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T. LaGrange, G. H. Campbell, J. D. Colvin, B.  
Reed, W. E. King

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# Nanosecond Time Resolved Electron Diffraction Studies of the $\alpha \rightarrow \beta$ Transition in Pure Ti Thin Films using the Dynamic Transmission Electron Microscope (DTEM)

Thomas LaGrange, Geoffrey H. Campbell, Jeffrey D. Colvin, Bryan Reed and Wayne E. King  
University of California, Lawrence Livermore National Laboratory, Livermore, CA 94550

## ABSTRACT

The transient events of the  $\alpha$ - $\beta$  martensitic transformation in nanocrystalline Ti films were explored via single shot electron diffraction patterns with 1.5 ns temporal resolution. The diffraction patterns were acquired with a newly constructed dynamic transmission electron microscope (DTEM), which combines nanosecond pulsed laser systems and pump-probe techniques with a conventional TEM. With the DTEM, the transient events of fundamental material processes, that are far too fast to be studied by conventional bulk techniques, can be captured in the form of electron diffraction patterns or images with nanosecond temporal resolution. The transient phenomena of the martensitic transformations in nanocrystalline Ti is ideally suited for study in the DTEM, with their rapid nucleation, characteristic interface velocities  $\sim 1$  km/s, and significant irreversible microstructural changes. Free-standing 40-nm-thick Ti films were laser-heated at a rate of  $\sim 10^{10}$  K/s to a temperature above the 1155 K transition point, then probed at various time intervals with a 1.5-ns-long, intense electron pulse. Diffraction patterns show an almost complete transition to the  $\beta$  phase within 500 ns. Post-mortem analysis (after the sample is allowed to cool) shows a reversion to the  $\alpha$  phase coupled with substantial grain growth, lath formation, and texture modification. The cooled material also shows a complete lack of apparent dislocations, suggesting the possible importance of a "massive" short-range diffusion transformation mechanism.

## INTRODUCTION

Martensitic transformations have been studied for over a century, 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 [1]. 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 high temporal resolution. One such instrument has been constructed at Lawrence Livermore National Laboratory (LLNL), the dynamic transmission electron microscope or DTEM. This provides a means to observe the dynamics of rapid material processes such as the martensitic transformation.

The LLNL DTEM is a next-generation version of instruments developed at Technische Universität Berlin [2], but with better time resolution, and improved electron optics. The high temporal resolution in DTEM is accomplished by using short, intense packets of electrons to illuminate the specimen. The electron pulses are generated via photoemission by irradiating a photocathode with nanosecond UV laser pulses. Each packet contains  $\sim 10^7$  electrons, sufficient to produce a good-quality diffraction pattern with a single shot from a small region ( $\sim 5$   $\mu\text{m}$  in

diameter). The related technique of ultrafast electron diffraction (UED) has typically had to average a large number of shots (with  $\sim 10^5$  electrons each) over an area  $\sim 100 \mu\text{m}$  in diameter [3]. The DTEM thus has an advantage both in spatial resolution and in the study of processes that cannot be driven reversibly.

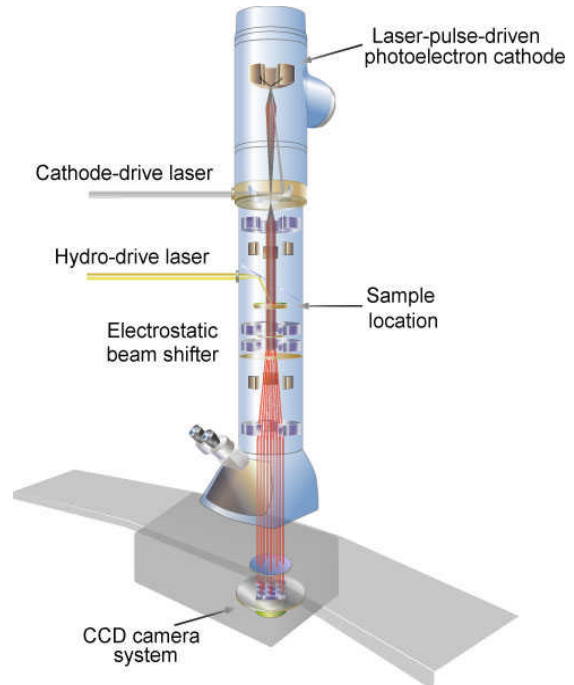
Typical DTEM time resolved experiments involve pumping a TEM specimen with a short laser pulse to induce transient heating or high pressure states and probing these transient states with a synchronized photo-electron pulse (figure 1). Since this technique is coupled to a standard TEM column, data can 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 attractive for studying rapid phase transformations such as the  $\alpha \rightarrow \beta$  transition in Ti.

