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Final Report, Fundamental Mechanisms of Transient States in Materials Quantified by DTEM

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Final Report

FUNDAMENTAL MECHANISMS OF TRANSIENT STATES IN MATERIALS QUANTIFIED BY DTEM

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Executive Summary

At the project's inception, there was growing evidence that the time domain for *in situ* observations of material evolution held great promise for allowing measurements to be made in never previously contemplated regimes. Also, central to the development of the project was the knowledge that phase transformations are of central importance to the development of materials microstructure and hence properties. We addressed this opportunity by developing a transmission electron microscope that could be operated in the pulsed mode (DTEM), with exposure times down to 20 ns and interframe times down to 20 ns in the nine-frame movie mode, designed with the intent of performing *in situ* experiments. This unprecedented capability allowed us to investigate structural phase transformations, intermetallic formation reactions, crystallization from the amorphous phase, rapid solidification of liquid metals, transformations in phase change materials, and catalyst nanoparticles. The ability of the electron microscope to create images with high spatial resolution allows for the accurate measurement of position. Common to all of the transformations mentioned above is the presence of a distinct interface between the old phase and the growing new phase. Measuring the position of the interface as a function of time, combined with the ability to count nucleation sites as a function of time, allowed for the exceptionally accurate measure of transformation kinetics. These measurements were used to guide and constrain the development of models and simulation methods for the classes of transformations studied.

I. Narrative

Phase transformations are integral to the manipulation of materials and control of their properties. The overarching hypothesis of this work was that in order to control materials properties, the formation of its structure at the microscale (and nanoscale) must be understood, meaning that the connections between processing conditions, driving forces, and microstructural evolution must be understood. Typically, the structure of a material is determined after a process step, such that evolution must be deduced indirectly. *In situ* techniques provide opportunity to observe structure formation while it occurs to reveal mechanistic details, though these approaches are extremely challenging as many important materials processes are inherently fast.

In situ transmission electron microscopy (TEM) is a powerful characterization tool with high spatial resolution for observations and measurements of structure formation and evolution [1-7]. The ever-expanding role of *in situ* TEM as a materials characterization tool demonstrates the need to identify through imaging the transient states of processes, which are often far more important than just the starting and end states. *In situ* TEM has been largely constrained by conventional video frame rates (30 Hz or ~33ms), though recent advances in CMOS-based and direct detection cameras have in some cases reduced these frame rates to the sub-millisecond regime. However, many dynamic processes occur across length and time scales that require temporal resolutions of nanoseconds or higher—especially when driving forces are large and the process is far from equilibrium.

These limitations were overcome by the development of the dynamic transmission electron microscope (DTEM) [10-12], which increased the time resolution for *in situ* TEM experiments by orders of magnitude to the nanosecond regime. The development of the DTEM was a significant advancement over a standard TEM, providing the capability to capture transient states in irreversible materials processes with nanosecond temporal resolution. This high time resolution was achieved using laser-induced photoemission to produce a short burst of electrons to acquire images with spatial resolution of the order of ~10 nm and sufficient signal and coherence to image defect structures that control materials properties, as shown in Figure 1. A second laser synchronized to the photoemission laser drives specific reactions in the specimen, and a snapshot image or diffraction pattern of the reaction was acquired after a defined time interval (e.g., 10 ns, 100 ns, etc.). By combining several of these snapshot images or diffraction patterns from repeated experiments at different delay times, a time sequence of the on-average evolution of the reaction could be acquired to provide the intrinsic details of the dynamic reaction rather than merely inferring the complex reaction pathway from postmortem analysis.

