

## Thermomechanical High-Density Data Storage in a Metallic Material Via the Shape-Memory Effect\*\*

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Information storage technology has undergone a revolution within the past 60 years. Information previously contained on a printed page now occupies  $\sim 100 \mu\text{m}^2$  of digital-media space. An entire small library can be stored on a commercially available magnetic hard disk and read in less than fifteen minutes by state-of-the-art small computer system interface devices. Recent advances have been propelled by innovations in giant magnetoresistance,<sup>[1]</sup> tribology,<sup>[2]</sup> and improvements to platen materials;<sup>[3]</sup> however, the magnetic storage paradigm is close to reaching a fundamental limit.

As the bit size decreases, so must the size of the platen's magnetic domains. Below a certain size threshold (around 100 atoms), the magnetic anisotropy energy of the domains becomes small enough that fluctuations in temperature are enough to change the magnetic moment of the domain, thereby randomizing the moments of the magnetic domains of the media, and erasing the data stored therein.<sup>[4]</sup> This phenomenon has become known as the superparamagnetic limit, and it restricts the maximum bit density in traditional planar magnetic information storage media to  $\sim 100 \text{ Gbit in.}^{-2}$  (i.e.,  $\sim 6500 \text{ nm}^2 \text{ bit}^{-1}$ ).<sup>[5]</sup>

Several clever techniques have been proposed to circumvent the superparamagnetic limit, including holography,<sup>[6]</sup> the use of higher coercivity materials, as in Seagate's heat-assisted magnetic recording technology, or the use of patterned media to isolate individual magnetic nanoparticles.<sup>[5]</sup> Concurrently,

a new paradigm is emerging in data storage technology. The new concept involves the mechanical manipulation of matter on the nanometer scale using sharp probe tips. The ultimate possibilities of this approach are well documented,<sup>[7]</sup> and a prototype device, known as the Millipede, has been developed by IBM.<sup>[8]</sup>

The Millipede is an array of individually addressable scanning probe tips (similar to the probe tips of atomic force microscopes) that makes precisely positioned indentations in a polymer thin film. The Millipede is scanned to address a large area for data storage. The indentations are bits of digital information, and write, read, erase, and re-write operations have been documented. The Millipede has also extended storage density into the  $\text{Tbit in.}^{-2}$  ( $\sim 650 \text{ nm}^2 \text{ bit}^{-1}$ ) range, and data-transfer rates into the range of up to a few  $\text{Mbit s}^{-1}$ .

In this paper, we examine the feasibility of using thin-film NiTi shape-memory alloys (SMAs) for thermomechanical data storage as an alternative to the polymer thin film used as the data storage medium in the IBM Millipede device.<sup>[8]</sup> NiTi is a potentially more robust and rapid storage medium than the polymer films currently used for thermomechanical data storage. For example, the poly(methyl methacrylate) (PMMA) medium documented by IBM is prone to charring at the temperatures necessary for device operation (around  $350^\circ\text{C}$ ).<sup>[9]</sup> At the shape-memory effect's normal operation temperature (around  $70^\circ\text{C}$ ), NiTi is largely impervious to normal environmental effects once its passive oxide layer has formed, and the shape recovery over millions of cycles has been documented.<sup>[10]</sup> In addition, its lower operating temperature requires less power for operation. SMAs do not require heating for the write operation to be carried out, as do the polymer films, and since SMAs have a much higher thermal conductivity and lower heat capacity than PMMA,<sup>[11]</sup> erase operations can be conducted more rapidly.

Our prior work,<sup>[12]</sup> and that of others,<sup>[13,14]</sup> has shown that nanometer-scale indentations in NiTi SMA thin films can recover substantially upon heating. In this study, we examine the effect of repeated thermomechanical cycling of indentations as well as the effect of indent proximity, both of which are critical for a device to carry out repeated write, read, and erase operations. We demonstrate a series of write, read, erase, and re-write operations for the thermomechanical data storage technique using a NiTi thin film as the storage medium. The data storage cycles are repeated several times and found to be robust within the range tested. In addition, the indents can be placed very close together, although a space roughly equal to the indent size must be allowed between adjacent bits.

