Shock Compression Techniques for Developing Multiphase Equations of State

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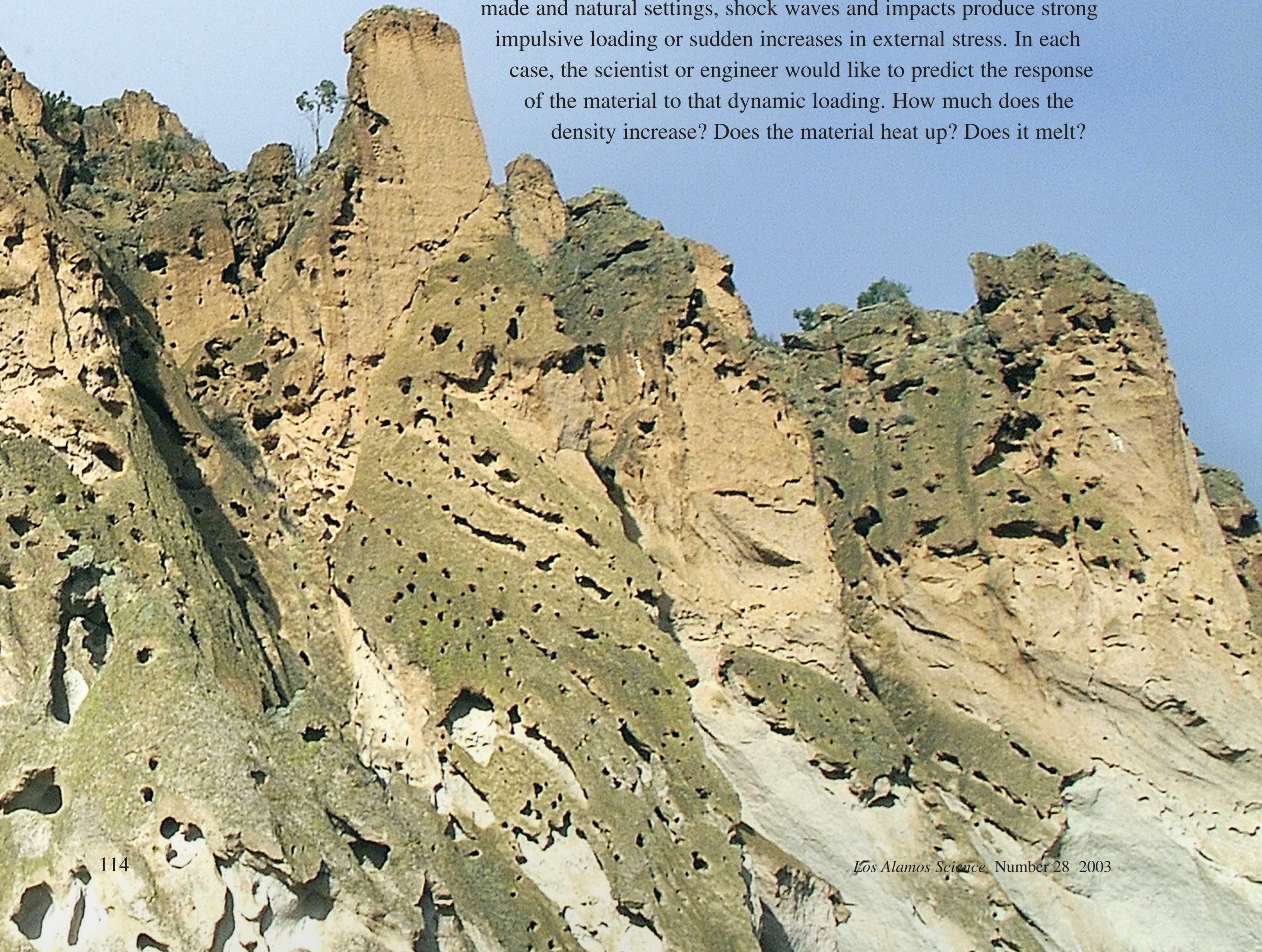
An airplane accidentally hits a mountainside, a bird gets sucked into the turbine blades of a jet engine, a meteorite strikes a satellite or a planet, explosives blast a cavity in the earth for a building foundation, a hammer strikes metal to forge a new part, a blast wave from a nuclear explosion strikes objects in its path—in both man-made and natural settings, shock waves and impacts produce strong impulsive loading or sudden increases in external stress. In each case, the scientist or engineer would like to predict the response of the material to that dynamic loading. How much does the density increase? Does the material heat up? Does it melt?



