Role of atomic variability and mechanical constraints on the martensitic phase transformation of a model disordered shape memory alloy via molecular dynamics

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Role of atomic variability and mechanical constraints on the martensitic phase transformation of a model disordered shape memory alloy via molecular dynamics

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Abstract

We use molecular dynamics (MD) with an embedded atom model potential parameterized for NiAl to study martensitic phase transformations in a disordered shape memory alloy. We focus on the role of intrinsic atomic-level variability and mechanical constraints on the martensite and austenite transformation temperatures and on the martensite microstructure for specimens with varying size. We find that periodic system size has a weak effect on transformation temperature all the way to the nanometer scale, with the entropy-stabilized austenite phase slightly penalized with decreasing size. Atomic-level variability in these random alloys leads to significant sample-to-sample variability in transformation temperature. The uncertainty in the austenite transformation temperature increases with decreasing size, reaching ~10% of the mean value for samples 10 nm on the side. Interestingly, the variability of the high-temperature martensite transition shows little size dependence. We find that a critical size of ~40 nm is required to develop multidomain martensite microstructures, and mechanical constraints reduce this critical size to ~7 nm, while significantly affecting the transformation temperatures. These results contribute to the understanding of martensitic transformation in nanocrystalline samples and of the fundamental limits of miniaturization of these alloys.

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

1. Introduction

Shape memory alloys (SMAs) are used in a wide variety of applications, including medical implants, microactuators and for mechanical damping [1,2]. The unique properties of these materials, shape memory and superelasticity, originate from a solid-to-solid martensite transformation, and the microstructure development during the transformation plays an important role in their performance. Martensitic transformations are diffusionless, solid-to-solid transitions between a high-symmetry, high-temperature phase called austenite (and stabilized by entropy) and a low-temperature phase called martensite, which has lower symmetry than the austenite [3]. For example, in Ni$_x$Al$_{1-x}$ disordered alloys that exhibit shape memory for $x$ between 62 and 64% [4], the martensite transformation is between a B2-based austenite and monoclinic martensite [5,6]. In these alloys shape memory is observed if the samples are quenched to room temperature to avoid the occurrence of the Ni$_3$Al$_3$ phase, which is stable below 700 °C [4]. During the transformation from austenite, the martensite phase develops a multiple-domain (or multivariant) structure in order to accommodate the elastic strain and retain the original shape of the sample. Plastic deformation in the martensite phase occurs via domain wall motion rather
than dislocation glide; thus, every atom retains its nearest neighbors. As a result, upon heating and transforming back to austenite, the material will have the same atomic configuration, resulting in shape memory [7]. Our understanding of the development of the martensite microstructure is incomplete; this is particularly true regarding the role of size and mechanical constraints that dominate the properties in nanostructured or nanocrystalline samples. These challenges are compounded in disordered SMAs, such as NiAl, where the intrinsic atomic variability can affect the behavior of nanoscale specimens.

The martensitic transformation involves significant multiaxial strain that causes complex internal stress distributions in polycrystalline samples which are expected to affect transformation temperature or stress and the development of multidomain microstructures. Experimental work is beginning to shed light on the details of the transformation process in polycrystalline samples and size effects. Under stress, the transformation originates in grains that are favorably oriented; these occur randomly throughout the material and lead to a homogeneous transformation macroscopically, but significant heterogeneities at length scales comparable to those of the grains. Furthermore, grains that attempt to transform become physically constrained by neighboring ones, resulting in the need for increasingly larger stress or degree of undercooling to complete the transformation [2]. Another important aspect is the release of latent heat upon transformation, which increases the local temperature of the material and further restricts the transformation [2,8]. Recent experimental work on sheets of NiTi SMAs under uniaxial loading has characterized the propagation of the martensitic transformation through the sample at the microscale; the authors characterized the strain distribution of the transformed material as well as the effect of texture on the transformation [9,10]. Experimental work on NiTiCu nanocrystals ranging from 10 to 50 nm in diameter and dispersed in a Ni50Ti25Cu25 matrix revealed size-dependent transformation temperatures. All nanocrystals >25 nm showed complete martensitic transformation upon cooling to room temperature, while nanocrystals between 15 and 25 nm showed partial transformation [11], whereas other work [12] reported nanograins of NiTi not transforming to martensite below 50 nm. Interestingly, no significant size effects were observed in In-21 at.% Ti nanowires with diameters between 10 and 650 nm [13]. Experimental work has also shed light on how the shape memory effect works in NiTi [14], and how deformation of the martensite stabilizes the structure, and changes the austenite transformation temperature [15].

