Towards a Nonlinear Elastic Representation of Finite Compression and Instability of Boron Carbide Ceramic

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16. SUBJECT TERMS

- nonlinear elasticity
- anisotropy
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Towards a nonlinear elastic representation of finite compression and instability of boron carbide ceramic

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Keywords: nonlinear elasticity; anisotropy; stability; rhombohedral structure; ceramic; boron carbide

1. Introduction

In nonlinear elasticity theory of ideal crystals, loss of mechanical stability can be associated with loss of positive-definiteness of various elastic stiffness tensors under loading conditions corresponding to a homogeneous stress state. Such a loss of stability implies that large deformations may result from little or no change in applied forces, or that bifurcations, i.e., non-unique load–displacement paths, are admissible [1]. In the context of real materials, loss of stability may correlate with the
onset of various heterogeneous physical behaviors, e.g., phase transformations, amorphization, slip, twinning, cavitation, or fracture [2–4].

The particular material of interest in the present work, boron carbide, is known to undergo amorphization when subjected to high pressure (compressive) loading. Shock-induced amorphization of boron carbide was first discovered following post-mortem examination of fragments recovered from ballistic experiments [5]. Therein, it was suggested that the onset of amorphization may be associated with loss of elastic stability.

Subsequent theoretical [Density Functional Theory (DFT)] calculations of hydrostatic loading [6] predicted collapse of the crystal structure of boron carbide into amorphous regions consisting of a mixture of carbon and boron icosahedra, with such amorphization energetically favorable for the particular polytype \( B_{12}^{\text{CCC}} \), denoted herein as “CCC”. In a later work [7], first principles calculations suggested that amorphization follows cross-linking of C-B-C atomic chains of the boron carbide unit cell with icosahedra at the vertices of the rhombohedral unit cell in the \( B_{11}^{\text{CBC}} \) polytype (i.e., “polar” polytype). The cross-linked structure is unstable at ambient pressure; hence, amorphization and fracture may occur on decompression. Such cross-linking was found to occur for uniaxial straining along the c-axis ([0001]-direction) but was not observed for hydrostatic compression. Local amorphous bands have also been observed in indented boron carbide [8].

Recent quantum mechanical calculations [9] report variations of elastic stiffness components of several polytypes of boron carbide with increasing applied hydrostatic pressure. Noteworthy was the discovery of a decreasing tangent elastic coefficient \( C_{44} \) with increasing pressure, leading to a predicted vanishing eigenvalue of stiffness tensor \( C_{\alpha\beta} \) at pressure \( p \approx 44 \text{ GPa} \) in the CCC polytype and \( p \approx 68 \text{ GPa} \) in the polar polytype.

Boron carbide exhibits a rhombohedral (i.e., trigonal) crystal structure: space group \( R3m \), centrosymmetric point group \( 3m \), and Laue group [10,11] RI. As indicated earlier, various polytypes exist, with the polar polytype most stable and usually most common [6]; stoichiometry of boron carbide may also depart from the ideal boron-to-carbon ratio of \( B_4C \), with lower carbon content typical, since \( B_4C \) represents the carbon-rich single phase limit [12]. Because of its high hardness (\( \approx 30 \text{ GPa} \)), high elastic stiffness (polycrystalline Young’s modulus 470 GPa [13]), and low mass density (theoretical density 2.52 g/cm\(^3\)), boron carbide is used in military protection systems (i.e., armors). Instability, amorphization, and subsequent fracture under ballistic loading (shock pressures of 10–40 GPa) may pose the greatest limitation to the material’s utility for such applications. The present study seeks an improved understanding of behavior of boron carbide through development of a nonlinear elasticity model and stability/failure criteria valid for this range of compressive stress states. In addition, application of the model towards behavior of polycrystals provides information supplementing that from plate impact studies. Though a number of such shock physics experiments have been conducted, the current understanding of material behavior remains incomplete [14–17].

Notably, several other crystals belong to the same crystallographic point group as boron carbide: quartz, calcite, and sapphire. The \( \alpha \) phase of quartz is known to undergo transformation to an amorphous phase at pressures in excess of 20 GPa,
and such behavior has been linked, at least qualitatively, to loss of elastic stiffness and stability [18]. In particular, the tangent elastic coefficient $C_{44}$ decreases at high pressure in quartz, as it does in boron carbide. Calcite undergoes a polymorphic transformation to a monoclinic structure at pressures on the order of 1.5 GPa [19] and is known to twin easily under concentrated loading [20]; it has been suggested that twinning in calcite may be facilitated by a loss of elastic stability associated with shear softening reflected by its third-order elastic constants [21]. Sapphire (i.e., single crystal alumina) does not exhibit any known loss of elastic stability and maintains its $\alpha$ phase to pressures of at least 79 GPa, but does demonstrate twinning [20,22,23]. Point defects, partial dislocations and stacking faults, and deformation twins have been observed in boron carbide [5,24]; however, such defects are thought to be relatively immobile, with threshold driving forces for their motion larger than those for amorphization and fracture; the latter two phenomena are thought to dominate inelasticity of boron carbide under ballistic or impact loading [5,17].

Following early work of Born [25], a number of criteria for stability of homogeneously strained solids have been derived [1–3,26–29]. Four such criteria, each corresponding to a vanishing eigenvalue of a different elastic stiffness matrix, are considered in the present work. It is found that for the material and loading conditions of present interest, the criterion for instability attained first (i.e., at the lowest applied load or strain) corresponds to loss of positive definiteness of a symmetric form of the matrix governing the change in Cauchy stress with incremental spatial strain. This incremental stiffness matrix is derived directly in the present work without any kinematic approximations; the end result is identical to some incremental stiffness matrices derived in different ways in previous studies [2–4,29,30].

In the current work, a nonlinear anisotropic elasticity model incorporating elastic constants up to third order [10,11,30] is applied. Elastic stiffness constants are obtained for polar and CCC polytypes such that tangent elastic moduli at 0% and $\approx 20\%$ volumetric compression (0 and $\approx 80$ GPa pressure, respectively) match those predicted theoretically from first principles [9]. Because available data are insufficient to specify all independent third-order elastic constants for this trigonal single crystal, selective assumptions of reduced anisotropy are used to eliminate certain unknown third-order constants not associated with shearing modes when such assumptions do not conflict with known pressure dependencies of tangent moduli. Prescribed third-order elastic coefficients affecting pressure dependence of $C_{44}$ reflect the loss of stability of boron carbide compressed along the c-axis. Third-order elasticity theory has been applied in previous works towards various other ceramics and minerals deformed to moderate compressions [22,23,31–33]; the present study represents the first application of such a model towards boron carbide, and to the author’s knowledge, the first analysis of elastic instability in the context of third-order elasticity.