Upon heating above the characteristic martensitic start temperature of 1155 K, Ti transforms from the HCP,  $\alpha$ -phase to the BCC coordinated,  $\beta$ -phase that is stable up to the melting temperature (1936 K). The broad temperature ranges for which the  $\alpha$  and  $\beta$  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 the high number of 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

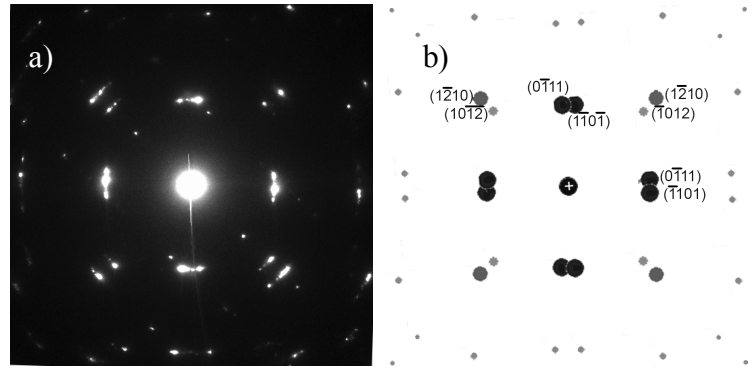
Pure Ti thin films with a 40 nm thickness were fabricated by sputter-deposition onto NaCl single crystalline substrates heated to 573 K. As-deposited films were sectioned into 2 mm x 2 mm squares by cleaving the crystal along (100) planes of the NaCl crystal. These sections were placed into distilled water to release the film from the salt substrate, and the resulting free-standing films were then floated onto 150 mesh copper TEM grids. The Ti films were nanocrystalline with grain sizes ranging from 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 the  $[10\bar{1}1]$  zone axis and had two in-plane orientation variants rotated  $90^\circ$  with respect to each other about the foil normal.

In-situ observations of the phase transformation were performed in the DTEM. Table I lists the respective parameters of laser systems and photo-electron pulses. The present capabilities of the DTEM limit data acquisition to the diffraction mode, since the number of electrons per pulse



**Figure 1.** Schematic of LLNL DTEM

( $10^7$ ) is too low to produce interpretable (low noise) single shot images<sup>1</sup>. 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 pulses. At present, only one single shot diffraction pattern can be acquired for each pump laser heating pulse. Thus, for consistency, a new region was studied for pump-probe experiment and the results compared. This was applicable since films used in this study had uniform thickness and homogenous microstructure.



**Figure 2.** a) Static experimental electron diffraction pattern, b) Two simulated  $[10\bar{1}1]$  Z.A. electron diffraction patterns rotated  $90^\circ$  degree with respects to each other. The simulation was computed using JEMS<sup>®</sup>.

**Table I.** Laser and electron pulse parameters

	Pulse Energy Range	Wavelength (nm)	Pulse Duration FWHM (ns)	Spot Size FWHM( $\mu\text{m}$ )
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  $35^\circ$  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 (which optimized the total charge per pulse). The C1 setting was not varied in the experiments.

## RESULTS

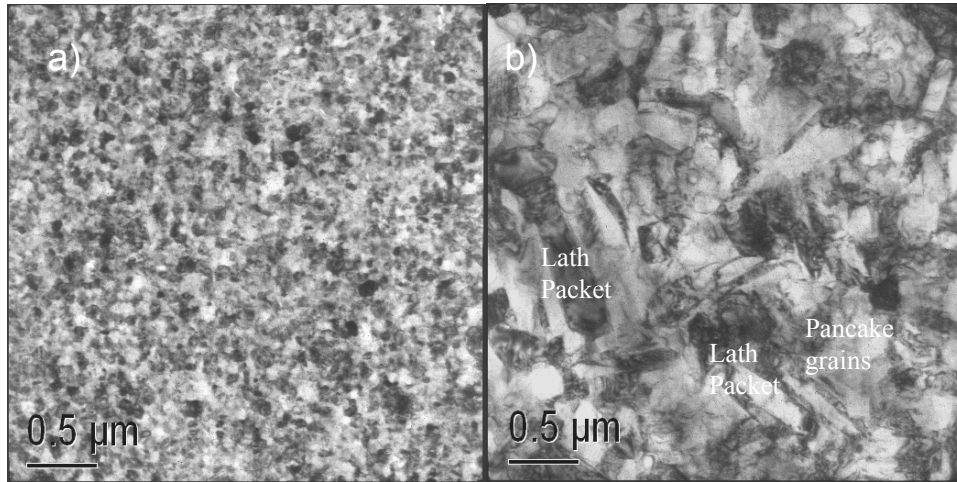
Before presenting time-resolved patterns, it is useful to first show the effects of laser irradiation on the nanocrystalline Ti microstructure. Post-mortem TEM observation of laser-treated films revealed that the film underwent substantial grain growth and morphological changes. The comparison of figures 3a and 3b clearly shows the dramatic increase in grain size.

