Role of grain size on the martensitic transformation and ultra-fast superelasticity in shape memory alloys

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Abstract

We use multi-million-atom molecular dynamics (MD) simulations with an embedded atom model potential parameterized for NiAl to study temperature- and stress-induced martensitic phase transformations in nanocrystalline shape memory alloys. Nucleation of the martensite phase occurs in the grain interiors and grows outwards up to the point where further transformation is hindered by the constraints imposed by neighboring grains. Decreasing grain size inhibits the transformation process and the temperature-induced transformation is completely suppressed for samples with average grain sizes of 7.5 nm and less. Interestingly, mechanical loads can induce the martensitic transformation in samples with ultra-fine grains and, quite surprisingly, the sample with 7.5 nm grain size exhibits improved, ultra-fast, superelasticity as compared with its coarser grain counterparts. The simulations provide a picture of the processes that govern the performance and fundamental limits of nanocrystalline shape memory alloys with atomistic resolution.

Keywords: Molecular dynamics; Shape memory alloy; NiAl; Martensite; Phase transformation

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1. Introduction

Shape memory alloys (SMAs) are an important class of active materials utilized in a range of applications, including medical implants, micro-actuators, mechanical damping, and noise reduction [1–4]. Shape memory and superelasticity, the unique properties of these materials, are a result of a diffusionless, solid-solid phase transformation between a high temperature, high symmetry austenite phase and a low temperature, lower symmetry martensite phase [5]. For example, in $\text{Ni}_x\text{Al}_{1-x}$ alloys, that exhibit shape memory for x between 61 and 65 at.% [6], the martensite transformation is between a B2-based austenite, with cubic symmetry, and a monoclinic martensite phase denoted M14 [7,8]. In these alloys, shape memory is observed if the sample is quenched to room temperature to avoid the formation of the Ni_5Al_3 phase which is stable below 700°C [6]. During transformation, the martensite phase develops a complex multi-domain microstructure that is key to the shape memory effect. Plastic deformation in the martensite phase of SMAs occurs via the motion of domain walls leaving atomic neighbors unchanged, rather than by dislocation glide where bonds are broken and formed. Therefore, upon heating the sample back to the austenite phase, the material recovers its original shape and atomic configuration [9]. Superelasticity occurs when the austenite phase is deformed and a martensitic phase transformation is induced by stress before significant irreversible plastic deformation occurs; upon unloading the material transforms back to austenite recovering a significant amount of the *plastic* strain. Despite the importance of these materials, our understanding of the temperature- and stress-induced martensitic transformation and the development of the martensitic microstructure is incomplete. This is particularly true in nanocrystalline or nanostructured alloys of interest in applications that require high strength. In

this paper we present the first molecular dynamics (MD) simulations of stress- and temperature-induced martensitic transformation in nanocrystalline samples with realistic grains. We focus on the role of average grain size on the martensite transformation temperature and superelasticity.

When polycrystalline samples undergo martensitic transformations, the significant multi-axial strain at the unit cell level leads to a complex internal stress distribution which, in turn, affect the transformation temperature or stress as well as the martensitic microstructure. Experimental efforts are providing important insight into the effect of grain and specimen size on the transformation of nanocrystalline SMAs. When stress or temperature drives the martensitic transformation, favorably disposed grains (either due to their orientation, internal stress, or geometry) will begin to transform before others. The different crystallographic orientation between neighboring grains mechanically constrain their deformation and transformation, increasing the stress or undercooling that is required for the transformation to progress [10]. Latent heat also results in the suppression of the transformation [10,11]. These effects are more dominant in fine-grain alloys and experimental studies have shown that reducing the grain size of polycrystalline SMAs to the nanoscale hinders martensitic transformation, both reducing the martensite start temperature (M_s) and the amount transformed [12]. In fact, the transformation is believed to be completely suppressed for grain sizes in the tens of nanometers [13]. For example, a study on NiTiCu SMA nanocrystals within a $\text{Ni}_{50}\text{Ti}_{25}\text{Cu}_{25}$ matrix showed complete transformation for grains with size over 25 nm, while smaller nanocrystals showed partial transformation [14]. A separate study in NiTi, revealed that grains under 50 nm in diameter did not transform [15]. In contrast, increasing grain constraints

have been shown to increase the complexity of martensite variants [16], and could lead to unique martensitic structures such as dot-like domains [17]. While recent dynamic TEM [18] and pulsed x-ray experiments [19] are providing information about the transformation with unprecedented resolution current experimental techniques lack the ability to characterize the nucleation and propagation of transformations in ultra-fine SMAs and significant questions remain unanswered.