Molecular dynamics (MD) simulations are also contributing to our understanding of these phenomena. Rahman and Parrinello [16] pioneered work on solid-solid phase transformations using MD and even warned of the limitations of using small system sizes with periodic boundary conditions. The limited size of MD simulation cells had a strong effect on early MD work on martensitic transformations [17,18]. More recent work [19] showed only two martensite variants during the body-centered cubic (bcc)–hexagonal close-packed (hcp) transition in Zr for systems with 40,000 atoms, indicating strong size effects at these sizes. Boundary conditions and shape also affect size effects in martensitic transformations. MD was used to characterize size effects on the martensitic microstructure of Zr and Fe nanowires [20,21], revealing that the size and shape of nanoscale specimens have a strong effect on microstructure and transition temperature, and that metastable phases are often present, minimizing the overall strain and domain wall energy. Ackland and collaborators [22,23] used MD simulations to produce realistic NiAl martensitic microstructures in 2-D systems consisting of parallel microtwins with opposite shear and characterized their formation. Such simulations are contributing to a deeper understanding of martensitic transformations [19,24–33], martensite nanostructures [19,24,25,27,30,32,33], size effects on mechanical behavior and hysteresis [26], surface effects on the transformation [31,34] and the effects of grain size [30]. Recent MD simulations [19,33] revealed how martensite nucleation and growth works in Zr. Martensite nucleates within the crystal upon cooling and imposes strain on the lattice. Different variants of martensite will then nucleate to compensate for this strain. Studies of the B2 to B19 phase transition in SMAs [33] revealed a twinning hierarchy. Microtwins formed within the martensite variants, in addition to the macrotwinning along the bar that is responsible for shape memory by responding to shear and propagating the domain wall. Despite such progress, several aspects of the martensite transformation remain poorly understood; among these are the effects of size and mechanical constraints on transformation temperature and on the resulting microstructure. The present paper focuses on the role of specimen size and mechanical constraints on sample-to-sample variability of the properties and microstructure of disordered SMAs modeled after a Ni63Al37 system.

The remainder of the paper is organized as follows. Section 2 describes the details of our simulations. Section 3 discusses size effects on the austenite and martensite transformation. Section 4 illustrates size effects on the martensitic microstructure. Section 5 describes the effects of mechanical constraints on the martensite structure and transformation. Finally, conclusions are drawn in Section 6.

2. Simulation details

The initial atomistic structures of the Ni63Al37 alloys were created by replicating a two-atom cubic B2 NiAl unit cell in all directions until the desired size was reached. We studied systems ranging in size from 6,750 atoms (which corresponds to a simulation cell length of 4.29 nm at 600 K), to 5,971,968 atoms (corresponding to a simulation cell length of 41.99 nm at 600 K). The simulations used periodic boundary conditions and the size refers to the length of the periodic cell.
To create the random alloy structures, Al atoms were randomly selected and replaced with Ni until the desired composition was achieved. One of our goals is to characterize sample-to-sample variability, and consequently several statistically independent samples were created for each size. We point out that our random alloys ignore possible correlations between substitutional atoms. Grand Canonical Monte Carlo simulations [35] can be used to obtain an ensemble of structures consistent with the equilibrium probabilities. Our choice of a random alloy enables us to evaluate the worst-case scenario in sample-to-sample variability and to establish an upper bound to its consequence in terms of properties. In addition, the actual distribution of atoms in Ni_{x}Al_{1−x} SMA samples is expected to be very dependent on processing conditions given that quenching is necessary to avoid the formation of the Ni_{3}Al_{1} phase.