This paper is organized as follows. Fundamental relationships of nonlinear elasticity and stability measures, applicable towards any hyperelastic solid, are discussed in Section 2. Application of the theory to boron carbide single crystals is addressed in Section 3. Application to boron carbide polycrystals is given in Section 4. Discussion and conclusions follow in Sections 5 and 6. Cartesian coordinates are used throughout, with summation applied over repeated indices.
2. Nonlinear elasticity and stability

2.1. Nonlinear elasticity of crystals

Let $x$ and $X$ denote current and reference coordinates of a material element, related at time $t$ by the twice differentiable one-to-one mappings

$$x = x(X, t), \quad X = X(x, t). \quad \text{(2.1)}$$

Components of the deformation gradient $F$ and its inverse are

$$F_{ij} = \frac{\partial x_i}{\partial X_j}, \quad F^{-1}_{ij} = \frac{\partial X_i}{\partial x_j}, \quad \text{(2.2)}$$

where $\frac{\partial x_i}{\partial X_j} = \frac{\partial x_i}{\partial x_j} F_{ij}$. Referential coordinate indices are capitalized; spatial coordinate indices are not. The Green elastic strain tensor $E$ is

$$E = \frac{1}{2} (F^T F - I), \quad E_{ij} = \frac{1}{2} (F^{-1}_{ij} F_{ij} - \delta_{ij}), \quad \text{(2.3)}$$

with $\delta_{ij}$ Kronecker’s delta and $(\cdot)^T$ the transpose. The ratio of deformed to initial volume for an element of material is the Jacobian determinant $J$:

$$J = V/V_0 = \det F = \frac{1}{6} \varepsilon_{ijk} \varepsilon_{IJK} F_{ij} F_{jk} = [\det(2E + I)]^{1/2} > 0, \quad \text{(2.4)}$$

with $\varepsilon_{ijk}$ and $\varepsilon_{IJK}$ permutation symbols. The following identities apply [11]:

$$\partial_i F_{lj} = \partial_j F_{li}, \quad \partial_i F^{-1}_{lj} = \partial_j F^{-1}_{li}, \quad \text{(2.5)}$$

$$\frac{\partial F^{-1}_{lj}}{\partial F_{ij}} = -F^{-1}_{lj} F^{-1}_{ij}, \quad \frac{\partial F_{lj}}{\partial F^{-1}_{ij}} = -F_{lj} F^{-1}_{ij}, \quad \text{(2.6)}$$

$$\frac{\partial J}{\partial F_{lj}} = J F^{-1}_{lj}, \quad \frac{\partial J^{-1}}{\partial F^{-1}_{lj}} = J^{-1} F_{lj}, \quad \partial_k (J F^{-1}_{kj}) = 0, \quad \partial_k (J^{-1} F_{kj}) = 0. \quad \text{(2.7)}$$

By the polar decomposition theorem applied to deformation gradient $F$, rotation $R$ and right stretch tensor $U$ are determined uniquely since $F$ is non-singular [11,27]:

$$F = RU, \quad F_{lj} = R_{lj} U_{lj}, \quad U_{lj} = U_{lj}, \quad \text{(2.9)}$$

where $R$ is proper orthogonal since $J = \det U > 0$. In the absence of rotation, $F$ is a pure stretch:

$$F_{lj} = \delta_{lj} U_{lj} = \delta_{lj} \partial_j x_i = \delta_{lj} \partial_l x_j = \delta_{lj} \partial_j \partial_l \varphi, \quad \text{(2.10)}$$

where $\varphi(X, t)$ is a displacement potential [27]. Green strain is uniquely related to stretch via

$$E = \frac{1}{2} (U^2 - I), \quad U = (2E + I)^{1/2}. \quad \text{(2.11)}$$

In the absence of body forces, the local balance of linear momentum is

$$\partial_k \sigma_{lk} = F^{-1}_{kk} \partial_k (J^{-1} F_{kl} P_{il}) = J^{-1} \partial_k P_{lk} = \rho \ddot{x}_l, \quad \text{(2.12)}$$
where the superposed dot denotes a material time derivative, i.e., \( \partial(\cdot)/\partial t \) at fixed \( X \). Symmetric Cauchy stress \( \sigma \) and first Piola–Kirchhoff stress \( P \) are related by

\[
\sigma = J^{-1} P F^T = J^{-1} F S F^T,
\]

and \( S \) denotes the symmetric second Piola–Kirchhoff stress tensor, often referred to in physics literature as “thermodynamic tension”. Referential and spatial mass density are related by

\[
\rho_0 = \rho J, \quad \dot{\rho} = -\rho \partial_k \dot{x}_k.
\]

Cauchy pressure is

\[
p = -\frac{1}{3} \sigma_{kk} = -\frac{1}{3J} F_{kl} F_{kj} S_{lj}.
\]

For a homogeneous hyperelastic solid, strain energy per unit reference volume is of the functional form

\[
U = U[E(F)].
\]

Stresses are

\[
P = \frac{\partial U}{\partial F}, \quad S = \frac{\partial U}{\partial E}.
\]

Corresponding tangent elastic moduli, which generally vary with \( F \) or \( E \), are

\[
A_{ijkl} = \frac{\partial P_{ij}}{\partial F_{kl}} = \frac{\partial^2 U}{\partial F_{ij} \partial F_{kl}} = A_{kl}^{ij},
\]

\[
C_{ijkl} = \frac{\partial S_{ij}}{\partial E_{kl}} = \frac{\partial^2 U}{\partial E_{ij} \partial E_{kl}} = C_{kl}^{ij}.
\]

From the symmetry of \( E \),

\[
C_{ijkl} = C_{jikl} = C_{ijlk} = C_{jilk}.
\]

At any value of deformation gradient, tangent moduli are related by [11]

\[
A_{ijkl} = F_{il} F_{kj} C_{ijkl} + S_{jl} \delta_{ik}.
\]

Notice that \( A \) directly enters momentum balance (2.12), and hence the wave propagation equations:

\[
\rho_0 \ddot{x}_i = \partial_j P_{ij} = \frac{\partial^2 U}{\partial F_{ij} \partial X_j} = \frac{\partial^2 U}{\partial F_{ij} \partial F_{kl}} \frac{\partial F_{kl}}{\partial X_j} = A_{ijkl} \partial_j F_{kl} = A_{il}^{jk} \partial_j F_{kl},
\]

where the final equality follows from (2.5).

The following relationships are derived using (2.6), (2.7), (2.13), and (2.18):

\[
J^{-1} A_{ijkl} = \frac{\partial \sigma_{im}}{\partial F_{kl}} F_{jm}^{-1} + \sigma_{im} (F_{jm}^{-1} F_{lk}^{-1} - F_{jk}^{-1} F_{im}^{-1}),
\]