MD simulations are also contributing to our understanding of SMAs and their size effects. The study of solid-solid phase transformations using MD was pioneered by Rahman and Parrinello. These authors warned that such simulations, involving small systems and periodic boundary conditions, would be flawed due to size effects [20] and the early MD simulations of martensite transformations [21,22] were limited due to the small system size. More recent MD work [23,24] characterized effect of size and shape of Zr and Fe nanowires on the martensitic transformation. Ackland and collaborators showed that MD simulations can produce realistic martensite microstructures of NiAl SMAs in 2-D and describe its formation [25,26]. MD simulations are also greatly enhancing our knowledge of martensite nanostructures [27–33], the transformation to martensite [27–37], grain size [31], surface effects [37,38], and mechanical properties of SMAs [34].

However, despite such progress on the experimental and theoretical sides, several aspects of the martensite transformation remain poorly understood. Among these are the effects of grain size and mechanical constraints on the nucleation and propagation of the martensitic transformation and the resulting microstructure. We report on an MD study of the effect of

grain size on the martensitic transformation of nanocrystalline samples. The simulations shed light into the atomistic processes that govern the phase transition and show that while the martensitic transformation is gradually suppressed with reducing grain size, nanocrystalline samples with average grain diameter as small as 7.5 nm can exhibit enhanced superelasticity.

The remainder of the paper is organized as follows: Section 2 describes the details of our simulations. Section 3 discusses the temperature induced phase transformation. Section 4 illustrates the stress induced phase transformation and superelasticity. Finally, conclusions are drawn in Section 5.

2. Model and simulation details

2.1 Model shape memory alloy after NiAl

Our MD simulations use an embedded atom model (EAM) interatomic potential developed by Farkas et al. [39] to describe NiAl alloys. The potential was parameterized for the B2 phase of NiAl and the Ni_5Al_3 phases, and is able to match properties such as lattice parameters, elastic constants, and stacking fault energies[39]. For compositions between 61 and 66 at. % Ni the potential describes a martensitic transformation between the B2 austenite to a monoclinic martensite. As discussed previously, [40] the martensitic structure predicted by the potential differs from the M14 observed experimentally; see supplementary material of Ref. [40] for a detailed comparison between the structures. Thus, as in prior publications [40,41], our simulation should be taken to correspond to a model shape memory material only approximately equivalent to NiAl.

2.2 Nanocrystalline samples

The nanocrystalline structures were generated using the Voronoi method [42]. Average grain size serves as an input to the code, which then generates randomly oriented grains with a distribution of grain sizes around that average. First, the grains are populated with B2 equiatomic NiAl. Then, Al atoms are randomly selected and replaced by Ni until the composition of 63 at.% Ni is reached. It is important to note that we ignore possible correlations between substitutional atoms, and grand canonical Monte Carlo simulations could be used to generate structures using their statistical weight[43]. However, given that fact that NiAl SMAs need to be quenched and are away from equilibrium even such methods should be used with care. The grain sizes studied ranged from 2.5 nm (with simulation cell lengths of 20 nm and a total of 606,419 atoms) to 20 nm (with simulation cell lengths of 80 nm and a total of 43,103,735 atoms). Snapshots of selected equilibrated structures are shown in Figure 1. All simulations use periodic boundary conditions in three dimensions.

2.3 Thermal- and stress-induced phase transformations and analysis

Prior to annealing or deformation the nanocrystalline samples described above are equilibrated at 300K for 200 ps using a Nose-Hoover thermostat with coupling constant of 0.1 ps and Parrinello-Rahman barostat with coupling constant of 1 ps.

Temperature-induced martensitic transformations were studied using isobaric, isothermal MD simulations (NPT ensemble); the equilibrated samples at $T=300$ K are cooled down to 1K at a rate of -0.5K/ps . The temperature is changed continuously (at every MD step). The barostat used to maintain stress at 1 atm allows all cell parameters to vary independently. The low-

temperature structures and then heated to a temperature above the martensitic transformation at a rate of 0.5 K/ps using the same procedure as in the cooling.