This choice of periodic boundary conditions enables us to focus on the inherent effects of the reduction in the number of atoms and maximum wavelength associated with microstructure. Other boundary conditions including free surfaces [36] (clean or passivated) and those imposed on a crystalline grain by neighboring grains in a polycrystalline sample are of great importance but beyond the scope of this paper.

We use an embedded atom model (EAM) interatomic potential developed by Farkas et al. [37] for all the MD simulations. The potential was parameterized to reproduce elastic constants, lattice parameters and stacking fault energies of the B2 NiAl and Ni_{3}Al_{1} phases [37]. Desirable features include a description of the martensitic phase transformation in several NiAl alloys [38], and the capture of the strong Ni compositional dependence of the transformation temperature [39].

The martensite and austenite transitions were studied using isobaric, isothermal MD simulations (NPT ensemble) with a cooling/heating procedure that used rates of ±0.5 K ps⁻¹. Equations of motion were integrated with a timestep of 1 fs, and a Nosé–Hoover thermostat and Parrinello–Rahman barostat [16] were used to control the temperature and maintain atmospheric pressure in all directions. The barostat allows for the simulation cell lengths and angles to evolve independently but the cell angles remained constant. Coupling constants of 0.1 and 1.0 ps were used for the thermostat and barostat, respectively. In order to study how mechanical constraints affect the martensite transformation, we performed additional simulations where cell angles were kept at 90°.

During the martensitic transformation, see Fig. 1, the cubic austenite phase undergoes a transformation to martensite with a monoclinic unit cell. Prior reports, using the same interatomic potential [37], have reported the martensite structure to be 3R L1₀ [37] and tetragonal L1₀ [40]. For completeness, we compare our structure with the 7R structure [5], also known as 14 M [6], reported from experiments in NiAl alloys of similar compositions. Noda et al. [5] obtained a monoclinic angle \( \beta = 85.63^\circ \) and lattice parameters of \( a_m = 4.172 \text{ Å}, \quad b_m = 2.690 \text{ Å} \) and \( c_m = 14.450 \text{ Å} \) from neutron-diffraction experiments for the Ni_{62.5}Al_{37.5} martensite. When we outline a comparable martensite structure to be 3R L1₀, we find \( \beta = 88.29^\circ \) and lattice parameters of \( a_m = 4.33 \text{ Å}, \quad b_m = 2.60 \text{ Å} \) and \( c_m = 14.52 \text{ Å} \) (see snapshots in the online Supplementary material). However, this unit cell is not a periodic repeating unit of the structure. The reason for this difference is that the experimental structure [5] shows a (5, −2) stacking sequence of (110) planes, while our structure has an alternating stacking sequence. We note that the main results of the paper are independent of the details of the martensitic crystal structure and we stress that our simulations should be thought of as representing a model shape memory material, in the same spirit as Ref. [41].

Finally, in order to study the role of mechanical constraints on the phase transformation, we performed separate series of simulations in which the simulation cells were forced to remain orthorhombic; the cell lengths were allowed to vary independently but the cell angles remained at 90°. This study is motivated by the fact that individual grains in polycrystalline SMAs would experience similar constraints, the details of which depend on their neighboring grains. An extensive set of heating/cooling simulations were run, with up to 50 different samples for each size.

3. Size effects on martensite and austenite transformation

3.1. Transformation under heating and cooling

Fig. 1 shows the temperature dependence of the lattice parameters during cooling and heating for a Ni_{63}Al_{37} disordered shape memory alloy with 746,496 atoms. As the high-temperature, cubic austenite phase is cooled down, it transforms to martensite at a temperature of \( \sim 150 \text{ K} \). The martensitic phase transformation involves expansion along two \([100]_{\text{Bcc}}\) directions and compression along the remaining \([100]_{\text{Bcc}}\). This is accompanied by a change in the cell angles from cubic to monoclinic (\( \alpha = \delta = 90^\circ, \quad \beta \neq 90^\circ \)). Upon reheating, the martensite transforms back into austenite at a higher temperature than the transformation to
martensite, indicating significant hysteresis in the process. This is consistent with prior MD simulations [35,39,40].

