Equation of State and Evidence of Enhanced Phase Transformation for the Shock Compression of Distended Compounds

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Abstract

Shear stress and deformation is inherent to shock-wave compression. Shear deformation is enhanced when the material subject to shock compression is in an initial distended state. Shock Hugoniot data for full-density and porous compounds of boron carbide, silicon dioxide, tantalum oxide, uranium dioxide and playa alluvium are investigated for purposes of equation-of-state representation of intense shock compression. Hugoniot data of distended materials reveal evidence of accelerated solid-solid phase transition as a consequence of shock compaction and accompanying enhance shear deformation. A phenomenological thermo-elastic equation-of-state model is constructed that accounts for both deformation-induced phase transformation and the extreme shock compaction of distended solids, and applied to the compounds studied.

Keywords: equation of state, boron carbide, silicon dioxide, tantalum oxide, uranium dioxide, alluvium

1. Introduction

Many compounds undergo solid-solid crystallographic phase transformation in the shock-wave environment. Forces leading to phase instability through the time history of the shock compression process are not well understood. Adequate shock pressure is certainly central to achieving phase transformation at the Hugoniot state. There is experimental evidence that shear stress and deformation also play a prominent role in the shock-induced phase transformation.

The underlying physics of shear in the acceleration of phase transformation in the shock environment is less clear. A state of shear can lead to localized shear deformation with attendant localized heating, defect production and amorphization. Alternatively, or additionally, shear stresses lead to distortional elastic strain energy that lower energy barriers to crystal structure transformation.

Conditions that generate shear in the shock compression process are also complex. A homogeneous solid experiences shear in the uniaxial environment of the shock wave with the extent of shear stress, shear deformation, and elastic shear strain energy determined by the intensity of the shock and the crystal strength of the material. Granularity and crystal anisotropy will additionally amplify shock-induced shear. Shear in the shock compression event is further intensified when the initial material is distended (initially porous or powder state).
The interrelationship of shear deformation and molecular change of state in the shock-wave event has been pursued in earlier studies. Teller [1] speculated on the importance of shear in the chemical transformation within the shock wave. Although emphasis was on energetic reactions in the shock wave event, the physical arguments of Teller generally apply to the genesis of any molecular transformation in the shock process. Effects of shear deformation on the phase transformation under shock in silicate and carbonate minerals has been pursued with emphasis on underlying microscopic mechanisms [2].

In the present study shock Hugoniot data for high-strength compounds, including boron carbide, silicon dioxide, uranium dioxide and tantalum pentoxide, are all shown to exhibit features consistent with the influence of shear on the shock-induced phase transformation. The consequences of shear on the shock equation-of-state description of a solid are explored. A phenomenological equation-of-state model is developed that incorporates the enhancement of phase transformation brought about by shock compaction induce shear deformation and applied to the materials studied. The Rice-Walsh equation-of-state framework, rather than the more common Mie-Gruneisen equation of state, is employed and shown appropriate for the applications of concern. In particular, characterization is undertaken of the intense-pressure shock equation of state of moderate and highly distended solid compounds.

2. Shear and the Shock Phase Transformation

There is both theoretical and experimental evidence that shear stresses and accompanying shear deformation augment the shock-induced phase transformation. In particular, shock Hugoniot data for the compounds in this study reveal the enhancement of phase transformation brought about by shock compaction and accompanying shear deformation. Also, recent diamond anvil cell (DAC) experiments and molecular dynamics calculations on boron carbide further support the requirement of a shear component in the high-pressure phase transition.

![Fig. 1. Comparison of Hugoniot states for near-full-density material (solid points) and porous material (open points) illustrating increased compressibility at lower shock pressures for the more distended material. Data suggests phase transformation is enhanced by increased deformation of the more porous material. Third-order Birch equation of state representation of initial phase compressibility reveals increased Hugoniot densification for the three materials.](image-url)

Shock Hugoniot data for full density and 42% porosity α-quartz [3] are compared on the left in Fig. 1. Full density quartzite exhibits a Hugoniot elastic limit (HEL) strength of about 8 GPa [4]. Subsequent Hugoniot states traverse the mixed low and high pressure phase region, achieving complete transformation to the six-fold coordination stishovite phase at about 40 GPa. Hugoniot states for the porous α-quartz between about 10-30 GPa reside substantially to the left (higher density) of the comparable-pressure full-density Hugoniot. Although at significantly higher temperature due to the excessive shock heating, increased densification of the porous quartz at comparable Hugoniot pressures suggests enhanced phase transformation brought about by the shock deformation process. At the highest pressures the porous quartz Hugoniot resides to the right (lower density) of the fully density Hugoniot data due the different levels of shock heating and thermal expansion. The α-quartz-to-stishovite shock-induced phase transformation is reasonably well understood through numerous shock wave and DAC studies.