Interestingly, the laser treated films exhibit two main grain morphologies, small ‘pancake’ grains and large laths, where the pancake 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 [1,4,5], but may not exist in film cycled with extreme heating and cooling rates. To estimate the heating rates in 40 nm thick films, heating curves were calculated using a 1-D lagrangian hydrodynamics simulation<sup>2</sup> and pump laser parameters listed in table I for two different laser energies, 21  $\mu\text{J}$  and 56  $\mu\text{J}$ . The predicted heating rates ( $10^{10}$  K/s and  $2.4 \times 10^{10}$

<sup>1</sup> Single-shot imaging requires  $10^6$ - $10^8$  detected electrons per pulse, depending on the contrast formation mechanism and desired observation. In the present study, it is estimated that  $5 \times 10^7$  e/pulse are needed for appropriate imaging.

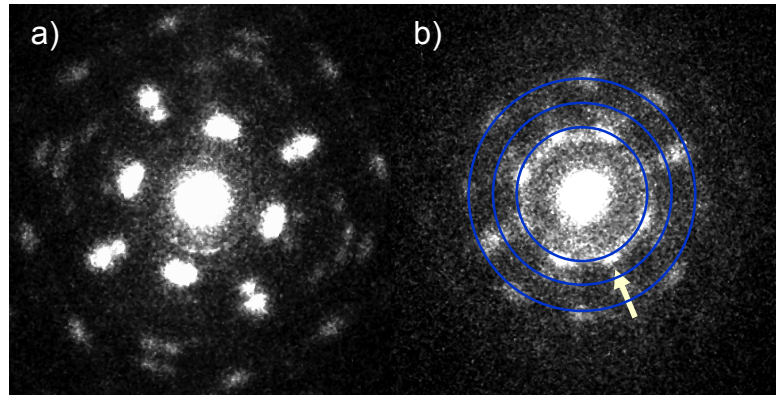
<sup>2</sup> The 1-D approach was used to reduce computing time and was assumed valid based on the argument that electron probe size is much smaller than incident laser spot size.

K/s, respectively) are remarkably high compared to traditional bulk studies (by 7 orders of magnitude [6]) but are easily accessed in the case of thin-film short-pulse-laser experiments.



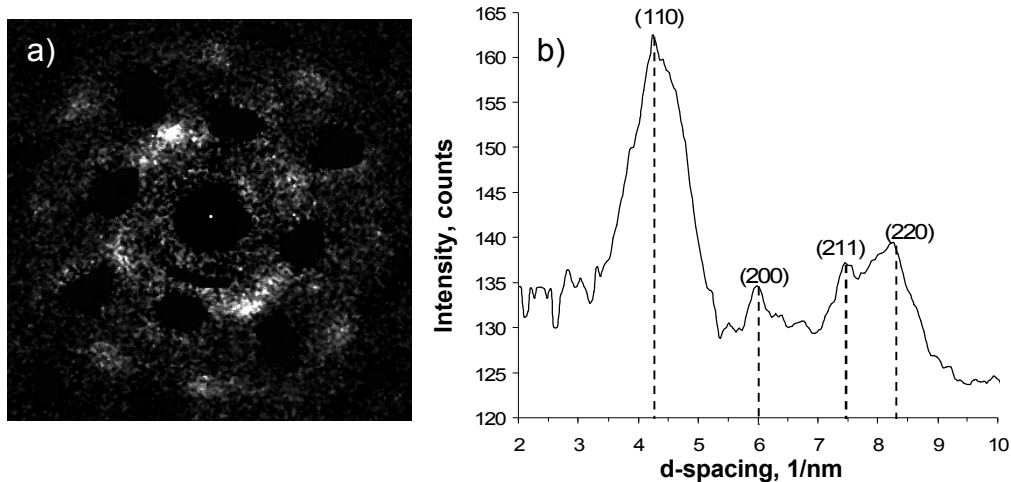
**Figure 3.** a) As-deposited Ti film microstructure, b) After laser