The DTEM's initial single-pump/single-probe, single-shot DTEM (SS-DTEM), mode of operation was applied to, for example, phase transitions in nanocrystalline Ti [13,14], transient structures and morphologies of moving reaction fronts in Ni/Al reactive multilayer foils (RMLFs) [15,16], studies combining nanocalorimetry with DTEM [17], crystallization processes in Ni-Ti metallic glass [18], GeTe [19,20] and $Ge_2Sb_2Te_5$ [21] phase-change materials, and amorphous Ge [22,23] thin films, rapid solidification in pure Al [24] and Al-based alloys [25], *in situ* heating of Al nanoparticle aggregates [26], and pulsed-laser-induced dewetting of Ni [27] and Co-Cu [28]thin films. This work using SS-DTEM demonstrated the significant capability to image transient states of strongly driven, highly non-equilibrium phase transformations with measurements of the kinetics of these rapidly evolving processes. However, there is inherent

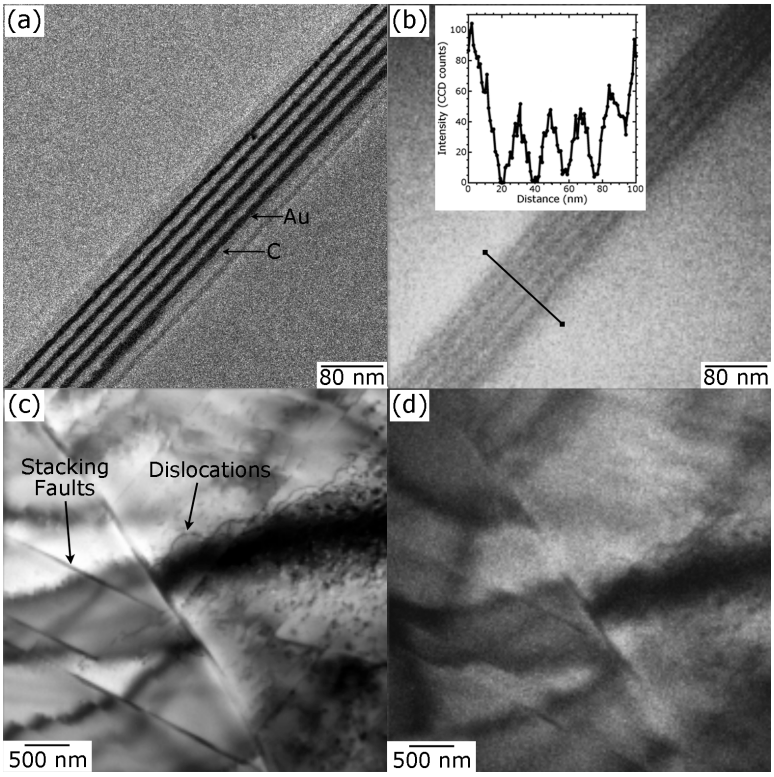

Figure 1. (a) Conventional continuous wave (CW) bright-field TEM image of a Au-C multilayer foil with 10-nm-thick layers, for comparison with (b) a 15-ns pulsed DTEM image of the same multilayer foil. The layers are clearly resolved in the pulsed image. The inset line profile in (b) shows the pixel intensity across the multilayer, with the intensity from the layers visible above the background, indicating that the resolution is ~10 nm. (c) CW bright-field TEM image of a stainless-steel microstructure, including dislocations and stacking faults, for comparison with (d) a 15-ns pulsed image of the same microstructure. Despite the difference in exposure times of nearly eight orders of magnitude, most of the microstructural features evident in the CW image are visible in the pulsed image. These images were not processed apart from standard dark count and flat-field corrections. Images adapted from references [8,9].

variability associated with the single-shot approach to irreversible processes, as there may be small differences in the evolution of the process from experiment to experiment as well as variation in experimental parameters such as the laser energy used to drive the process.

In order to alleviate these issues, the DTEM was upgraded to a single-pump/multi-probe mode of operation, or Movie Mode DTEM (MM-DTEM) [29-31]. Instead of providing a single snapshot (time-delay image) of an event, a multi-frame movie can now be acquired. Like SS-DTEM, MM-DTEM is based on a TEM that incorporates two pulsed lasers: the specimen drive laser and the cathode laser (see Figure 2). MM-DTEM incorporates three significant upgrades in the DTEM hardware: (1) A laser system based on an arbitrary waveform generator (AWG), capable of producing essentially any temporal pattern of pulses within a window of ~100 μs, (2) a set of high-speed electrostatic deflectors placed in the space between the electron lenses and the CCD camera, and (3) a fully programmable electronic timing and control system that orchestrates the entire process.