Similar behavior is exhibited by uranium dioxide in the center plot where Hugoniot states for nominally 6% porous and 42% porous UO₂ are compared [5]. Phase transformation on the solid material Hugoniot is less conclusive than that for SiO₂. Gust [6] proposes a Hugoniot transformation in the range of 44-54 GPa. DAC
studies report transformation in UO$_2$ between about 33-40 GPa [7]. Again, Hugoniot states between about 10-40 GPa for the porous UO$_2$ reside at markedly higher density states, indicative of enhanced phase transformation under shock compression.

A similar plot is shown on the right comparing near-full density (3-7% porosity) boron carbide with more porous (22-25%) B$_4$C. Pressure-induced phase transformation in boron carbide is uncertain, although detailed analysis of shock Hugoniot data [8] and DAC studies [9] are suggestive of a solid-solid phase transition. Enhanced compression, and possibly phase transformation, of the more porous boron carbide within the lower-pressure Hugoniot regime is indicated by the Hugoniot data, although less definitive than the behavior of SiO$_2$ and UO$_2$.

The shock Hugoniot data contrasting near-full-density and distended samples of the same compounds shown in Fig. 1 collectively support the effects of enhanced Hugoniot compressibility with increasing distention. The proximity with known or suspected phase transformation on the Hugoniot supports increasing phase transformation with increasing shock deformation associated with the initial state of distention.

3. Thermo-Elastic Equation of State

An isochoric Taylor expansion of the $P(\nu,E)$ partial equation of state, and keeping only the linear term in the thermal energy, leads to the commonly used Gruneisen equation of state,

$$P(\nu,E) = P_r(\nu) + \frac{\gamma(\nu)}{\nu}(E - E_r(\nu)),$$  

(1)

where $P_r(\nu)$ and $E_r(\nu)$ are the reference state at which the Taylor expansion is centered.

Less common is the partial equation of state developed by Rice and Walsh [10] to describe the high-pressure shock-wave properties of water,

$$\nu(P,H) = \nu_r(P) + \eta(P)(H - H_r(P)).$$

(2)

The Rice-Walsh equation of state follows from an isobaric Taylor expansion of the specific volume, truncated to the linear term in the specific enthalpy. Whether Eq. (1) or Eq. (2) has theoretical precedence over the shock-wave equation-of-state surface spanned by the range of distended compounds of interest in the present study is debatable. The Rice-Walsh equation of state has computational convenience in addressing the backward leaning and multivalued Hugoniot relations occurring in the shock compression of highly distended solids, and is used in the present applications.

Construction of the Rice-Walsh equation of state requires a reference equation of state that provides the specific volume $\nu_r(P)$ and specific enthalpy $H_r(P)$ on some identified pressure path. Also necessary is a thermal equation of state specified by a pressure-dependent relation for the Rice-Walsh factor $\eta(P)$. The Rice-Walsh factor can be specified directly, or if the isentropic bulk modulus $K_s(P)$ is known on the reference equation of state path, is provided by the Gruneisen parameter $\Gamma$ and the bulk modulus through the thermodynamic identity,

$$\eta = \Gamma / K_s.$$  

(3)

In this study, equations of state are constructed to describe the shock Hugoniot properties of porous media that include the silicon dioxide, uranium dioxide and boron carbide illustrated in Fig. 1, as well as tantalum pentoxide and a naturally occurring silicate mixture, playa alluvium, for which appropriate shock Hugoniot data are available. Equation of state development focuses on the reference and the thermal equations of state that are constructed to account for the shear-enhanced phase transformation observed to occur on the Hugoniot of increasingly distended samples of the compounds investigated.