\[
\frac{\partial \sigma_{im}}{\partial F_{kl}} = J^{-1} A_{ijkl} F_{mj} + \sigma_{jm} (F_{lj}^{-1} \delta_{km} - F_{lk}^{-1} \delta_{jm}).
\]
Furthermore, from (2.13), Cauchy stress depends on Green strain and rotation:
\[
\sigma(F) = J^{-1}F[S(E)]F^T = \sigma(U, R) = \sigma(E, R). \tag{2.25}
\]
Application of the chain rule gives
\[
\frac{\partial \sigma_{ij}}{\partial F_{KL}} = \frac{\partial \sigma_{ij}}{\partial E_{KL}} \bigg|_{R=\text{const.}} F_{KK} + \frac{\partial \sigma_{ij}}{\partial R_{KM}} \bigg|_{E=\text{const.}} U_{LM}^{-1}, \tag{2.26}
\]
where
\[
\frac{\partial \sigma_{ij}}{\partial R_{KM}} \bigg|_{E=\text{const.}} = J^{-1}(\delta_{ik} F_{jN} U_{ML} + \delta_{jk} F_{iL} U_{MN}) S_{LN}, \tag{2.27}
\]
leading to the total tangent moduli
\[
\frac{\partial \sigma_{ij}}{\partial E_{KL}} \bigg|_{R=\text{const.}} = J^{-1}A_{[Mnk} F_{jM} F_{lN}^{-1} F_{Km} - \sigma_{ij} F_{Lm}^{-1} F_{Kn}^{-1} F_{Lm} - \sigma_{ij} F_{Lm}^{-1} F_{Km}^{-1} F_{Ln} - \sigma_{ij} F_{Lm}^{-1} F_{Km}^{-1} F_{Ln}. \tag{2.28}
\]
A tangent modulus used later in this work, written as \(Z\), is obtained by assuming \(\sigma = \sigma(E)\) such that the rightmost term can be omitted in (2.26) or the rightmost two terms can be omitted in (2.28). This assumption is valid if and only if (2.10) holds. Symmetrizing over indices \(K, L\) then gives the following result:
\[
Z_{ijKL} = \frac{\partial \sigma_{ij}(E)}{\partial E_{KL}} = J^{-1}F_{[Ij} F_{jK} C_{IJKL} - \frac{1}{2} \left( 2\sigma_{ij} F_{Kn}^{-1} F_{Ln}^{-1} F_{Kn}^{-1} F_{Ln} - \sigma_{ij} F_{Lm}^{-1} F_{Kn}^{-1} F_{Lm} - \sigma_{ij} F_{Lm}^{-1} F_{Km}^{-1} F_{Ln} - \sigma_{ij} F_{Lm}^{-1} F_{Km}^{-1} F_{Ln} \right). \tag{2.29}
\]
Fourth-order two-point tensor \(Z\) obeys the symmetry relations
\[
Z_{ijKL} = Z_{jiKL} = Z_{ijLK} = Z_{jikL}, \tag{2.30}
\]
but in general \(Z_{ijKL} \delta_{il} \delta_{jL} \neq Z_{klij} \delta_{ik} \delta_{jL}\).

The following incremental stiffness tensor \([2,4,30,34]\) is also considered:
\[
B_{ijkl} = \hat{C}_{ijkl} - \frac{1}{2} (2\sigma_{ij} \delta_{kl} - \sigma_{ij} \delta_{ik} - \sigma_{ij} \delta_{ik} - \sigma_{jk} \delta_{il} - \sigma_{ik} \delta_{jl}). \tag{2.31}
\]
Fourth-order tensor \(B\) of (2.31) obeys the symmetry relations
\[
B_{ijkl} = B_{jikl} = B_{ijk} = B_{jikl}, \tag{2.32}
\]
but in general \(B_{ijkl} \neq B_{klji}\).

Incremental (tangent) modulus \(B\) has been derived in different ways \([2–4,30,34]\) and has been attributed various physical meanings. The definition of \(\hat{C}\) entering \(B\) depends on the (possibly stressed) reference state from which Green strain is measured, and as shown in Appendix B, when the current configuration is taken as the reference state, is \([34]\)
\[
\hat{C}_{ijkl} = J^{-1}F_{[Ij} F_{jK} F_{lL} C_{IJKL}. \tag{2.33}
\]

Tensor \(\hat{C}\) exhibits the same complete Voigt symmetry as \(C\), i.e., contains up to 21 independent entries.
In the usual context of nonlinear elasticity of crystals \([10,11,30]\), strain energy density is expressed as the following Taylor polynomial in terms of \(E\):

\[
U(E) = U_0 + \frac{\partial U}{\partial E_{IJ}}|_{0} E_{IJ} + \frac{1}{2!} \frac{\partial^2 U}{\partial E_{IJ} \partial E_{KL}}|_{0} E_{IJ} E_{KL} \\
+ \frac{1}{3!} \frac{\partial^3 U}{\partial E_{IJ} \partial E_{KL} \partial E_{MN}}|_{0} E_{IJ} E_{KL} E_{MN} + \cdots
\]

(2.34)

where \((\cdot)|_0\) denotes a quantity evaluated at a reference state. Presuming energy density and stress vanish at the reference state where \(F = 1\) and \(E = 0\):

\[
U_0 = 0, \quad C_{IJ}|_0 = 0,
\]

(2.35)

and introducing Voigt notation \([10,11,30]\) where Greek indices run from 1 to 6:

\[
11 \leftrightarrow 1, \quad 22 \leftrightarrow 2, \quad 33 \leftrightarrow 3, \quad 23 \leftrightarrow 4, \quad 31 \leftrightarrow 5, \quad 12 \leftrightarrow 6,
\]

(2.36)

strain energy density can be written as follows, upon truncation at third order:

\[
U = \frac{1}{2} C_{\alpha\beta}|_0 E_{\alpha} E_{\beta} + \frac{1}{6} C_{\alpha\beta\chi}|_0 E_{\alpha} E_{\beta} E_{\chi}.
\]

(2.37)

Second-order elastic constants at the reference state are \(C_{\alpha\beta}|_0\), and third-order elastic constants at the reference state are \(C_{\alpha\beta\chi}|_0\). For isothermal problems, \(U\) can represent free energy at constant temperature, in which case isothermal elastic constants should be used. For isentropic problems (e.g., many applications involving wave propagation or high rates of elastic loading), \(U\) can represent internal energy at constant entropy, in which case isentropic (adiabatic) elastic constants should be used. For non-ideal cases wherein heat conduction or dissipation are non-negligible – cases which fall outside the scope of the present study – thermoelastic coupling terms should be incorporated into the energy potentials. In the context of lattice statics and homogeneous deformation of crystals \([35]\), second-order constants are related to harmonic contributions to the interatomic potential, and third-order constants depend on harmonic and anharmonic contributions \([11,21,30,36]\).

From (2.37), second Piola–Kirchhoff stresses and second-order tangent moduli of (2.19) are

\[
S_{IJ} = C_{IJKL}|_0 E_{KL} + \frac{1}{2} C_{IJKLMN}|_0 E_{KL} E_{MN}
\]

\[
\leftrightarrow S_{\alpha} = C_{\alpha\beta}|_0 E_{\beta} + \frac{1}{2} C_{\alpha\beta\chi}|_0 E_{\beta} E_{\chi};
\]

(2.38)

\[
C_{IJKL} = C_{IJKL}|_0 + C_{IJKLMN}|_0 E_{MN} \leftrightarrow C_{\alpha\beta} = C_{\alpha\beta}|_0 + C_{\alpha\beta\chi}|_0 E_{\chi}.
\]

(2.39)

Coefficients such as \(C_{\alpha\beta}(E)\) are often referred to in physics literature as “elastic constants” even though they generally vary with strain, stress, volume, pressure, etc. Only in linear elastic solids for which elastic constants of orders three and higher
vanish by definition do $C_{\alpha\beta} = C_{\alpha\beta} |_0 = \text{constant.}$ With $S$ and $C$ known for a given $F,$ other stiffness coefficients $A$, $Z$, and $B$ can be computed directly using (2.21), (2.29), and (2.31).

For crystals of minimal symmetry (i.e., triclinic point groups), $C_{\alpha\beta} |_0$ consists of up to 21 independent terms and $C_{\alpha\beta} |_0$ up to 56. It is remarked that Taylor polynomial (2.34), while convenient, is not the most general form of the strain energy function of a material with a given symmetry. For a hyperelastic material, the most general functional form of $U$ is

$$U = U(I_1, I_2, \ldots, I_N),$$

where $I_K (K = 1, \ldots, N)$ are scalar invariant functions of the symmetric deformation tensor $F^T F$ (or of $E$) relative to the group $G$ consisting of orthogonal tensors in the material symmetry group [37]. For standard crystalline solids, $G$ is determined by the crystallographic point group (one of 32) to which the particular crystal structure of interest belongs.

