Imaging of Transient Structures Using Nanosecond in Situ TEM

Judy S. Kim, Thomas LaGrange, Bryan W. Reed, Mitra L. Taheri, Michael R. Armstrong, Wayne E. King, Nigel D. Browning, Geoffrey H. Campbell

The microstructure and properties of a material depend on dynamic processes such as defect motion, nucleation and growth, and phase transitions. Transmission electron microscopy (TEM) can spatially resolve these nanoscale phenomena but lacks the time resolution for direct observation. We used a photoemitted electron pulse to probe dynamic events with "snapshot" diffraction and imaging at 15-nanosecond resolution inside of a dynamic TEM. With the use of this capability, the moving reaction front of reactive nanolaminates is observed in situ. Time-resolved images and diffraction show a transient cellular morphology in a dynamically mixing, self-propagating reaction front, revealing brief phase separation during cooling, and thus provide insights into the mechanisms driving the self-propagating high-temperature synthesis.

Transmission electron microscopy (TEM) has evolved dramatically in recent years with the development of monochromation and spherical aberration correction (1–3) facilitating sub-angstrom spatial resolution. In situ TEM studies have also progressed from simple heating and cooling experiments to include capabilities such as nanoindentation (4) and environmental cells (5, 6). The TEM is already a powerful tool for material characterization in diverse scien-

References and Notes
23. Materials and methods are available as supporting material on Science Online.
32. This study was partially supported by the Grant-in-Aid for Scientific Research (Kakeshi, Wakate 5), the Special Coordination Funds for Promoting and Technology. We thank T. Sakurai and M. Takamaya of University of Tokyo for invaluable discussion; Y. Komatsu of Dainik copolymer; and A. Kosaka of Exploratory Research for Advanced Technology-Solution Oriented Research for Science and Technology Nanospace Project, Japan Science and Technology Agency, for technical support. T. Someya and T. Sekitani have filed a provisional U.S. patent (61/064,024) on this work.
33. www.sciencemag.org
34. Supporting Online Material www.sciencemag.org/cgi/content/full/1160309/DC1
35. Materials and Methods
36. Figs. S1 to S4
37. References
38. 12 May 2008; accepted 21 July 2008
39. Published online 7 August 2008; 10.1126/science.1160309
40. Include this information when citing this paper.
tific fields, but there is a need to incorporate fast time-resolution capabilities into EM.

In the past, direct electron imaging has been essential to uncover phenomena that are difficult to distinguish with diffraction (7–9), for instance, dislocation dynamics. Electron interrogation methods also have the potential to provide higher sensitivity and resolution compared with laser or x-ray methods. This is possible because of bright electron sources, the ability to control and focus electrons for different contrast mechanisms, and the stronger interaction of electrons with matter (10), resulting in a broad class of observable samples and length scales.

Traditional in situ TEM spatially resolves microstructural details of phase, structure, and morphology; however, it cannot collect data with acquisition times less than 1 ms. This is often orders of magnitude too slow to capture the essential material details of interface motion, crystal formation, twinning, and many other fundamental material processes. Many such processes are nonrecurring, necessitating single-shot techniques that capture images or diffraction patterns in a single brief exposure. At nanosecond time scales, such transient data are only attainable with the use of a single, short electron bunch with very high peak current by TEM standards (microamperes to milliamperes). Nanosecond-scale in situ TEM has been achieved using a conventional TEM modified to introduce a laser for stimulating the process that will later be captured by the electron pulse. The time delay between the laser and electron pulse were varied from ~0.7 to 25 μs, before the arrival and long after the front has passed.

Reactive multilayer foils (RMLFs), also termed nanostructured metastable intermolecular composites, are layers of reactant materials that undergo exothermic, self-propagating reactions when layer mixing is induced by an external energy source (Fig. 1). These nano foils exhibit mobile, high-temperature reaction zones where atoms of adjoining layers diffuse across the interfaces, wherein velocity and temperature can be manipulated by composition and geometry of the component materials (14–16). They are used as customized heat sources for rapid fuses, biological neutralization, and joining of materials by means of localized heating rather than global device heating (17, 18).