The isentrope or the principal Hugoniot of the fully-dense solid is frequently used as the reference equation of state when constructing shock-wave equations of state for porous materials. Here the principal Hugoniot of
the full-density solid is used as the reference equation of state. Most single-component analytic forms for the reference equation of state (Birch, Murnaghan or Vinet equations for example) are adequate for the present development. Here a particularly convenient form is used that results from an assumed linear dependence on pressure of the inertial modulus [11] of the material $Z(P) = \rho K = Z_o + Z'_o P = \rho_0 K_o + \rho_0 (K'_o + 1)P$. Namely,

$$
\nu_{ho}(P) = \nu_o \left[ 1 - \frac{1}{K'_o + 1} \ln \left( 1 + \frac{P}{K_o} \right) \right],
$$

(4)

where $\nu_{ho}(P)$ is the relation for the principal Hugoniot of the material. The reference equation of state for a material undergoing phase transformation on the Hugoniot is then formed through an additive mixing of the compression relations for the low-pressure and the high-pressure phases of the material,

$$
\nu_{ho}(P) = (1 - \mu(P, \alpha))\nu_{h1}(P) + \mu(P, \alpha)\nu_{h2}(P),
$$

(5)

where $\mu(P, \alpha)$ is the Hugoniot transformation function and mass fraction of the high-pressure phase. The functional forms for $\nu_{h1}(P)$ and $\nu_{h2}(P)$ are provided by Eq. (4). The transformation function has the form,

$$
\mu(P, \alpha) = 1 - e^{-(P/\sigma)^n}.
$$

(6)

The transformation pressure on the Hugoniot is provided by the scale parameter $\sigma$ while the shape parameter $n$ determines the spread in pressure over which transformation proceeds. A premise of the present study, supported by arguments offered in the preceding section, is that shear deformation in the shock compaction process accelerates phase transformation on the Hugoniot and that increasing porosity of the test material enhances shear deformation. This aspect of the model is implemented by allowing the scale and shape parameters in Eq. (6), $\sigma(\alpha)$ and $n(\alpha)$, to be phenomenological functions of the initial distention $\alpha$ of the porous material.

Hugoniot expressions for the distended materials are readily calculated from Eq. (2). Hugoniot energy conservation relations for the principal Hugoniont and the distended media Hugoniot are,

$$
H_{ho}(P) = \frac{1}{2} P(\nu_o + \nu_{ho}(P)), \quad H_h(P) = \frac{1}{2} P(\nu_{oo} + \nu_h(P)),
$$

(7)

where $\nu_o$ and $\nu_{oo}$ are initial specific volumes of the full-density and distended material, respectively. Introducing the Hugoniot relations in Eq. (7) into the equation-of-state expression in Eq. (2) and solving yields,

$$
\nu_h(P) = \nu_{ho}(P) + \frac{\eta}{1 - \eta P^2} \left[ \frac{1}{2} P(\nu_{oo} - \nu_o) \right].
$$

(8)

The second term provides the excess isobaric thermal expansion brought about by shock heating due to compaction of the distended material at the Hugoniot pressure $P$. Shock velocity and particle velocity corresponding to the Hugoniot state follow from,

$$
U_h(P) = \frac{P}{\rho_{oo}} \left( \frac{1 - \nu_h(P)}{\nu_{oo}} \right)^{-1}, \quad u_h(P) = \frac{P}{\rho_{oo}} \left( \frac{1 - \nu_h(P)}{\nu_{oo}} \right).
$$

(9)

Thermal-elastic properties of the equation of state are modeled with the Rice-Walsh factor as provided in Eq. (3). In construction of the equation of state it is found that a constant Gruneisen parameter or a Gruneisen parameter that modestly decreases with pressure adequately represents the available data. A pressure dependent Gruneisen parameter of the exponential form,

$$
\Gamma(P) = \Gamma_o e^{-P/P_o},
$$

(10)
is used in the equation-of-state description of the materials investigated. When combined with pressure dependence of the bulk modulus, the relation in Eq. (3) provides the required thermodynamic Rice-Walsh factor.

4. Shock Equation of State of Selected Compounds

The materials selected for equation-of-state studies all have available high pressure shock Hugoniot data that span a substantial range of initial distention. The Rice-Walsh form of the equation of state, along with the features of the equation-of-state model proposed to account for deformation-augmented phase transformation and thermo-elastic properties, are applied to each material. In general the equation-of-state model provides a satisfactory representation of the available shock Hugoniot data.

4.1 Silicon Dioxide

Shock Hugoniot data for full-density and a wide range of distended silicon dioxide materials are provided in the compendium of Trunin et al. [3]. The α-quartz to stishovite transition on the Hugoniot is perhaps the most widely studied and best understood of the many solid-solid phase transformations known to occur under shock compression. The α-ε transition in iron is probably a strong contender. The Hugoniot data described in Section 2 provides compelling evidence that enhanced deformation brought about by initial distention accelerates phase transformation on the Hugoniot. Compression relations for both the low-pressure (α-quartz) and the high-pressure (stishovite) phase of silicon dioxide are reasonably well known. The compressibility properties that constrain the compression for the low-pressure α-quartz phase are provided by the study of Anderson et al. [12] while that for the high-pressure stishovite phase are from Mizutani et al. [13].