The key to answering some of these questions lies in knowing those intrinsic properties of materials characterized by their equations of state. Like the familiar equation of state (EOS) of an ideal gas, $PV = n\mathrm{R}T$, the equation of state of a material specifies a definite relationship between three thermodynamic variables, pressure P, temperature T, and volume V (or density ρ = mass/V). Thus, it is not possible to adjust the three variables independently. Rather, if the density and temperature of a material are fixed, for example, then its pressure (as well as energy, entropy, and all other thermodynamic quantities) is a unique value determined by its EOS.

Los Alamos scientists have a long tradition of using dynamic loading techniques to develop the equations of state that describe solids and liquids at extremely high temperatures and pressures. During the Manhattan Project, Hans Bethe, Geoffrey I. Taylor, Cyril S. Smith, and others developed seminal theories of material response to shock wave compression. After World War II, experimentalists Stanley Minshall, John M. Walsh, Robert G. McQueen, and others developed plate impact techniques to make much more precise measurements of equations of state. Weapon designers use those equations of state, as well as others developed more recently, to improve the fidelity of their large-scale computer simulations of nuclear weapon designs.

Today the goal is to perform high-fidelity simulations that predict nuclear weapon performance and safety under a wide variety of scenarios. To achieve the required level of confidence, weapon designers need equations of state that faithfully account for the complex behavior of plutonium, uranium, and many other metals when they are dynamically compressed.

Under dynamic loading, metals can change not only from solid to liquid and liquid to vapor but also from one solid crystal structure to another. Here we describe how we are using new shock-compression techniques involving the preheating of materials to map out the boundaries between solid–solid and liquid–solid phases. We also outline how we use that information to construct sophisticated, semiempirical multiphase equations of state from which we can predict responses of materials in complex geometries, responses that have not been or cannot be directly measured experimentally. These equations of state help with our own interpretation of experiments and contribute to the development of other, more comprehensive equations of state for use in weapon design codes.

Zirconium Phase Diagram

To illustrate the development of an EOS, we will consider our work on the EOS of zirconium, a heavy element between titanium and hafnium in the group 4B metals. Figure 1, the phase diagram of zirconium, shows current best estimates for the phase boundaries of zirconium in the pressure–temperature (P–T) plane. At a constant pressure of 1 atmosphere, zirconium, which is a hexagonal, close-packed (hcp) structure at room temperature, will change to a less-dense, body-centered-cubic (bcc) structure when heated above 1136