Figure 4a 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 electron beam was converged in order to increase the signal. Figure 4b shows the time-resolved diffraction pattern of the crystal structure 500 ns after a 15  $\mu$ J laser pulse hit the foil. The concentric rings overlaid on the 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 4b. A clearer depiction of the change in phase was performed by taking the difference pattern (figure 5a) of the two diffraction patterns in figure 4, and plotting the radial averaged intensity of difference pattern with reciprocal lattice units (d-spacing). The peaks present in figure 5b show that it is indeed BCC. There was approximately  $75 \pm 5\%$  BCC,  $\beta$ -phase present in figure 4b, which was calculated first by fitting the peaks in figure 5b 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 4b–figure 5a).



**Figure 4.** 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 15  $\mu$ J pump laser pulse. Arrow indicates the appearance of new spots that did not exist in the HCP pattern.

Figure 6a shows the single-shot diffraction of same region after the material has cooled to room temperature (which takes less than a millisecond). The diffraction spots in this image are sharper, which indicates grain coarsening as observed in figure 3. The pattern also exhibits spots



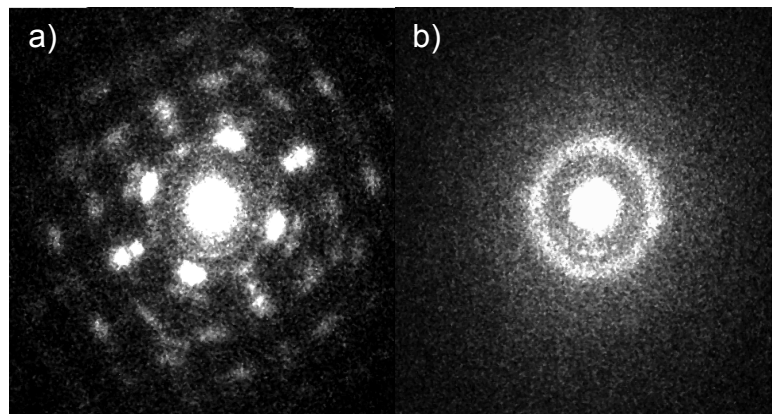
**Figure 5.** a) Difference pattern showing between figure 6a and b, showing residual BCC reflections, b) Radial intensity verse d-spacing for the rotational averaged pattern in figure 5a.

that are not present before laser heating, and some that appear to emanate from the prior  $\beta$ -phase texture. After this pattern was acquired, the region was hit with a second 30  $\mu\text{J}$  laser pulse that was sufficient to induce melting at 100 ns after impact (apparent from the diffuse ring in figure 6b). This study offers both a temperature calibration and means to validate the laser-absorption simulations. Unfortunately, the simulations overestimate the requisite energy by more than 40%, and work is in progress to bring the simulation and experiment into coincidence and to better estimate the heating rates.

## 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  $\beta$  phase, where films are expected to be at high temperature ( $\sim 1200$  K) for extended times ( $>5\mu\text{s}$ ) [7]. However, the appearance of the smaller pancake grains may indicate recrystallization and growth in the  $\alpha$  phase as well.

The additional spots observed in figure 6 are linked with the formation of laths and randomization of the microstructure. Randomization of the microstructure is expected since 12 hexagonal variants can form for each BCC crystal variant and the texture of the prior structure is 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



**Figure 6.** 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  $\mu\text{J}$  pump laser pulse, which was sufficient to induce melting.

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 possibility is that laths form from an incoherent nucleation and growth mechanism requiring diffusion, such as a massive transformation, which would also explain the randomization of the microstructure. In the absence of impurities, like Fe that strongly inhibit diffusion, pure Ti can undergo a massive type transformation at fast cooling rates [7]. 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 the transformation would certainly help to divulge the mechanism.

## CONCLUSIONS

The HCP  $\alpha$ Ti films were transformed rapidly to BCC phase using 80 ns, 1064 nm, 15  $\mu$ J laser pulses. Ex-situ examinations showed extreme grain growth after only one laser hit and in time scales on the order of microseconds. The reason for the lack of dislocations 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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