The reactive foils contain stored chemical energy in the form of layered structures with <1 nm of interdiffusion at the interfaces (fig. S2). The reaction-front velocity (reaching ~10 m/s) is related to bilayer thickness, with an exception in thin bilayers (~10 nm) where intermixing during deposition retards the reaction propagation (15). Maximum temperatures attained during mixing vary greatly based on composition and geometry, reaching upwards of 1750 K (19). Little is known about the dynamic and transient events that transpire in the proximity of the reaction front, although these will govern the structure, mechanical properties, and performance of the reacted materials. The combination of nanostructure and rapid velocity often make traditional characterization methods incapable of direct observation of the self-propagating high-temperature synthesis.

We use dynamic TEM (DTEM) to observe the RMLF reaction front for rapid phase-transition times and metastable morphologies. RMLF experimental samples are composed of five bilayers of Al/Ni$_{0.91}$V$_{0.09}$ (at a 2:3 atomic ratio, totaling 125 nm in thickness) and mounted in Cu mesh-clamping grids. Through fast optical imaging at 2 μs per frame (fig. S3 and movie S1), we found that when initiated by a 1064-nm laser pulse in an external vacuum chamber, the reaction front travels across the sample at a velocity of 13 m/s. Because the spatial resolution was 35 μm per pixel, the optical videos did not show additional definitive information. We then conducted DTEM experiments at the same pump-laser conditions [80-μm 1/e$^2$ radius, 12-μJ energy, 3-ns full width at half maximum (FWHM) pulse duration]. The orientation of the experimental setup illustrated in the schematic (fig. S1, inset, and fig. S3) shows how the reaction front radiates out in all directions from the reaction initiation site in the freestanding RMLF membrane. By initiating the mixing reaction several hundred micrometers away from the observation area, the reaction front of the intermetallic formation zone is observed while it is in a steady state of propagation. Delays between the reaction-front arrival and the probe electron pulse were varied from ~0.7 to 25 μs, before the arrival and long after the front has passed.

At low magnification with a field of view of ~500 μm$^2$, the reaction front is visible after 1 μs as it travels away from the drive-laser initiation site (fig. S4). At increased magnification, the bright field images (Fig. 2) demonstrate the transient morphology of the reaction front. The reaction front is closely followed by the elongated finger-like structure, defining the interface between the reacted and unreacted material. These cellular features of Fig. 2 have a periodicity of ~600 nm wide and are greater than 40 μm long (equivalent to 3 μs of propagation time), showing a distinct formation and gradual termination, which proves their transient character.

The images in Fig. 2 are in plan view (with the viewing direction perpendicular to the metallic layers), and the cellular features are normal to the bilayer structure in the direction of the yellow arrow in the schematic Fig. 1. The size scale of the transient structures (600-μm periodicity) greatly exceeds the bilayer periodicity of the RMLF (25 μm); thus, the observed cellular structures are not directly related to the metallic-layer structure but instead suggest a transverse patterning mechanism inherent in the reaction process. This is reminiscent of binary alloy solidification in the midst of slight undercooling and also of solid solution eutectoid transformation (20, 21). These models have shown that similar

---

1. Materials Science and Technology Division, Lawrence Livermore National Laboratory (LLNL), Livermore, CA 94550, USA.
2. Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA.
3. To whom correspondence should be addressed. E-mail: kim46@llnl.gov

---

**Fig. 1.** Schematic of RMLF reaction-front propagation where mixing is initiated by a laser and continues to travel along the foil until the layers are consumed and converted into reacted intermetallic.
structures are known to arise from the interplay of thermal gradients and atomic interdiffusion, the same physical principles that govern the RMLF front propagation.

Analysis of 15-ns-resolution diffraction data (Fig. 3) reveals the initial formation of the intermetallic ordered B2 phase, NiAl, from the separate face-centered cubic (fcc) Al and Ni$_{0.01}$V$_{0.09}$ layers. The NiAl formed in underseparate face-centered cubic (fcc) Al and termetallic ordered B2 phase, NiAl, from the same physical principles that govern the RMLF thermal gradients and atomic interdiffusion, the structures are known to arise from the interplay of thermal gradients and atomic interdiffusion, the same physical principles that govern the RMLF front propagation.

