

Focused Ion Beam Manufacturing Methods for Nickel-Titanium Shape-Memory Alloy Thin Films

G.A. Shaw, K.-H. Chung, B. Ming, A. Vldar

Manufacturing Engineering Laboratory
National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

Nickel-titanium shape-memory alloy is an interesting and technologically relevant material that can recover large amounts of mechanical strain through a thermally-activated phase transformation. Because of its unusual properties, it has been used widely for biomedical and microelectromechanical systems (MEMS) applications. Some of these desirable properties, namely chemical inertness and mechanical strength, make it difficult to process, however. In this study, focused ion beam (FIB) milling of nickel-titanium shape-memory alloy thin films was carried out in a scanning electron microscope (SEM). The effect of this micromachining method on the shape memory effect was then examined using instrumented indentation. FIB milling at high energy was found to affect the material's mechanical properties near the thin film surface, and methods for minimizing this damage were explored.

Introduction

Shape-memory alloys (SMAs) are a class of materials that can recover large amounts of mechanical strain through a solid-state phase change known as a martensitic transformation [1]. Thin films of nickel-titanium SMA have a great deal of promise for use as actuators in hybrid microelectromechanical systems (MEMS). The thermally-induced shape-memory effect (SME) in these alloys has one of the highest work densities of any actuation scheme, and is therefore ideal for applications where a large force must be applied by a small volume of material. In addition, NiTi SMA has proven to be both mechanically and chemically robust, and is therefore used in a wide variety of applications ranging from arterial stents [2] to computer memory [3]. Although this robustness is a major attribute in terms of device performance, it complicates manufacturing processes. Bulk NiTi is typically machined using electrical discharge machining (EDM); however this method cannot produce devices smaller than the millimeter-scale. Micromachining of NiTi is typically carried out using wet chemical methods applied to thin film material. The film is masked with a photoresist and then the exposed regions etched with hydrofluoric acid [4]. This approach also has its limitations, as the photoresist can be undercut, degrading control of the fabrication process.

An alternative method for use in micro- to nanoscale manufacturing is focused ion beam (FIB) milling. In this process, a high-energy beam of ionized gallium is used to ablate material from a surface. Although this is currently a low-throughput process, control of component geometries is possible down to the nanometer scale [5].

Previous work has shown that FIB milling NiTi thin film samples results in a polishing effect, however these studies do not address effect of the ion beam on the mechanical properties of the alloy [6]. It has also been shown that oxygen and nickel ion implantation can have a significant effect on the properties of NiTi SMA [7, 15], and also that indentations made on the surface of NiTi thin film material can recover through the shape memory effect [8]. In this study, we report indentation and atomic force microscope (AFM) studies of FIB milled NiTi samples in the martensite phase. The polishing effect described previously is observed, but we observe that the milled surface roughens again upon heating past the martensite transformation temperature. In addition, significant changes in mechanical properties were observed that depended on FIB energy.

Experimental

NiTi SMA thin films were obtained from TiNi Alloy Co*. The films were DC magnetron sputtered onto oxidized silicon to a depth of 1.7 μm . A rapid thermal anneal to a temperature of 550 $^{\circ}\text{C}$ was performed over a total time of five minutes. The films were determined to be in the martensite phase at room temperature by X-ray powder diffraction. In contrast to previous work, no chemical etch step was used to remove surface oxides.

To carry out the surface modification of NiTi shape memory thin films by focused ion beam milling, a FEI Helios NanoLab 600 DualBeam system was used. First, square-shaped patterns with 10 μm width were milled with an ion beam voltage of 30 kV and a beam current of 0.92 nA. This will be referred to as the high energy condition. The nominal milling depth was 200 nm. To study the effect of lower energy ion beams, patterns of the same shape, size and nominal depth were created at 5 kV and 2 kV beam voltages. The beam current values used were 1.0 nA and 0.56 nA, respectively, and will be referred to as the medium and low energy conditions. To ensure that the results are comparable, all milling patterns were made in one experiment on one NiTi thin film sample, with 10 μm spacing between them. Except for above mentioned changes in the beam voltage and current settings, no other beam adjustments took place during the milling process. The machined area was then imaged with both scanning ion microscopy and scanning electron microscopy as shown in Figure 1.