The write–read–erase–re-write operations were carried out using a combined nanoindenter and atomic force microscope system, which allowed an indentation to be precisely located (bit spaces with minimal variations in topography were preferred). Information was then written into the medium mechanically, in the form of an indentation in the martensite-phase film's surface. The load was applied and held for 10 s before unloading (the write step). The indentation was then

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scanned using the nanoindenter tip (the read step) and heated in situ to initiate the shape-memory effect (the erase step). The indent would typically recover 30–60 % of the indent depth, and this was verified by rescanning the residual impression. Subsequent re-write steps followed the same sequence of events.

Figure 1 shows the indent depths before heating ( $D_{bh}$ ) and after heating ( $D_{ah}$ ) over the course of 7 write, read, and erase cycles for two different indenter geometries. Berkovich and cube-corner indenters were loaded to 150 and 80  $\mu\text{N}$ , respectively, at a rate of 15  $\mu\text{N s}^{-1}$ . The indent depth was measured from the deepest point of the indent to the vertex of the triangular residual impression, using a profiling feature of the Digital Instruments' atomic force microscopy (AFM) software.

In the case of the cube-corner indentations,  $D_{bh}$  and  $D_{ah}$  reached consistent values after about 3 indentation cycles, whereas the Berkovich indentations required approximately 6 write–read–erase cycles to reach a steady indent depth. Because it has a larger radius of curvature and included angle, the Berkovich tip exhibits a lower maximum strain for indentation depths comparable to those in the cube-corner indentation experiments.<sup>[15]</sup> Therefore, a larger fraction of the indent depth is recovered upon heating, despite the higher applied load.<sup>[13]</sup>

The gradual increase in indent depth during constant-load cycling may be evidence of the accumulation of plastic deformation in the solid. Dislocations, which stabilize the martensite phase nearby, are introduced under the tip during indentation.<sup>[11]</sup> This limits the amount of deformation that can be recovered by the shape-memory processes in the area nearest the indenter tip, as these stabilized martensites may fail to transform upon heating. Even after multiple write–read–erase cycles, however, the indents recovered a roughly constant fraction of their depth upon heating (i.e.,  $D_{bh} - D_{ah} \sim \text{constant}$ ). One could compensate for changes in  $D_{ah}$  in a memory device by performing a formatting step, in which each bit-

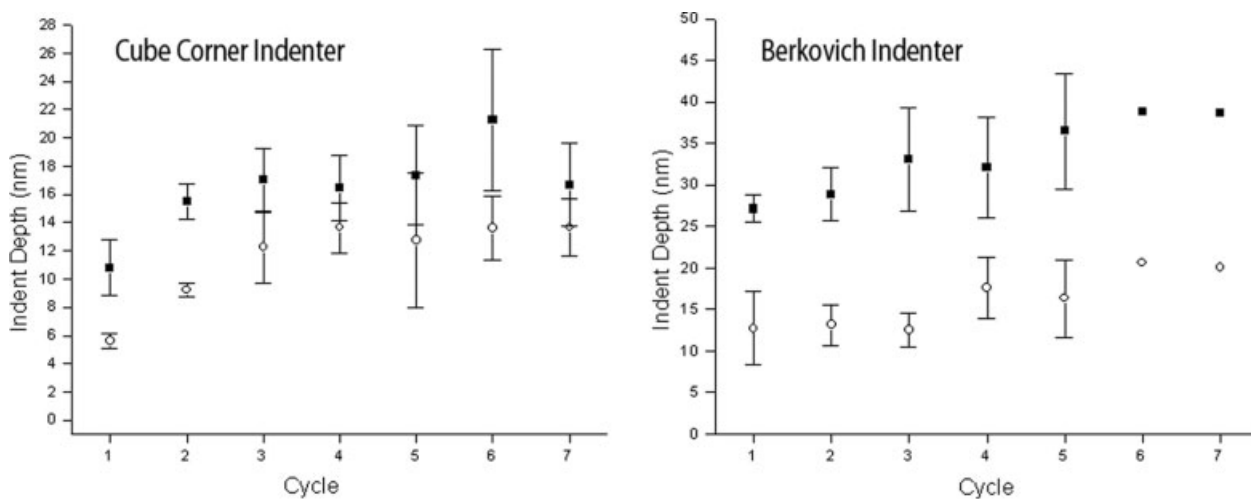
space is indented several times before being used for information storage.

This experiment demonstrates the feasibility of using shape-memory materials as media for rewritable mechanical data storage, with clear delineation between the indent depths before and after heating for the parameters tested.

