

MICROSTRUCTURAL EVOLUTION AND THERMO-MECHANICAL RESPONSE OF Ni ION IRRADIATED TiNi SMA THIN FILMS

T. B. Lagrange, R. Gotthardt*

Swiss Federal Institute of Technology, Lausanne (EPFL), Faculty of Basic Sciences, Institute of Physics of Complex Matter, Lausanne, Switzerland

The present study focuses on the effect of 5 MeV Ni ion irradiation of plastically strained ($\epsilon \sim 4\%$) martensitic TiNi thin films, which is used as a processing technique for a novel out of plane bending actuator. Conceptually, the frustration of the martensitic transformation due to ion beam damage in a 2 μm surface layer of a 6 μm thick film will create a sharp differential latent strain on reverse transformation. This latent strain causes a two-way bending motion during cyclic heating and cooling, and in addition, this thermal actuator can be used to do useful mechanical work on both heating and cooling. To better understand the behaviour of these ion irradiated thin films, TEM observations and motion experiments were conducted. Results are presented and discussed as they relate to the ion induced microstructure and its influence on the martensitic transformation and the shape memory effect.

(Received October 7, 2002; accepted March 12, 2003)

Keywords: Thin film, TiNi, Thermo-mechanical response

1. Introduction

Shape memory alloys (SMA) are accompanied by a technically usable effect, the shape memory effect (SME). The shape memory effect (SME) arises from a special martensitic transformation which is a displacive, diffusionless phase transformation that is crystallographically reversible, due to a so called "self-accommodated twin structure" [1]. SMAs are able to recover large plastic strains, and large recovery stresses can be generated during reverse martensitic transformation. Many applications have been developed that use their remarkable mechanical properties, which range from medical devices to eyeglass frames. Because the present research focuses on microdevice and thin film technologies, there is a current interest to develop applications which use SMA thin films as active elements in micro-electro-mechanical systems (MEMS), requiring large force and displacement outputs [2]. In MEMS applications, where a cyclic motion is desired, the design of SMA actuators must provide for repeated deformation of the low temperature martensite phase upon cooling, which is subsequently recovered by heating to high temperature austenite phase. A bias spring can be employed to reset the actuator, but external biasing elements are awkward to implement in planar photolithographic micromachines. There is, thus, an interest in developing high performance shape memory materials in which the actuator and bias spring can be realized in a single thin film element, using simple planar processing.

The martensitic transformation in TiNi SMA is very sensitive to crystalline defects, such as dislocations and point defects (vacancies, interstitials, anti-site defects, etc.), and the martensitic phase transformation can be suppressed by high defect concentrations induced, for example, by cold rolling and irradiation damage [1, 3-6]. In most studies, the effects of irradiation damage have been studied in order to assess its hindrance on the martensitic transformation and SME. In general, TiNi was shown to be easily amorphized at low doses (less than 0.5 displacements per atom or dpa) [4, 5], and the martensitic start temperature was shown to be considerably reduced at doses corresponding to

* Corresponding author: Rolf.Gotthardt@epfl.ch

< 0.2 dpa [6]. In the experiment of Grummon and Gotthardt [3], $6\text{ }\mu\text{m}$ thick pre-deformed martensitic TiNi thin films were irradiated with 5 MeV Ni^{2+} ions in order to suppress the martensite $\rightarrow$ austenite transformation in the beam-damaged layer, whose thickness was chosen to be of the order of $1/3$ the film thickness. Thus, during heating to recover the austenite phase, only the unmodified martensite layer contracts, and the differential strain between the damaged and unmodified layer causes the film to curl out of plane, away from the irradiated face. On subsequent cooling, the beam-damaged layer can act as an elastic spring that stores some of the strain energy released during prior heating, which is then available to redeform the martensite. Fig. 1 shows schematically the SMA thin film motion after the above mentioned irradiation structural modification. Pronounced, reversible out-of-plane bending motions, were achieved and were shown to generate appreciable force levels. Various complexities in the observed strain-temperature response suggested that transformational behaviour was sensitive to irradiation conditions, such as dose and temperature. The present work has thus been directed toward a better understanding of the effect of irradiation on transformation temperature, microstructure, and defect distribution, and the relationship of these factors on thermomechanical response.

