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In-situ Studies of the Martensitic Transformation in Ti Thin Films using the Dynamic Transmission Microscope (DTEM)

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ABSTRACT

The α to β transition in pure Ti occurs mainly by a 'martensitic type' phase transformation. In such transformations, growth rates and interface velocities tend to be very large, on the order of 10^3 m/s, making it difficult to observe the transformation experimentally. With thin films, it becomes even more difficult to observe, since the large surface augments the nucleation and transformation rates to levels that require nanosecond temporal resolution for experimental observations. The elucidation of the transformational mechanisms in these materials yearns for an apparatus that has both high spatial and temporal resolution. We have constructed such an instrument at LLNL (the dynamical transmission electron microscope or DTEM) that combines pulsed lasers systems and optical pump-probe techniques with a conventional TEM. We have used the DTEM to observe the transient events of the α-β transformation in nanocrystalline Ti films via single shot diffraction patterns with 1.5 ns resolution. With pulsed, nanosecond laser irradiation (pump laser), the films were heated at an extreme rate of 10^{10} K/s. was observed At 500 ns after the initial pump laser hit, the HCP, alpha phase was almost completely transformed to the BCC, beta phase. Post-mortem investigations of the laser treated films revealed that substantial grain growth occurred and lath microstructure, containing no apparent dislocations. The lack of dislocations may indicate that the α to β transformation may also proceed by a 'massive' type mechanism (short range diffusion).

INTRODUCTION

Martensitic transformations have been studied for over a century [1], and current understanding of these rapid transformations is still limited to phenomenological models based on postmortem observations of crystallographic relationships between the parent and product phases [2,3]. These limitations stem from the inability to directly observe the transformation due to the inherent rapid growth rates and interface velocities that can be on the order of 10^3 m/s. In spite of this, some kinetic models have been developed for alloy systems that exhibit time-dependent growth (isothermal) and have slow nucleation and growth rates [1]. The development of more sophisticated models that extend to other kinetic modes of the martensitic transformation, such as athermal modes, necessitates a technique that has both high spatial and temporal resolution. One such instrument has been constructed at LLNL, the dynamic transmission electron microscope or DTEM[1], and provides a means to observe the dynamics of rapid material processes, such as the martensitic transformation.

The high temporal resolution in DTEM is accomplished by using shot, intense packets of electrons to illuminate the specimen. The electron pulses are generated via photoemission by the

[1] It should be noted that the first DTEM was pioneered at Technische Universität Berlin, and a detailed summary of the instrument is provided in reference [4].

irradiation of a photocathode with nanosecond UV laser pulses. Due to the physical limitations in generated photoelectron currents and resulting low signals, every electron should be collected, and thus, a key element in the DTEM is the implementation of a single-electron sensitive CCD. Typical time resolved experiments involve pumping a TEM specimen with short laser pulse to induce transient heating or high pressure states and probing these transient states with a synchronized photo-electron pulse (see schematic in figure 1.). Since this technique is coupled to standard TEM column, data can be collected in the form of images or diffraction patterns. Furthermore, different delays can be set between the pump and probe pulses, and the entire evolution of the material process can be delineated, which makes the DTEM so attractive for studying rapid phase transformations, such $\alpha \rightarrow \beta$ transition in Ti.

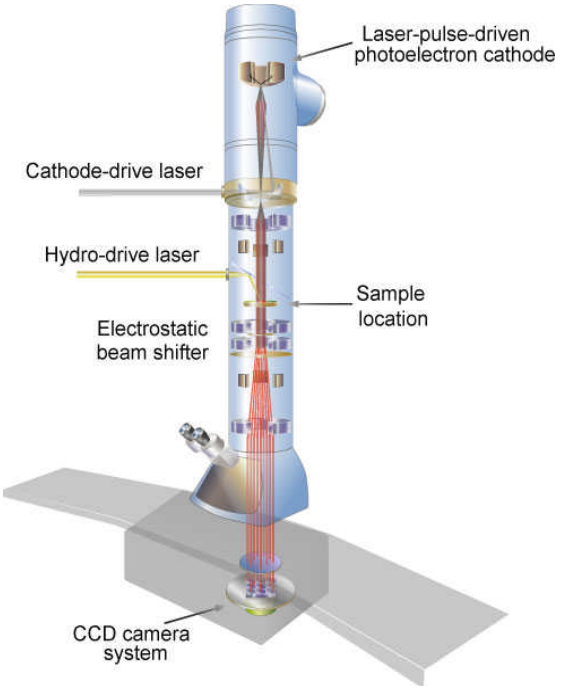

Figure 1. Schematic of LLNL DTEM

Upon heating above the characteristic martensitic start temperature of 1155 K, Ti transforms from the HCP, α-phase to the BCC coordinated, β-phase that is stable up to the melting temperature (1936 K). The board temperature range for which the α and β phases are stable make Ti an appropriate choice for the DTEM based experiments. Moreover, the transformation is speculated to be rapid in nanocrystalline thin films, like those used in this study, due to high number heterogeneous nucleation sites per volume. Using single-shot diffraction with nanosecond time resolution, preliminary investigations of the transformation were conducted. These results will be discussed in conjunction with post-mortem microstructure investigations of the laser treated Ti films.