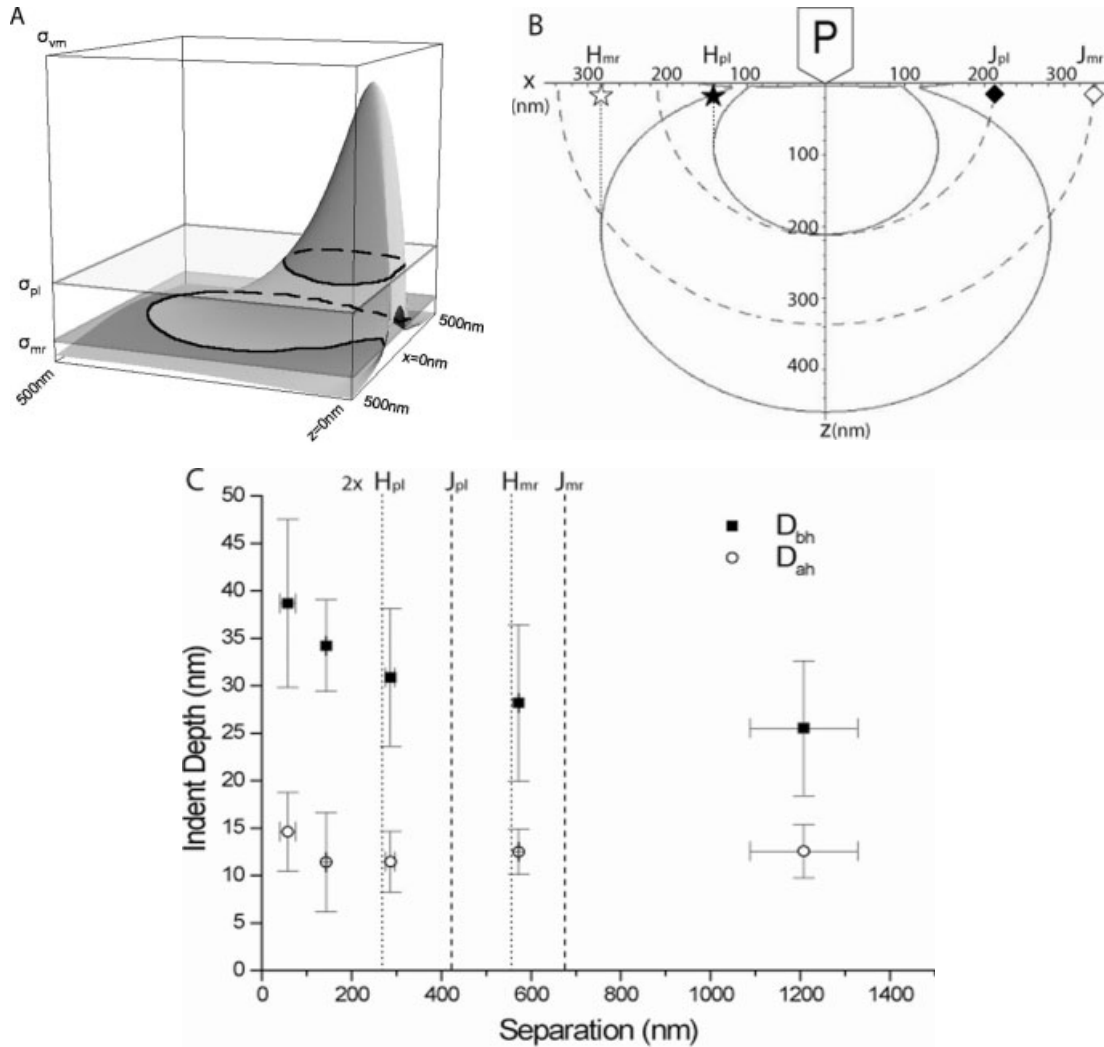
In order to determine the approximate maximum planar storage density of our medium, we have modeled the system using a Hertzian stress field<sup>[16]</sup> and the von Mises yield criterion. This approximate theoretical treatment models Hertzian loading of an isotropic elastic half space. It requires only a few input parameters: nanoindentation loading information (maximum load, indent depth, and indenter geometry), which was obtained experimentally, and the mechanical properties of NiTi (modulus, Poisson's ratio, twin rearrangement stress, and yield stress), which were taken from the literature.<sup>[10,17]</sup> The results are compared to an adaptation of Johnson's spherical-cavity model of elastic/plastic indentation.<sup>[12,18]</sup>