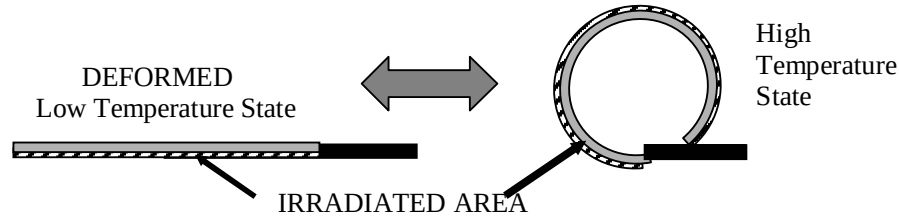


Fig. 1. Schematic of irradiated film motion.

2. Experimental procedures

The general experimental approach is outlined in Fig. 2. $6\text{ }\mu\text{m}$ thick binary TiNi thin films, with M_f above 300 K , R_s of 335 K , and A_s above 350 K , were fabricated as described in [3]. Free-standing martensitic films were cut into $3 \times 25\text{ mm}$ strips and deformed in uniaxial tension to a strain between $4\text{--}5\%$ using a micro-tensile machine. The deformed films were mounted to aluminium heat sink using conductive carbon cement and irradiated at $25\text{ }^\circ\text{C}$ with 5 MeV Ni^{2+} ions at four different total fluences, 1×10^{16} , 5×10^{15} , 1×10^{15} , 1×10^{14} , and $1 \times 10^{13}\text{ ions/cm}^2$, corresponding to 30 , 15 , 3 , 0.3 and 0.003 dpa , respectively. As irradiated films were mounted to a glass substrate in a precision temperature controlled furnace, and the motion of the films during thermal cycling was observed through an optical window using a stereomicroscope equipped with CCD camera. Images of the film shape were taken at intervals of $2.5\text{ }^\circ\text{C}$ during thermal cycling between 0 and $150\text{ }^\circ\text{C}$ with heating and cooling rates of $2\text{ }^\circ\text{C/min}$. The strain in the freestanding film was calculated as $\varepsilon = t/2\rho$, where ρ is the radius of curvature and t is the film thickness, and then plotted as function temperature. After the motion experiment, TEM cross-sectional samples were made by mechanical polishing and using a Gatan PIPS ion mill and observed in a Phillips CM20 and in a CM300 high resolution TEM, operating at 200 and 300 kV , respectively

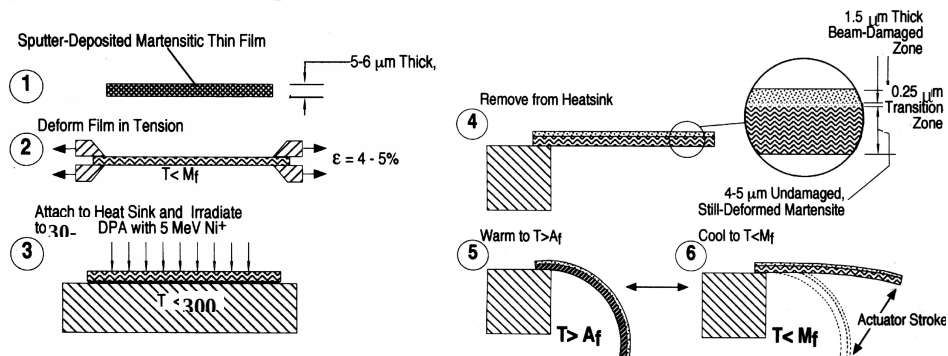


Fig. 2. Schematic of the ion implantation procedure.