The generation of a laser pulse train is essential for MM-DTEM to obtain a series of time-resolved nanosecond images of a transient event in a material. For increased flexibility in the laser system and to tailor the laser parameters for a given experiment, an AWG laser was designed and constructed. The AWG laser system can generate temporally shaped laser pulses, providing the capability to easily change the pulse duration and intensity and even to produce pulse trains with independent control over each individual pulse. This is an important breakthrough in the technology as it allows trade-offs to be made between temporal resolution, signal, coherence, and spatial resolution based on experimental needs. The AWG laser system allows for continuously variable and controlled electron pulse durations from ~1 μs down to 20 ns.

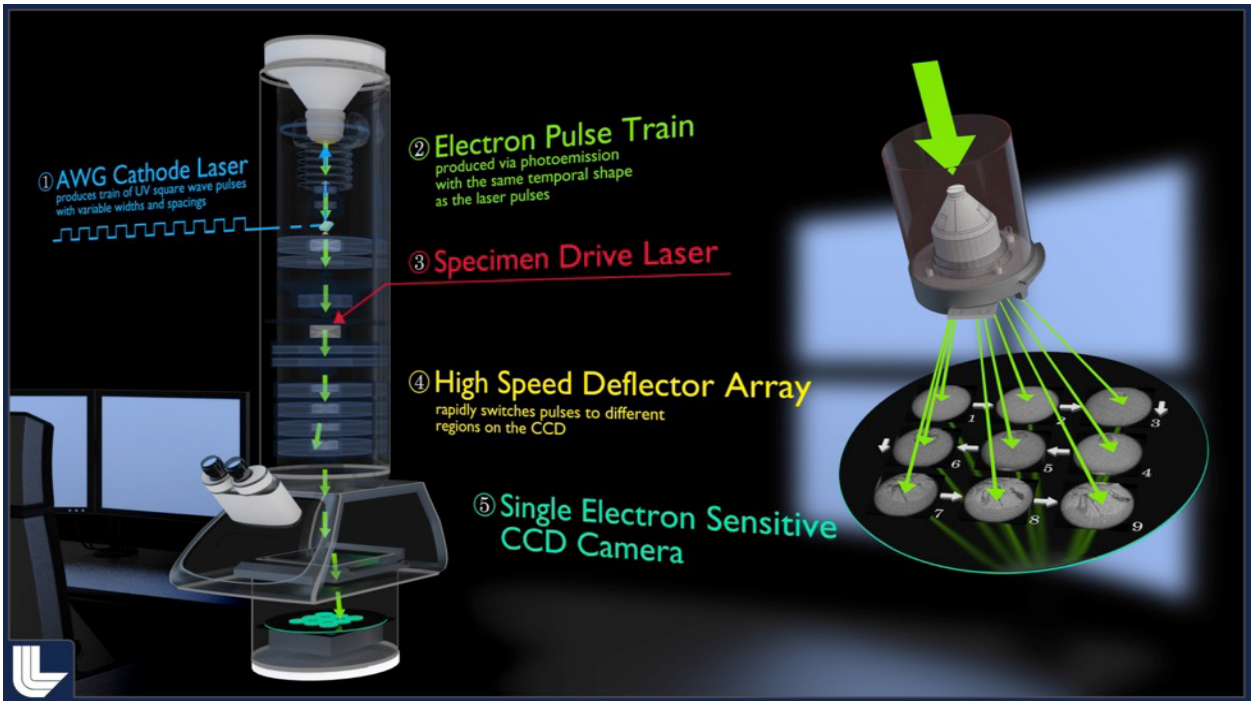

Figure 2. Schematic of the Movie Mode DTEM (MM-DTEM) technology, enabling single-pump/multi-probe operation and true *in situ* microscopy capabilities in the DTEM in which multi-frame movies of rapidly evolving materials dynamics can be acquired.

