated softening and hardening behavior during the fatigue test. In addition, the estimation of elastic strain can be further obscured if the stress-strain loops during the fatigue tests on the amorphous nanowires do not exhibit

well defined yield points, as shown in Fig. 1(b). Therefore, more accurate evaluation of the plastic strain should be used, for instance, the definition based on the loading cycle that is completed as in Fig. 1(b). The plastic strain measured here does include a small time-dependent irreversible visco-plastic component^{45,46}, without any reversible anelastic strain.

In our simulations, the exact control of plastic strain with accurate assessment of the elastic strain was implemented as follows. For each sample, we first conducted one cycle of loading with a total strain between 4 to 6%. The plastic strain measured during the first cycle was set as the target plastic strain. At the beginning of every cycle, the sample system was subjected first to a trial cycle with the total strain applied in the last cycle. If the plastic strain measured during the trial cycle is not within a 5% error of the target plastic strain, another trial cycle will be carried out on the system at the beginning of this cycle with an adjusted total strain (via a feedback loop based on the deviation from the target). For each initial total strain, we run five parallel tests, of which the target strain might be slightly different (see Fig. 3(a)) due to sample-to-sample variation.

The validity of the plastic strain controlled fatigue tests is demonstrated in Fig. 3(a). In order to keep the plastic strain at constant, the applied total strain in each accepted cycle varies. The variation of the applied total strain during the typical plastic-strain-controlled fatigue tests exhibit again a plastic-strain-dependent work hardening or softening behavior, which is very similar to the fatigue tests with constant total strains as shown in Fig. 1(c). While the softening or final fracture of the

amorphous nanowire is clearly associated with the shear band, the exact structural origin for hardening is not clear. As suggested by a recent atomic simulation on amorphous CuZr²¹, the subtle structural change associated with hardening induced by cyclic deformation requires better classification of the atomic structure of amorphous solids.

With plastic-strain-controlled fatigue tests, we can directly plot the fatigue life as a function of the plastic strain. As shown in Fig. 3(b), the fatigue life of the metallic glass nanowires varies with the plastic strain in a power-law relation as in $\varepsilon_p = \varepsilon_f \times N_f^c$, which is identical to the Coffin-Manson relation⁴³. The fatigue ductility exponent c is found to be - 0.6, similar to that of the crystalline metals in the range between - 0.5 and - 0.7¹⁵. The fatigue ductility coefficient ε_f is found to be 0.118. It is interesting to note that the Coffin-Manson relation was originally observed under the plastic strain controlled fatigue tests on the crystalline copper in experiment^{38,40}. Thus, the Coffin-Manson relation appears to be insensitive to the amorphous or crystalline atomic structure of the sample.

5. Understanding the power law from damage accumulation

We further explore why the Coffin-Manson relation is valid in the plastic strain controlled fatigue test for the model metallic glass nanowires. The Coffin-Manson relation is usually rationalized in terms of crack growth via the Paris law $\frac{da}{dN} = A(\Delta K)^p$,¹⁵ where a is the crack length, N is applied cycles, ΔK is the stress intensity factor range and A and p are two fitting parameters. However, in the model

metallic glass nanowire, no apparent crack is introduced or formed, except the very late stage of the low cycle fatigue tests. Therefore, fatigue damage evolution in terms of shear band development, instead of crack propagation should be considered here. Here, any atom with a higher than 20% local shear strain is considered part of the damaged region. As shown in Fig. 2, a threshold of 20% in the local shear strain delineates the local deformation very well. It should be noted that a different threshold strain for damage (such as 15% or 25%) will not affect the following analysis. Thus, the fatigue damage (D) can be quantified as the ratio of the number of atoms in the damaged region relative to the total number of atoms in the sample, similar to the deformation participation ratio used in an earlier report to quantify shear localization⁴⁷.