MATERIALS AND METHODS

Pure Ti thin films with a 40 nm thickness were fabricated by a sputter-deposition onto NaCl single crystalline substrates heated to 573 K. As-deposited films were sectioned into 2x2 mm squares by cleaving the crystal along (100) planes of the NaCl crystal. These sections were placed into distilled water to release the film from the salt substrate, and these free-standing films were then floated onto 150 mesh copper TEM grids. The Ti films were nanocrystalline, with grain sizes between 50-100nm and were highly textured (See figure 2a). Electron diffraction simulation of the HCP structure (figure 2b) indicated that the grains were preferentially oriented to [10-11] zone axis and had two in-plane orientation variants rotated 90° with respects to each other about the foil normal.

In-situ observations of the phase transformation were performed on DTEM shown in figure 1, and table I lists the respective parameters of laser systems and generated photo-electron pulses. The present capabilities of the DTEM limits data acquisition to the diffraction mode, since the number electron per pulse (10^7) is too low to produce interpretable (low noise) single shot

images [2]. Therefore, the transformation kinetics were only studied by a series of electron diffraction patterns acquired at different delays between the pump laser and electron probe pulse. At present, only one single shot diffraction pattern can be acquired for one pump laser heating pulse. However, since the $\alpha \rightarrow \beta$ transition is reversible with temperature, the evolution of the transformation can be studied by repeated laser shots of the same region.

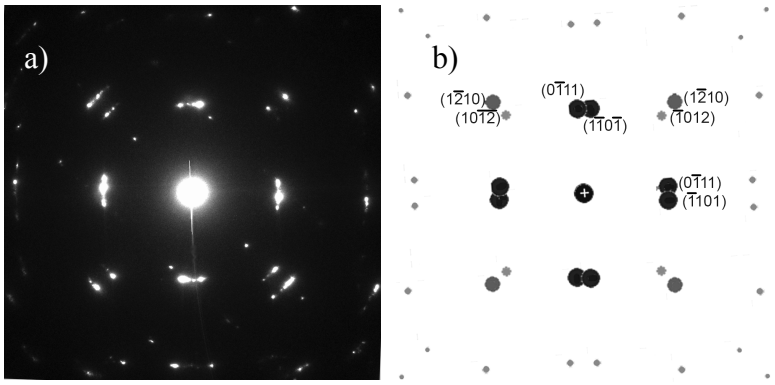

Figure 2. a) Experimental electron diffraction pattern, b) Two simulated [10-11] Z.A. electron diffraction patterns rotated 90° degree with respects to each other. The simulation was computed using JEMS© software package.

Table I. Laser and electron pulse parameters

	Pulse Energy Range	Wavelength (nm)	Pulse Duration FWHM (ns)	Spot Size FWHM(μm)
Photo cathode laser	10 nJ-1mJ	213	3	10^3
Specimen treatment laser	10 nJ-300mJ	1064	70	70 x 110*
Electron pulse	$10^7 e^-$ per pulse	0.00251	1.5	4**

* Since the incident beam is 35° to the specimen normal, the projected beam is elliptical.
** The table indicates the smallest possible electron illumination diameter, using the lowest C1 lens excitation setting that used for optimized collection and total charge per pulse. C1 setting was not varied in the experiments.

RESULTS

Before presenting time-resolved patterns, it is useful to first show the effects of laser irradiation on the nanocrystalline Ti microstructure. Post-mortem TEM observation of laser-treated films revealed that the film underwent substantial grain growth and morphological changes. The comparison of figure 4 a and b clearly show the dramatic

