

Interpreting the shock response of porous oxide systems

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Abstract. An energy based model is developed to describe the shock compression response of phase transitioning porous materials. Assuming the solid and porous materials transform to the same high pressure phase (HPP), the shock response of the solid material is used to define the energy limits E_1 , the energy at which the shocked solid begins to deviate from the Hugoniot of the low pressure phase, and E_2 , the energy at which the shocked solid begins to asymptote to the equilibrium HPP. With the Hugoniot of the HPP solid known, the porous Hugoniot is calculated using an isobaric (constant pressure) approach, with at present two variable parameters. The parameters are the thermodynamic value of the initial Grüneisen constant, γ_0 , and the yield/transition strength parameter, σ_Y . The approach is demonstrated for several different initial distortions of SiO_2 .

1. Introduction

Over the years, considerable effort has been directed toward developing equations of state that can relate the compression (shock, isothermal, isentropic) response of a material in its solid and porous states [1]. While the isochoric (constant volume) [2, 3] approach has typically been more prevalent, isobaric (constant pressure) [4, 5] approaches also exist, and are preferable for materials with high initial distortions [5]. For porous materials that also undergo phase transitions as a result of shock loading, additional complexities are present such that the onset of transition may be effected by the level of initial porosity [6, 7]. The present work develops a theoretical framework based on an isobaric equation of state (to describe the high pressure phase) and a compaction/transition model (to describe the mixed phase region), which are combined to capture the shock response of porous, initially quartz, SiO_2 over a wide range of impact pressures.

2. Theoretical Considerations

An isobaric approach similar to that originally proposed by Rice and Walsh [4] is used to determine the shock response of highly distorted materials in the equilibrium equation of state regime by relating the enthalpy, H , and volume, V of the porous and solid materials at constant pressure through [4]:

$$V(P, H) = V_S(P) + \xi[H(P) - H_S(P)] \quad \text{or} \quad \xi = \left(\frac{dV}{dH} \right)_P, \quad (1)$$



where ξ is a function of pressure, P , only, and the subscript S denotes values along the solid reference state. The thermodynamic identity for enthalpy $H = E + PV$ defines for the solid and porous Hugoniot:

$$H_S(P) = \frac{P}{2}(V_0 + V_S(P)) \quad \text{and} \quad H(P) = \frac{P}{2}(V_{00} + V(P)). \quad (2)$$

Insertion of both relations in equation (2) into equation (1) results in the Hugoniot for the porous material:

$$V(P) = V_S(P) + \left[\frac{\xi}{1 - \frac{P\xi}{2}} \right] \frac{P}{2}(V_{00} - V_0), \quad (3)$$

which describes the pressure dependence of volume for an initially porous material that crushes up to solid density at negligible pressures. Addition of a P - α crush model [8, 9], where α is a measure of the instantaneous distention such that $\alpha = V/V_S = P_S/P$ results in:

$$V(P) = \alpha V_S(\alpha P) + \left[\frac{\xi}{1 - \frac{\alpha P \xi}{2}} \right] \frac{\alpha P}{2}(V_{00} - \alpha V_0). \quad (4)$$

Solution of equations (3) and (4) require an expression for ξ , which can be determined from equation (1), which after the appropriate thermodynamic substitutions results in:

$$\xi = \frac{\gamma}{K_\eta} \quad \text{with} \quad K_\eta = \frac{P\gamma}{2} + \left(\frac{dP}{dV} \right)_S \left[\frac{\gamma}{2}(V_0 - V_S) - V_S \right] \quad (5)$$

where γ is the Grüneisen gamma, K_η is the isentropic bulk modulus [10], and $(dP/dV)_S$ is along the solid Hugoniot. Equation (4) also requires a definition for $\alpha(P)$, where the rate-independent formulation developed by Carroll and Holt is used [11]:

$$\alpha = 1/[1 - e^{-3P/2\sigma_Y}] \quad (P_C \leq P \leq \infty), \quad (6)$$

where σ_Y is, in the original formulation, the yield strength of the bulk material. The change in compaction during the initial elastic and elastic-plastic regions is neglected such that the initial distention α_0 remains constant until the critical pressure, P_C , is reached, where the critical pressure is further defined as [11]:

$$P_C = \frac{2}{3}\sigma_Y \ln[\alpha_0/(\alpha_0 - 1)]. \quad (7)$$

With this formulation the crush response is uniquely defined by the initial distention and the yield parameter σ_Y . Therefore, the solid Hugoniot given by equation (4) can be combined with equations (6) and (7) to describe both the low pressure compaction and high pressure equation of state response of highly distended porous materials. In the current approach equations (6) and (7) are used to describe not only the irreversible process of compaction, but also the transition from the initial phase to the high pressure phase.