In Fig. 4(a), the accumulative damage during plastic strain controlled fatigue tests are shown to increase with cycle N . The curves can be effectively described in the form of $D = K(\varepsilon_p)N^\alpha$, in which $K(\varepsilon_p)$ is the pre-factor that increases with the plastic strain ε_p . The exponent α is found to be approximately 1.5 (ranging from 1.3 to 1.6 for all the data). Consequently, the damage per cycle can be written as $\frac{dD}{dN} \propto N^{\frac{1}{2}}$ or $\frac{dD}{dN} \propto D^{\frac{1}{3}}$. Thus, the damage generation rate is proportional to $D^{\frac{1}{3}}$ (the size of a three-dimensional shear band nucleus). Next, $K(\varepsilon_p)$ can be obtained from Fig. 4(a) via fitting, assuming α to be 1.5. Fig. 4(b) shows that $K = A\varepsilon_p^\beta$, where $A = 11.8$ and $\beta = 2.4$. Therefore the accumulated damage can be written as $D = A\varepsilon_p^\beta N^\alpha$. Fig. 4(c) shows excellent data collapsing in the D vs. $\varepsilon_p^\beta N^\alpha$ graph, supporting the damage evolution relation.

The above damage accumulation relation provides a mechanistic explanation of why the fatigue life of the nanowire follows the Coffin-Manson relation. As shown in the inset of Fig. 4(a), the damage at fracture (D_f) is roughly a constant of 0.09 ± 0.03 for all fatigue tests. Therefore, one can assume fatigue fracture occurs when the damage D reaches a threshold value D_f . From $D_f = A\varepsilon_p^\beta N_f^\alpha$, we have $\varepsilon_p = (D_f / A)^{1/\beta} \times N_f^{-\alpha/\beta}$, identical to the Coffin-Manson relation. Here $(D_f / A)^{1/\beta}$ was estimated to be 0.13 ± 0.02 , very close to the fatigue coefficient ε_f measured as 0.118 in Fig. 3(b). In addition, the exponent $-\alpha / \beta$ can be calculated as -0.625, which is also very close to the fatigue ductility coefficient c measured as -0.6 in Fig. 3(b). Thus, the Coffin-Manson relation is recovered by connecting the microscopic accumulative damage with the macroscopic plastic strain.

Our simulation results reveal that the fatigue failure of metallic glass nanowires is a result of local damage accumulation, which is further controlled by the macroscopic plastic strain via a power law. In other words, if the plastic strain is zero, then no fatigue failure is expected because no damage will be accumulated. Therefore the fatigue limit of metallic glass samples free from defects should approach the yield strength itself. This is in line with a recent experimental finding¹⁶ that micrometer scale metallic glass samples have exceptionally high fatigue limits. Note that the fatigue limit of macroscopic samples will likely be degraded by the local damage accumulation triggered inevitably by defects or stress concentrators.

6. The effect of notch on fatigue behaviors of glassy nanowires

In addition to pristine as-quenched metallic glass nanowires, we also carried out plastic strain controlled fatigue tests on the same nanowires with a pre-existing surface crack. The crack was created by removing atoms within a wedge-shaped region between two intersecting planes such that the size of the surface crack is 2.8 nm with a maximum opening of 0.9 nm on the surface of the nanowire (as illustrated in Fig. 5). To reduce the computational time, three independent samples were simulated here. Moreover, three levels of plastic-strain-controlled fatigue tests with initial total strain amplitudes of 4%, 5% and 6% were carried out.

As shown in the deformation morphology in Fig. 5(b-d), all damages localize around the notch, without developing a 45-degree (off the nanowire axis) shear band as seen in notch-free nanowires (Fig. 2). Thus, the fatigue failure mode of the nanowires is the extension of the existing crack, instead of shear banding for pristine nanowires. The fatigue life as a function of the plastic strain is shown in Fig. 5(e), consistent with the Coffin-Manson relation. Fig. 5(f) shows the log-log plot of damage accumulation as a function of cycle number. According to $D = K(\varepsilon_p)N^\alpha$ from the preceding section, the exponent α is 1. Therefore, it appears that the fatigue damage increases linearly during cyclic loading. As the existing crack is substantial (the crack size is about half the nanowire radius), the accumulated damage does not lead to accelerated deformation. Furthermore, the prefactor K , or D/N^α , is shown as a function of the plastic strain ε_p in Fig. 5(g). Similar to the as-quenched sample, a power law emerges between K and ε_p : $K = A\varepsilon_p^\beta$, where $A = 9.57$ and $\beta = 1.92$ from fitting. Fig. 5(h) shows the fatigue damage data falling on a master

curve as a function of $\varepsilon_p^\beta N^\alpha$, analogous to Fig. 4(c). Following the same derivation presented in the preceding section, one can understand the Coffin-Manson relation in fatigue life from damage evolution. The fatigue ductility coefficient c equals $-\alpha/\beta$, which is calculated to be -0.52. Compared to the pristine nanowire samples (c is around -0.6), it can be seen that the notch facilitates fatigue failure.