Dynamic snapshot images of the mixing reaction-front zone reveal a transient cellular structure. In the reaction-front region, the intermetallic NiAl nucleates and continues to grow near the hot reaction front as the material enters a two-phase field of NiAl + liquid, consistent with known thermodynamics of Ni/Al binary mixtures (22). The Al atoms gain mobility because pure Al melts at the relatively low temperature of 933 K, far below the expected temperature of the reaction front. Basic calculations of heat emitted by the mixing of Al and Ni indicate that the temperature reaches ~1700 K [\(\Delta H = 77 \text{ kJ mol}^{-1}\), \(c_p = 24 \text{ J mol}^{-1} \text{ K}^{-1}\) (23, 24), where \(\Delta H\) is the change in enthalpy and \(c_p\) is heat capacity at constant volume], consistent with the measured ~2% thermal expansion from the NiAl diffraction, using \(\alpha = 15 \times 10^{-6} \text{ K}^{-1}\) (where \(\alpha\) is the coefficient of linear thermal expansion) (25). The as-grown layers are stoichiometrically close to NiAl at a 2:3 Ni-rich ratio, and the final reacted phase is NiAl (the B2 phase revealed by diffraction data, which is confirmed by the uninterrupted presence of distinct rings. The timing of the hot reaction-front velocity is measured by DTEM imaging of the front of the cellular structure. When this information is combined with the diffraction data, it is evident that the solid NiAl phase begins to form immediately after the arrival of the hot reaction front.

In the vicinity of the fully reacted foil retains cellular-type structures. The observation of such remnant features with mass-thickness contrast in high-angle annular dark field scanning TEM (fig. S5) reveals that after cooling to room temperature, the regions of narrow, dark intensity in Fig. 2 correspond to thickness modulations in the projected z direction. We confirmed the material thickness modulation using electron energy-loss spectroscopy to measure the ratio of elastically scattered to inelastically scattered electrons at varied positions along the specimen. The rows of increased thickness further support the idea that liquid, which may coalesce to reduce surface energy and cause this thickness modulation, is one of the phases present. This hypothesis is consistent with the thermodynamics and explains how the thickness modulations ~600-nm apart could form on.

**Fig. 2.** RMLF mixing front is defined in (A), and after longer times (2 μs), the structure moves further (B) and is no longer present (5 μs) after the Al/Ni layers have completed mixing (C). The images shown here are plan-view bright field images. Dynamic snapshot images of the mixing reaction-front zone reveal a transient cellular structure.

**Fig. 3.** Dynamic single-shot diffraction with 15-ns resolution of regions before, during, and after the exothermic mixing reaction front has passed. The times indicated at right are in relation to the reaction front, set at \(t = 0\) s. The crystal structure clearly changes from separate fcc Al/Ni and Ni/V layers to an intermetallic B2 structure NiAl phase within 300 ns after the arrival of the hot reaction front. a.u., arbitrary units.
the observed time and length scales (~100 ns judging from the micrometer-scale sharpness of the reaction front in Fig. 2A and the 13-m/s propagation speed). These time and length scales are not consistent with an alternative hypothesis that the structures arise from purely solid-state diffusive processes, which are orders of magnitude too slow, even at 1700 K (26).

The dark intensity between the cells fades away in the last micrograph of the series in Fig. 2, at a point in time where the reaction is long since complete. The solid solubility range of the NiAl B2 phase increases as the temperature drops (22), so that at room temperature nearly all of the excess Ni could be reabsorbed into a stable homogeneous B2 structure with a Ni:Al ratio close to 3:2. Post-mortem TEM examination indicates that this happens in nearly all cases, with frozen-in structures (such as those in fig. S5) being rare exceptions associated with defects. The cellular morphology is not normally present at completion.

We have obtained single-pulse nanosecond-scale TEM data in both diffraction and imaging modes, which are necessary to study the propagation and behavior of energetic nanolaminates in situ. With the use of 15-nm imaging, we have observed transient structures produced by the self-propagating high-temperature synthesis, revealing lines of mass-thickness contrast due to cellular phase formation of an ordered B2 NiAl phase and liquid. At such high formation temperatures (~1700 K), these materials are now known to exhibit transverse self-ordering reminiscent of cellular binary solidification mechanisms. We have established that the DTEM is proficient for nano-second science in a TEM for direct nanoscale characterization of irreversible, dynamic phenomena. It is notable and exciting to find spontaneous, rapid formation of ordered structures in materials far from equilibrium, which is also an important step for essential comprehension of RMLF performance in applications.