3. Results

3.1 Motion experiments

Results on the motion experiments of the specimen irradiated to 1×10^{15} ions/cm² are shown in Fig. 3, and bending was observed to occur away from the irradiated face on heating. It responded to thermal cycling in a way qualitatively similar to that reported in [3], although here the curvatures were more uniformly circular and tighter. For the results shown in Fig. 3(a), the temperature was cycled between 0 and 100 °C. During the first cycle, the film curled to a strain of 0.2 %, but the film did not completely return to its original shape during reverse transformation, leaving approximately ~0.1 % unrecovered strain. However during the second cycle, the film showed a completely reversible shape change with a reversible strain of ~0.1%. When this film was heated to 150 °C, as shown in Figure 3(b), it curled more tightly to a strain of ~1.4%, but still failed to recover completely, leaving ~0.6 % unrecovered strain. During the fourth thermal cycle (0 ↔ 150 °C), the overall shape change during heating was lower (~0.6%), but 0.5% strain was recovered, leaving only 0.1% unrecovered strain. At higher fluences (5×10^{15} and 1×10^{16} ions/cm²), the response was same as those for films irradiated to doses of 1×10^{15} ions/cm², showing similar curvatures and reversible shape strain values. The dose of 1×10^{14} ions/cm² showed a smaller two-way reversible shape strain (~0.2 %). The lowest dose (1×10^{13} ions/cm²) showed a complex and unpredicted motion as shown in Fig. 4. At first and by heating to temperature of 100 °C, the film curled in an opposite sense towards the irradiated surface rather than the predicted curling out plane, away from the irradiation damage layer. With a continued heating to 150 °C, the film uncurled and bent in the direction away from the irradiated surface. During cooling and continued thermal cycling, there was no additional film motion, indicating that the irradiation induced defects and microstructure have acquired a thermally stable configuration.

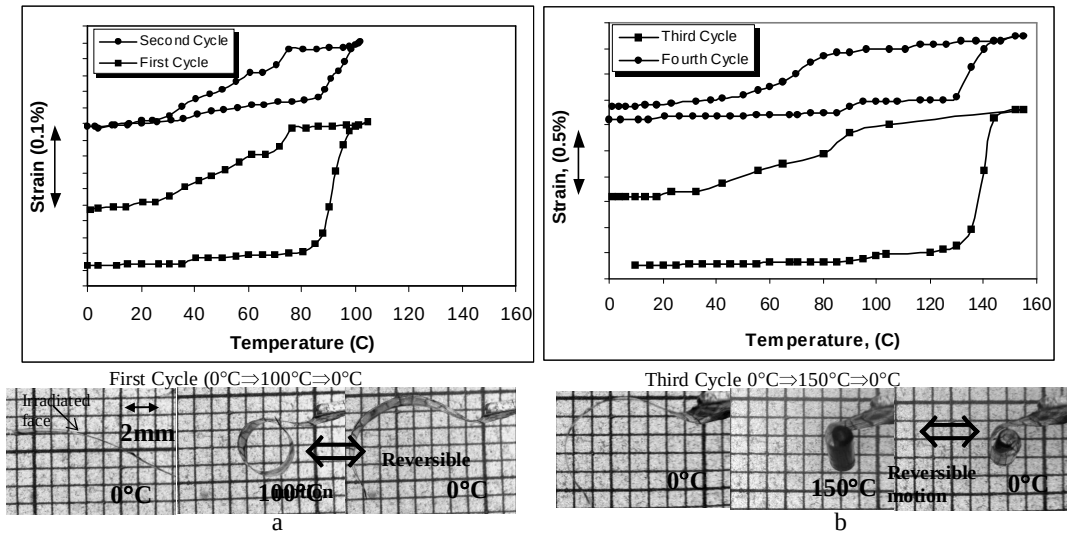


Fig. 3. a) Film curvature strain as a function of temperature a) thermally cycled through the martensite – R – phase transformation, b) thermally cycled through martensite - austenite phase transformation.

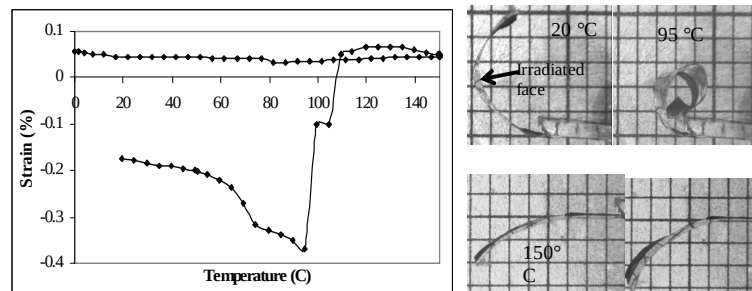


Fig. 4. Photographs and plot of 1×10^{13} ions/cm² irradiated film curvature strain as a function of temperature.