While the AWG laser can be programmed to create an arbitrary train of discrete electron pulses each with enough intensity to produce a high-quality image, without additional modification, all of the images would simply overlap at the camera, producing a multiply exposed image. A new high-speed electrostatic deflection system was designed and installed to direct each of the images to a separate region on the CCD camera. The camera itself does not need high time resolution. Rather, it remains in a receptive state throughout the entire experiment, so that all of the time resolution is in the electron pulse train and the electrostatic deflector. Thus, the interfame times are governed by the deflection speed. The current limits to the switching times range from ~20 ns to 10 μs between electron pulses. Typical MM-DTEM acquisitions are comprised of 9 frames, but this could be increased to 16 or even 25 frames with a higher-resolution CCD camera.

Examples of MM-DTEM experiments are provided in Figures 3 and 4 to illustrate the types of studies that have been conducted. Figure 3 shows crystallization in an amorphous GeTe film, where growth was captured following a single nucleation event [32]. Figure 4 shows the rapid solidification of an Al-4at.%Cu alloy [33], with the associated measurements of the kinetics of the transformation. Other applications of MM-DTEM include disorder-order transitions in 2D copper-intercalated MoO_3 [34], nanoscale condensed-phase reactions with Al and CuO nanoparticles [35], propagating fronts in reacting Ti-B nanolaminate films [31], crystallization kinetics of amorphous Ge [36-38] and $GeSb_6Te$ phase-change materials [39], dewetting of nanoscale Ni thin films on $SrTiO_3$ substrates [40], and rapid solidification of pure Al [41] and Al-based alloy [33,42] thin films.

In summary, the success of this project in developing an *in situ* dynamic TEM to study strongly driven, far-from-equilibrium phase transformations has significantly advanced our

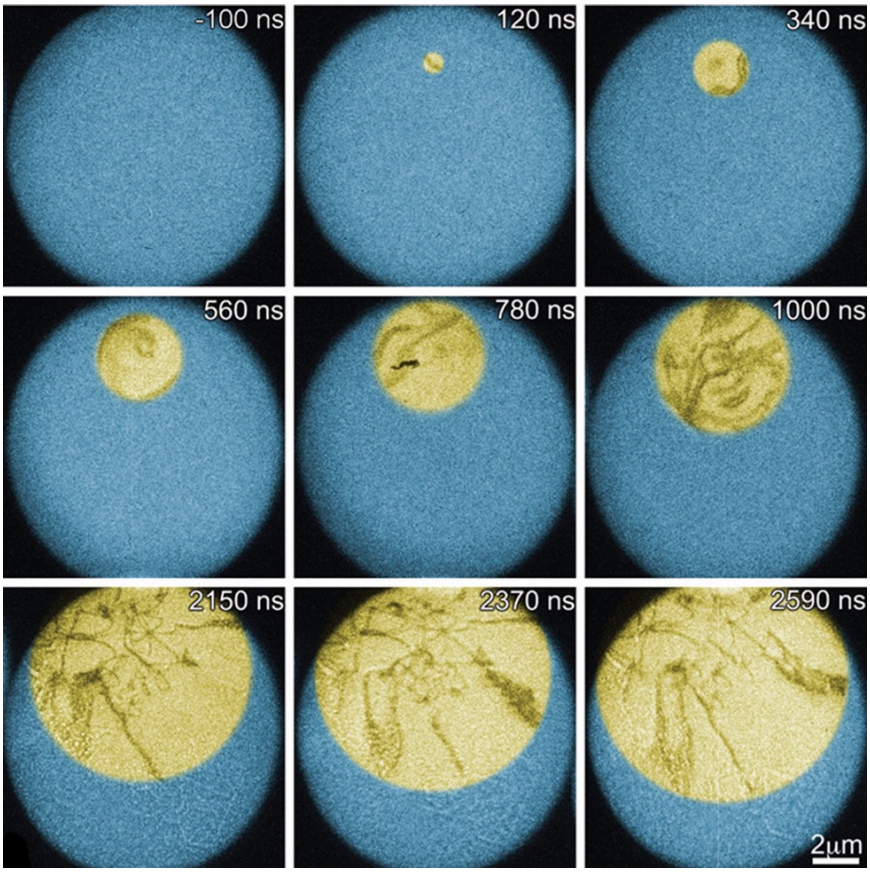

Figure 3. Movie Mode DTEM acquisition showing growth of crystalline regions (false-colored yellow) into amorphous GeTe (false-colored blue) in a nine-image series of 17.5-ns electron pulses after a 4.7 μJ laser shot. The time signature in each frame is relative to the time of the peak specimen laser intensity with an uncertainty of ±3 ns.