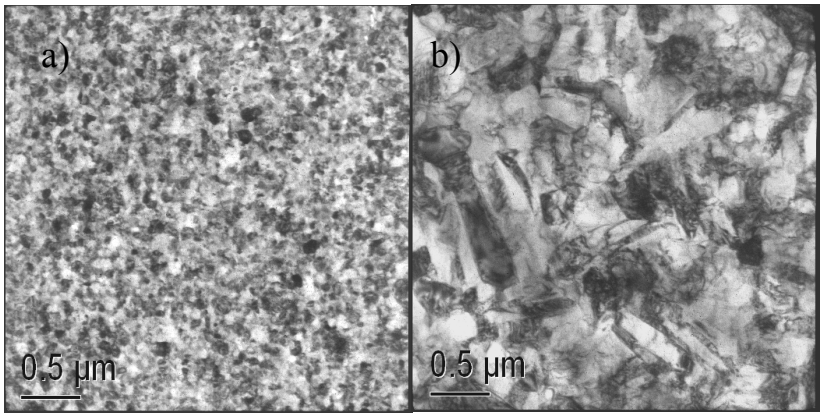

Figure 4. a) As-deposited Ti film microstructure, b) After laser treatment

[2] Single-shot imaging requires 10^6-10^8 electrons per pulses, and the image quality depend on the contrast formation mechanism and desired observation. In the present study, it is estimated that $5x10^7$ e/pulse are needed for appropriate imaging.

increase in grain size.

Interestingly, the laser treated films exhibit two main grain morphologies, small 'disk shaped' grains and large laths, where the disk shaped grains straddle the 'packets' of laths. Another notable feature is the lack of dislocations in the post-treated lath microstructure, which are commonly observed in bulk materials [1,5], but may not exist in film cycled with extreme heating and cooling rates. The predicted heating rates (10^{10} K/s) are remarkably high, 7 orders of magnitude higher than previous studies in bulk (millimeter thick) Ti materials [6].

Figure 5a shows a typical single-shot diffraction pattern for a textured, nanocrystalline Ti film. The pattern is similar to conventional TEM SADP shown in figure 2a, although the spots are slightly broader, since the selected area is much larger and the electron beam was converged. Large selected areas and a converged beam are used to increase the signal, but at the expense of resolution. Figure 5b shows the time-resolved diffraction pattern of the crystal structure 500 ns after 15 μJ laser pulse hit foil. The concentric rings overlaid on diffraction pattern show that the crystal structure was primarily BCC. The change in crystal structure is especially notable by the appearance of the new diffraction spots, as indicated by the white arrow in figure 5b. A clearer depiction of the change in phase was preformed by taking the difference pattern (figure 6a) of the two diffraction patterns in figure 5, and plotting the radial averaged intensity with reciprocal lattice units (d-spacing). The peaks present in figure 6b show that it is indeed BCC. There was approximately 75 ± 5% BCC, β-phase present in figure 5b, which was calculated first by fitting the peaks in figure 6b with a Lorentzian profile function and determining their integrated intensities that were then compared with the integrated intensities of difference pattern containing only HCP reflections (figure 5b–figure 6a). Figure 7a shows the single-shot diffraction of same region after the material has cooled to room temperature (which takes less than a millisecond). The

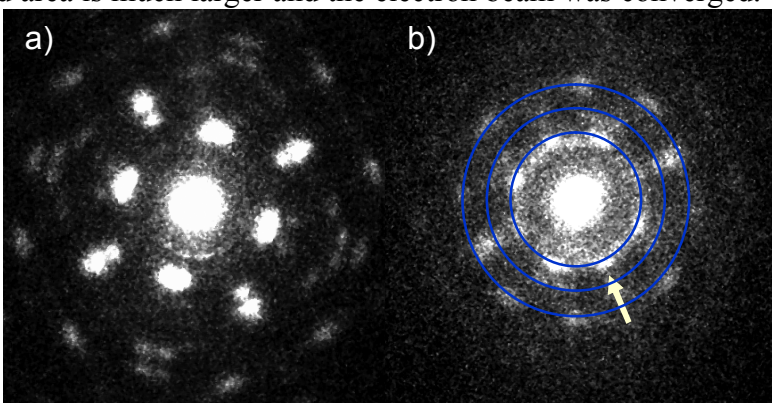

Figure 5. Single shot diffraction patterns recorded with 1.5 ns time resolution, a) HCP structure acquired at room temperature before laser treatment, b) Indexed as BCC structure and was acquired 500 ns after the 12 μJ pump laser pulse. Arrow indicates the appearance of new spots that did not exist in HCP pattern.