3.2 TEM observations

TEM images of the material irradiated to 1×10^{14} ions/cm² and 5×10^{15} ions/cm² are shown in Fig. 5. Fig. 5(a) shows amorphous material in the beam-damaged layer and a sharp interface between amorphous (damaged layer) and crystalline material (undamaged). The beam-damaged layer thickness of $1.75 \mu\text{m}$ is consistent with Monte Carlo transport simulations [8]. In the darkfield TEM images shown in Fig. 5(b), bright speckles, 1-5 nm in diameter, were observed in beam-damaged layer. The three dark-field images were taken using different segments of the diffuse amorphous ring in the electron diffraction pattern and show slight variations that indicate the diffuse ring is a combination of many smaller diffraction spots coming from spherical nanocrystalline structures and the diffuse scattering of the amorphous matrix.

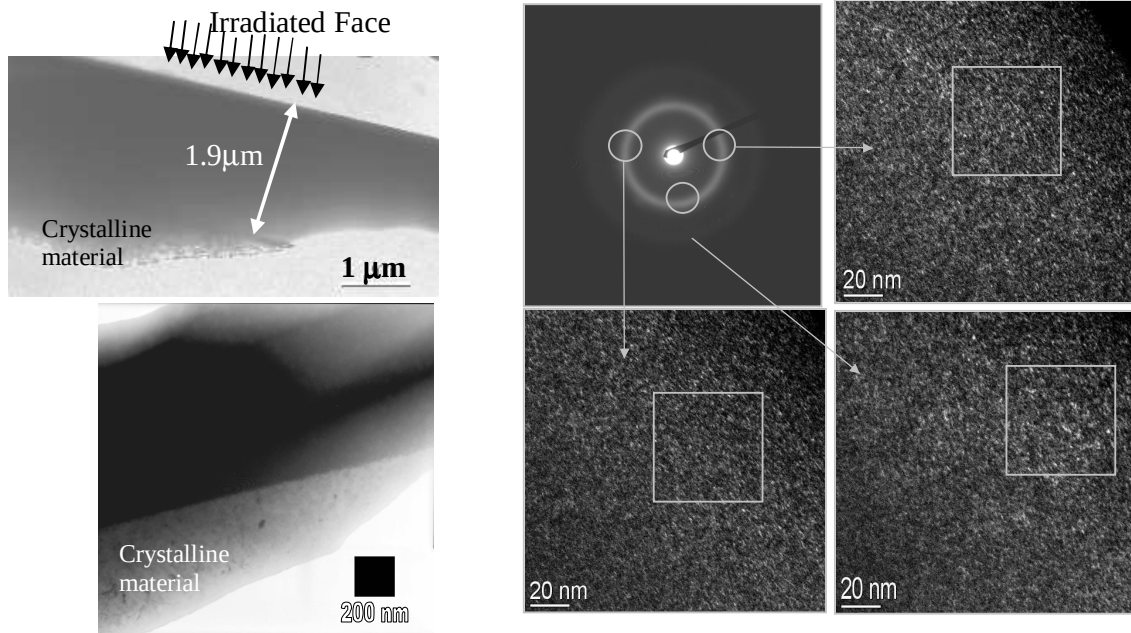


Fig. 5. a) Low magnification bright field TEM images of the implanted layer (1×10^{14} ions/cm²), b) dark field TEM images of irradiated zone showing bright speckle contrast associated to nanocrystals (5×10^{15} ions/cm²).

The high-resolution images in Fig. 6 show that the irradiation damage in $1 \times 10^{15} \text{ cm}^{-3}$ specimen consists of nanocrystals surrounded by an amorphous matrix. The Fourier transforms in the insets of Fig. 6 a) and b) taken from the marked (square box) regions indicate that these nanocrystals have a monoclinic (B19') and BCC crystal structure, respectively. The BCC crystals were found to have a lattice symmetry and constant similar to the high temperature austenitic phase (B2), while the monoclinic phase was found to be similar to the low temperature martensitic phase. The size of both types of crystals decreased with increasing dose; with a maximum size around 10 nm at 1×10^{14} ions/cm² and a minimum size of 1-2 nm for 1×10^{16} ions/cm². The lowest dose did not show any amorphous material, nanostructures, or common irradiation defects, like loops and voids, however the damage layer contained B2 austenite, which indicates a phase transformation occurred during irradiation.