Inherent in this approach are that $\gamma(P)$ and $K_\eta(P)$ are known. If the reference solid material can be described by a linear shock velocity-particle velocity (U_S - u_P) relationship such that $U_S = C_0 + Su_P$, where C_0 is the ambient sound speed and S is a linear fitting parameter, the volume of the solid material is:

$$V_S(P) = \frac{S-1}{S}V_0 + \frac{C_0^2}{2S^2P} \left[-1 + \left(1 + \frac{4SPV_0}{C_0^2} \right)^{1/2} \right]. \quad (8)$$

For $\gamma(P)$, the assumption is made that $\gamma/V = \gamma_0/V_0$ and that $\gamma_S(V) = \gamma_S(P) = \gamma(P)$ [12].

3. Model Development

An energy-based model is proposed to capture the mixed and high pressure phase equation of state response for phase transitioning porous metal-oxides. In the present analysis initially quartz SiO_2 is used as the example system for development of the model. The basis for this framework lies in the ability to determine the shock energies at which the onset and completion of phase transition occur for the solid material, and then apply those energies to describe the similar onset and completion of transition for the porous material. For solid and porous materials, the total energy imparted during shock loading is described by:

$$E_S = \frac{1}{2}P(V_0 - V) \quad \text{and} \quad E = \frac{1}{2}P(V_{00} - V), \quad (9)$$

where it has been assumed that the initial energy for the solid, E_0 , and porous, E_{00} , materials are equivalent and small compared to the total shock energy such that they can be neglected, as are the initial pressures P_0 and P_{00} . The Hugoniot response of solid SiO_2 is shown in figure 1(a), where a clear transition from the calculated quartz Hugoniot at E_1 to the high pressure phase (HPP) Hugoniot at E_2 is observed. These same energies, E_1 and E_2 , also define the onset and completion of phase transition in the porous material. Data from the literature [7] for several different initial distentions of SiO_2 are shown in figure 1(b), and are plotted within the current model framework such that the open symbols reflect Hugoniot experiments where the shock energies are $E < E_1$, the half-filled symbols are for $E_1 < E < E_2$, and solid symbols reflect data for which $E > E_2$.

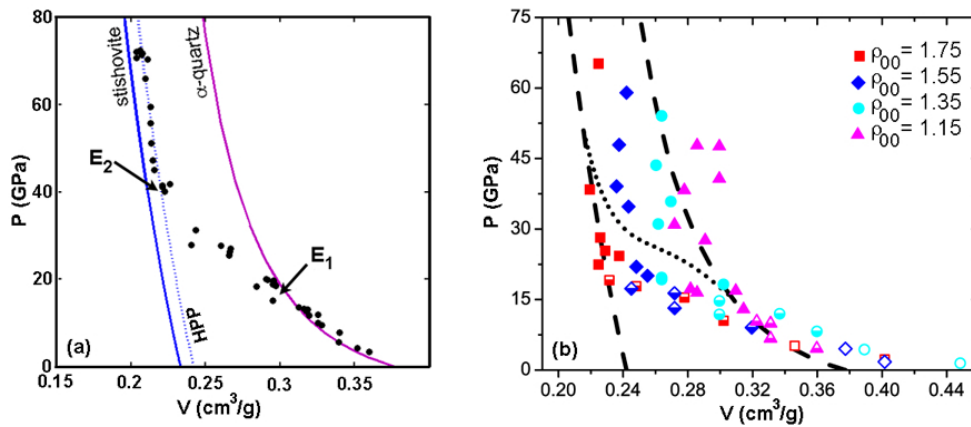


Figure 1. Shock response of (a) solid SiO_2 with calculated α -quartz and stishovite Hugoniots [13], experimental data from [7, 14], where dotted line is the HPP, which is the stishovite phase shifted in volume to align with the high pressure phase shock data. Data in (b) is for porous SiO_2 at initial densities 1.75, 1.55, 1.35, and 1.15 g/cm^3 , where dashed lines are quartz and HPP Hugoniots and dotted line is path followed by the solid under shock compression. All data for porous SiO_2 taken from [7].