The mechanically induced martensite transformations were performed by controlling the cell dimensions along the tensile axis with a strain rate of $2 \times 10^8 \text{ s}^{-1}$. The lateral dimensions of the simulation cell are allowed to vary to maintain normal stress of 1 atm. The subsequent unloading and relaxation simulations switched from strain controlled to stress controlled to unload the stress over 500ps and relax an additional 500ps. The unloaded structures were subsequently annealed for 500ps at 300K, then heated to annealing temperatures ranging from 400K to 800K and held there for an additional 500ps. This high-temperature annealing is performed to accelerate the transformation back to austenite given the restriction on timescales achievable through MD simulations. The annealed structures were then quenched to room temperature over 50ps to calculate remnant strain and martensite percentage. The equations of motion were integrated using a 1 femtosecond timestep for all simulations.

The microstructures corresponding to the various stages of our studies were analyzed using the Ovito visualization package[44], with the different phases identified based on the local environments of the atoms. Local crystal structures were identified using the adaptive common neighbor analysis method (a-CNA)[45] that uses the common neighbor analysis technique[46], but with a radial cutoff that is calculated on the fly based on the first 12 nearest neighbors of each atom. The analysis is performed on instantaneous atomic configurations obtained from the MD trajectories. Atoms with local environments classified as bcc signified the B2 austenite phase and will be colored blue, atoms classified as hcp (red) denote the martensite phase, and atoms classified as fcc (green) represent stacking faults within the martensite. We calculate

martensite percentage by taking the sum of hcp and fcc atoms over the total number of atoms, but we exclude atoms in grain boundaries, which remain unclassified due to the disorder at grain boundaries. We note that grain boundary atoms constitute a significant portion of the samples at extremely small grain sizes (up to 0.67 fraction).

3. Temperature Induced Transformation

Figure 2 shows the martensite fraction as a function of temperature during cooling and heating for various grain sizes. Nanocrystals with average grain diameter of 15 and 20 nm undergo clear martensitic transformations. Due to the computational cost of simulating samples with the largest grain size we stopped the heating simulations once the transformation was clear. Reducing grain size reduces the transformation temperature and makes the transformation more gradual and less complete; similar trends have been reported in similar MD work in nanocrystalline Fe-Ni [47] and experiments [34,48]. Interestingly, below a critical grain size of 7.5 nm the transformation is completely hindered. This is consistent with previous experimental work on NiTiCu nanocrystals which reported complete suppression of martensite for sizes below 16 nm [14]. For these ultra-fine grain nanocrystals we find a coexistence of austenite and martensite phases since the cells are created. The martensite phase is often located around the grain boundaries and we attribute their formation to the large internal stresses at grain boundaries during the creation of the initial microstructures. As can be seen in Figure 1, we observe similar small, isolated clusters of martensite atoms near grain boundaries for all the grain sizes studied. The fraction of martensitic atoms in the ultra-fine grained samples is only weakly temperature dependent and no phase transformation is observed.

Figure 3 shows atomistic snapshots during cooling for samples with three different grain sizes and at various temperatures. In the samples with average grain size of 10 and 15 nm we observe the martensite phase initially nucleates in the inside of the grains and not at grain boundaries. This indicates that the mechanical constraints imposed by neighboring grains with different orientations are significant. After nucleation, the martensite phase propagates outward towards the grain boundaries, see Fig. 3 and animations provided in the Supplementary Material. Often, the constraints preclude the martensite from reaching the grain boundaries and we observe a layer of austenite. The D=15 nm sample exhibits multi-domain grains while most of the martensite regions in the D=10 nm case consist of a single domain. The D=7.5 nm case does not transform at all, consistent with Fig. 2. Stress analysis, shown in the Supplementary Material, shows that stress increases during cooling, with a large increase in stress for the D=20 nm case upon transformation to martensite. Large stresses were observed in grains corresponding to the regions of martensite. However, not all of the martensite is highly stressed. We note that heating and cooling rates could affect the transformations; such studies are beyond the scope of this first work on 3D nanocrystalline SMAs.

During heating, the systems with grain diameters 10 nm and larger transform back to austenite. We note that the austenite transformation temperature is higher than the martensite one, but the thermal hysteresis is significantly smaller than in the perfect crystal cases studied previously [40], where the hysteresis ranges between 150 and 1250 K.