4. Discussion

The first most pronounced result was the very uniform and sharply defined amorphous matrix seen in specimens irradiated to 1×10^{14} ions/cm² or more. This is unusual since the damage profile in ion irradiation has a very heterogeneous distribution with a sharp peak at the end of the ion range.

For the ion energy used in our experiments (5 MeV), most of cascade damage from nuclear stopping events should occur at a depth of 1.4 μm (as calculated from TRIM [8]).

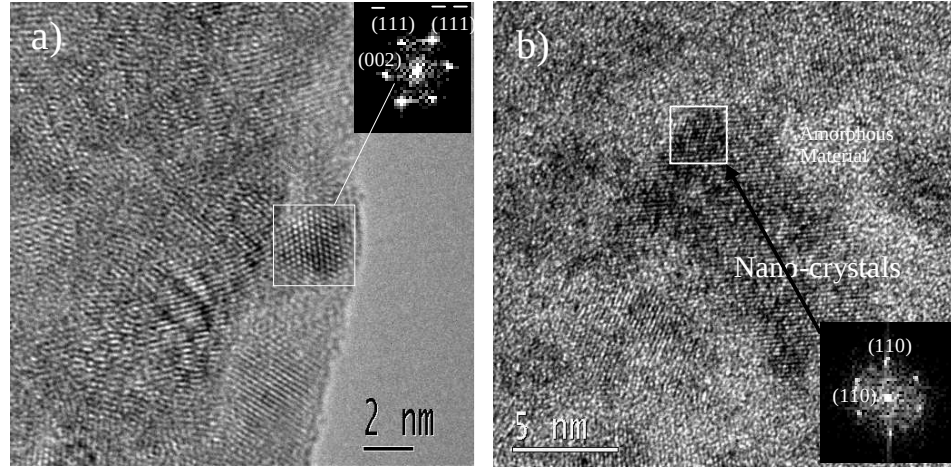


Fig. 6. a) High resolution TEM image of Irradiated Zone showing B19' nanocrystalline phase with a 110 zone axis in an amorphous matrix in the 1×10^{15} ions/cm², b) the same sample showing B2 nanocrystals with a 111 zone axis.

The experiments of Moine et al [5] and Brimhall et al. [4] showed that at room temperature overlapping cascades (from nuclear stopping) were necessary to amorphize TiNi at an average deposited energy density (in a cascade) of 0.01 eV/atom, which was much higher than our experimental value of 0.0015 eV/atom (all values were calculated from TRIM). In general, amorphization is easier at higher deposition energies, and it can occur either directly within a cascade or by cascade damage accumulation [7]. The sharp transition between amorphous damage layer and crystalline material and the lack of amorphous zones in the lowest dose specimen (1×10^{13} ions/cm²) verify that it is damage accumulation process since direct amorphous was not observed in the low dose. Thus, a threshold value to which damage accumulates must be achieved to raise the free energy enough to cause a crystalline to amorphous transformation. In contrary, near the irradiation surface, the cascade density from nuclear stopping is very low, and the damage accumulation is thus low, especially due to the annealing effects at room temperature, like point defect diffusion to large free surface sinks. Therefore, it is not expected that amorphization occurs in this area. Nevertheless, it was observed, and thus, it can be concluded that nuclear stopping is not solely responsible for the observed amorphization throughout the beam-damaged layer. It is not clear which irradiation mechanisms are responsible for the observed damage, however experiments are in progress to explore the role of electronic stopping in the damage production.