understanding of these materials processes. Measurements of how metastable structural dynamics develop under these far-from-equilibrium conditions are critical to controlling materials properties and developing predictive modeling capabilities. The development of the Movie Mode DTEM represents a major advance in instrumentation development to enable transformational science and energy-related technologies, addressing identified needs to image materials far from equilibrium and to understand the critical roles of heterogeneities, interfaces, and disorder in materials. The imaging of structural states in a complex system with both spatial and temporal resolutions is a critical, existing challenge to understanding non-equilibrium materials evolution and driven transformations. The work performed under this project using both SS-DTEM and MM-DTEM demonstrated the potential of the technique to address this challenge. Many opportunities still exist, particularly in areas such as nanoscale solid-liquid interfaces for energy storage and materials synthesis, *in situ* corrosion studies, geochemical reactions at fluid-solid interfaces, and controlling microstructure as it develops under non-equilibrium conditions present, for example, during additive manufacturing. The DTEM continues to be a unique instrument, providing data that no other instrument in the world can produce.

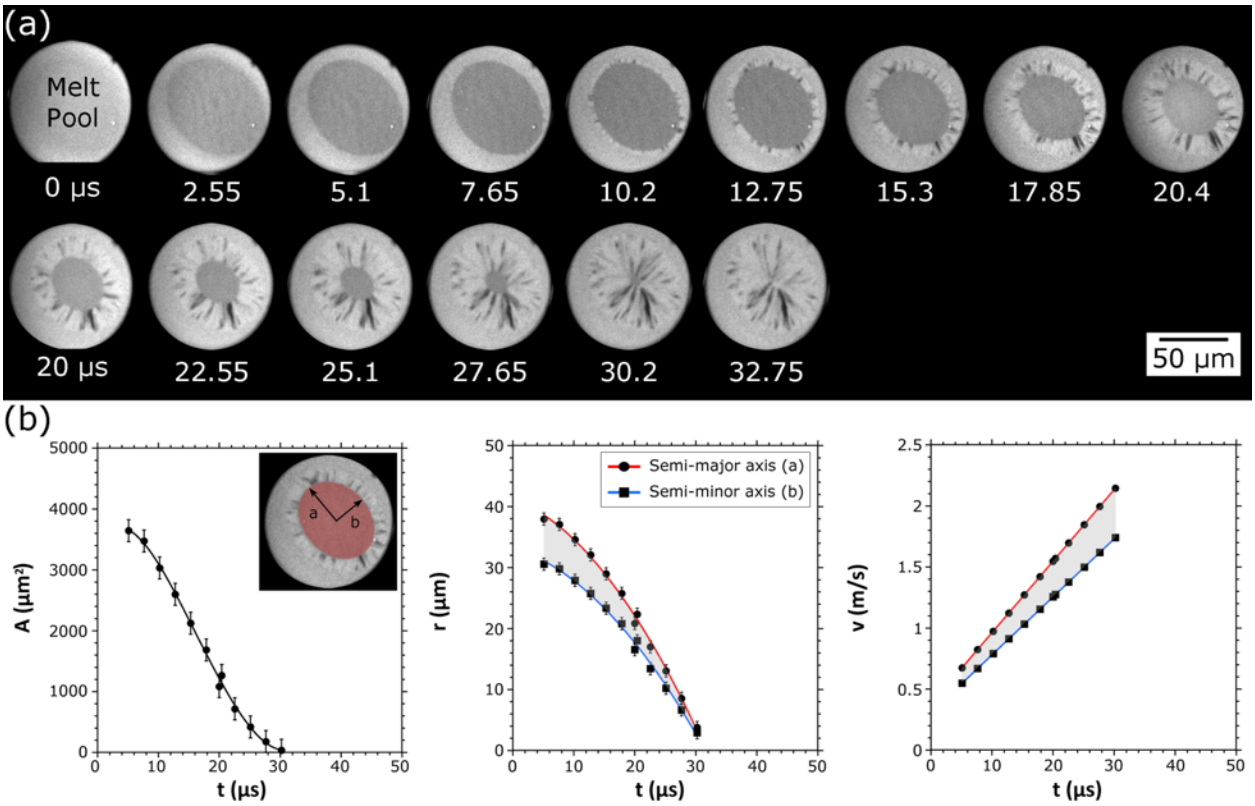

Figure 4. (a) Dynamic time-delay sequence of images recorded during rapid solidification in an Al-4at.%Cu thin-film alloy. The indicated times below each image are the delays (in μs) between the peak of the Gaussian laser pulse used to melt the film and the 50-ns electron pulse used to form the image. (b) Time evolution of the (left) melt pool area, (middle) semi-major and semi-minor axes of the elliptical melt pool, and (right) solidification front velocity. The gray areas bounded by the semi-major and semi-minor axes represent the ranges of (middle) axis length and (right) velocity along the solid-liquid interface.

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IV. Collaborations Fostered

Numerous collaborations were fostered through this FWP:

- Fabrizio Carbone, École Polytechnique Fédérale de Lausanne
- Amy J. Clarke, Colorado School of Mines
- Philip D. Rack, University of Tennessee
- Simone Raoux, IBM
- Federico Rosei, Université du Québec
- Bradley J. Siwick, McGill University
- Klaus van Benthem, University of California, Davis
- Timothy P. Weihs, Johns Hopkins University
