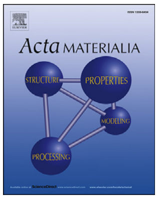
Acta Materialia 123 (2017) 90–101

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat



Full length article

Atomic scale processes of phase transformations in nanocrystalline NiTi shape-memory alloys

Won-Seok Ko [a, b, *], Sascha B. Maisel [b], Blazej Grabowski [b], Jong Bae Jeon [c], Jörg Neugebauer [b]

[a] School of Materials Science and Engineering, University of Ulsan, Ulsan 44610, Republic of Korea
[b] Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany
[c] Functional Components and Materials R&D Group, Korea Institute of Industrial Technology (KITECH), Busan 618-230, Republic of Korea

ARTICLE INFO

Article history:
Received 6 August 2016
Received in revised form
30 September 2016
Accepted 7 October 2016

Keywords:
Shape-memory alloy
Nickel-titanium
Nanocrystalline material
Phase transformation
Molecular dynamics simulation

ABSTRACT

Molecular dynamics simulations are performed to investigate temperature- and stress-induced phase transformations in nanocrystalline nickel-titanium shape-memory alloys. Our results provide detailed insights into the origins of the experimentally reported characteristics of phase transformations at the nanoscale, such as the decrease of the transformation temperature with grain size and the disappearance of the plateau in the stress-strain response. The relevant atomic scale processes, such as nucleation, growth, and twinning are analyzed and explained. We suggest that a single, unified mechanism—dominated by the contribution of a local transformation strain—explains the characteristics of both temperature- and stress-induced phase transformations in nanocrystalline nickel-titanium.

1. Introduction

Shape-memory alloys have been widely used for many applications utilizing their unique properties of shape-memory behavior and superelasticity. Among the various shape-memory alloys discovered so far, nickel-titanium (NiTi) shape-memory alloys with equiatomic or nearly equiatomic compositions have received great attention owing to their excellent mechanical properties, biocompatibility, corrosion resistance, and their ability to transform close to room temperature [1]. In NiTi alloys, the reversible temperature- and stress-induced phase transformation between B2 austenite and B19′ martensite results in the shape-memory effect and in superelasticity, respectively [1].

Recently, nanocrystalline NiTi shape-memory alloys have attracted special attention because of their excellent strength, thermomechanical cyclic stability, linear superelasticity, and the large temperature window for superelasticity [2–5]. Because these exceptional properties are likely related to unique characteristics of phase transformations at the nanoscale, experimental studies on phase transformations in nanocrystalline NiTi are ongoing [2–8]. A noticeable characteristic of nanocrystalline NiTi is an over-stabilization of the austenite phase with respect to the martensite phase. In the case of the temperature-induced phase transformation, it has been reported that the transformation temperature decreases with decreasing grain size and that the transformation to martensite is completely suppressed below a critical grain size [9–11]. In the case of the stress-induced phase transformation, a steep hardening in the stress-strain response has been reported for nanocrystalline NiTi, while polycrystalline NiTi with larger grains shows a clear plateau in the stress-strain curve [2–4]. Consequently, the transformation in nanocrystalline NiTi occurs at higher stress levels, indicating again an over-stabilization of the austenite phase [2–4].

This over-stabilization of the austenite phase has not only been reported for nanocrystalline materials, but also for shape-memory nanoparticles with different boundary conditions, such as free standing particles or nanoparticles embedded in bulk metallic glass [11]. It is reasonable to expect that the fundamental mechanism underlying phase transformations at the nanoscale differs from its bulk counterpart. Several candidate mechanisms have been proposed to explain the over-stabilization of the austenite phase. The first one is the "*interfacial energy contribution mechanism*" [11–13]

---

[*] Corresponding author. School of Materials Science and Engineering, University of Ulsan, Ulsan 44610, Republic of Korea.
E-mail address: wonsko@ulsan.ac.kr (W.-S. Ko).

http://dx.doi.org/10.1016/j.actamat.2016.10.019
1359-6454/

which promotes the relative difference between the interfacial energy of the austenite and martensite phase. For example, if the grain boundary energy of the austenite phase is lower than that of the martensite phase, a decrease in the transformation temperature is expected with smaller grain size. The second one is the "*internal defect contribution mechanism*" [11,14] which promotes the role of internal defects, e.g., dislocations, as heterogeneous nucleation sites. Based on the assumption that a larger grain or particle contains more internal defects than a smaller one, the suppression of the martensitic phase transformation is expected with smaller grain or particle size. The final mechanism is the "*strain-contribution mechanism*" [4,10,11] which promotes a mechanical constraint by the presence of interfaces. Following this idea, the phase transformation is suppressed with smaller grain or particle size, because the increased transformation strain energy due to the strong mechanical constraint can contribute to an increase in the free energy.

Among these mechanisms, the strain-contribution mechanism has been supported by a recent experiment on the stress-induced phase transformation in nanocrystalline NiTi alloys [4]. The experiment reported X-ray diffraction profiles recorded during *in situ* tensile loading and unloading. The results indicate a gradual degeneration of the diffraction profiles from a multiple-peaks mode to a continuous, single-peak mode with decreasing grain size. This is an indicator of lattice strains inside the transformed structure due to strong mechanical constraints by grain boundaries.

