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Effect of indentation temperature on nickel-titanium indentation-induced two-way shape-memory surfaces

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ABSTRACT

This study investigated the effect of temperature on indentation-induced one-way and two-way shape memory properties in Ti-50.3 at% Ni alloy. Indentation temperatures ranged from below the martensite finish temperature (M_f) to above the austenite finish temperature (A_f) with the explicit intent of varying the indented phase. Samples used in the study were characterized by differential scanning calorimetry and transmission electron microscopy (TEM). The topographical behavior of the shape memory effect was investigated through Vickers indentation and laser scanning 3D confocal measurements. The magnitudes of deformation recovery associated with the one-way and two-way shape-memory effect (OWSME, TWSME) decreased with increasing indentation temperatures, which is a reflection of the decreasing volume of material experiencing martensitic reorientation during indentation. Indented and subsequently planarized samples exhibited TWSME protrusions when thermally cycled. Laser scanning measurements were used to characterize the height of the protrusions as increasing depths of material were polished away, which provided insight into the overall affected volume beneath the indent. As indentation temperatures increased, both the height of the protrusions, and consequently the polish depth necessary to completely remove the effect, decreased. TEM investigations revealed that directly underneath a nanoindent the microstructure was very fine due to the high-strain deformation; this was contrasted with a much coarser grain size in the undeformed bulk material. Overall these results strongly imply that the deformation recovery associated with the OWSME and TWSME can be maximized by indenting at temperatures at M_f or below because the volume of deformed microstructure beneath the indent is maximized. This finding has important practical value for any potential application that utilizes indentation-induced phase transformation deformation recovery in NiTi.

1. Introduction

Near-equiatomic nickel-titanium (NiTi) alloys exhibit shape memory properties that can recover apparent permanent deformations upon heating (shape memory) or spontaneously during unloading (pseudoelasticity) [1,2,3,4,5]. The shape memory deformation recovery is owed to a reversible phase transformation from a B19' martensitic crystal structure to a B2 austenitic structure upon heating [3]. This one-way shape memory effect (OWSME) has been observed for any loading condition including tension [6,7,8,9,10], compression [6,9,11,12,13], and indentation [14,15,16,17,18]. The phase transformation behavior is extremely dependent on alloy composition and deformation processing history. Increasing the relative nickel content decreases the phase transformation temperatures by approximately 220°C/at% Ni [19], which will have a profound effect on stress-strain behavior. Plastic deformation associated with deformation processing has a similar effect, impeding the stress-induced phase transformation, although the microstructural effects are more complex [20,21,22,23].

NiTi also exhibits a two-way shape memory effect (TWSME) [9,24,25]. This TWSME is the material's ability to "remember" both a hot and a cold state and subsequently transition between these two states based on a phase transition from martensite to austenite and vice-versa. It has been noted that the methods of eliciting the TWSME can be categorized into three general methods:

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thermo-mechanical training [26,27,28,29,30], severe deformation below the martensite start temperature (M_s) [1,24,25,26,31,32], and stress-assisted aging [33,34,35,36]. More recently it has been shown that the TWSME can be induced in NiTi through an indentation method [16,37,38]. Not only has the indentation-induced shape memory effect been observed in materials below the martensite finish temperature (M_f), it has also been observed for indentation of austenitic NiTi [39,40]. Additionally, it has been shown that subsequently planarizing these indents followed by thermal cycling leads to reversible TWSME surface protrusions that are reversible over several cycles [39,40,41,42,43]. Although a handful investigations have proposed theories on the underlying mechanisms leading to this indentation induced TWSME [37,41,43], the complex mechanisms on the microstructural scale remain to be experimentally uncovered and a comprehensive understanding has not yet been widely agreed upon.

In a recent publication, Qin et al. investigated the indentation-induced OWSME and TWSME in a NiTi alloy which is in the austenite phase at room temperature. Transmission electron microscopy (TEM) uncovered that both dislocations and thermally stable martensitic plates are present and parallel to the indenter geometry at temperatures in which the material is expected to be fully austenitic [40]. Complementary to those results, a separate study has shown that indentation-induced TWSME diminishes and disappears with heating to temperatures well above the austenite finish temperature (A_f), indicating that the thermally stable martensite underneath the indent reverts to austenite above A_f [39]. Combined, these studies strongly suggest that residual, stress-stabilized martensite plays a dominant role in indentation-induced TWSME.