- Jörg M.K. Wiezorek, University of Pittsburgh
- Michael R. Zachariah, University of Maryland

V. Technologies

This project allowed the development of the dynamic transmission electron microscope (DTEM). When this instrument first started making pulsed electron images in 2006 it was a unique instrument. It is still today a unique instrument, producing data that no other instrument in the world is producing.

VI. Patents

1. B.W. Reed, R.M. Shuttlesworth, T.B. LaGrange, D.J. Gibson, "Single-shot high performance dynamic transmission electron microscope (DTEM) for e.g. X-ray spectroscopy, has camera chamber which is positioned below condenser lens system for housing single electron sensitive camera," Patent No. US2011168888-A1.
2. B.W. Reed, "Ponderomotive phase plate system for use in transmission electron microscope for high-resolution and biological phase contrast imaging, has transport system transporting laser beam into post-sample electron beam drift space of lens system," Patent No. US2011220791-A1; US8217352-B2
3. B.W. Reed, W.J. DeHope, G. Huete, T.B. LaGrange, R.M. Shuttlesworth, "Electron microscope has control system to set inter-pulse spacing between sequentially generated ones of electron pulses that are independently controlled by programmable control system," Patent No. WO2014100835-A1.
4. B.W. Reed, "Scanning transmission electron microscopy system for use in sensing system for mathematical techniques for post-measurement reconstruction for research application, has subsystem for mathematically analyzing dataset to predict information," Patent No. US8933401-B1; WO2015061037-A1; CA2921307-A1; AU2014340580-A1; KR2016077072-A; CN105745736-A; EP3061118-A1; IN201627004615-A; JP2016538681-W; EP3061118-A4.
5. B.W. Reed, W.J. DeHope, G. Huete, T.B. LaGrange, R.M. Shuttlesworth, "Electron microscope, such as dynamic transmission electron microscopy microscope, has arbitrary waveform generation laser system to produce train of temporally-shaped laser pulses of predefined pulse duration and waveform," Patent No. US2015235800-A1; US9165743-B2.
6. B.W. Reed, W.J. DeHope, G. Huete, T.B. LaGrange, R.M. Shuttlesworth, "High-speed multi-frame dynamic transmission electron microscope, has control system for providing spacings between electron pulses that are variable, programmable and independently controlled by controller," Patent No. US2016005567-A1; US9373479-B2.

VII. Licensing Agreements

Many of the patents listed above have been licensed to Integrated Dynamic Electron Solutions (IDES), Inc.