7. The structural origin of hardening/softening upon cyclic loading

Lastly, we explored the structural origin of the cyclic hardening at low loads and cyclic softening at high loads, which can be seen in the total-strain controlled tests (Fig. 1c). In other words, we wish to find the local preferred structural signatures that are responsible to the resistance to deformation in this glassy sample. In previous studies, Shi and Falk found that the concentration of local structures rich of tetrahedra (for instance, an icosahedral cluster has twenty tetrahedra) is high in low temperature glasses, and low in high temperature liquids³². Thus, these local structures are solid-like in a binary structural view, and thus are considered as “back-bones” for model metallic glass formers⁴⁸. However, such structural criterion to associate tetrahedra-rich clusters to solid-like regions only applies to model glasses conform to hard-sphere descriptions, not for systems that deviate from hard-sphere descriptions³². For instance, the well-studied Kob-Andersen⁴⁹ binary Lennard-Jones system features a bond length of AB smaller than the average of AA and BB bonds, thus cannot be

described as a hardsphere system. Consequently, icosahedral clusters are not relevant as a structural indicator for the Kob-Andersen system.³²

The mBLJ potential used here (Eq. 1) features an energy penalty beyond the first nearest neighbors, which leads to covalency in bonding. This covalency is evident by the fact that the glassy structure is substantially less dense (about 25% less dense than the original BLJ system), and that there emerges a new 90 degrees angular peak with a diminished peak at 60 degrees²³. In other words, the atomic packing becomes more open and less close-packed. Therefore, the mBLJ potential does not conform to the hardsphere models. Consequently, the tetrahedra-rich local structures do not represent solid-like regions, nor serve as back-bones in the mBLJ system. To the contrary, the tetrahedral clusters characterize the liquid-like regions and fertile spots for shear. Let us consider a tetrahedron cluster composing of four atoms. The energy penalty, from the additional bump term, does not affect first-nearest neighbors, therefore it is still energetically favorable to assemble an efficiently packed *isolated* tetrahedron. However, in *bulk* glass, it is difficult for other surrounding atoms to bond near this tetrahedron due to the repulsive force from the energy penalty term. Such repulsive force is almost isotropic around the tetrahedron, precisely because of its high packing efficiency.

To examine the efficacy of the tetrahedral clusters in serving as the structural indicator of soft spots, we first examined the tetrahedral cluster population during vitrification. The tetrahedral clusters are identified by the connectivity: four atoms are mutually nearest neighbors. A pair of atoms is considered to be the nearest neighbors

if the separation is within 0.38, 0.34, 0.30 nm, for $L-L$, $L-S$ and $S-S$ pairs. These distances are the average values of the first and second peaks in the species-dependent pair distribution functions. Fig. 6(a) shows that the number of tetrahedral clusters decreases as the temperature decreases during the vitrification process. The sample was cooled using the same protocol described in Section 2. It should be noted that, in order to avoid the surface effect that complicates the structural characterization, a 32000-atom bulk sample (with periodic conditions in all three directions) was used, instead of a nanowire sample. It is clear that the soft regions of tetrahedral clusters decreases as the system undergoes the glass transition (the glass transition is estimated to be around 290 K²³). The high temperature liquid and low temperature glass can be structurally distinguished by the amount of tetrahedral clusters: high concentration of tetrahedral clusters represents liquid-like region and vice versa.

Next, we examined how the tetrahedral cluster population evolves during cyclic loading. Total-strain-controlled fatigue tests with a total strain of 4% and 6% were selected as representatives for cyclic hardening and cyclic softening, respectively. The system configurations were selected at the end of the compression cycles, which retain its original sample length. All five independent samples were analyzed. Figure 6(b) shows that the tetrahedral cluster population decreases for the cyclic loadings with a total strain of 4%, indicating the reduction of liquid-like regions. This can be considered an aging process aided by mechanical agitation of cyclic loading. For the cyclic loadings with a total strain of 6%, there seems to be some aging initially as the

tetrahedra population decreases slightly from 0 to 5 cycles, followed by rapid surge of tetrahedral population indicating significant deformation-induced structural softening.