Inspection of figure 1(b) reveals three important features, characteristic of phase transitioning porous oxides: 1) the introduction of porosity appears to lower the threshold pressure for the onset and completion of transition, 2) with increasing porosity the Hugoniots vary from "normal" to "anomalous" (increased pressures result in expansion), and 3) it is difficult to discern how much of the total volume reduction is due to pore collapse and how much is due to the phase transition. Figure 1(b) also shows that for $E < E_1$ (open symbols) all of the experimental data lies to the right of the quartz Hugoniot, such that the total volume reduction for experiments in

this regime result from pore collapse only. For $E_1 < E < E_2$ (half-filled symbols) the Hugoniot points in figure 1(b) span a wide range of compressions, where at higher initial densities the points fall exclusively between the quartz and HPP Hugoniots, and at lower initial densities the points lie to the right and left of the quartz Hugoniot. At the highest shock energies for which $E > E_2$ (solid symbols), the response for each initial density appears to asymptote to nearly linear behavior at high pressures. For the three lower initial density samples, it also appears that at high pressures the systems exhibit traits of "anomalous" compaction. With the data for $E < E_1$ occurring at relatively low pressures, the proposed model attempts to capture the trends observed in figure 1(b) for $E > E_1$ by combining the isobaric equation of state and P - α compaction/transition model, as given by equation (4)

3.1. Isobaric Response

In the current framework the isobaric equation of state is meant to capture the Hugoniot response of the high pressure phase, which in this analysis is assumed to be the stishovite Hugoniot shifted to align with the solid data of figure 1(a) and is described by the parameters, $V_0 = 0.242 \text{ cm}^3/\text{g}$, $C_0 = 9.42 \text{ km/s}$, $S = 1.02$, such that the reference specific volume is that of the high pressure phase. With the reference state of the solid defined, the porous Hugoniot is given by equation (3), and the best-fit results using γ_0 as the adjustable parameter are shown in figure 2. It is observed that by allowing γ_0 to vary between 0.5 to 2.5 as the initial density is decreased from 1.75 to 1.15 g/cm³, good agreement is obtained for most all of the data with energies $E > E_2$ (solid symbols). It should be noted that the ambient Grüneisen coefficient for the quartz, coesite, and stishovite phases of SiO₂ are $\gamma_0 = 0.65$, 0.40, and 1.22, respectively [13]. Therefore, the assigned γ_0 values for the two highest initial density samples, which are found to capture all of the data for $E > E_2$, are well within the ranges of γ_0 values for the different phases of SiO₂. It is only when the initial distention becomes quite large that γ_0 must be increased significantly. This suggests the current approximation for $\gamma(P)$ is insufficient to capture the large thermal excursions experienced during the shock compression of low density specimens.

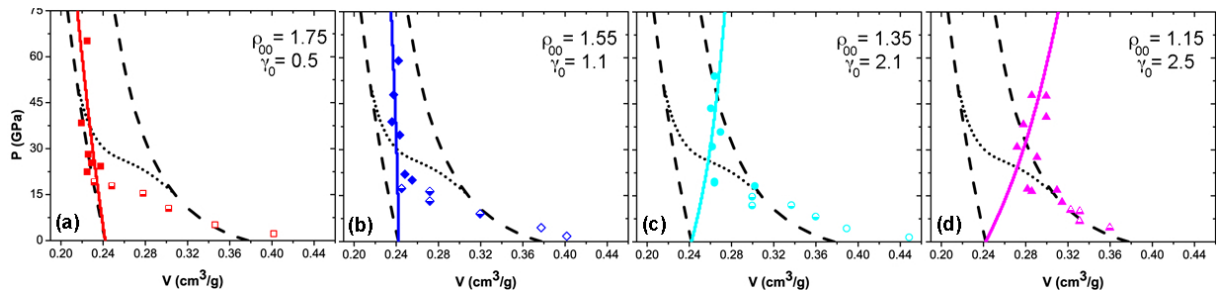


Figure 2. Calculated response of initially distended SiO₂ assuming material crushes to HPP at negligible pressures (solid lines) with experimental porous data and solid quartz and HPP Hugoniots. Open symbols are for $E < E_1$, half-filled symbols for $E_1 < E < E_2$, and filled symbols for $E > E_2$.

3.2. Mixed Phase Response

With sufficient agreement obtained between the experimental data and the isobaric equation of state response at high pressures, the P - α compaction model defined by equations (6) and (7) is applied to fit the remainder of the data in the mixed phase regime (half-filled symbols). Assigning a value of $\sigma_Y = 11 \text{ GPa}$ yields the results shown in figure 3, where the data for all experiments with $E > E_1$ falls on, or within close proximity to, the calculated porous Hugoniot indicated

by the solid line. Only at the lowest pressures and lowest initial density ($\rho_{00} = 1.15 \text{ g/cm}^3$) does there appear to be any noticeable deviation from the calculated response. With regard to the best-fit value of 11 GPa for σ_Y , in the original P - α formulation σ_Y simply represented the yield strength of the material under compression. However, in the current investigation σ_Y encompasses not only the yield properties of the material (controlling the process of pore collapse), but also the extent to which the material is undergoing a transition to the second phase. Comparing the best-fit value for σ_Y to the reported Hugoniot elastic limit (HEL) for the different crystallographic orientations of quartz [15]: x-cut = 3.5-8.5, y-cut = 5.5-8.5, and z-cut = 10-15 GPa, respectively, it appears that σ_Y is in the range of the HEL for at least the z-cut orientation. However, caution must be exercised when relating σ_Y to the HEL, as σ_Y reflects both the yield and phase transitioning properties of SiO_2 .