References and Notes

The Magnetic Memory of Titan's Ionized Atmosphere

C. Bertucci,1,2*, N. Achilleos,3,2 M. K. Dougherty,4 R. Modolo,4 A. J. Coates,5,2 K. Szeg6, A. Masters,4 Y. Ma,4 F. M. Neubauer,9 P. Garnier,9 J.-E. Wahlund,9 D. T. Young10

After 3 years and 31 close flybys of Titan by the Cassini Orbiter, Titan was finally observed in the shocked solar wind, outside of Saturn’s magnetosphere. These observations revealed that Titan’s flow-induced magnetosphere was populated by “fossil” fields originating from Saturn, to which the satellite was exposed before its excursion through the magnetopause. In addition, strong magnetic shear observed at the edge of Titan’s induced magnetosphere suggests that reconnection may have been involved in the replacement of the fossil fields by the interplanetary magnetic field.

The absence of a substantial intrinsic magnetic field at Titan results in a direct interaction between the moon’s chemically complex atmosphere and its plasma environment (J). This interaction consists of electromagnetic coupling between charged particles resulting from the ionization of Titan’s atmosphere and neutral corona, and the external wind of magnetized plasma. As external plasma approaches Titan, it is mass-loaded by these locally produced ions (2) and its speed progressively decreases. Because the plasma is virtually collisionless, a magnetic field is frozen into the plasma, causing external field lines to drape around the moon. Magnetic field lines then pile up near the sub-flow point and stretch along the flow direction in the flanks and the downstream sector, creating an induced magnetosphere and magnetotail. In a Titan-centered frame of reference, the magnetotail consists of “away” and “toward” lobes containing, respectively, draped field lines parallel and antiparallel to the external flow (J, 4). This interaction leads to the removal of ionized atmospheric constituents as they acquire the linear momentum lost by the external flow (5).

Titan orbits Saturn at an average distance of 20.2 Saturn radii [1 Saturn radius (R_S) = 60,268 km], spending most of its time in Saturn’s partially corotating magnetospheric flow (Fig. 1A). This flow, consisting of charged particles from sources such as the E ring and Enceladus (6), transports Saturn’s magnetic field, which encircles Titan at speeds of ~100 km/s (J). Hence, the angle between the magnetospheric flow and the solar photons responsible for the ionization of Titan’s atmosphere—and therefore the interaction—depends on the moon’s local time with respect to Saturn [Saturn local time (SLT)] (7). At SLT near noon, Titan can also interact with the shocked solar wind and the interplanetary magnetic field (IMF) during periods of high solar wind dynamic pressure (P_{SW}) (8), as the pressure balance at the magnetopause occurs at lower Kronocentric distances, leaving Titan in the magnetosheath (Fig. 1B).

1Space and Atmospheric Physics Group, Imperial College London, The Blackett Laboratory, Prince Consort Road, London SW7 2AZ, UK. 2Astrophysics Physics Laboratory, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK. 3Centre for Planetary Sciences, University College London, London, UK. 4Department of Physics and Astronomy, University of Iowa, 613 Van Allen Hall, Iowa City, IA 52242-1479, USA. 5Mullard Space Science Laboratory, University College London, Holmbury St. Mary, Dorking, Surrey RH5 6NT, UK. 6KFKI Research Institute for Particle and Nuclear Physics, Konkoly Thege Street 29-33, Building III, H-1121 Budapest, Hungary. 7Institute of Geophysics and Planetary Physics, University of California Los Angeles, Los Angeles, CA 90025, USA. 8Institute for Geophysics and Meteorology, KU Leuven, 30923 Kiel, Germany. 9Swedish Institute of Space Physics, Box 537, SE-751 21 Uppsala, Sweden. 10Southwest Research Institute, Post Office Box 28510, San Antonio, Texas 78227-1301, USA.

*Present address: Instituto de Astronomia y Fisica del Espacio, Ciudad Universitaria, Buenos Aires, Argentina. †To whom correspondence should be addressed. E-mail: cbertucci@iafe.uba.ar