The stress-level necessary to induce martensite varies linearly with elevating temperatures following the Clausius-Clapeyron relation, thus with an increase in temperature, the stress required to initiate and propagate this transformation also increases [44,45]. However, there is a critical temperature at which this stress-induced martensite is no longer energetically favorable and the deformation mechanism of the NiTi is ultimately shifted to plastic deformation of the austenite [46]. In contrast to uniaxial loading, indentation produces a much more complex stress state and several studies have demonstrated indentation-induced recovery when indented at temperatures above A_f. It is believed that the large component of hydrostatic stress from indentation [47,48] assists in shifting the transformation temperatures [18,49]. As thermally stable martensite has been uncovered in indented austenitic NiTi [40], this stress-induced transformation may play a pivotal role in the manifestation of the indentation-induced TWSME.

The goal of this study was to further understand the inherent mechanisms necessary for the TWSME to occur, as a function of the temperature at which the sample is indented. A Ti-50.3 at% Ni alloy was indented at temperatures ranging from 19°C below M_f to 31°C above A_f; thereby, these temperatures span the martensitic and austenitic states. The recovery ratios of both the OWSME and the TWSME were measured as a function of increasing indentation temperature. Through this, an understanding of the volume of material that affects the TWSME could be reached and related to indentation temperature. In addition to these experiments, indented samples were investigated using transmission electron microscopy (TEM) and the microstructure of the material exhibiting the TWSME was examined.

2. Experimental

The material used in this study was a commercially available NiTi with a composition of Ti-50.3 at% Ni (Ti-55.4 wt% Ni). As the bulk plate was likely heavily deformed during material processing, the material was solutionized at 1000°C for 24 hours and immediately water quenched. The phase transition temperatures of both the solutionized and as-received materials were measured using differential scanning calorimetry (DSC) on a Mettler Toledo DSC1 Star System. Tests were conducted using a heating/cooling rate of 10°C/min starting from room temperature, initially heating to 120°C and cycled to a low temperature of -80°C before returning to the start temperature. Masses of the samples analyzed were between 10 mg and 30 mg. Three full heating and cooling cycles were performed for both the as-received and solutionized samples. Using the DSC data, the transformation temperatures were calculated using a two-tangent method.

For indentation, samples were prepared perpendicular to the drawing direction and cut from the bulk sample to a working size of 5 mm × 8 mm. Prior to indentation, these samples were cold mounted in epoxy and ground using a progressively lower grit size to 1200 (P-4000) grit SiC paper followed by a 1 μm diamond suspension and a 50 nm colloidal silica polish. Finally, samples were electropolished in an electrolyte solution consisting of 20% volume H_2SO_4 and 80% volume methanol at room temperature.

Microindentation was performed on an MTS 858 Mini Bionix® II load frame equipped with a Vickers indenter tip. A maximum load of 50 N at a loading rate of 1 μm/sec was used for each indent. This load was held constant for 30 s prior to unloading at the same rate. Samples were indented at temperatures ranging from -10°C to 120°C with the aim to examine the magnitude of the shape memory effects with changing temperature. Indentation at temperatures other than room temperature was achieved using either an MTS 651 environmental chamber (temperatures -10°C to 85°C) or using a heat gun (indentation at 90°C and above).

All samples, regardless of indentation temperature, were first fully cooled below M_f before being heated to their indentation temperature, such that samples were fully martensitic at indentation temperatures below A_s. Similarly, between A_s and A_f, samples are expected to have some combination of phases during indentation, and indentation temperatures above A_f ensured a fully austenitic phase.

Samples for measuring the recovery ratio were each indented four times spaced 750 μm apart. Subsequently, the indentation depths of the samples were measured with an Olympus OLS4000 laser scanning confocal microscope capable of 3D measurements with a depth resolution of 10 nm. To determine the magnitude of both the OWSME and TWSME, indents were measured in three states: initially after indentation, heated above A_f, and cooled below M_f. Heating of samples was performed *in situ* using a ceramic heater underneath the microscope. Comparison of the initial indent with the heated indent yielded the OWSME. The reversible TWSME was observed through measurements of the initial, heated, and cooled indentation depths.

To measure the recovery of the protrusions as a function of polishing depth, samples were initially indented at the corners of the rectangular samples with a 120° diamond spheroconical indenter to much larger indentation depths of about 120 μm. These indents were used as reference for the amount of material polished away. Afterwards, the samples were microindented six times in a similar fashion as previously described and post-indentations were thermally cycled to recover the shape change induced by the OWSME. The samples were then planarized and polished until the initial indents were removed, leaving only the deeper reference indentations. Measurement of the subsequent protrusion height upon heating above A_f was accomplished using an identical *in situ* heating method as described for the recovery ratio samples using the confocal microscope. After measuring the protrusion height, samples were cooled below M_f and further polished until roughly 3–5 μm of material was removed. Then the