Shape Memory and Pseudoelasticity in Metal Nanowires

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(Received 22 July 2005; published 15 December 2005)

Various researchers have demonstrated that fcc nanowires can undergo unique structural reorientations and transformations based on size, thermal energy, and the type of defects formed during inelastic deformation. By utilizing atomistic simulations, we show that certain fcc nanowires can exhibit both shape memory and pseudoelastic behavior. We also show that the formation of defect-free twins, a process related to the material stacking fault energy, nanometer size scale, and surface stresses is the mechanism that controls the ability of fcc nanowires of different materials to show a reversible transition between two crystal orientations during loading and thus shape memory and pseudoelasticity.

DOI: 10.1103/PhysRevLett.95.255504

PACS numbers: 61.46.+w, 62.25.+g, 64.70.Nd, 68.65.–k

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temperature below the melting temperature of the nanowire. Specifically, the pseudoelasticity and shape memory effects disappear at a rate directly proportional to the inverse of wire diameter since the surface stress-induced driving force for the transition between the two wire states also diminishes at a rate directly proportional to the inverse of wire diameter [6].

We investigate the fundamental mechanisms controlling shape memory and pseudoelasticity in fcc metal nanowires via molecular dynamics (MD) simulations using embedded atom (EAM) [9] potentials for gold [10], nickel [11], and copper [12]; relevant potential parameters are summarized in Table I. The potentials were chosen for their accurate representations of the materials respective SFEs. The wires were created using atomic positions from a bulk fcc crystal with an initial \(\langle 100\rangle\) orientation, square cross section, and \(\langle 100\rangle\) surfaces. The wire length was 50 cubic lattice units long in the \(z\) direction, with cross sectional lengths less than or equal to 6 cubic lattice units in the \(x\) and \(y\) directions; no periodic boundary conditions were utilized at any stage in the simulations, which were performed using the Sandia-developed code WARPMED [13,14].

We note that the numerically determined values for \(T_c\) in Table I represent lower bound estimates for each material; this is because EAM potentials typically underestimate surface stresses [15] while also lacking fidelity in thermal transport properties.

We first demonstrate that \(\langle 100\rangle\) wires can reorient to the energetically favorable \(\langle 110\rangle/\langle 111\rangle\) orientation at \(T_c\). By constraining the wire ends to move only in the \(z\) direction and applying a velocity scaling thermostat at \(T_c\), the \(\langle 100\rangle\) nanowires contract in the \(z\) direction, eventually reorienting to \(\langle 110\rangle/\langle 111\rangle\) nanowires; an example of the reorientation process via twinning is shown in Figs. 2(a)–2(d) for a 1.76 nm \(\times\) 1.76 nm nickel nanowire at 640 K. The boundary conditions were chosen to mimic the situation of a nanowire bonded to connected leads that permit extension or contraction of the wire while constraining the wire ends to move in axial directions only. The thermo-electromechanical nature of this connection will play an important role in influencing the shape memory behavior of the nanowires, and should be investigated in future experimental and theoretical studies.

The reorientation begins with the formation of a single twin in the wire interior which gradually increases in size to allow the complete \(\langle 100\rangle\) to \(\langle 110\rangle/\langle 111\rangle\) reorientation to occur. Gold and copper also reoriented from \(\langle 100\rangle\) to \(\langle 110\rangle/\langle 111\rangle\) via the formation of twins at temperatures close to their respective \(T_c\). The difference in \(T_c\) for copper and gold, which have similar SFES, is due to the fact that the \(\langle 100\rangle\) surface stress for gold is nearly double that of copper [15], indicating that less thermal energy is needed to assist the surface stresses in forming the lower energy \(\langle 111\rangle\) surfaces. Below \(T_c\), the wires partially reorient via spatially distributed twinning from \(\langle 100\rangle\) to \(\langle 110\rangle/\langle 111\rangle\), where twin boundaries in the nanowire separate \(\langle 100\rangle\) and \(\langle 110\rangle/\langle 111\rangle\) single crystals.

After reorientation was complete, the \(\langle 110\rangle/\langle 111\rangle\) nanowires were loaded in tension in the \(z\) direction to test for pseudoelastic behavior. Pseudoelasticity is demonstrated if the \(\langle 110\rangle/\langle 111\rangle\) wires can reorient back to the initial, defect-free \(\langle 100\rangle\) orientation under external stress at a temperature greater than \(T_c\) as it was already demonstrated that wires will return to the \(\langle 110\rangle/\langle 111\rangle\) orientation once the external loading is removed at this temperature. Figures 3(g)–3(i) show that the 2.45 nm \(\times\) 2.45 nm gold nanowire eventually fails via the formation and subsequent fracture of thin atom thick chains [10] before complete reorientation back to \(\langle 100\rangle\) can occur. Interestingly, only a minimal amount of detwinnning is observed during the reorientation back to \(\langle 100\rangle\) is seen in Fig. 3(i), even though the initial reorientation from \(\langle 100\rangle\) to \(\langle 110\rangle/\langle 111\rangle\) was twinning dominated.