After FIB milling, instrumented indentation was used to test the mechanical properties of the thin films. The Hysitron Triboscope used for these experiments was used as a scanning probe instrument, mapping the surface topography of the areas to be tested prior to indentation with the cube corner indenter tip. Indentations were performed at maximum applied forces of 3000 μN , 1000 μN , 500 μN , 200 μN , and 80 μN in control areas which had not been milled with the FIB, but were within 500 μm of the milled area. Four indentations were performed at each of these forces. It may be important to note, however, that a very small Ga ion flux may have been incident on the control areas as a result of scanning ion imaging. An identical set of indentations were performed in the area milled with the high energy beam. A set of four indentations at maximum forces of 200 μN and 80 μN were also performed on the areas milled with medium and low energy FIBs. Young's modulus was determined for each indentation using the Oliver-Pharr method [16].

Atomic force microscopy (AFM) was carried out to examine the effect of the martensitic transformation on the FIB milled surface. The surface topography of the control and FIB areas were imaged after indentation, and the films were then heated to approximately 200 $^{\circ}\text{C}$ with a heat gun. A change in surface reflectivity was observed as the film transformed from the martensite phase to the austenite phase and back again. The relevant areas of the films were then re-imaged after transformation.

Results and Discussion

Figure 2 shows representative AFM topographical images of an area milled at 30 kV, and a control area before and after heating past the transformation temperature. Qualitatively, it can be observed that the FIB-milled area is flatter than the control sample before heating. Protruding

features were subject to a greater ion flux, and therefore apparently etched more rapidly. This leads to the polishing effect previously observed [6]. After heating the samples, the films transform from the martensite phase to the austenite phase. It is at this point that the shape memory effect occurs. Upon cooling, the sample topography for the control samples is altered only slightly, as evidenced by the similarity between images A and B; whereas the FIB-milled surfaces undergo large changes in topography, as evidenced by the obvious difference between images C and D. This effect was observed regardless of the energy of the FIB used.

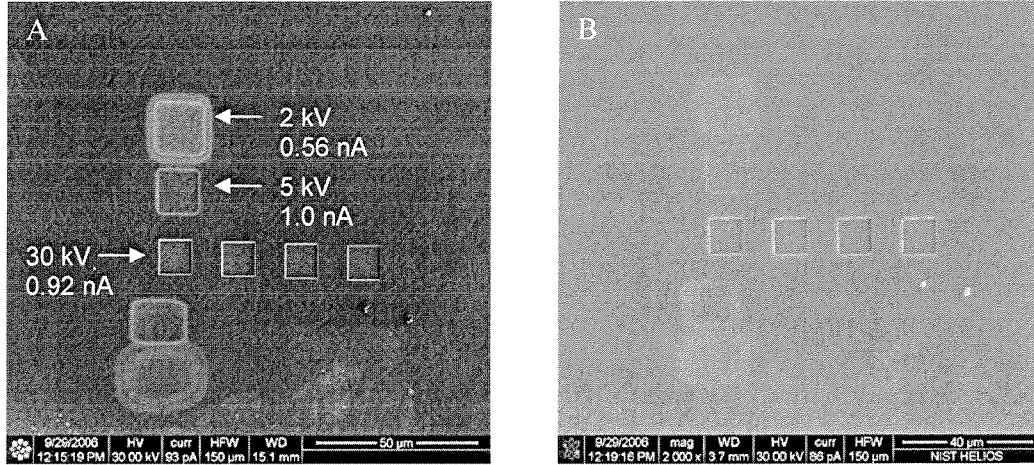


Figure 1. The scanning ion microscope image is shown in A, and the scanning electron microscope image is shown in B. The lower two machined areas were used as a test for machining parameters, and were not examined in this study. The upper two machined areas were machined at low (top) and medium (middle) energy, as described in the article text. The row of four machined areas were machined at high energy.

