Atomistic simulation of a NiZr model metallic glass under hydrostatic pressure

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Compressive behavior of a model NiZr metallic glass under hydrostatic pressure is simulated using molecular dynamics. The equation of state obtained exhibits two distinct regimes, one at low and the other at high pressure, along with an intermediate region in between. The densification is associated with topological rearrangement of atoms at low pressure and hard-sphere-like compaction dictated by the strong interatomic repulsion at high pressure. Different from many isotropic materials, the atomic rearrangement in the metallic glass during compression is accompanied by strong local topological structure change and chemical short-range (re)ordering. The possibility of a pressure-induced phase transition is briefly discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3077862]

The equation of state (EOS) relating the volume or density to pressure, temperature, and other state variables is one of the most fundamental thermodynamic properties from which the stability of a phase can be measured. The EOS is related closely to both atomic structures and specific interatomic interactions. One example is the abundance of the polymorphic phase transitions (PPTs) present in crystalline materials. For amorphous metals (AMs), due to the absence of the long-range symmetry, a much simpler case is expected for the EOS. Recent high pressure experiments on liquids and amorphous materials, however, gave a quite different picture. Some of the pressure-volume relations measured up to high pressure (~40 GPa) did not obey some of the well-established EOS models, namely, the Birch–Murnaghan EOS. The recent plate impact experiment with pressure up to 123 GPa shows a density change in a Zr-based bulk metallic glass (BMG) at around 26 GPa, indicating a possible (first order) “phase transition.” An obvious kink reported in the bulk modulus at around 14 GPa suggests a second order PPT (Ref. 5) in a La-based BMG. As compared with crystalline materials, the underlying atomistic mechanisms of compression, in particular, a possible PPT in amorphous solids is far subtle because there exists an infinite number of metastable states, many of which may be separated from each other only minutely. As a result, many (local atomic) amorphous structures could exist or coexist at different pressures and the transitions among these states are certainly not unique, making it hard to specify a well-defined thermodynamic transition. On the atomic level, due to the limitation in pressure range and structure detection, the lack of detailed knowledge of atomic movement during compression seriously confines our understanding of the EOS in AMs.

In this letter, we report an atomistic simulation of high-pressure compression of a model Ni$_40$Zr$_60$ AM. The emphasis here is on detailed atomic structure change and the EOS for the AM with a specific interatomic interaction without invoking explicitly the electronic structure changes as suggested in the recent work. To this end, we employed classical molecular dynamics (MD) simulation. A semiempirical many-body potential including electronic or volume contributions was used for the system. We would like to make a special note that the repulsive potentials for the interatomic interactions are obtained by the nearly free-electron-tight-binding approach and was fitted by thermodynamic and structural properties of NiZr metallic glasses at ambient pressure. Nose–Hoover const-temperature ensemble and Parrinello–Rahman (PR) constant-pressure MD (Ref. 15) was implemented with periodical boundary conditions. A fifth order predictor-corrector method was used to solve the equation of motion with a time step of 2.5 fs. The samples used for high-pressure compression test were obtained by cooling the equilibrated glass-forming liquid to 300 K. The details of the sample preparation can be found in Ref. 17. No significant size effect was found in samples made of 4000, 32 000, and 4 000 000 atoms (although smaller samples with a few thousand atoms or less may exhibit statistical irregularities). The results presented here are thus for the samples with 4000 atoms only. The hydrostatic pressure is applied directly to the sample through the PR MD. The system is equilibrated for 250 ps after each pressure increment of 1.0 GPa. Different pressure rates (from 1 MPa to 10 GPa for 250 ps) were tested and found no obvious difference in the results. The average structural properties and the EOS were measured by taking a thermal average of over 50 ps in the equilibrated state in the last segment of each pressure interval (total of 250 ps). The same procedures were also used in decompression by changing simply the sign of the pressure rate.

Figure 1 shows the volume changes during compression and decompression. We performed additional compression and decompression cycles with the same pressure rate of 1 GPa, each starting with the completely unloaded sample at zero pressure from the previous loading cycle. The volume decreases monotonically as pressure is applied up to 200 GPa. The decompression is activated at 200 GPa. Except in the first cycle after which the system sustained a permanent residual volume change, in the subsequent cycles the remnant volumes at different unloaded states remain almost the same. Furthermore, the decompression curve retraces the

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the Ni–Zr PRDF pressure goes up, the hump decreases and becomes less dis-
of the unlike elements do not change much as pressure goes
level of amorphous solids. The compression and decompres-
phases are stable and macroscopically reversible.

Since the short-range order is represented by the first peak,
indicating possibly large reordering of the Zr atoms. Above 10
GPa, the ratio between the positions of the second and the
first peak is about 1.40–1.50, which is close to that in the fcc
structure (~1.414). To examine further the detailed local
atomic structure change, we checked the three most prev-
Honeycutt and Andersen (HA) parameters with indices of
4–4–1, 5–5–1, and 6–6–1, totaling about 60% of all the
bonds, and found that the 5–5–1 pair begins to decrease at
about 15 GPa while the 4–4–1 and 6–6–1 begin to increase at
about 13 GPa (Fig. 3). The 5–5–1 pair is a characteristic for
icosahedral packing and the 4–4–1 and 6–6–1 are for the
cubic/crystal-like structure. These results show that at high
pressure the atomic structure tends to be more densely
packed; but due to slow kinetics at increasing hydrostatic
pressure or possibly short time window in atomistic simula-
tion, actual crystallization does not occur in our system.

The EOS obtained shows no abrupt change in volume or
density, signaling no apparent first order transition. The bulk
modulus B obtained also demonstrates that a higher order
transition is unlikely. We calculated the isothermal B from
\[ B = -\frac{\partial (\beta V / \beta V)}{\partial (\beta V)} \] by numerically fitting the EOS (Fig. 1) with a
seventh order polynomial and by using thermal fluctuation,
\[ B = NkT / \langle \delta V^2 \rangle, \] in the Gibbs ensemble, where \( \langle \delta V^2 \rangle \) is the
volume fluctuation and \( T \) is the temperature. The numerical
fitting gives a more accurate result than that from the fluct-
uation method, which is limited by the sample size and
simulation time. Figure 4 shows that at below 8 GPa, B
increases with pressure. From 8 to 23 GPa, it decreases
slightly. Above 23 GPa, it increases nearly linearly again.
The initial increase is dominated by free volume reduction. In the subsequent compression-decompression cycles, this region becomes flatter. For denser systems, we should expect that the hump in $B$ decreases further and eventually should approach a linear function between 0 and 15 GPa.

In conclusion, we found that the densification process from a low-density state to a high-density state is a gradual one without apparent discontinuities in either the volumes or the bulk modulus. The EOS behaves though differently in the two regimes, which may lead to different responses in dynamic behaviors and difficulties as well in employing the Birch–Murnaghan EOS. The atomic rearrangement consists of both local topological structure change and chemical (re)ordering. Moreover, since our atomistic model uses an (semi)empirical potential, the remarkably good qualitative agreement with the experimental result raises the question of how large the contribution is from electronic structure change to the EOS in metallic glasses in general, as suggested from rare-earth metal-based systems.

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