Fig. 2 shows the average transformation temperatures as a function of the simulation cell length obtained from a minimum of 10 independent simulations at each system size. The MD simulations show that decreasing the sample size leads to a slight increase in the transformation temperature for both austenite and martensite. This indicates that reducing the periodic sample size penalizes (from a free energy point of view) the high-symmetry austenite phase more than the lower-symmetry martensite; we attribute this observation to the fact that the high-temperature austenite phase is stabilized by entropy which would be affected by the reduction in periodic boundary conditions that restrict the maximum wavelength of allowed phonons.

3.2. Variability in transformation temperature: role of size

We now turn our attention to the role of atomic-level, sample-to-sample variability in transformation temperature. For small system sizes, we expect the specific atomic configuration (location of the substitutional, randomly placed Ni atoms) to affect the relative energy of the austenite and martensite phases, and affect the transition temperature; for large specimens, the deviations of the various local configurations would cancel out, and we would expect the samples to behave more homogeneously. Thus, we expect this variability to increase with decreasing sample size, potentially limiting the use of random alloys in nanoscale applications.

Fig. 3 shows the relative fluctuation in transformation temperatures (ratio between standard deviation to mean) for a range of system sizes. As expected, this variability in the martensite transition temperature increases with decreasing system size and is over 10% of the mean value for samples of ~10 nm on the side. Surprisingly, the variability in the austenite transition temperature is relatively independent of system size. We attribute this to the high temperature associated with this transition; at such temperatures entropy dominates free energy (remember entropy does internal energy).

4. Martensite microstructure: role of periodic system size

Fig. 4 shows atomistic snapshots during the cooling of two samples of different size, one with 746,496 atoms (periodic \( L = 20 \text{ nm} \)) and a second one with 5,971,968 atoms (periodic \( L = 40 \text{ nm} \)). We color atoms according to their local atomic packing determined from common neighbor analysis. Atoms with bcc environments are shown as blue spheres and represent austenite, red spheres denote local hcp environments and mark the martensite phase, and green denotes face-centered cubic (fcc) environments which correspond to stacking faults. fcc-like atoms denote defects in the martensite and are useful to identify variants and the evolution of the transformation process. As exemplified in Fig. 4, we find that samples with periodic length up to \( L = 20 \text{ nm} \) transform into a single-domain martensite; whereas the \( L = 40 \text{ nm} \) ones lead to multidomain martensite, indicating a threshold size for multidomain structures. The multidomain structure consists of two martensite domains with different orientations (this can be verified by the different orientation of the fcc atoms). Both the stacking faults and domain walls occur along \{110\}_\text{bcc} planes. It is interesting to note that during the transformation of the sample with \( L = 20 \text{ nm} \) (top snapshots in Fig. 4) a two-domain structure is originally formed but the domain walls separating them are very mobile and the structure transforms to a single-domain one within a few picoseconds. These two domains differ only by the monoclinic angle and the transformation to a single-domain structure is accompanied by a change in the angle of the simulation cell. The multiple-domain structure of the \( L = 40 \text{ nm} \) cell exhibits two domains differing in more than the monoclinic angle. We speculate that the domain walls present in the larger system have lower mobility, stabilizing the multidomain structure even in the absence of mechanical constraints. Characterizing the mobility of the various walls would be of interest but is beyond the scope of this paper. Upon heating, all the martensite structures (regardless of whether they are single or multidomain) transform back to a single-domain austenite identical to the original structure.
5. Role of mechanical constraints on transformation temperature and martensite microstructure

Most SMAs are polycrystalline and the relative orientation of neighboring grains leads to significant mechanical constraints as transformation begins. In this section we explore how mechanical constraints affect the transformation temperature and martensitic microstructure. Explicit polycrystal simulations would require extremely large simulation cells leading to computationally intensive simulations. Thus, in this paper we impose mechanical constraints by forcing the simulation cells to remain orthorhombic; the cell lengths are allowed to vary independently, but the angles are fixed at 90°.

