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# 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 outward 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.



## 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 $Ni_xAl_{1-x}$ 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 by 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, affects 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 constrains their deformation and transformation, increasing the stress or

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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 (Ms) 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 $Ni_{50}Ti_{25}Cu_{25}$ 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 the 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 the 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 Fig. 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 300 K 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 1 K at a rate of $-0.5$ K/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 are 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 $2 \times 10^8$ $s^{-1}$. 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 500 ps and relax an additional 500 ps. The unloaded structures were subsequently annealed for 500 ps at 300 K, then heated to annealing temperatures ranging from 400 K to 800 K and held there for an additional 500 ps. 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 50 ps 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