However, several uncertainties remain, which have so far prohibited the conclusion that the strain-contribution mechanism indeed governs phase transformations in nanocrystalline NiTi. Most notably, the experiment in Ref. [4] presented only limited information on the microstructure during the phase transformation. Generally, it is known that the evolution of the microstructure—especially the twinning behavior—is critical for phase transformations in shape-memory alloys [1], but the twinning in nanocrystalline NiTi and its role during the phase transformation are still uncertain. Further, it is questionable whether a single, unified mechanism governs both temperature- and stress-induced phase transformations. Contrary to experiments on the stress-induced phase transformation, experiments on the temperature-induced phase transformation of nanocrystalline materials are rather challenging and generally limited because of the following difficulties: The temperature-induced phase transformation of nanocrystalline NiTi usually involves the formation of an interfering intermediate R-phase during cooling induced by the presence of metastable Ni_4Ti_3 precipitates [1,7–9]. Moreover, the availability of *in situ* experiments is greatly limited because the transformation temperature of nanocrystalline NiTi can approach 0 K, limiting experimental capabilities [11].

In order to overcome these difficulties and to supplement experiment, theoretical approaches by means of mesoscale [15] and atomistic simulations are useful. Especially, molecular dynamics (MD) simulations combined with semi-empirical interatomic potentials can enable a detailed understanding of the underlying mechanisms. For example, MD simulations have been successfully used to elucidate the deformation behavior of metallic nanocrystalline materials [16–18] and phase transformations of shape-memory alloys [19–22]. As for the phase transformations in nanocrystalline shape-memory alloys, there has been a recent MD simulation work [23] focusing on a related shape-memory alloy system (NiAl). However, because the work in Ref. [23] was based on an interatomic potential which predicts a wrong martensite structure as compared to experiment [23,24], the respective conclusions are rather limited.

In the present study, we have investigated phase transformations in nanocrystalline NiTi shape-memory alloys based on a recently developed interatomic potential [22] that correctly reproduces the experimentally reported phase transformation between B2 austenite and B19′ martensite. We present MD simulation results that are consistent with available experimental information. Based on the results we are able to shed light on the atomistic processes involved during the phase transformations, such as nucleation and growth, the twinning behavior, and the occurrence of an irrecoverable strain. The governing mechanism of temperature- and stress-induced phase transformations in nanocrystalline alloys is critically discussed by confronting the proposed mechanisms with our simulation results and available experimental data.

2. Methodology

The MD simulations were performed based on the second nearest neighbor modified embedded-atom method (2NN MEAM) with an interatomic potential specifically designed for the Ni–Ti binary system [22]. This potential was developed with the aim to accurately reproduce the temperature- and stress-induced phase transformations in equiatomic NiTi. It reproduces the phase transformation between the B2 austenite and B19′ martensite phase as well as the fundamental physical properties (structural, thermodynamic, and defect properties) of the relevant intermetallic compounds and solid solutions. All of the present simulations were performed with a radial cutoff distance of 5.0 Å, which is larger than the second nearest-neighbor distance of B2 NiTi. A detailed formulation of the 2NN MEAM formalism is available in the literature [25–27].

Nanocrystalline cells were generated using the Voronoi construction method [28] with random positions and crystallographic orientations for each grain. Initially, cube-shaped cells with the B2 structure were generated considering designated average grain sizes. Most of the cells were composed of 30 grains, but the cell with the largest average grain size (30 nm) was generated with only 5 grains to render the computations feasible. The resulting average grain diameter (D), number of grains, cell dimensions, and number of atoms for each cell are summarized in Table 1.

A series of MD simulations was then performed using the LAMMPS code [29] with a time step of 2 fs. The Nosé-Hoover thermostat [30,31] and the Parrinello-Rahman barostat [32] were used for controlling temperature and pressure, respectively. Periodic boundary conditions were applied along all three dimensions to remove spurious surface effects. During the simulations, cell dimensions, cell angles, and individual atomic positions were allowed to fully relax. Initially, the generated cells were subjected to an energy minimization process using the conjugate gradient method to avoid unstable atomic positions near the generated grain boundary configurations. Annealing at 400 K, i.e., above the austenite finish (A_f) temperature, was applied to recover the initial B2 austenite structure.

The temperature-induced phase transformation was investigated by performing MD simulations in an isobaric-isothermal (*NPT*) ensemble at zero-pressure. From the initial temperature of 400 K, the temperature was gradually decreased to 10 K and increased again to 400 K with cooling and heating rates of ±0.5 K/ps. During the simulations, atomic volumes at the specific temperature and their changes were recorded to observe the occurrence of phase transformations.

The stress-induced phase transformation was likewise investigated with MD simulations in an *NPT* ensemble. Prior to loading, zero-stress transformation temperatures for each nanocrystalline cell were obtained from simulation results of the temperature-induced phase transformation. The A_f temperature of every nanocrystalline cell turned out to be lower than 400 K. Knowing this result, the temperature was kept at 400 K to maintain the B2