5.1. Transformation temperatures

Fig. 5 shows the transformation temperatures for all system sizes when cell angles are artificially constrained to remain at 90°. The simulations show that the martensitic transformation temperatures remain rather similar to the unconstrained case. However, the austenite transformation temperature shows strong size dependence; the transformation temperature decreases with system size by approximately a factor of 2. This is due to the fact that constrained martensite phase has a significantly higher free energy than the unconstrained case of Sections 3 and 4. The origin of the size dependence is as follows: with increasing system size the martensite can develop a multidomain structure in order to release some of the internal stresses caused by the constraint, and the transformation temperature approaches that of the unconstrained systems.

Fig. 6 shows the sample-to-sample variability in the transformation temperatures for all system sizes when artificially constrained. The simulations show an increased variability in the transformation back to austenite upon heating for smaller sizes. This is likely due to the much lower transformation temperature in the mechanically constrained case, providing additional support to our argument that sample-to-sample atomic variability affects the relative entropy between the two phases less than it does internal energy.

5.2. Martensite microstructure: role of mechanical constraints

Fig. 7 shows martensite microstructures obtained from the MD simulations at various sizes with and without mechanical constraints. The unconstrained case exhibits a multidomain structure only for the largest size simulated (40 nm), while the constrained case shows multidomain structures for all sizes except the smallest size of 4.2 nm.
We found that in mechanically unconstrained systems, the effect of periodic system size on transformation temperature is very weak, and this leads to a slight increase in the transformation temperature; this indicates that the entropy-stabilized austenite is penalized with the reduction of simulation cell size. Sample-to-sample variability leads to an increase in the uncertainty in the austenite temperature with decreasing system size, reaching 10% of the mean value for samples of ~10 nm on the side. Interestingly, the variability in the martensite transition temperature is independent of system size. This might place a fundamental limit on the miniaturization of this class of materials. We note that surface effects (ignored in our periodic simulations) would also affect the transformation temperature of nanoscale samples and should be taken into account to understand miniaturization. The focus of this paper is on sample-to-sample variability due to the disordered nature of the alloy.

In addition, our simulations show that mechanical constraints can change the transformation temperature by as much as 50%. This is important to understand the behavior of polycrystalline samples, where the relative orientation of neighboring grains leads to constraints as the transformation occurs. Our simulations assume that the austenite phase is strain free and the constraint penalizes the martensite structure. Thus, the martensite transformation temperature remains similar to the unconstrained case. Interestingly, we also find that mechanical constraints have a strong effect on martensite microstructure. The unconstrained samples exhibit critical size for multidomain structures of 40 nm; below this critical size samples exhibit a single domain structure. On the other hand, mechanical constraints favor a multidomain martensite that accommodates internal stresses and reduces this critical size. We observe multidomain structures in constrained samples as small as 7 nm on the side. The motion of domain boundaries is critical for shape memory and superelasticity, and consequently understanding this critical size for multidomain structures is critical to understanding the performance of this material, especially when its characteristic size is reduced to the nanoscale.

6. Conclusions

We carried out an extensive set of MD simulations of disordered SMAs using an EAM potential parameterized for NiAl to characterize the effect of sample size, atomic-level variability and mechanical constraints on the phase transformation temperature and martensite microstructure. The use of periodic boundary conditions enables us to assess the intrinsic role of the number of atoms and constraints in the maximum wavelength of structural fluctuations or features without the effects of specific surface terminations or grain boundaries. We note that finite size effects appear to still be playing a large role in the behavior for up to 5 million atoms.
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