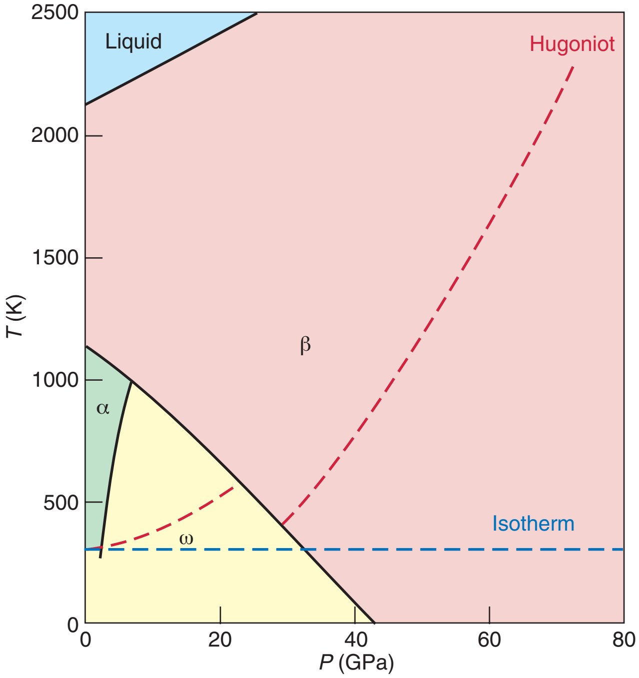


Figure 1. Zirconium Phase Diagram

This diagram by Carl Greeff of Los Alamos shows current best estimates for the phase boundaries of zirconium in the pressure–temperature (P–T) plane. The estimates are based on shock compression work and analyses from the literature. Boundaries separate the three solid phases—α (hcp), ω (hex), and β (bcc)—and the liquid phase. Each P–T point along a phase boundary defines a state in which mixtures of the two phases can coexist in equilibrium. The locus of P–T states in which a liquid and a solid phase can coexist is called the coexistence curve, the melt curve, or the phase boundary. The locus of states in which two solid phases can coexist is called a coexistence curve or phase boundary. Two coexistence curves intersect at a "triple point," and at that temperature and pressure, three phases can coexist. Also shown is the principal Hugoniot, a locus of end states reached by shock compression starting from room temperature and pressure.

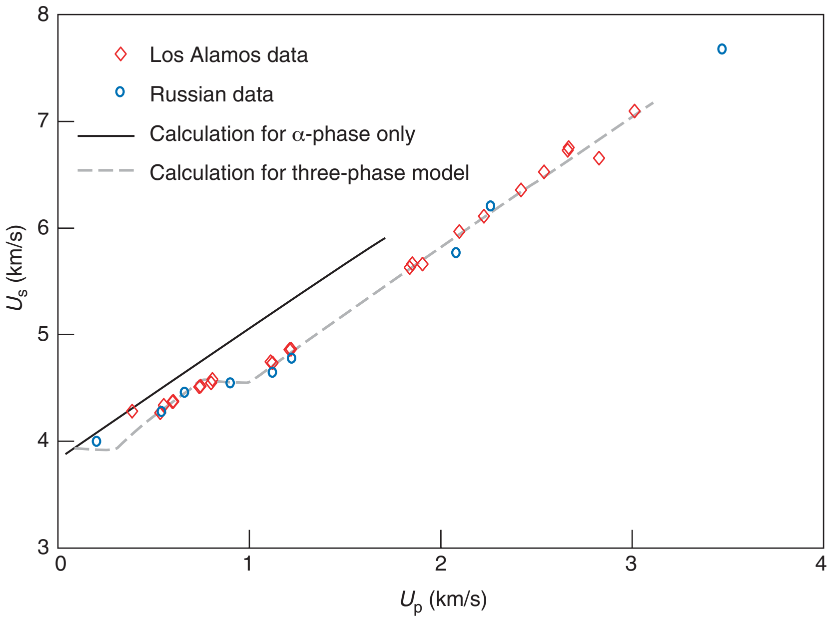


Figure 2. The Zirconium Shock Hugoniot

The shock Hugoniot for zirconium, a plot of shock velocity (U_s) vs particle velocity (U_p), was determined from Los Alamos and Russian shock-compression measurements and from calculations (dashed curves) using the multiphase model developed by Greeff. The cusps in the data indicate that successively higher-impact stresses bring the metal to final states with different crystalline phases: the α (hcp), ω (hex), or β (bcc) phase. This shock Hugoniot was used to calculate the *P–T* Hugoniot displayed in Figure 1.

kelvins. At still higher temperatures, it melts. Similarly, if the metal is kept at room temperature, the hcp phase of zirconium will transform to a new, higher-density hexagonal phase when the pressure is increased. (Note that for some metals, the high-pressure phase is less dense than the low-pressure phase.)

Using Shock Waves to Develop Equations of State

Also shown in Figure 1 is the "principal" Hugoniot[1] for zirconium. This dashed curve is the locus of end states that can be reached through shock wave compression. The Hugoniot rises steeply in the *P–T* plane, whereas an isotherm, a locus of states reached through static compression (slow increase in pressure) with temperature held constant, is by definition, flat in the *P–T* plane. Both the Hugoniot and the isotherm are useful in developing an EOS for a material, but they must be combined with other thermodynamic information, such as the material's heat capacity. In general, phase diagrams and properties of the pure phases can be experimentally determined with either static or dynamic techniques. Results may differ because of the differences in the experimental time scale. Sometimes, those differences are explained by time-dependent equilibration, but other differences reflect the fact that a material responds differently to high strain rates than it does to low strain rates.