The second interesting result was the observation of nanocrystals in the amorphous matrix, even at the high doses (1×10^{16} ions/cm²). This was not observed in previous studies [4, 5], which found complete amorphization at doses of 0.1 dpa (lower than those used in this experiment) and asserted that the martensite did not transform to austenite before becoming amorphous. Further, these nanocrystals were observed to have two different structures, B19' and BCC. The BCC structures had lattice spacings that correspond to a dilated TiNi B2 austenite. We postulate that increased irradiation damage defect concentrations created at low doses (1×10^{13} ions/cm² or less) causes a phase transformation from the martensite to austenite. This austenite then becomes chemically disorder with continued irradiation to higher fluences until damage accumulates to a threshold value, causing a crystal to amorphous transition. However, it is unclear why these nanocrystals are stable, even at high doses and damage. In contrary to the above-mentioned mechanism, the existence of a monoclinic martensite phase would rather suppose that it is a direct amorphization mechanism which is responsible for the observed microstructure. Direct amorphization can occur within a cascade or in areas where cascades overlap. Therefore, it can be conceived that the martensitic regions between cascades or overlapped cascades areas will not amorphize and remain as crystalline islands in an

amorphous matrix. The complexities of ion irradiation and the observed microstructure from current experiments make it difficult to deconvolute and to determine the exact mechanism of transformation. However, it is most likely a combination of a damage accumulation and a direct amorphization by cascade overlapping process.

As previously observed [3], the films were observed to curl away from the irradiated face during heating as a result of shape-memory contraction in the undamaged crystalline material. However, the complete reversible motion of the film was not observed for the first deformation cycle. This is most likely related to plastic deformation of the beam-damaged layer, and to the fact that the beam-damaged layer must overcome the 'detwinning' flow stress of the martensite phase. The latter requirement may explain why full reversibility was not achieved even for the case of 0.2 % curvature strains in the low-dose experiment. It has been shown that after the first cycle, two-way motion can be stabilized for 0.1 % reversed strain. The fact that reversibility was incomplete for continued cycling at higher temperatures (150 °C) suggests that the higher strains are plastically deforming the beam-damaged layer. The nanocrystals may play an important role in the deformation characteristics of the irradiated layer, which may limit the elastic strength of the layer. This can be confirmed by the results in the low dose (1×10^{14} ions/cm²) specimen, which was associated with larger nanocrystal size and lower volume fraction and showed lower reversible strains. The lowest dose did not have a reversible motion and did not have amorphous material. Although, the motion results have shown clearly that the irradiation had an effect on microstructure. The TEM results only showed a transformation to austenite in the layer, and smaller defects like loops and voids were not observed. This defect structure acquired a stable orientation after the first heating that relaxed the stressed layer, eliminating the reversible motion of film. Thus, if reversible motion is desired, the irradiation dose at room temperature must be equal to or higher than 1×10^{14} ions/cm².

5. Conclusions

The observations of the sharply defined continuous amorphous matrix that contains monoclinic and BCC nanocrystals are very interesting and have not been reported in other investigations. The most likely mechanism for amorphization is a combination of cascade overlapping and damage accumulation from both nuclear and electron stopping, but the kinetics and the specific mechanisms of irradiations are at present unclear. Lastly, the plastic deformation in the implanted layer, due to the presence of nanocrystals that reduce its elastic strength, limits the full two-way shape recovery of the film.

Acknowledgements

The authors are grateful to the Swiss National Science Foundations for funding this project. We additionally thank the personnel at the Center Interdepartmental Electron Microscopy (CIME) at EPFL, Jinping Zhang for preparation of the thin films used in this study, and Dr. Christian Abromeit for his many fruitful discussions on this subject.

References

- [1] T. W. Duerig, K. N. Melton, D. Stockel, C. M. Wayman, *Engineering Aspects of Shape Memory Alloys*, Butterworth-Heinemann: London 1990.
- [2] R. H. Wolf, A. H. Huer, *J. Microelectromech. Syst.* **4**, 1057 (1995).
- [3] D. S. Grummon, R. Gotthardt, *Acta. Mater.* **48**, 635-46 (2000).
- [4] J. Brimhall, H. Kissinger, A. Pelton, *Radiat. Eff.* **90**, 241 (1985).
- [5] P. Moine, C. Jaoen, *J. Alloys Compounds* **194**, 373-80 (1993).
- [6] F. Goldberg, E. Knystuatas, *Thin Solid Films* **342**, 67-73 (1999).
- [7] A. T. Motta, *J. Nucl. Mater.* **244**, 277-50 (1997).
- [8] J. P. Biersack, L. G. Haggmark, *Nucl. Instr. and Meth.* **182/183**, 199 (1981).