The extent to which initial distention of the material augments the phase transformation is not known. In this study the constants \( \sigma(\alpha) \) and \( \eta(\alpha) \) in the Eq. (6) transformation function are selected for each of the silicon dioxide materials that provide a best agreement with the experimental Hugoniot data.

Equation-of-state calculations for the distended material Hugoniot from Eq. (8) are compared with the shock Hugoniot data of Trunin et al. [3] in Fig. 2. An initial Gruneisen parameter of \( \Gamma_o = 1.35 \) and reduction pressure of \( P_o = 200 \text{ GPa} \) in the Eq. (10) Gruneisen relation provide the Hugoniot equation-of-state predictions shown in the plots. Notable is the equation-of-state model predictions of enhanced phase transformation on the Hugoniot for increased distention materials. The Rice-Walsh equation of state also provided a reasonable description of the markedly hotter intermediate and large distention Hugoniot data. The ambient Gruneisen parameter for stishovite is 1.7. McQueen et al. [14], and also Ahrens et al. [15], propose equations of state for stishovite for which shock Hugoniot data are best described by a Gruneisen parameter closer to 0.9 to 1.0. The present model
is best fit to the data by an ambient Gruneisen parameter of 1.35 that reduces to about 0.9 at the upper pressure range of the data.

4.2 Uranium Dioxide

High-pressure Hugoniot data is provided by the experimental study of Goplen [5] on a modestly porous (4-6%) sintered uranium dioxide ceramic and on UO₂ powder with three initial distention densities. Uranium dioxide also undergoes shock-induced solid-solid phase transformation on the Hugoniot. Again, the Rice-Walsh equation of state as outlined in Eq. (2) through (10) is constrained by and applied to the shock Hugoniot data. The influence of increased porosity on the Hugoniot phase transformation is most clearly seen in comparison of the Hugoniot characteristics of the sintered ceramic and the lowest distention UO₂ powder shown previously in Fig. 1. Hugoniot data for the four uranium dioxide sample densities tested by Goplen [5] are plotted in Fig. 3 and shown with the equation-of-state description of the material.

![Graph showing Uranium Dioxide Hugoniot data](image)

Fig. 3. Rice-Walsh equation-of-state model representation of shock Hugoniot data for selected densities of uranium dioxide (Goplen, 1970). Distension levels are identified for the selected porosities for which Hugoniot data are plotted.

The near-full-density (α = 1.06) data of Goplen is normalized to crystal density (α = 1.00) and provides the alternative plot of the shock velocity particle velocity data on the left in Fig. 3. The latter plot of the data is used in construction of the reference equation of state. An ambient Gruneisen parameter of Γ₀ = 1.7, and a reduction pressure of P₀ = 900 GPa, provide the Hugoniot equation-of-state representations compared with the data in the plots.

4.3 Boron Carbide, Tantalum Oxide, Playa Alluvium

Comparable equation of state analysis is undertaken for boron carbide, tantalum oxide and playa alluvium. The results contribute further support for the occurrence of accelerated phase transformation brought about by compaction-induced shear deformation in the Hugoniot compression process. The experimental data are comparably well represented by a Rice-Walsh thermo-elastic equation of state. More detail discussion is provided in the extended publication [16].

5. Closure

Central to the present study is the thermo-elastic equation-of-state description of high-pressure shock compression of compounds that occur in the initial state over a wide range of initial distention. The less-commonly used Rice-Walsh form of the equation-of-state surface is applied in the present study. The Rice-Walsh equation of state exhibits features that lend its application to shock-wave computation where often multi-valued Hugoniot compression curves are the rule.
The study also reveals that shock-induced phase transformation on the Hugoniot is common to many of the compounds of interest. Further, the extent of phase transformation is shown from the experimental Hugoniot data to be dependent on the initial distention of the test material. Analysis of the present data along with other supporting experimental and theoretical work offers compelling evidence that high pressure combined with compaction-induced shear deformation are necessary to the shock phase transformation. Dependence of phase transformation on the initial state of distention of the material is incorporated into the equation-of-state model.

Shock Hugoniot data available from the literature for near-full-density and porous silicon dioxide, boron carbide, uranium dioxide, tantalum pentoxide and playa alluvium are investigated with the present equation-of-state model. Generally, the wide-ranging Hugoniot data are sensibly represented by the Rice-Walsh equation of state accounting for phase transformation.

References