### 2.2. Elastic stability

Several criteria for mechanical elastic stability are discussed in what follows. A criterion credited to Born [25] and considered or applied in a number of subsequent works [1,18,28,35] can be expressed as the inequality

$$d^2 U_C = dS_{IJ} dE_{IJ} = \frac{\partial S_{IJ}}{\partial E_{KL}} dE_{KL} dE_{IJ} = C_{IJKL} dE_{KL} dE_{IJ} = C_{\alpha\beta} dE_\alpha dE_\beta > 0,$$

where $d^2 U_C$ is a second-order increment in potential energy associated with increment in Green strain $dE_\alpha \neq 0.$ Stability requires that potential energy must increase for any nonzero strain increment, leading to the requirement that tangent modulus $C_{\alpha\beta}$ be positive definite. A necessary and sufficient condition for (2.41) to hold is positiveness of the determinant of the symmetric $6 \times 6$ matrix $[C_{\alpha\beta}(E)]:$

$$\text{det}[C_{\alpha\beta}] > 0 \iff d^2 U_C > 0 \ \ (\forall dE_\alpha \neq 0).$$

During a deformation history, onset of instability can be associated with attainment of strain state $E^*_\alpha$ corresponding to the tensor of moduli becoming positive semi-definite [28]:

$$\text{det}[C_{\alpha\beta}(E^*)] = 0, \quad C_{\alpha\beta}(E^*) dE^*_\beta dE^*_\alpha = dS^*_\alpha dE^*_\alpha = 0.$$

Eigenmode $dE^*_\alpha$ associated with a zero eigenvalue of $[C_{\alpha\beta}]$ corresponds to a strain increment to which stress increment $dS^*_\alpha$ is orthogonal. Deformation along such a path would result in no second-order change in potential energy and no additional resistance from mechanical stress. In a real material, such an eigenmode would likely correspond to the strain direction associated with structural transformation, strain localization, fracture, etc. A criterion like (2.41) can be formulated in terms of tangent stiffness tensor $\hat{C}$ of (2.33) [2,3,28], i.e., $J^{-1}d^2 U_C = \hat{C}_{ijkl} dE_{ij} dE_{kl} > 0,$ where $d\hat{E}_{ij} = dE_{ij} F^{-1}_{hi} F^{-1}_{lj}$ is an increment in Green strain measured from the current state.
A second stability criterion can be expressed in terms of increments in deformation gradient rather than Green's strain \([1,28,30,38]\):

\[
d^2 U_A = dP_{ij} dF_{ij} = \frac{\partial P_{ij}}{\partial F_{kl}} dF_{kl} dF_{ij} = A_{iikl} dF_{kl} dF_{ij} > 0, \tag{2.44}
\]

where \(d^2 U_A\) is a second-order increment in potential energy associated with increment in deformation gradient \(dF_{ij} \neq 0\). Criterion (2.44) can be simplified for deformation paths wherein rotations vanish. A symmetric increment in stretch is

\[
dU_{ij} = dU_{ji} = \frac{\partial I}{\partial J} d': \tag{2.45}
\]

Criterion (2.44) becomes

\[
d^2 U_A = A_{iikl} dF_{kl} dF_{ij} = A_{iikl} \delta_{ik} \delta_{kL} dU_{KL} dU_{IJ} = A_{ijkl} dF_{ij} dF_{kl} > 0,
\]

where

\[
A_{ijkl} = \frac{1}{4} (A_{ijkl} \delta_{ij} \delta_{kL} + A_{ijkl} \delta_{ij} \delta_{kL} + A_{ijkl} \delta_{ij} \delta_{IL} + A_{ijkl} \delta_{ij} \delta_{IL}), \tag{2.47}
\]

\[
A_{ij} = A_{ji}. \tag{2.48}
\]

Therefore, stability with respect to increments in stretch corresponds to positive definiteness of the symmetric \(6 \times 6\) matrix \([A_{ij}]\):

\[
\text{det}[A_{ij}] > 0 \iff d^2 U_A > 0 \quad (\forall dU_{ij} \neq 0). \tag{2.49}
\]

Conditions marking the onset of instability are

\[
\text{det}[A_{ij}(F^*)] = 0, \quad A_{ij}(F^*) dU^*_i dU^*_j = dP^*_i dU^*_a = 0. \tag{2.50}
\]

Eigenmode \(dU^*_a\) associated with a zero eigenvalue of \([A_{ij}]\) corresponds to a stretch increment to which stress increment \(dP^*_a\) is orthogonal.

A third criterion follows from the so-called GCN\(^+\) condition of Coleman and Noll [26,27], which can be written

\[
d^2 U_D = J^{-1} A_{ijkl} F_{ij} F_{kl} dE_{ij} dE_{kl} = D_{ijkl} dE_{ij} dE_{kl} = D_{ij} dE_{ij} dE_{ij} > 0, \quad (\forall dE_{ij} = dE_{ij} \neq 0), \tag{2.51}
\]

with de a symmetric nonzero, but otherwise arbitrary, second-order tensor and

\[
D_{ijkl} = \frac{1}{4J} (A_{ijkl} F_{ij} F_{kl} + A_{ijkl} F_{ij} F_{kl} + A_{ijkl} F_{ij} F_{kl} + A_{ijkl} F_{ij} F_{kl}). \tag{2.52}
\]

This condition requires that the transformation from deformation to first Piola–Kirchhoff stress be monotone with respect to pairs of deformations differing by a pure stretch [27]. Stability with respect to increments in spatial strain measure \(e^*_a\) corresponds to positive definiteness of the symmetric \(6 \times 6\) matrix \([D_{ij}]\):

\[
\text{det}[D_{ij}] > 0. \tag{2.53}
\]

Conditions marking the onset of instability are

\[
\text{det}[D_{ij}(F^*)] = 0, \quad D_{ij}(F^*) dE^*_i dE^*_j = dS^*_i dE^*_a = 0, \tag{2.54}
\]

Therefore, stability with respect to increments in stretch corresponds to positive definiteness of the symmetric \(6 \times 6\) matrix \([A_{ij}]\):

\[
\text{det}[A_{ij}] > 0 \iff d^2 U_A > 0 \quad (\forall dU_{ij} \neq 0). \tag{2.49}
\]

Conditions marking the onset of instability are

\[
\text{det}[A_{ij}(F^*)] = 0, \quad A_{ij}(F^*) dU^*_i dU^*_j = dP^*_i dU^*_a = 0. \tag{2.50}
\]

Eigenmode \(dU^*_a\) associated with a zero eigenvalue of \([A_{ij}]\) corresponds to a stretch increment to which stress increment \(dP^*_a\) is orthogonal.