4. Stress Induced Transformation and Superelasticity

The martensite transformation can also be achieved by mechanically loading the austenite and, as discussed above, this transformation is the basis for superelasticity. Figure 4 shows stress as a function of engineering strain for a range of grain sizes with samples uniaxially loaded in tension to 4% and 10% at a strain rate of $2 \times 10^8 \text{ s}^{-1}$ and $T=300\text{K}$ followed by unloading over a period of 500 ps and relaxation for an additional 500 ps. Figure 5 shows the corresponding martensite fraction for selected cases and Fig. 6 shows snapshots for $D=3.5, 7.5$ and 15 nm during loading, unloading and after annealing.

Following elastic loading, the samples with larger grain size exhibit a well-defined yield point followed by softening; as can be seen in Figs. 5 and 6 this yield corresponds to the nucleation of the martensite phase in a few, preferentially oriented grains, and their growth. Interestingly, as the martensite impinges on grain boundaries the samples exhibit significant hardening associated with the nucleation and propagation of martensite in less preferably oriented grains.

Reducing the grain size down to 5 nm results in an increase of the yield stress (Hall-Petch behavior) followed by a slight weakening for average grain diameters below 5 nm (inverse Hall Petch). The finer grain samples show a high yield stress and significantly less work hardening. The plots in Fig. 5 and snapshots in Fig. 6 show that stress induces an increase in the martensite fraction even in ultra-fine grains. However, the transformation becomes more gradual and less complete with decreasing grain size. We see that some grains fully transform while others

remain in the austenite phase. This supports the idea that favorable grains transform first, and that local stresses can severely hinder transformation in certain regions[10,49].

The snapshots in Fig. 6 show that after the martensite transformation is complete, additional strain is accommodated by dislocations; see high-density of stacking faults in the martensite.

4.1 Plastic strain recovery and superelasticity

There is great interest in the material's ability to recover its original shape following large deformation. Following unloading and relaxation the samples are annealed at various temperatures to favor the transformation back to austenite, after maintaining them at the annealing temperature for 500ps we quench them back to $T=300$ K. Figure 7 shows the remnant strain as a function of annealing temperature together with the martensite fraction for the various cases. Figure 8 shows remnant strain as a function of grain size for each of the annealing temperatures. We find that grain size has a strong effect on the pseudoelasticity of the samples. Increasing the annealing temperature results in lower remnant strain and this correlates to the reduction of the martensite fraction in almost all cases. Samples with grains larger than 5 nm exhibit significant superelasticity, with remnant strain of approximately 1% after a 10% deformation and about 0.25% after 4% strain. Smaller grains fail to recover their strain and this correlates with the significantly less preponderant role the martensite transformation plays as a deformation mechanism during loading.

Interestingly, the superelastic performance of the alloys is not monotonous with grain size especially for low annealing temperatures or no annealing. The sample with mean grain

diameter of 7.5 nm, which failed to undergo a martensitic transformation under cooling, shows the lowest remnant strain and smaller martensitic fraction for no or low annealing temperatures. For this grain size the martensite phase is not favored even at low temperatures but can be induced with strain; thus the sample rapidly transform back to austenite upon removal of the mechanical load. This agrees with work on nanostructured superelastic NiTi where grain size reduction gradually weakened the hysteresis associated with the transformation [50].

We note that the short simulation timescales in MD limits the transformation back to austenite after the mechanical load is removed for the larger-grain samples. These samples are likely to continue transforming and recovering their strain with time; it is possible that the non-monotonous behavior of the remnant strain with grain size would disappear if the simulation time could be extended to seconds. This seems to be confirmed by the annealing simulations that accelerate the austenite transition. The bottom panels in Figure 6 show the extent of austenite recovery following annealing at 800K for 500 ps, with near complete austenite recovery seen for the largest grain size. Nevertheless, the observation of strain recovery in nanosecond timescales for fine-grained nanocrystals is of interest in applications where ultra-fast shape recovery is required.

5. Conclusions

Large-scale MD simulations of the martensitic transformation and superelasticity in nanocrystalline SMAs shed light into the atomic mechanisms that govern these processes. The simulations agree with the experimental observation that reducing the grain size to the

nanoscale hinders the martensitic transformation, but interestingly, this can be used to obtain superior ultrafast superelasticity. We find that the transformation is completely hindered for grain sizes below 10 nm. An analysis of the MD trajectories shows that the martensite phase nucleates in the interior of grains and propagates toward the grain boundaries. This indicates that the mechanical constraints imposed by neighboring grains with different orientations hinder nucleation in grain boundaries; our simulations disprove the postulated increase in martensite nucleation sites with reduced grain size [18].