In martensitic NiTi, the deformation caused by an indenter can be accommodated by elastic deformation, martensitic twin rearrangement, or plastic flow. The region nearest to the indenter tip is subject to very high stresses, resulting in plastic deformation. Slightly farther from the tip, stresses decrease and are accommodated by martensitic twin rearrangements, which can be recovered upon heating. Still farther from the indenter tip, stresses are low enough that all deformation is elastically accommodated. The boundaries delineating the regions in which deformation proceeds by twin rearrangement and plastic flow can be calculated using the twin-rearrangement yield stress and the plastic yield stress in the models described below.

A constant von Mises stress surface for the three-dimensional Hertzian load is shown in Figure 2A. In this plot, the 135  $\mu\text{N}$  Hertzian load is applied at the origin, where  $z$  is perpendicular to the free surface. The critical twin-rearrangement stress,  $\sigma_{mr}$ , and plastic yield stress,  $\sigma_{pl}$ , of NiTi are indi-



**Figure 1.** Effect of repeated cycling on the shape-memory effect in nanoindentation of a NiTi thin film using cube-corner and Berkovich indenters. Closed squares represent  $D_{bh}$  and open circles represent  $D_{ah}$ . The final two data points lack error bars because only two trials were conducted.



**Figure 2.** Behavior of NiTi during cube-corner indentation to load  $P=135 \mu\text{N}$ , where  $\sigma_{mr}$  is the twin-rearrangement stress and  $\sigma_{pl}$  is the plastic yield stress. Results shown in (A) are for the constant von Mises stress surface below the indenter, calculated from the Hertzian model (load applied at  $x=z=0$  nm). Loci of points at the intersection of the constant  $\sigma_{vm}$  stress surface with  $\sigma_{mr} = 200$  MPa and  $\sigma_{pl} = 800$  MPa are shown in (B), where  $H_{mr}$  and  $H_{pl}$  are twin-rearrangement and plastic-yield boundaries, as predicted by the Hertzian model.  $J_{mr}$  and  $J_{pl}$  are twin-rearrangement and plastic-yield boundaries, as predicted by Johnson's model. Stars or diamonds are located at maximum lateral extents of affected zones for each boundary. The experimental results in (C) show the influence of indent separation on the shape-memory effect. The theoretical predictions of the Johnson and Hertzian models are indicated by vertical lines, denoting twice the value of the affected lateral extent for plastic and twin-rearrangement processes.

cated by the planes at 200 MPa and 800 MPa, respectively. The intersection of the constant von Mises stress surface with these planes is shown in Figure 2B.  $H_{mr}$  and  $H_{pl}$  represent the loci of points that meet, respectively, the martensitic twin-rearrangement and plastic yield stress of NiTi, as predicted by the Hertzian model. Given that this is an elasticity solution, stresses should not exceed the plastic-stress criterion. However, it has been shown that in the case of a mode I crack in an elastic/plastic material, elasticity theory provides a remarkably accurate approximation of the size and shape of the plastic zone of the crack tip.<sup>[19]</sup>  $J_{mr}$  and  $J_{pl}$  represent these martensitic twin-rearrangement and plasticity-zone boundaries in Johnson's model, respectively. Previous work has shown that

the spherical-cavity method can predict the approximate progression of the shape-memory zone during indentation, although the same work indicates that the plastic zone may be smaller than predicted at indentation depths less than 100 nm.<sup>[20]</sup> The size of the plastic zone estimated from the spherical-cavity model can therefore be viewed more as an upper limit.