A third criterion follows from the so-called GCN\(^+\) condition of Coleman and Noll [26,27], which can be written

\[
d^2 U_D = J^{-1} A_{ijkl} F_{ij} F_{kl} dE_{ij} dE_{kl} = D_{ijkl} dE_{ij} dE_{kl} = D_{ij} dE_{ij} dE_{ij} > 0, \quad (\forall dE_{ij} = dE_{ij} \neq 0), \tag{2.51}
\]

with de a symmetric nonzero, but otherwise arbitrary, second-order tensor and

\[
D_{ijkl} = \frac{1}{4J} (A_{ijkl} F_{ij} F_{kl} + A_{ijkl} F_{ij} F_{kl} + A_{ijkl} F_{ij} F_{kl} + A_{ijkl} F_{ij} F_{kl}). \tag{2.52}
\]

This condition requires that the transformation from deformation to first Piola–Kirchhoff stress be monotone with respect to pairs of deformations differing by a pure stretch [27]. Stability with respect to increments in spatial strain measure \(e^*_a\) corresponds to positive definiteness of the symmetric \(6 \times 6\) matrix \([D_{ij}]\):

\[
\text{det}[D_{ij}] > 0. \tag{2.53}
\]

Conditions marking the onset of instability are

\[
\text{det}[D_{ij}(F^*)] = 0, \quad D_{ij}(F^*) dE^*_i dE^*_j = dS^*_i dE^*_a = 0, \tag{2.54}
\]
where $\delta e^\alpha_a$ is the eigenmode (spatial strain increment) associated with a vanishing
eigenvale of $[D_{\alpha\beta}]$ and $\delta \sigma^\alpha_a$ is the corresponding stress increment. Notice that
$\delta^2 U_B = J^{-1} \delta^2 U_A$ when $2\delta e_{ij} = F_{iK}^{-1} dF_{iK} + F_{jK}^{-1} dF_{jK}$.

A fourth elastic stability criterion can be written [2–4,29]

$$\delta^2 U_B = B_{ijkl} \delta \epsilon_{ij} \delta \epsilon_{kl} = B_{\alpha\beta} \delta \epsilon_{\alpha} \delta \epsilon_{\beta} > 0,$$

(2.55)

where the symmetrized incremental tangent stiffness

$$\tilde{B}_{ijkl} = \frac{1}{2} (B_{ijkl} + B_{klij}),$$

(2.56)

and with $B_{\alpha\beta}$ denoting the symmetrized stiffness $\tilde{B}_{ijkl}$ in Voigt’s notation:

$$B_{\alpha\beta} = B_{\beta\alpha}.$$

(2.57)

The first-order incremental potential energy change per unit spatial volume is

$$J^{-1} S_{ij} dE_{ij} = F_{li}^{-1} F_{lj}^{-1} \sigma_{ij} dE_{ij} = \sigma_{ij} d\epsilon_{ij};$$

(2.58)

therefore, incremental strain measures are related by [4]

$$dE_{ij} = F_{li} F_{lj} d\epsilon_{ij}.$$

(2.59)

Conditions (2.55) are typically applied under loading paths for which $F$ is
symmetric [i.e., a pure stretch $F = U = (2E + 1)^{1/2}$], such that Cauchy stress $\sigma$ and $B$
depend only on $E$ [3,4]. Stability with respect to increments in strain $\delta \epsilon_{\alpha}$ corresponds
to positive definiteness of the symmetric $6 \times 6$ matrix $[B_{\alpha\beta}(E)]$:

$$\det[B_{\alpha\beta}] > 0 \iff \delta^2 U_B > 0 \quad (\forall \delta \epsilon_{\alpha} \neq 0).$$

(2.60)

Conditions marking onset of instability at critical strain $E^*$ are

$$\det[B_{\alpha\beta}(E^*)] = 0, \quad B_{\alpha\beta}(E^*) \delta \epsilon^\alpha_a \delta \epsilon^\alpha_a = d\sigma^\alpha_a d\epsilon^\alpha_a = 0,$$

(2.61)

where $\delta \epsilon^\alpha_a$ is the eigenmode associated with a vanishing eigenvale of $[B_{\alpha\beta}]$ and $d\sigma^\alpha_a$
is the corresponding stress increment, identified definitively later with Cauchy stress.
Conditions $\delta^2 U_B > 0$ are analogous to positivity of a Gibbs-type integral derived
in [3]. Instability conditions (2.61) imply that increment in Cauchy stress $d\sigma$ becomes
orthogonal to strain increment $d\epsilon$ at instability.

Criterion (2.55) is derived in a new, direct way in the present work as follows:

$$\delta^2 U_Z = d\sigma_{ij} d\epsilon_{ij} = \frac{\partial \sigma_{ij}}{\partial E_{KL}} dE_{KL} d\epsilon_{ij}$$

(2.62)

$$= Z_{ijkl} dE_{KL} d\epsilon_{ij} = Z_{ijkl} d\epsilon_{kl} d\epsilon_{ij}$$

(2.62)

$$= \tilde{Z}_{ijkl} d\epsilon_{kl} d\epsilon_{ij} = Z_{\alpha\beta}^* d\epsilon_{\alpha} d\epsilon_{\beta} > 0.$$

Mapping and symmetrization of $Z$ are defined, upon use of (2.59), as

$$Z_{ijkl} = Z_{ijkl} F_{iK} F_{lL}, \quad \tilde{Z}_{ijkl} = \frac{1}{2} (Z_{ijkl} + Z_{klij}), \quad Z_{\alpha\beta} = Z_{\beta\alpha}.$$

(2.63)

Substituting (2.29) into (2.63), it follows that

$$Z_{ijkl} = B_{ijkl}, \quad Z_{\alpha\beta} = B_{\alpha\beta}, \quad \delta^2 U_Z = \delta^2 U_B.$$

(2.64)
The above steps avoid linear series approximations of the deformation gradient and its determinant (or their inverses) in calculation of \( \partial \sigma / \partial E \) used previously [3,4,30], demonstrating that \( B_{ijkl} \) of (2.31) is an exact representation of incremental stiffness entering (2.62). In other words, the present derivations have proven directly using tensor calculus that \( d \sigma_{ijkl} d e_{ij} = B_{ijkl} \) when \( \sigma = \sigma(E) \).

The four stability criteria listed above, each corresponding to a different positive definite tangent or incremental stiffness matrix, can be summarized as follows:

\[
\begin{align*}
C \text{ stable: } & d^2 U_C > 0 \iff \det[C_{\alpha \beta}] > 0 \iff \lambda_C > 0; \\
A \text{ stable: } & d^2 U_A > 0 \iff \det[A_{\alpha \beta}] > 0 \iff \lambda_A > 0; \\
D \text{ stable: } & d^2 U_D > 0 \iff \det[D_{\alpha \beta}] > 0 \iff \lambda_D > 0; \\
B \text{ stable: } & d^2 U_B > 0 \iff \det[B_{\alpha \beta}] > 0 \iff \lambda_B > 0. \\
\end{align*}
\]  

(2.65)

The \( \lambda_C, \lambda_A, \) etc. refer to the minimum eigenvalue of the corresponding symmetric 6 \times 6 matrices from \( C, A, \) etc. Instability, conversely, is attained as \( \lambda \to 0 \).

Criteria (2.41) and (2.46), along with others involving deformed unit cell parameters [39], have been analyzed for cubic crystals stretched volumetrically or in one or more principal directions [1], leading to implications on which instability criterion would be attained first for loading of a particular sign or direction. Criterion (2.55) has been favored in recent literature [2–4,29]. This \( B \) criterion was found to correlate with observed physical instabilities in molecular dynamics simulations of monatomic cubic crystals subjected to hydrostatic tension, uniaxial stress extension, and stress-free heating, while the \( C \) criterion was unable to predict physically observed instabilities in such simulations [2,3]. For hydrostatic loading, molecular dynamics [3] predicted \( B \) instability associated with decreasing bulk modulus along the primary load path of hydrostatic expansion leading to cavitation, whereas DFT [29] predicted \( B \) instability associated with decreasing rhombohedral shear stiffness representing a stability bifurcation deviating from the primary load path. The latter situation is of particular relevance in the context of the present work, since it will be shown later that boron carbide demonstrates a loss of shear stiffness (\( B_{44} \) or \( B_{55} \)) when the primary load path is spherical or uniaxial (c-axis) compression. Criterion (2.46) was used in a study of thermally induced solid-solid phase transformations in unstressed bi-atomic crystals [40].