For the Hugoniot shown in Figure 1, the temperatures were not measured directly but were calculated from the EOS that we constructed using the Los Alamos and Russian data displayed in Figure 2. This representation of the shock Hugoniot is a plot of shock velocity (U_s) versus particle velocity (U_p). Each cusp, or sudden change in slope, signals the location of a solid–solid phase boundary. The cusp forms because the shock pressure is sufficient to induce a phase change, and the resulting density change causes the shock velocity to change and the single shock to split into two shocks, one following the other.

Figure 3 describes how we use time-resolved laser-interferometric techniques to locate the position of that cusp, or solid–solid phase change, in the *P–T* plane. Work is under way to use different initial temperatures of the material and thereby map out all the points on the phase boundaries in Figure 1.

The gas gun facility where we perform the experiments is shown in Figure 3(a). The gas gun accelerates a projectile carrying a thin impactor toward a flat, very thin zirconium target held in place by its edges—refer to Figure 3(b). At the back of the target is a laser probe connected by fiber-optic cables to a VISAR[2] (velocity interferometer system for any reflector)—refer to Figure 3(c). By determining the frequency of the laser light reflected from the center of the target's back surface, the VISAR determines the velocity history of that surface after impact. As explained in Figure 3(d), the velocity history of the back surface directly reflects the structure of the shock waves that have propagated through the sample and, in turn, the effects of

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[1] This curve is named after the nineteenth century French scientist.

[2] The VISAR was invented around 1970 by Lynn Baker at Sandia National Laboratories. It is the tool of choice worldwide for shockwave work.