We have identified that the tetrahedral clusters in the mBLJ system serve as the structural indicator for liquid-like regions. Although such specific structural signatures in a highly simplified model glass former of mBLJ system cannot be directly applied to experimental systems, it provides us a useful insight: the tetrahedral clusters, representing solid-like region in hardsphere models, denote liquid-like regions in non-hardsphere models upon the introduction of covalent bonding. The relevance of tetrahedra-rich local structures, such as the icosahedral cluster, serving as structural signature of metallic glasses is likely to be contingent on the bonding nature of the glass, which could be affected by minor alloying^{50,51}.

8. Conclusions

By means of molecular dynamics simulations, low cycle fatigue behaviors of model metallic glass nanowires were investigated. During fatigue loading, the nanowires cyclic hardens under low strain amplitudes, while softens under high strain amplitudes. It was found that the structural origin of the observed hardening/softening is the decrease/increase of tetrahedral clusters, as a result of the non-hardsphere nature of the glass model. Shear banding appears to be the main failure mode for model metallic glass nanowires under low cycle fatigue tests. The fatigue life of metallic glass nanowires in plastic-strain-controlled cyclic loading obeys the Coffin-Manson

relation. The accumulation of the local atomic damage was found to be controlled by the macroscopic plastic strain via a power law, from which the Coffin-Manson relation can be derived. Upon the introduction of a notch, the nanowire fails via crack extension instead of shear banding, yet the fatigue life still obeys the Coffin-Manson relation. Our study provides a quantitative relation to assess the fatigue reliability of nanoscale metallic glass samples under cyclic loading.

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Reference

- (1) Kumar, G.; Desai, A.; Schroers, J. *Advanced Materials* **2011**, *23*, 461–476.
- (2) Chen, M. *NPG Asia Materials* **2011**, *3*, 82–90.
- (3) Kumar, G.; Tang, H. X.; Schroers, J. *Nature* **2009**, *457*, 868–872.
- (4) Jang, D.; Greer, J. R. *Nature Materials* **2010**, *9*, 215–219.
- (5) Tian, L.; Cheng, Y.-Q.; Shan, Z.-W.; Li, J.; Wang, C.-C.; Han, X.-D.; Sun, J.; Ma, E. *Nature Communications* **2012**, *3*, 609.
- (6) Jiang, Q. K.; Liu, P.; Ma, Y.; Cao, Q. P.; Wang, X. D.; Zhang, D. X.; Han, X. D.; Zhang, Z.; Jiang, J. Z. *Scientific Reports* **2012**, *2*, 852.
- (7) Tian, L.; Shan, Z.-W.; Ma, E. *Acta Materialia* **2013**, *61*, 4823–4830.
- (8) Guo, H.; Yan, P. F.; Wang, Y. B.; Tan, J.; Zhang, Z. F.; Sui, M. L.; Ma, E. *Nature Materials* **2007**, *6*, 735–739.
- (9) Ashby, M.; Greer, A. *Scripta Materialia* **2006**, *54*, 321–326.
- (10) Sharma, P.; Kaushik, N.; Kimura, H.; Saotome, Y.; Inoue, A. *Nanotechnology* **2007**, *18*, 035302.
- (11) Schroers, J.; Kumar, G.; Hodges, T. M.; Chan, S.; Kyriakides, T. R. *JOM* **2009**, *61*, 21–29.
- (12) Hofmann, D. C.; Suh, J.-Y.; Wiest, A.; Duan, G.; Lind, M.-L.; Demetriou, M. D.; Johnson, W. L. *Nature* **2008**, *451*, 1085–1089.
- (13) Kim, J.-Y.; Jang, D.; Greer, J. R. *Advanced Functional Materials* **2011**, *21*, 4550–4554.
- (14) Brothers, A. H.; Dunand, D. C. *Advanced Materials* **2005**, *17*, 484–486.
- (15) Dieter, G. E. *Mechanical metallurgy*; McGraw-Hill: New York, 1986.
- (16) Jang, D.; Maaß, R.; Wang, G.; Liaw, P. K.; Greer, J. R. *Scripta Materialia* **2013**, *68*, 773–776.
- (17) Launey, M. E.; Hofmann, D. C.; Johnson, W. L.; Ritchie, R. O. *Proceedings of the National Academy of Sciences* **2009**, *106*, 4986–4991.
- (18) Packard, C. E.; Witmer, L. M.; Schuh, C. A. *Applied Physics Letters* **2008**, *92*, 171911.
- (19) Cameron, K.; Dauskardt, R. *Scripta Materialia* **2006**, *54*, 349–353.
- (20) Shi, Y.; Louca, D.; Wang, G.; Liaw, P. K. *Journal of Applied Physics* **2011**, *110*, 023523.
- (21) Deng, C.; Schuh, C. A. *Applied Physics Letters* **2012**, *100*, 251909.
- (22) Wang, C.-C.; Mao, Y.-W.; Shan, Z.-W.; Dao, M.; Li, J.; Sun, J.; Ma, E.; Suresh, S. *Proceedings of the National Academy of Sciences* **2013**, *110*, 19725–19730.
- (23) Shi, Y.; Luo, J.; Yuan, F.; Huang, L. *Journal of Applied Physics* **2014**, *115*, 043528.
- (24) Wahnström, G. *Physical Review A* **1991**, *44*, 3752–3764.
- (25) Shi, Y. *Applied Physics Letters* **2010**, *96*, 121909.
- (26) Plimpton, S. *Journal of Computational Physics* **1995**, *117*, 1–19.
- (27) Shi, Y. F.; Falk, M. L. *Applied Physics Letters* **2005**, *86*, 011914.
- (28) Dzugutov, M. *Physical Review A* **1992**, *46*, R2984–R2987.
- (29) Dzugutov, M.; Simdyankin, S. I.; Zetterling, F. H. M. *Physical Review Letters*