None of the criteria in (2.65) reflect instability induced by incremental rotations. For more general situations in which \( dF \) is non-symmetric (and thereby includes differential rotations), the \( A \) criterion in (2.50) can be replaced with vanishing of the determinant of the 9 \times 9 matrix \( [A_{\Phi \Gamma}] \), where \( \Phi, \Gamma \) correspond to one of nine independent components of \( F \), and where \( A_{\Phi \Gamma} = \partial^2 U/\partial F_{\Phi} \partial F_{\Gamma} \) [28]. A criterion involving \( \partial \sigma / \partial F \) of (2.26) might also apply in such cases, e.g., \( d \sigma_{ij} F_{ij}^{-1} dF_{ij} = (d \sigma_{ij} / dF_{ij}) F_{ij}^{-1} dF_{ij} > 0 \). Utility of criteria involving rotations is questionable, however, since the unstressed and undeformed state is a boundary point of the (un)stable domain [28].

Because all moduli reduce to second-order elastic constants when \( F = I \), i.e.,

\[
C_{ijkl} |_{o} = A_{ijkl} |_{o} \delta_{il} \delta_{kj} = D_{ijkl} |_{o} \delta_{il} \delta_{kj} \delta_{IL} = B_{ijkl} |_{o} \delta_{il} \delta_{kj} \delta_{IL},
\]  

(2.66)
all four stability criteria above (involving respective stiffness tensors $C, A, D, \text{ and } B$) reduce to the simple requirement [25]

$$\det\left[ C_{\alpha\beta} \right] > 0$$

(2.67)

at the stress free reference state. Finally, conditions on mechanical elastic stability and positive determinants listed above should be distinguished from the strong ellipticity condition [27]

$$D_{ijkl} u_i v_j u_k v_l > 0, \quad (\forall u, v \neq 0)$$

(2.68)

where $u$ and $v$ are any two nonzero vectors. Condition (2.68) is necessary and sufficient that the acoustic tensor for acceleration waves be positive definite. Replacing $>$ in (2.68) with the weaker requirement $\geq$ results in Hadamard’s condition, which is necessary for stability of any equilibrium configuration of an elastic body subject to a given body force distribution and mixed boundary conditions [27].

3. Boron carbide: single crystal response

3.1. Material properties

Relevant physical properties of boron carbide ceramic are listed in Tables 1 and 2. The referential coordinate system is oriented in the conventional way for crystals of trigonal symmetry [37] such that $X_1$ is parallel to the a-axis ([2110] in hexagonal Miller indices), $X_3$ is parallel to the c-axis ([111] in the rhombohedral structure or [0001] in hexagonal Miller indices), and $X_2$ is orthogonal to $X_1$ and $X_3$ such that $\{X_1, X_2, X_3\}$ form a right-handed triad. In the hexagonal system, $X_1$ and $X_3$ lie in the basal (0001) plane, and $X_3$ is normal to this plane. In the boron carbide unit cell, CCC or CBC atomic chains are aligned with the [0001] direction and thread the basal layers of icosohedra located at the rhombohedral vertices [7,24]. Strictly, structural parameters listed in Table 1 apply for the CCC polytype with ideal stoichiometry $\text{B}_4\text{C}$; slight distortion from listed lattice parameter values may occur in other polytypes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_0$</td>
<td>2.52</td>
<td>Mass density (g/cm$^3$) [13]</td>
</tr>
<tr>
<td>$a_0$</td>
<td>5.17</td>
<td>Rhombohedral lattice parameter (Å) [24]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>65.6°</td>
<td>Rhombohedral angle [24]</td>
</tr>
<tr>
<td>$a$</td>
<td>5.60</td>
<td>Hexagonal lattice parameter (Å) [13]</td>
</tr>
<tr>
<td>$c$</td>
<td>12.12</td>
<td>Hexagonal lattice parameter (Å) [13]</td>
</tr>
</tbody>
</table>

Space group: R$3m$

Point group: $3m$

Atoms/unit cell: 15

$C_{\alpha\beta}$

$C_{\alpha\beta\chi}$

Second-order constants

Third-order constants

(any crystal belonging to Laue group RI)
Experimentally measured elastic constants in Table 2 correspond to a single crystal with stoichiometry B$_{5.6}$C [13] except measurements of the polycrystalline shear modulus $G_0$ and its pressure derivative under hydrostatic loading $G_0|_p = \left( \frac{\partial G}{\partial p} \right)|_p = -18$ that correspond to a polycrystal of 99.7% theoretical density [12]. Tangent elastic coefficients $^\perp C_11/C_12/C_13$ except $^\perp C_14$, particular to polar (CBC) and CCC polytypes have been calculated using first principles as functions of pressure under hydrostatic loading [9]. The value of $C_{14}|_0$ in Table 2 corresponds to the CBC polytype and was computed in a different theoretical study of boron compounds [41]. Values of $^\perp C_j/C_11/C_12|$ listed in Table 2 correspond to a hydrostatic pressure of $p = 80$ GPa and a volume ratio of $V/V_0 = J = 0.79$, the upper limit of pressure reported in [9].

Under hydrostatic loading, an accurate representation of pressure is given by the relationships [14,17]

$$
p = \frac{B|_0(1 - J)}{[1 - s(1 - J)]^2} \approx \frac{3}{2} B|_0(1 - J^{2/3})J^{-7/3} \left[ 1 + \frac{3}{4} (B'|_0 - 4)(J^{-2/3} - 1) \right], \quad (3.1)
$$

where $B|_0$ is the bulk modulus at the reference state and $B'|_0 = (\partial B/\partial p)|_p = 0$ is its initial pressure derivative. The bulk modulus of a single crystal of trigonal symmetry is [41]

$$
B|_0 = \frac{C_{33|0}(C_{11|0} + C_{12|0}) - 2C_{13|0}^2}{C_{11|0} + C_{12|0} - 4C_{13|0} + 2C_{33|0}}, \quad (3.2)
$$

and the two pressure–volume equations-of-state in (3.1) are coincident to second order when [14,17]

$$
s = \frac{1}{4} (B'|_0 + 1). \quad (3.3)
$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment [Ref.]</th>
<th>Polar [Ref.]</th>
<th>CCC [Ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{14</td>
<td>0}$ [GPa]</td>
<td>-18 [41]</td>
<td>-18 [assumed]</td>
</tr>
<tr>
<td>$B</td>
<td>_0$ [GPa]</td>
<td>237 [eq. (3.2)]</td>
<td>236 [eq. (3.2)]</td>
</tr>
<tr>
<td>$s$</td>
<td>1.43 [eq. (3.3)]</td>
<td>1.08 [eq. (3.3)]</td>
<td>1.13 [eq. (3.3)]</td>
</tr>
<tr>
<td>$G'</td>
<td>_0$ [GPa]</td>
<td>0.8 [12]</td>
<td>0.8 [12]</td>
</tr>
</tbody>
</table>

Table 2. Elastic constants of boron carbide.
coefficients are related to third-order elastic constants via

$$ \frac{\partial C_{IJKL}}{\partial p} \bigg|_0 = \frac{\partial C_{IJKL}}{\partial \varepsilon_{MN}} \frac{\partial \varepsilon_{PQ}}{\partial p} \bigg|_0 = -C_{IJLMN}\varepsilon_{0MNP}, $$