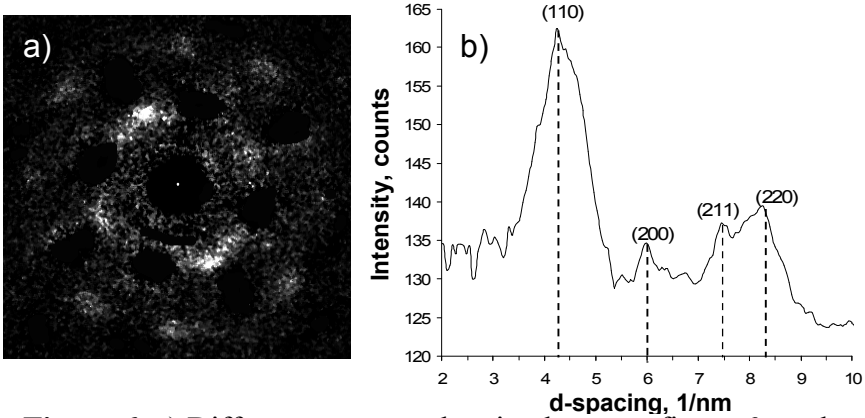

Figure 6. a) Difference pattern showing between figure 6a and b, showing residual BCC reflections, b) Radial intensity verse d-spacing for the rotational averaged pattern in figure 7a.

diffraction spots in this image are sharper, which indicates grain coarsening as observed in figure 4. The pattern also exhibits spots that are not present before laser heating, and some that appear to emanate from the prior β-phase texture. The laser energy was increased to 30 μJ, and the region was hit with a second laser pulse that was sufficient to induce melting at 100 ns after impact (apparent form the diffuse ring in figure 7b). This study was useful since it offers a calibration and means to validate the simulations in figure 5.

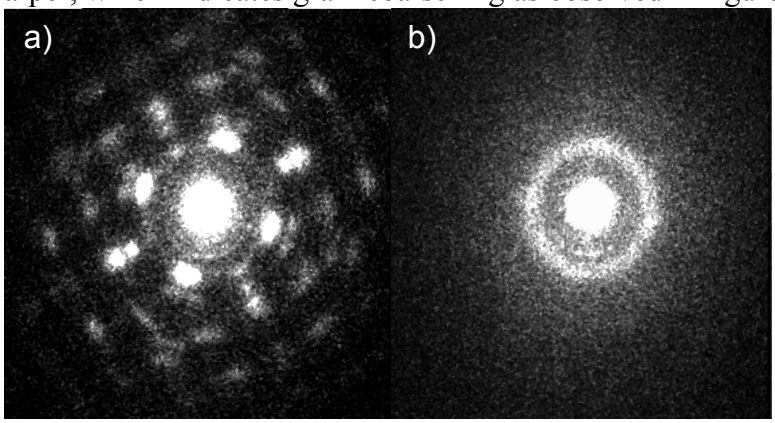

Figure 7. Single shot diffraction patterns recorded with 1.5 ns time resolution, a) acquired at room temperature after laser treatment, HCP structure as indexed in figure 2. The diffraction pattern in b) was acquired 100 ns after a 30 μJ pump laser pulse, which was sufficient to induce melting.

DISCUSSION

It first should be noted that the phenomenal grain growth observed in the post-mortem TEM studies occurs at time scales less than a millisecond. The extensive grain growth most likely occurs in the β phase, where films are expected to be at high temperature (~1200 K) for extended times (>5μs) [7]. However, the appearance of the smaller disk shaped grains my indicated recrystallization in α phase as well.

The additional spots observed in figure 8 are linked with the formation of laths and randomization of the microstructure. Randomization of the microstructure expected since 12 hexagonal variants can form for each BCC crystal variants and the texture of prior structure partially lost due to the nucleation and growth of different HCP variants. The lack of dislocation in the lath microstructure is intriguing. The nucleation of dislocations typically accompanies martensitic transformations and acts to relieve the stress caused by the nucleating martensite variant (strain energy minimization). However, the extremely high heating and cooling rates in the experiment may inhibit the slower dislocation nucleation processes. It is also possible that dislocation formation may not be necessary due to large free surfaces that relieve the excess strain energy.

The second possible is that laths form from an incoherent nucleation and growth mechanism, requiring diffusion, such a massive transformation, which would also explain the randomization of the microstructure. In the absence of impurities, like Fe that inhibit diffusion, pure Ti can undergo a massive type transformation at fast cooling rates. A further argument is that high concentrations (>1 at.%) of oxygen, which is an alpha stabilizer, can favor a massive type transformation mode, which may exist in nanocrystalline films. However, this requires more investigation. Observing the interfaces through single-shot imaging during transformation would certainly divulge mechanism.

CONCLUSIONS

The HCP alpha Ti film were transformed rapidly to BCC phase using 80 ns, 1064 nm, 15 μJ laser pulses. Ex-situ examinations showed extreme grain growth after only one laser hit and in

time scales on the order of microseconds. The lack dislocation in the lath microstructure is not clear, and more experiments using single-shot time resolved imaging are needed to further illuminate the transformation mechanisms in Ti thin films. Clearly, the preliminary results show the capabilities of the LLNL DTEM for time resolved diffraction based experiments. Future studies in the DTEM will unveil fundamental materials science processes on time and length scales not previously accessible by other techniques.

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