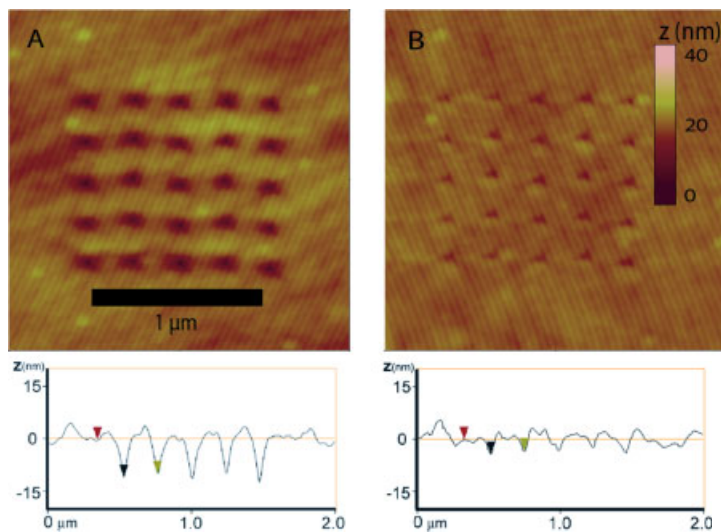
We have employed a continuum mechanics analysis for the entire range of indentation depths presented in this paper. This is clearly valid for the larger depths; we employ it also for the smaller depths as a first analysis of the problem, and with the justification that evidence for the validity of continuum mechanics down to extremely small size scales continues

to mount. Two examples of this evidence are the dislocation interaction studies of Liu et al.,<sup>[21]</sup> and the nanometer-scale fracture analyses of Starr, Drugan and co-workers.<sup>[22,23]</sup> Additionally, it is noted that reducing the three-dimensional nature of an SMA phase transformation to a threshold value of a composite von Mises stress is a significant simplification. However, it has been shown that this approach yields reasonably accurate predictions.<sup>[24–26]</sup>

For the case of a spherical indenter, the Hertzian model describes the indentation process more accurately than the spherical-cavity model. Whereas Johnson's yield surface extends as far laterally as it penetrates into the material (an artifact of disregarding the boundary condition of a traction-free surface), the Hertzian solution's yield surface is smaller in extent near the free surface. This solution is a more physical description of the yield surface.<sup>[27]</sup> A consequence of this affected zone shape is that the footprint of a single bit must be measured by the maximum lateral extent of the zone boundary, as shown in Figure 2B. However, since the indenters used behave as sharp indenters at large indent depths and as spherical indenters at shallow indent depths because of their blunt tips, it is important to consider both of the models mentioned above.

To place this theoretical modeling in the context of the experimental data, Figure 2C shows the effect of indent spacing on neighboring indents of different separation widths. The vertical lines mark the indent separations at which the twin-arrangement and plastic zones of the two indents would overlap for both the Johnson and Hertzian models. The upward trend at small indent separation widths indicates that the second indent is affected by the residual fields of the first indent at these small separation widths. As was the case in the cyclic indentations of Figure 1, the presence of dislocations in the stress field of the indenter increases residual indentation depth. It may be reasoned that an overlap of SMA twin-arrangement zones may not affect a neighboring indent due to the ability of the martensite to simply re-orient to the new favorable variant. However, overlapping plastic zones should significantly affect neighboring indents, because SMAs respond differently after being plastically deformed. Figure 2C shows that neighboring indents begin to affect each other at  $\sim 280$  nm, as expected from the lateral extent of the plastic zone predicted by the Hertzian model. At the applied load of  $135 \mu\text{N}$ , this bit footprint corresponds to a theoretical storage density of  $8 \text{ Gbit in.}^{-2}$  ( $\sim 81\,000 \text{ nm}^2 \text{ bit}^{-1}$ ).

A data array with a storage density of  $10 \text{ Gbit in.}^{-2}$  is demonstrated in Figure 3, where an array of five-by-five bits is written into the NiTi thin film using a cube-corner indenter loaded to  $73 \mu\text{N}$  and then erased by heating. Performing the same calculations as above, with an experimentally determined maximum indent depth of  $26 \text{ nm}$ ,  $H_{\text{pl}}$  and  $J_{\text{pl}}$  are  $104$  and  $79 \text{ nm}$ , respectively. Accordingly, these models predict a minimum indent separation of between  $208$  and  $158 \text{ nm}$



**Figure 3.** An indent data array A) before and B) after heating past the martensitic transformation temperature. Insets below images show profiles drawn through a row of indentations.

to avoid overlapping plastic zones. The array in Figure 3 has an indent spacing of roughly  $240 \text{ nm}$ , and recovers substantially upon heating. However, recovery was largely inhibited in an identical array with an indent spacing of  $140 \text{ nm}$ , in agreement with our models. Optimizing the indentation process may extend the storage density much further. Using the Johnson model to estimate the footprint of a probe tip with a  $10 \text{ nm}$  radius of curvature penetrating the surface to a depth of  $5 \text{ nm}$ , we find a plastic-zone radius of  $15 \text{ nm}$ , yielding a storage density of approximately  $0.5 \text{ Tbit in.}^{-2}$  ( $\sim 1300 \text{ nm}^2 \text{ bit}^{-1}$ ).