(3.4)

where, in Voigt’s notation, $[M_{\alpha\beta}] = [C_{\alpha\beta}]^{-1}$ is the elastic compliance matrix at the reference state obeying $M_{\alpha\beta}C_{\alpha\beta}\varepsilon_0 = \delta_{\alpha\beta}$. For trigonal crystals of Laue group RI, this reduces to [42]

$$ C_{\alpha\beta}\varepsilon_0 = \frac{\partial C_{\alpha\beta}}{\partial p} \bigg|_0 = -M_1(C_{\alpha\beta}\varepsilon_0 + C_{\alpha\beta}\varepsilon_0) - M_3(C_{\alpha\beta}\varepsilon_0); $$

(3.5)

$$ M_1 = M_{11} + M_{12} + M_{13}, \quad M_3 = 2M_{13} + M_{33}. $$

(3.6)

Proposed third-order constants for polar and CCC polytypes are listed in Table 3. These are determined upon use of Table 2 and comparison with predicted coefficients obtained during spherical and uniaxial compression, as described in Sections 3.2, 3.3, and 3.4. Parameter $\xi$ will be defined explicitly later in Section 3.4. Corresponding pressure derivatives computed from (3.5) are listed in Table 4; these do not depend appreciably on $\xi$.

### 3.2. Spherical compression

Consider a single crystal subjected to spherical (i.e., isotropic) compression. In this case, the deformation gradient $F$, Green strain $E$, and tangent elastic modulus tensors $C$ and $\hat{C}$ are all explicit functions of volume ratio $J$:

$$ F_{IJ} = J^{1/3}\delta_{IJ} = (V/V_0)^{1/3}\delta_{IJ}; $$

(3.7)

$$ E_{IJ} = \frac{1}{2}(J^{2/3} - 1)\delta_{IJ} = E\delta_{IJ}, \quad E = \frac{1}{2}(J^{2/3} - 1); $$

(3.8)

$$ C_{IJKL}\varepsilon_0 = C_{IJKL}\varepsilon_0 + C_{IJLMN}\varepsilon_0; $$

(3.9)

$$ \hat{C}_{ijkl}\varepsilon_0 = J^{1/3}\delta_{ij}\delta_{jk}\delta_{kl}C_{ijkl}\varepsilon_0. $$

(3.10)
For a crystal with RI group symmetry, noting that $C_{2330} = C_{1330}$, $C_{2440} = C_{1550}$ and $C_{1220} = C_{1110} + C_{1120} - C_{2220}$ [11], (3.9) yields the following six independent equations in Voigt’s notation:

$$C_{11\xi} = C_{11\xi_0} + \left(C_{111\xi_0} + C_{112\xi_0} + C_{113\xi_0}\right)E,$$  \hspace{1cm} (3.11)

$$C_{12\xi} = C_{12\xi_0} + \left(C_{111\xi_0} + 2C_{112\xi_0} + C_{123\xi_0} - C_{222\xi_0}\right)E,$$  \hspace{1cm} (3.12)

$$C_{13\xi} = C_{13\xi_0} + \left(C_{113\xi_0} + C_{123\xi_0} + C_{133\xi_0}\right)E,$$  \hspace{1cm} (3.13)

$$C_{33\xi} = C_{33\xi_0} + \left(2C_{133\xi_0} + C_{333\xi_0}\right)E,$$  \hspace{1cm} (3.14)

$$C_{44\xi} = C_{44\xi_0} + \left(C_{144\xi_0} + C_{155\xi_0} + C_{344\xi_0}\right)E,$$  \hspace{1cm} (3.15)

$$C_{14\xi} = C_{14\xi_0} + \left(C_{114\xi_0} + C_{124\xi_0} + C_{134\xi_0}\right)E.$$  \hspace{1cm} (3.16)

Stresses and pressure are

$$S_{ij} = C_{ijkl\xi_0}E + \frac{1}{2}C_{ijklm\xi_0}E^2;$$  \hspace{1cm} (3.17)

$$\sigma_{ij} = J^{-1/3}S_{ij}\delta_{ij}, \hspace{0.5cm} p = -\frac{1}{3}J^{-1/3}S_{kk}.$$  \hspace{1cm} (3.18)

Maximum shear stress is defined as half the difference between maximum and minimum principal values of Cauchy stress ($\sigma_1 \geq \sigma_2 \geq \sigma_3$):

$$\tau = \frac{1}{2}(\sigma_1 - \sigma_3).$$  \hspace{1cm} (3.19)

Tangent moduli $A$, $D$, and $B$ of Section 2.2 are computed readily from (3.9), (3.10) and the above expressions for deformation gradient and stresses.

3.3. Uniaxial strain compression

Consider a single crystal subjected to uniaxial compression along, for example, the $X_1$ direction. In this case, the deformation gradient $F$, volume ratio $J$, Green strain $E$, and...
and tangent elastic modulus tensor $C$ are all explicit functions of compression ratio $F = F_{11} = \partial x_1 / \partial X_1$:

$$[F_{ij}] = \begin{bmatrix} F & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix};$$

(3.20)

$$J = V/V_0 = \det[F_{ij}] = F;$$

(3.21)

$$[E_{ij}] = \begin{bmatrix} E & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad E = \frac{1}{2} (F^2 - 1);$$

(3.22)

$$C_{ijkl}\big|_F = C_{ijkl}\big|_0 + C_{ijkl11}\big|_0 E.$$  

(3.23)

Second Piola–Kirchhoff and diagonal Cauchy stress components and pressure are

$$S_{ij} = C_{ijkl}\big|_0 E + \frac{1}{2} C_{ijkl11}\big|_0 E^2;$$

(3.24)

$$\sigma_{11} = FS_{11}, \quad \sigma_{22} = F^{-1} S_{22}, \quad \sigma_{33} = F^{-1} S_{33};$$

(3.25)

$$p = -\frac{1}{3F} (F^2 S_{11} + S_{22} + S_{33}).$$

(3.26)

Maximum shear stress is found as in (3.19). Tangent moduli $A$, $D$, and $B$ of Section 2.2 are computed readily from (3.20–3.25).

3.4. Estimation of third-order constants

Crystals belonging to Laue group RI have up to 14 independent third-order elastic constants $C_{\alpha\beta\gamma\delta}|_0$, as listed in Table 1. An indeterminate set of third-order elastic constants for each of the boron carbide polytypes (polar and CCC) is proposed here with the following assertions:

1. Tangent elastic coefficients $C(p)$ measured under hydrostatic compression are approximately equivalent to tangent coefficients $C(J)$ obtained under spherical compression, that is

$$C_{\alpha\beta}|_p \approx C_{\alpha\beta}|_J \Leftrightarrow J^{-1/3} \hat{C}_{\alpha\beta}|_J \approx J^{-1/3} \hat{C}_{\alpha\beta}|_p,$$

(3.27)

where $p$ and $J$ are related through (3.1) and the second equality corresponds to (3.10), which in turn is an application of (2.33). Values of $\hat{C}_{\alpha\beta}|_p$ corresponding to $p \approx 80$ GPa are given in Table 2; inversion of (3.1) yields a volume ratio $J \approx 0.79$ for both polytypes at this pressure. Assumption (3.27) would be strictly valid for a material with isotropic or cubic symmetry; for a trigonal crystal, it is an approximation because anisotropy leads to shear stresses under spherical compression and to shape changes under hydrostatic compression. (Hydrostatic compression is defined as loading in which the
imposed Cauchy stress state is \( \sigma_{ij} = -p \delta_{ij} \), with \( p \) the pressure.) However, as will be demonstrated later (Figure 2), shear stresses \( \tau \) produced during spherical compression are very small relative to axial stresses and pressure, and hence this assumption is deemed reasonable. Use of (3.27) with (3.11–3.16) and values of \( \hat{C}_{ab \mid p} \) in Table 2 provide five independent equations for each polytype, e.g.,

\[
C_{11 \mid p} = C_{11 \mid 0} + (C_{111 \mid 0} + C_{112 \mid 0} + C_{113 \mid 0})E, \tag{3.28}
\]

where \( E \approx -0.072 \) at this pressure. The analogous equation associated with \( C_{14 \mid p} \) is assumed to be \( C_{14 \mid p} = C_{14 \mid 0} \) because the variation of \( C_{14 \mid p} \) with pressure has not been computed theoretically [9]; this equation is counted later in (3.31).