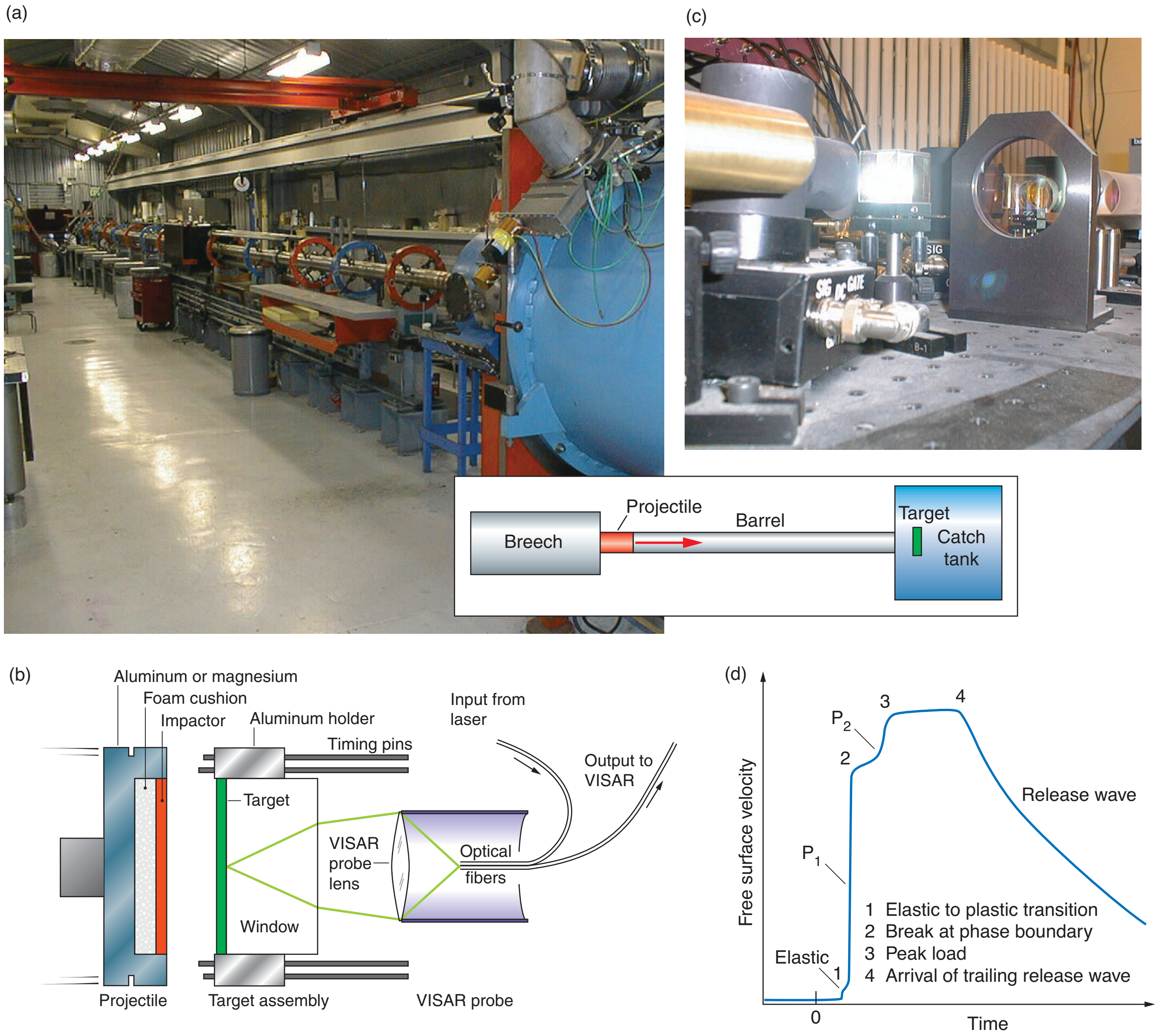

Figure 3. VISAR Measurements of Shock Wave Structure

(a) Both photo and schematic (inset) show a gas gun facility at Ancho Canyon, where we perform shock compression experiments. Typically, a projectile is accelerated by compressed gas, or sometimes by gunpowder, down a long barrel (10 to 40 ft long) and impacts a stationary target at speeds of 0.1 to 8 km/s. (b) In our equation-of-state experiments, a flat, thin impactor carried by the projectile strikes a flat, very thin zirconium sample and sends a compression wave through that target. A laser probe at the back of the target focuses laser light from one optical fiber onto a spot at the center of the zirconium plate. The light reflected from the moving surface is focused onto a second optical fiber that leads back to a laser-velocity interferometer, called a VISAR, located in the recording room (c). The VISAR determines the reflected light's frequency shift as a function of time and thus the velocity history of the back surface of the zirconium sample. The wafer is so thin and the aspect ratio so large (say, 40 to 1) that measurements take less than 2 μs following impact, before any edge effects could travel to the target center and affect the measurements. This technique determines the time-resolved velocity history of a moving surface with the times accurate to ± 1 ns and the velocities accurate to ± 1%. (d) The shape of the surface velocity history reflects the propagation of the shock wave through a multiphase material. Between 0 and 1, an elastic wave reaches the target's back surface; between 1 and 2, a plastic (deforming) wave called P1 increases the pressure to the point 2 where the material begins to change phase. Between 2 and 3, a second plastic wave (P2) increases the pressure slowly as more of the material changes phase until the peak load is reached at 3. Finally, at 4, a trailing release (rarefaction) wave, initiated by reflection of the shock wave from the impactor's back surface, arrives at the target's back surface.