- 2002**, 89, 195701.
- (30) Dzugutov, M. *Physical Review Letters* **1993**, 70, 2924–2927.
 - (31) Dzugutov, M. *Physical Review A* **1992**, 46, R2984–R2987.
 - (32) Shi, Y. F.; Falk, M. L. *Physical Review B* **2006**, 73, 214201.
 - (33) Nose, S. *J Chem Phys J Chem Phys* **1984**, 81, 511–519.
 - (34) Hoover, W. G. *Physical Review A* **1985**, 31, 1695–1697.
 - (35) Falk, M. L. *Physical Review B* **1999**, 60, 7062–7070.
 - (36) Menzel, B. C.; Dauskardt, R. H. *Acta Materialia* **2008**, 56, 2955–2965.
 - (37) Chuang, C.-P.; Yuan, T.; Dmowski, W.; Wang, G.-Y.; Freels, M.; Liaw, P. K.; Li, R.; Zhang, T. *Scientific Reports* **2013**, 3, 2578.
 - (38) Polák, J.; Obrtlík, K.; Hájek, M.; Vasek, A. *Materials Science and Engineering: A* **1992**, 151, 19–27.
 - (39) Polak, J.; Vasek, A. *International Journal of Fatigue* **1994**, 16, 403–408.
 - (40) Cheng, A. S.; Laird, C. *Materials Science and Engineering* **1981**, 51, 55–60.
 - (41) Winter, A. T. *Philosophical Magazine* **1973**, 28, 57–64.
 - (42) Hess, P.; Menzel, B.; Dauskardt, R. *Scripta Materialia* **2006**, 54, 355–361.
 - (43) Manson, S.S., Hirschberg, M.H. *In Fatigue – An Interdisciplinary Approach, Proceedings of the 10th Sagamore Army Research Conference, Raquette Lake, NY 1963*.
 - (44) Vinogradov, A.; Kaneko, Y.; Kitagawa, K.; Hashimoto, S.; Stolyarov, V.; Valiev, R. *Scripta Materialia* **1997**, 36, 1345–1351.
 - (45) Tomida, T.; Egami, T. *Physical Review B* **1993**, 48, 3048–3057.
 - (46) Zhang, Y.; Mattern, N.; Eckert, J. *Intermetallics* **2012**, 30, 154–157.
 - (47) Shi, Y.; Falk, M. *Physical Review Letters* **2005**, 95, 095502.
 - (48) Shi, Y.; Falk, M. *Scripta Materialia* **2006**, 54, 381–386.
 - (49) Kob, W. *Physical Review E* **1995**, 51, 4626–4641.
 - (50) Wang, W. *Progress in Materials Science* **2007**, 52, 540–596.
 - (51) Yuan, C.; Xiang, J.; Xi, X.; Wang, W. *Physical Review Letters* **2011**, 107.