In addition, the Young's modulus of the milled surfaces increases in the near-surface region. Figure 3 shows reduced modulus (E_r) as a function of maximum indentation depth (h_{max}). Reduced modulus is defined as

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (1)$$

where E and E_i are the Young's moduli of the material under test and the material of the indenter, respectively, whereas ν and ν_i are the Poisson ratios of the material under test and indenter, respectively. The deepest indentations were a significant fraction of the film thickness. The increase in modulus observed at these indent depths may reflect the contribution of the silicon oxide substrate [14]. Previously, a significant indentation size effect has been reported for SMA thin films [9], the effects of strain gradient plasticity are also observed in these experiments as the increase in modulus of the control sample at small indent depths show. The increase in modulus at shallow indent depths is much greater for the milled areas, particularly in the case of the medium energy FIB conditions. The oxide layer of NiTi is primarily composed of TiO_2 , and the Young's modulus of single crystal rutile titania is 489 GPa, as determined by indentation [10]. The increase in modulus at shallow indentation depths could be explained by the presence of a significant oxide layer, since no chemical etch step was used to thin the oxide prior to testing. However, as can be seen in Figure 3, the FIB processing increases modulus near the sample surface relative to the unprocessed control areas. Since the FIB is expected to partially remove the surface oxide layer, the TiO_2 is not likely to be responsible for the change in mechanical properties from the milling process.

There are several possible mechanisms for the observed changes in topography and modulus. It is well known that high energy ion beams such as those used for FIB milling are capable of amorphizing crystalline material. The Young's modulus of martensite-phase NiTi has been reported as 60 GPa to 70 GPa depending on indentation depth [9], and the modulus of amorphous NiTi films has been determined to be approximately 100 GPa [11]. The observed increased Young's modulus of the FIB-milled areas would be consistent with the formation of a thin amorphous layer near the surface of the thin film. Time-dependent redistribution of material by low-energy FIBs has also been reported [12]. The removal rate of the lowest energy ion beam was extremely small, so this mechanism may be operative at lower energies. The extent of localized heating is not yet known, the properties of NiTi have been shown to be sensitive to processing temperature [1]. A fourth mechanism may also contribute: implantation of gallium ions. Oxygen ion implantation and nickel ion implantation have both been shown to significantly affect the mechanical properties of NiTi SMA [7, 15], and the implantation of gallium atoms could have a similar effect. A more detailed study is being carried out to determine which mechanism is active in the surface modification.