The major drawbacks of the system employed in this study are its slow speed, its inability to allow the erasure of individual bits, its strong dependence on film planarity, and the issue of tip wear. The nanoindentation/atomic force microscope apparatus used is designed for precision application of force and measurement of distance. As such, a single write–read–erase–write cycle takes approximately  $1 \text{ h}$ . Since the process is in the exploratory phase, the control of experimental variables is more important than speed. To be a viable commercial device, however, data-transfer rates would need to be increased to levels of several hundred megabits per second. This can be accomplished through the use of multiple read/write probes, as well as devices optimized for speed, such as the Millipede. Currently, the NiTi device requires a global erase step, in which the entire film is heated to initiate the martensitic transformation and shape-memory effect. A heated probe tip will be necessary to erase individual indentations. During annealing, the martensite thin films undergo buckling due to mismatch in the thermal expansion coefficients of the film and substrate.<sup>[28]</sup> As a result, some regions of the film have topographical excursions of  $100 \text{ nm}$  or more. A chemomechanical planarization processing step could serve to alleviate this problem, as could the judicious choice of processing condi-

tions during thin-film deposition. Although current microelectromechanical system processes can allow a root-mean-square roughness of 5.5 nm,<sup>[29]</sup> this has not yet been achieved for NiTi, and the ultimate storage density of the device depends on the maximization of film planarity. The tip wear will also become an issue, as scanning probes made of even the hardest materials eventually have their tips worn away through contact with a metal surface. This can be mitigated by the use of a friction-reducing coating.

The results presented here reveal a promising future for SMA thin films as media for computer data storage. Multiple write, read, erase, and re-write operations can be carried out on the same data bit using a mechanical probe to make an indentation, then removing the indentation by heating. The use of sharper probes than the relatively blunt diamond indenters used in this study could increase storage density beyond that of the preliminary small array demonstrated herein, although the problems associated with data-transfer rate, selective erasing of individual bits, film planarity, and tip wear must still be overcome. The two models presented showed good agreement with the experimental findings for the parameters tested and suggest that storage density could be increased to as much as  $\sim 0.5$  Tbit in.<sup>-2</sup> ( $\sim 1300$  nm<sup>2</sup> bit<sup>-1</sup>) well exceeding the 10 Gbit in.<sup>-2</sup> ( $\sim 65\,000$  nm<sup>2</sup> bit<sup>-1</sup>) storage density already demonstrated experimentally. Although this approach has not yet been optimized, the experimental evidence and theoretical predictions show SMA thin films are an appropriate medium for thermomechanical data storage. Shape-memory films may well provide a more robust and rapid new alternative for mechanical data storage than the polymer films currently used.

## Experimental

NiTi thin films were deposited at TiNi Alloy Co. in San Leandro, CA, using a direct-current magnetron sputtering technique [30]. The films were grown on an oxidized silicon substrate to a thickness of approximately 700 nm and annealed at 550 °C in vacuum.

Indentation experiments were performed on a combined Hysitron Triboscope Nanoindenter/Digital Instruments Multimode atomic force microscope. The combined nanoindenter/atomic force microscope allowed for indents to be precisely positioned. Topographical images were obtained in situ using the indenter tip as the probe. Both Berkovich and cube-corner indenters were used for the multiple write-read-erase experiments, and a cube-corner indenter was used for the experiments examining the effect of indent proximity and the demonstration of an indentation data array. It should be noted that the topographical data would have been subject to tip-broadening effects, as the indenter tips were relatively blunt (radius of curvature  $\sim 100$  nm); however, imaging with sharper standard atomic force microscope cantilever tips showed that the effect of tip broadening on the relevant data was within experimental error.

After indentations were made, the sample was heated in situ to initiate the shape-memory effect. The heater used was a Peltier cell from Melcor that was magnetically attached to the scanner tube of the microscope. The sample was then mounted onto a ferrous sample puck with thermally conductive epoxy, and magnetically attached to the heater. The maximum temperature, approximately 90 °C, was held for 5 min to ensure complete transformation.

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