In contrast, nickel and copper both show different behavior during tensile loading of the reoriented \(\langle 110\rangle/\langle 111\rangle\) nanowire; the stress-induced reorientation from

<table>
<thead>
<tr>
<th>Metal</th>
<th>(\gamma_{sf})</th>
<th>(\gamma_{usf})</th>
<th>(\gamma_{100})</th>
<th>(\gamma_{111})</th>
<th>(T_c/T_m)</th>
<th>(T_m)</th>
<th>(\gamma_{111}/\gamma_{100})</th>
<th>(\gamma_{usf}/\gamma_{sf})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>32</td>
<td>92</td>
<td>1090</td>
<td>1180</td>
<td>0.0374</td>
<td>1337</td>
<td>0.924</td>
<td>2.88</td>
</tr>
<tr>
<td>Copper</td>
<td>39</td>
<td>133</td>
<td>1351</td>
<td>1452</td>
<td>0.3134</td>
<td>1356</td>
<td>0.930</td>
<td>3.43</td>
</tr>
<tr>
<td>Nickel</td>
<td>125</td>
<td>264</td>
<td>1928</td>
<td>2060</td>
<td>0.4345</td>
<td>1726</td>
<td>0.936</td>
<td>2.11</td>
</tr>
</tbody>
</table>

TABLE I. Intrinsic \((\gamma_{sf})\) and unstable \((\gamma_{usf})\) stacking fault energies and ratios \((\gamma_{usf}/\gamma_{sf})\), \(\{100\}\) \((\gamma_{100})\) and \(\{111\}\) \((\gamma_{111})\) surface energies and ratios \((\gamma_{111}/\gamma_{100})\) for EAM potentials of nickel, copper, and gold. \(T_c/T_m\) calculated for 6 \(\times\) 6 \(\times\) 50 cubic lattice unit nanowires. Energetic units are in eV.}

![Figure 2](https://example.com/figure2.png)

**FIG. 2** (color online). Steps (a)–(d) show snapshots of the \(\langle 100\rangle\) to \(\langle 110\rangle/\langle 111\rangle\) thermal reorientation process at 640 K for 1.76 nm \(\times\) 1.76 nm nickel nanowire. The potential energy values are in eV.
\{110\}/\{111\} back to the original \(\{100\}\) configuration is illustrated for a 1.76 nm \(\times\) 1.76 nm nickel nanowire at 640 K at a strain rate of \(\dot{\varepsilon} = 10^9\) s\(^{-1}\) in Figs. 3(a)–3(c). As seen in Fig. 3(b), nickel is able to obtain its original \(\{100\}\) configuration by the creation and subsequent annihilation of twins as reported for copper by Liang and Zhou [5]. Upon continued tensile loading, the twin boundaries are pushed together, and finally annihilate each other to allow complete reorientation back to the original \(\{100\}\) configuration. After the original \(\{100\}\) orientation is reached, the load is removed. Because the nickel wire is above the critical reorientation temperature \(T_c\), it reorients back to the \(\{110\}/\{111\}\) configuration in Figs. 3(c)–3(e) following the unloading stress-strain path seen in Fig. 3(f). The pseudoelastic loop seen in Fig. 3(f) is the same observed when bulk shape memory alloys are deformed above their austenite finish temperature and experience a forward and reverse thermoelastic martensitic transformation. The reverse loading from \(\{110\}/\{111\}\) to \(\{100\}\) was tested over three decades of strain rates from \(10^8\) s\(^{-1}\) to \(10^{10}\) s\(^{-1}\); the strain rates did not appear to deleteriously affect the shape memory or pseudoelastic behavior.

In order to test for shape memory effects, the reoriented \(\{110\}/\{111\}\) wires were thermally equilibrated at 10 K \((T < T_c\), Fig. 1) for 60 ps before tensile loading. The wires were loaded in tension at a strain rate of \(10^9\) s\(^{-1}\) as shown in Figs. 4(a)–4(c) for copper, and reached the initial \(\{100\}\) orientation at which point loading was removed. The resulting stress-induced 1.81 nm \(\times\) 1.81 nm \(\{100\}\) wire in Fig. 4(c) is stable at very low temperatures with respect to \(T_c\). Finally, the temperature of the stable \(\{100\}\) wire was increased by 50 K every 100 ps until complete reorientation back to \(\{110\}/\{111\}\) occurred as shown in Figs. 4(d)–4(f); the reorientation occurs via the initiation and propagation of twins as in Fig. 2. The wire shows shape memory since it is capable of being deformed to nearly 40% strain through a reorientation to \(\{100\}\) while subsequent heating causes reverse reorientation back to \(\{110\}/\{111\}\).

To answer why nickel and copper exhibit shape memory and pseudoelasticity while gold does not despite the fact that all three materials reoriented from \(\{100\}\) to \(\{110\}/\{111\}\) via twinning, we analyzed the initial defect structure formed in each material during the original \(\{100\}\) to \(\{110\}/\{111\}\) reorientation. We find that the initial defect structure formed during the \(\{100\}\) to \(\{110\}/\{111\}\) reorienta-
it was found that copper and nickel still regained the twin interior, did not regain the initial to the more complex defect and stacking fault structure in reloading of the partially reoriented has a lower SFE than copper and nickel, was shown to form h can show shape memory and pseudoelastic behavior to continue. It is critical to note that the present results imply that standard metals at the nanoscale may exhibit both reversible shape memory behavior previously observed only in exotic alloys such as NiTi [19] as well as pseudoelasticity and pseudoelastic strains previously observed only in polycrystalline shape memory alloys [19] and copper nanowires [5]; these effects are not observed by the metals in bulk form. In addition, the theoretical maximum recoverable strain in NiTi is approximately 10%, while these nanowires have predicted recoverable strains on the order of 40%. Since researchers have more experience growing monolithic metallic nanowires, the potential of such wires to experience shape memory and pseudoelasticity is critical to guiding basic research efforts in nanoscience and nanotechnology.

We would like to thank E. Dave Reedy and Neville R. Moody for their support of this research. We would also like to thank Stephen M. Foiles for his help with characterizing the EAM potential and Gregory J. Wagner for his assistance with using the WARP code. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

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