Loading austenitic samples mechanically show that the martensite transformation can be induced in nanocrystals with minimal irreversible plastic deformation even for large strains as long as the grain size is larger than a critical value of approximately 5 nm. Interestingly, samples with grain size near the suppression of thermal martensitic transformation (7.5 nm grain size in our case) exhibit the best performance in terms of ultra-fast psuedoelasticity since they were able to transform back to the austenite phase more promptly than coarse grain samples. This explains the use of ultrafine grain samples in superelasticity applications [50].

Acknowledgements

This work was supported by the United States Department of Energy Basic Energy Sciences (DoE-BES) program under Program No. DE-FG02-07ER46399 (Program Manager John Vetrano) and by the US Defense Threat Reduction Agency, Contract No. HDTRA1-10-1-0119 (Program Manager Suhithi Peiris). Computational resources of nanoHUB.org are gratefully acknowledged.

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(Color online) Figure 1: Representative initial nanocrystalline structures. Average grain diameters range from 2.5 to 20 nm, simulation cell lengths from 15 to 60 nm and number of atoms from 265K to 18M. B2 are colored blue, martensite is red, stacking faults in the martensite are green while unclassified atoms are colored white.

(Color online) Figure 2: Temperature-induced austenite and martensite transition. Martensite fraction as a function of temperature during (a) cooling and (b) heating; samples with average grain size of 10 nm and higher exhibit a martensitic transformation, which is hindered completely for $D \leq 7.5$ nm.

(Color online) Figure 3: Atomistic snapshots of martensite structures during cooling for a range of grain sizes of $\text{Ni}_{63}\text{Al}_{37}$ disordered SMAs. Transformation is hindered as grain size is reduced. B2 are colored blue, martensite is red, stacking faults in the martensite are green while unclassified atoms are colored white.

(Color online) Figure 4: Stress as a function of strain during uniaxial deformation to (a) 4% and (b) 10% strain for the various samples followed by unloading to zero stress and relaxation.

(Color online) Figure 5: Martensite fraction as a function of strain during uniaxial deformation for various grain sizes.

(Color online) Figure 6: Snapshots of nanocrystalline samples for various grain sizes during uniaxial deformation, after unloading, and after annealing at 800K for 500ps. B2 are colored blue, martensite is red, stacking faults in the martensite are green while unclassified atoms are colored white.

(Color online) Figure 7: Martensite fraction and remnant strain after uniaxial deformation to (left) 4% and (right) 10% as a function of annealing temperature. We observe that the samples with a grain size of 7.5 nm exhibit improved shape memory for low annealing temperatures as compared to structures with a larger grain size.

(Color online) Figure 8: Remnant strain as a function of grain size for various annealing temperatures up to 800K. The 7.5 nm grain size shows the best recovery for lower annealing temperatures, while larger grains are able to match it at higher annealing temperatures.

Figures

D=2.5nm, 606K atoms

D=3.5nm, 265K atoms

D=5 nm, 644K atoms

D=7.5 nm, 2.2 M atoms

D=10 nm, 5.3 M atoms

D=15 nm, 18 M atoms

Figure 1

Figure 2

D=7.5 nm

T=150 K

D=10 nm

T=300 K

D=15 nm

T=139 K

T=116 K

T=116 K

T=116 K

T=1 K

T=1 K

T=1 K

Figure 3

Figure 4

Figure 5

L=3.5 nm

$\varepsilon = 0.0$

L=7.5 nm

$\varepsilon = 0.0$

L=15 nm

$\varepsilon = 0.0$

$\varepsilon = 0.04$

$\varepsilon = 0.04$

$\varepsilon = 0.04$

Uniaxial strain

$\varepsilon = 0.1$

$\varepsilon = 0.1$

$\varepsilon = 0.1$

$\varepsilon = 0.052$

$\varepsilon = 0.051$

$\varepsilon = 0.056$

Relaxed

$\varepsilon = 0.032$

$\varepsilon = 0.014$

$\varepsilon = 0.012$

Annealed at
800K for 500ps

Figure 6

Figure 7

Figure 8