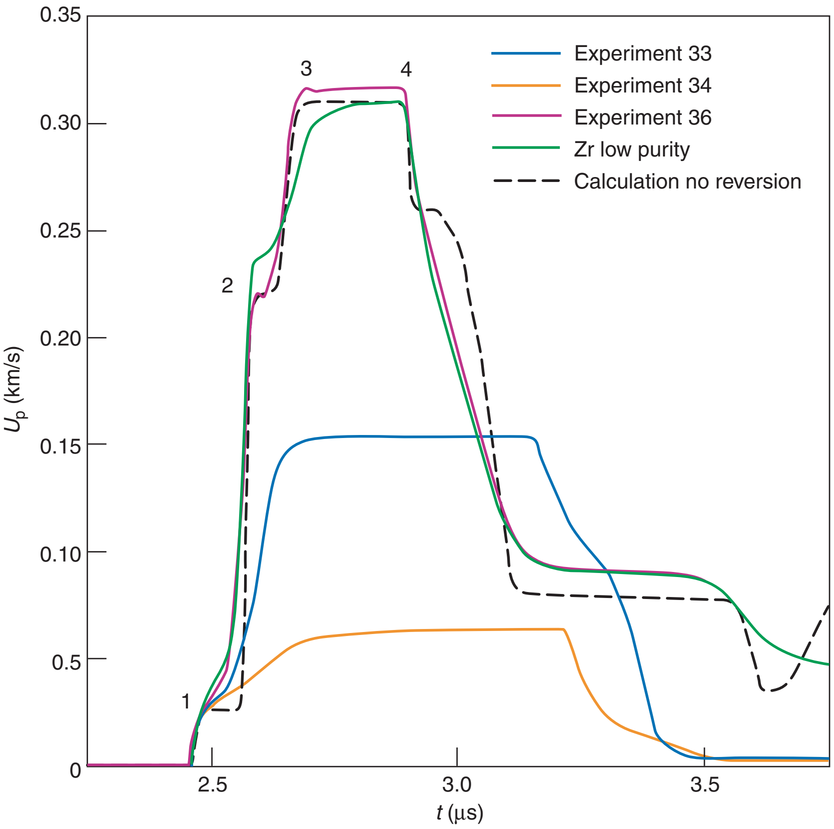

Figure 4. Measured Wave Profiles at Different Impact Stresses

Under high impact stresses (strong shock compression), the (particle velociy) wave profiles for high-purity zirconium (red) and low-purity zirconium (green) display features labeled 1–4, corresponding to the features described in Figure 3(d). In particular, the cusp at point 2 indicates the stress (or pressure) at which a solid–solid phase transformation begins in the material, producing a second plastic wave P2. Note that low-purity zirconium changes phase at a higher pressure than high-purity zirconium, and its phase transformation is more sluggish—the pressure rises more slowly as the phase transformation proceeds between points 2 and 3. The impact stresses reached in Experiments 33 and 34 (also done on high-purity zirconium) were lower than the pressures at which phase change begins, so the wave profiles are smooth, indicating no phase change. These profiles were measured by Paulo Rigg of Los Alamos.

shock compression on the material. In particular, if shock compression causes the material to change to a denser phase (for example, to cross the α–ω boundary or the ω–β boundary in Figure 1), the shock wave is unstable and breaks into two shock waves, or deforming/plastic waves, called P1 and P2. The first deforming wave P1 has a pressure corresponding to the stress at which the principal Hugoniot intersects the phase boundary in Figure 1. It brings the material to point 2 in Figure 3(d). The second, slower plastic wave P2 brings the material to its ultimate loading stress shown as point 3 in Figure 3(d). The detailed shape of the transmitted compression wave, therefore, contains information about the location of one point on the phase boundary. The small initial elastic wave (between point 0 and point 1) complicates interpretation of this record and is discussed below.

By changing the initial temperature of the sample, we can shift the starting point of the Hugoniot curve so that it will cross the phase boundaries at a different longitudinal stress in the material and thereby map out all the points on the phase boundaries. Such techniques for preheated shock compression are currently being developed at Los Alamos.

Multiphase Equations of State

Development. After locating the boundaries between different phases of a material, we use that information to help develop sophisticated, thermodynamically consistent equations of state that take into account some or all the possible structures of the material. We then use these multiphase equations of state to do high-fidelity computer simulations of experiments that involve dynamic loading.

We model the EOS for each pure phase with, for example, a semiempirical, analytical form for the Helmholtz free energy (HFE) and determine the parameters in the model from shock wave experiments, isothermal compression data, and any other available data. To get a thermodynamically complete HFE in the mixed-phase region, we must also specify the entropy and energy at one reference point. We know that two phases have the same Gibbs free energy (GFE) along their coexistence curve. Therefore, by requiring that the calculated coexistence curves (that is, the points at which the calculated GFE for the two phases are equal) match the measured phase boundaries, we can determine uniquely all the pure-phase reference energies and entropies.