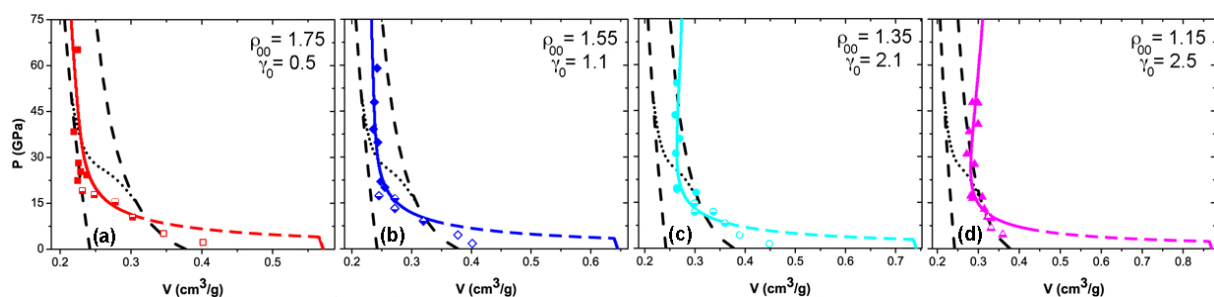


Figure 3. Calculated equation of state and crush response of initially distended SiO_2 with addition of P - α model (solid lines) also showing experimental porous data and solid quartz and HPP Hugoniot. Open symbols are for $E < E_1$, half-filled symbols for $E_1 < E < E_2$, and filled symbols for $E > E_2$.

4. Conclusions

A model was developed that can predict the onset and completion of phase transition in porous oxide systems by equating the energies at which these transition occur for the solid and porous materials. The energy criteria was applied to available experimental data for SiO_2 , and it was found that by using the solid Hugoniot of the high pressure phase as the reference state, an isobaric equation of state could successfully capture the trends exhibited by the Hugoniot responses for a wide range of initial density samples, provided the ambient Grüneisen constant was allowed to vary. In addition, a rate-independent P - α compaction/transition model was also applied, and it was found that the combination of these two approaches could successfully describe the Hugoniot behavior for all experiments in the mixed ($E_1 < E < E_2$) and high pressure ($E > E_2$) phase regimes. With the appropriate relationships developed between the best-fit values for γ_0 and the initial sample density, or a more robust definition for $\gamma(P)$, it may be possible to utilize the current framework to predict the Hugoniot response for a wide range of initial density samples.

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References

- [1] Davison L 2008 *Fundamentals of Shock Wave Propagation in Solids* (Berlin: Springer-Verlag)
- [2] Zel'dovich Y and Razier Y 2002 *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (New York: Dover)
- [3] Simons G and Legner H 1982 *J. Appl. Phys.* **53** 943
- [4] Rice M H and Walsh J M 1957 *J. Chem. Phys.* **26** 824
- [5] Oh K-H and Persson P A 1989 *J. Appl. Phys.* **65** 3852
- [6] Marsh S P 1980 *LASL Shock Hugoniot Data* (Berkley: University of California Press)
- [7] Trunin R F 2001 *Experimental Data on Shock Compression and Adiabatic Expansion of Condensed Matter* (Sarov: RFNC-VNIIEF)
- [8] Herrmann W 1969 *J. Appl. Phys.* **40** 2490
- [9] Carroll M M and Holt A C 1972 *J. Appl. Phys.* **43** 759
- [10] McQueen R G, Marsh S P and Fritz J N 1967 *J. Appl. Phys.* **72** 4999
- [11] Carroll M M and Holt A C 1972 *J. Appl. Phys.* **43** 1626
- [12] Fredenburg D A and Thadhani N N 2013 *J. Appl. Phys.* **113** 223513
- [13] Boettger J C 1992 *J. Appl. Phys.* **72** 5500
- [14] Wackerle J 1962 *J. Appl. Phys.* **33** 2319
- [15] Swegle J W 1990 *J. Appl. Phys.* **68** 1563