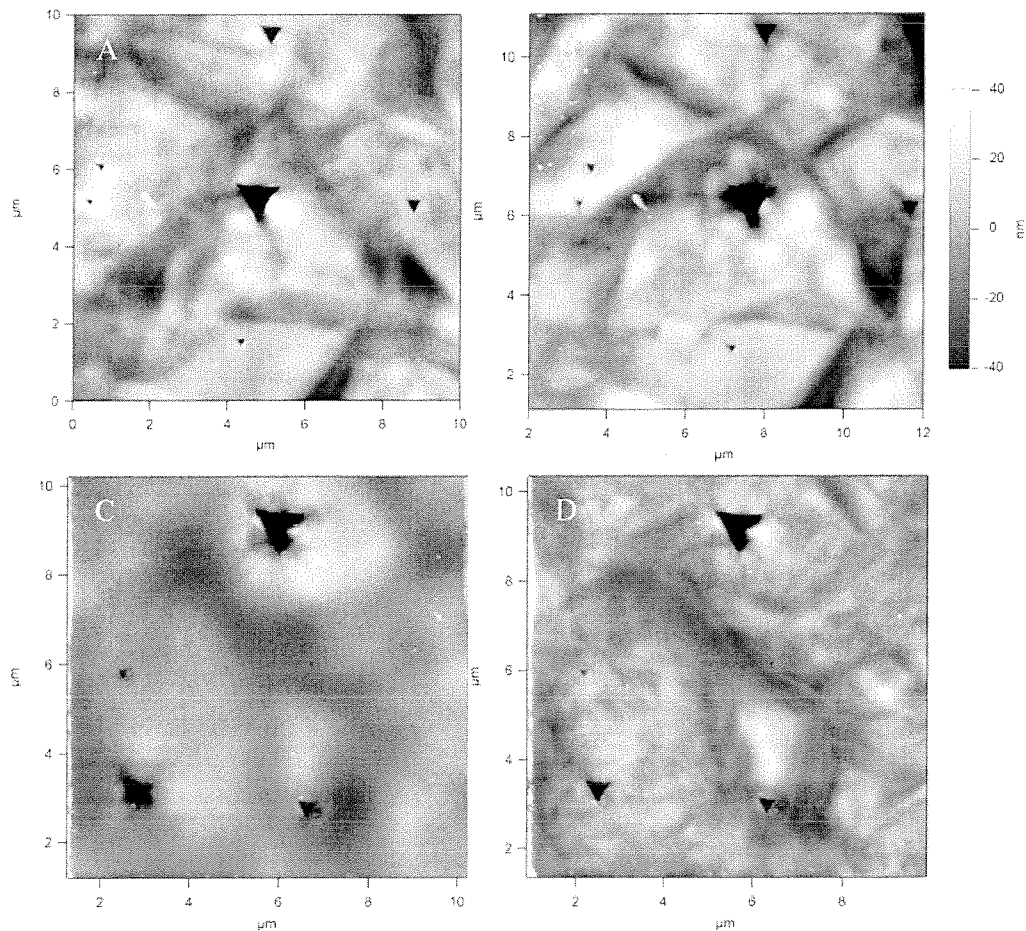


Figure 2. AFM topographical images of indented NiTi samples. The indentations can be observed as black triangles in the images. Control areas of NiTi sample before (A) and after (B) heating. Areas milled with the high energy FIB before (C) and after (D)

Regardless of the mechanism, the changes in surface topography of the milled areas upon transformation imply the existence of a certain degree of surface stress generated by the milling

process. Wafer curvature studies have shown that a significant compressive stress is generated in NiTi thin films by the annealing process [13]. As the films cool and transform from austenite to martensite, the films buckle to relieve this stress, thereby generating the large topographical excursions seen in the control sample of Figure 2. The changes in surface topography observed in the milled areas of Figure 2 upon transformation may be the result of surface stress generated by the milling process. The martensitic transformation may then relieve the stress by a buckling mechanism similar to the one described previously [13].

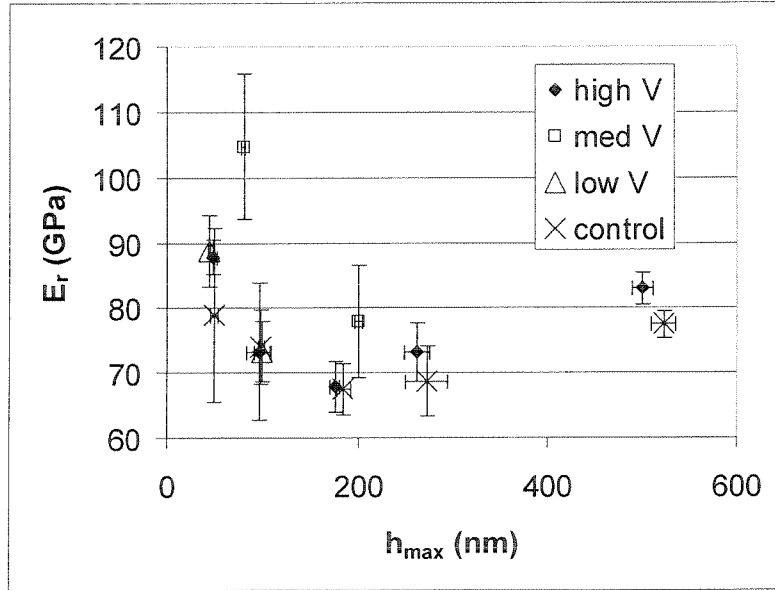


Figure 3. Young's modulus of NiTi thin film samples as determined by instrumented indentation for various FIB process conditions. Error bars denote one standard deviation of four measurements, and this statistical (type A) uncertainty is the only component of uncertainty included in this analysis.

Conclusion

The effects of FIB milling on NiTi shape-memory alloy thin films have been examined. The Young's modulus near the surface of the material is found to increase as a result of the milling process. In addition, the martensitic transformation is found to increase surface roughness qualitatively. This can be explained by the generation of a thin strained layer near the surface of the thin film during FIB milling.

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