Application. To implement a computational technique (say, a hydrodynamic calculation involving shock loading) that accounts for the behavior of mixtures of phases, we must make some additional assumptions. One-dimensional shock wave experiments measure longitudinal stress, whereas the thermodynamic properties depend upon pressure. For solids, longitudinal stress and pressure are different. In most cases, it is satisfactory to treat strength effects as being elastic/perfectly plastic, which is our usual assumption. We further assume that crystallites of the individual phases in a mixture are small enough that pressure and temperature are locally equilibrated, although the mixture need not otherwise be in thermodynamic equilibrium. We also assume that the shock response is rapid enough that all processes are adiabatic although not isentropic. Problem closure is achieved if rules are specified for the rates of transformation between phases. Because our goal is to interpret experimental results, we use semiempirical rules. In our most elementary models, we assume that the transformation rate between two phases is proportional to the calculated GFE difference between the two phases and inversely proportional to a characteristic time for that particular transformation. Our experiments show that characteristic times for a forward phase transformation (from a low- to a high-pressure phase) are not always the same as those for the reverse transformation. We have shown this numerical approach to be quite robust because it easily handles very complex, nonequilibrium mixtures of many phases during computations of wave propagation in a phase-changing material.

Systems with complex geometries often defy direct measurement of the details of the response to impulsive loading so that often the only alternative is to develop computational models. Many materials in systems of interest undergo multiple, and sometimes nonequilibrium phase changes, when they are shocked. The equations of state and locations of phase boundaries of these materials are measured in simple experiments and the behavior is captured in a multiphase EOS. Then modeling provides the necessary bridge between the world of physics and application.

Transmitted wave profiles that are measured in these experiments contain much more information on material behavior than just wave speeds and locations of phase boundaries. Most materials display a variety of nonequilibrium effects that are prominent in shock and release experiments. Some phase changes are sluggish, and this feature is reflected in the rather broad rise time in Figure 4. (See the broad rise time between points 2 and 3 compared with the sharp rise time between points 1 and 2.) The forward transformation sometimes slows abruptly after only partial completion, clearly a nonequilibrium phenomenon, and this affects the speed of the wave between points 2 and 3 in Figure 4. There may be big differences in the speeds of the forward and reverse transformations, which will affect both the peak particle velocity and the detailed structure of the release wave. Space limitations do not allow us to go into these aspects in any detail. But it is important to recognize that these experiments provide unique data on phase change kinetics and nonequilibrium effects that are invaluable for generation or validation of fundamental theories of the phase change processes at high strain rates.■

Acknowledgments

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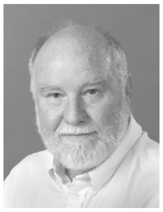

Robert Hixson received his bachelor's degree in physics from California State University, Hayward in 1973 and his Ph.D. in physics from Washington State University in 1980. After a brief postdoctoral appointment, also at Washington State University, Robert joined Los Alamos National Laboratory working in the Applied Physics group. He remained here until 1982 and moved to the Dynamic Experimentation Division where he is currently acting deputy group leader. He has worked in the field of shock compression physics for his entire professional career, authoring and co-authoring many experimental research papers. Robert's current research interests include studying shock-induced phase transitions, leading to development of multi-phase equations-of-state.

George T. "Rusty" Gray III received a Ph.D. in metallurgical engineering and materials science from Carnegie-Mellon University in 1981.Rusty worked as a post-doctoral researcher and then staff member at the Technical University of Hamburg-Harburg in Germany from 1982-1984. He is currently the leader of the Dynamic Materials Properties Testing and Modeling team in the Materials Science and Technology Division at Los Alamos National Laboratory. His research interests are focused on investigations of the influence of material microstructure on the dynamic and shock response of materials.

Dennis Hayes received a Ph.D. in physics from Washington State University in 1972. His research efforts at Sandia Labs focused on shock-induced phase changes and radiation effects. In 1996 he became the president of Lockheed Martin Nevada Technologies where he was responsible for execution of all US DOE NV programs. Dennis' efforts at Los Alamos have focused on multi-phase plutonium models, shock-melting in copper, twinning in uranium alloys and many other endeavors aimed at extracting a physics understanding of materials at the high temperatures and pressures generated in a shock wave environment.