(2) Longitudinal third-order elastic constants along the principal axes can be approximated as having cubic (or isotropic) symmetry:

\[
C_{111 \mid 0} \approx C_{222 \mid 0} \approx C_{333 \mid 0}. \tag{3.29}
\]

Such an approximation holds reasonably well for sapphire [22,23] and calcite [21], but fails for quartz [42], which has a significantly higher third-order stiffness for compression along the c-axis relative to the other two principal (a- and b-) directions. Other possible assumptions of increased symmetry or isotropy of third-order elastic constants affecting the spherical response (e.g., \( C_{112 \mid 0} \approx C_{113 \mid 0} \) and/or \( C_{113 \mid 0} \approx C_{133 \mid 0} \)) were found to be incompatible with the observed pressure dependencies of \( \hat{C}_{ab \mid p} \), i.e., are incompatible with (3.27). Assumption (3.29) provides two additional equations, bringing the total to seven.

(3) Loss of shear stiffness and elastic instability result primarily from compression along the c-axis (i.e., compression along c-axis [0001]). This behavior has been observed for the CBC (polar) polytype, whereafter cross-linking of C-B-C atomic chains with icosahedra at the vertices of the rhombohedral unit cell leads to amorphization on decompression from a uniaxially strained state [7]. It is suggested here that loss of stability associated with a decreasing \( C_{44} \) with increasing uniaxial strain compression along the c-axis enables easy shearing of the unit cell in directions orthogonal to [0001], leading to progressive instability, buckling, and cross-linking of the C-B-C chain. It is also suggested here that while cross-linking has not been reported for CCC polytype – no boron atom exists in the CCC chain that could bond with icosahedral atoms – elastic instability associated with [0001] compression also occurs in that polytype. Since the reported instability [7] does not occur under hydrostatic compression, it is further assumed that \( C_{44} \) does not soften with compression along the orthogonal a- and b-axes. Tangent elastic coefficient \( C_{44} \) under uniaxial strain in each principal direction is, from (3.23),

\[
C_{44 \mid F} = C_{44 \mid 0} + (C_{144 \mid 0})E_{11} \quad \text{(a-axis compression)},
\]
\[
C_{44 \mid F} = C_{44 \mid 0} + (C_{155 \mid 0})E_{22} \quad \text{(b-axis compression)},
\]
\[
C_{44 \mid F} = C_{44 \mid 0} + (C_{344 \mid 0})E_{33} \quad \text{(c-axis compression)}. \tag{3.30}
\]
It follows from the foregoing assumptions on $C_{44F}$ that
\[ C_{1440} \approx C_{1550} \approx 0, \quad (3.31) \]
and $C_{3440} > 0$ to produce a reduction in $C_{44F}$ on compression $E_{33} < 0$. Coefficient $C_{44}$ does not affect axial stresses or pressure for spherical compression or uniaxial strain compression along a-, b-, and c-axes. Assumption (3.31) provides two more equations, bringing the total to nine.

(4) Variation in tangent coefficient $C_{14}$ under spherical compression and uniaxial compression along the principal axes can be ignored, as can variation of $C_{44}$ under shear $E_4 = 2E_{23}$, leading to
\[ C_{1140} \approx C_{1240} \approx C_{1340} \approx C_{4440} \approx 0. \quad (3.32) \]
Assumption (3.32) would hold identically for a material with hexagonal, cubic, or isotropic symmetry, and is consistent with the assumption $C_{14\rho} = C_{140}$ made following (3.28). Coefficient $C_{14}$ does not affect pressure or axial stress under such loading conditions. Values of $C_{14}$ are not available at pressures other than ambient [9], and the value reported by [41] is much smaller in magnitude than the other five second-order constants. Variation of $C_{44}$ under pure shear is unknown and does not affect the response under spherical or uniaxial strain deformation along the principal axes. Equation (3.32) provides four additional equations, bringing the total to 13.

The above statements and assumptions provide, for each polytype of boron carbide, 13 independent equations relating 14 independent third-order elastic constants $C_{\alpha\beta\chi0}$. This indeterminacy can be represented via the parameter
\[ \xi = \frac{C_{1330}}{C_{3330}}. \quad (3.33) \]
For a given value of $\xi$ (1 equation), all 14 third-order constants can be determined analytically using (3.27) (5 equations), (3.29) (2 equations), (3.31) (2 equations), and (3.32) (4 equations). Solution of this set of equations is algebraically straightforward and leads to the third-order elastic constants in Table 3.

The following features of these constants are noteworthy. Magnitudes of third-order constants range from $\approx 400$–$4000$ GPa (4–40 Mbar), similar to those of sapphire [22,23], another hard ceramic belonging to point group 3m. All nonzero third-order constants are negative in sign except for $C_{3440}$. Negative constants generally yield increasing tangent stiffness with increasing compression, while positive third-order constants do the opposite. The strongly positive value of $C_{3440}$ leads to a decrease in tangent elastic coefficient $\acute{C}_{44}$ with increasing volumetric compression and with increasing compression along the c-axis. Values of $\xi$ examined herein (1/2, 1, and 2) are thought to probe a sensible range of longitudinal constants to enable assessment of the choice of $\xi$ on results of interest. For example, as shown in Table 4, initial pressure derivatives of second-order moduli are nearly independent of $\xi$. On the other hand, values of longitudinal constants $C_{1110}$, $C_{2220}$, and $C_{3330}$ are sensitive to the choice of $\xi$. In each of calcite, quartz, and sapphire, $C_{1330}$ and the longitudinal third-order constants are all of the same order of magnitude. In boron
carbide, the proposed negative values of large magnitude for $C_{1120}$ and $C_{1230}$ enable the large increase in $\hat{C}_{12}$ with increasing pressure computed from DFT [9].

Figures 1a and b show tangent elastic moduli $\hat{C}_{\alpha\beta\gamma\delta}$ computed under spherical compression conditions described in Section 3.2. From Figure 1a, moduli vary nearly linearly with compression ratio $J = V/V_0$ over this pressure range. The variation in moduli with pressure (i.e., the slope) decreases slightly as pressure increases as shown in Figure 1b, a result of the increase in tangent bulk modulus with decreasing volume. Trends shown in Figure 1 are in reasonable agreement with atomic theory [9], and tangent moduli are in exact agreement with [9] at pressures of 0 and 80 GPa. Elastic moduli of the polar polytype are stiffer than those of the CCC polytype except $\hat{C}_{12}$ and $\hat{C}_{13}$, which are similar for both polytypes. Shear modulus $\hat{C}_{44}$ decreases with increasing compression, i.e., with decreasing volume; all other moduli increase with increasing compression. The response, including stresses and moduli, is independent of $\xi$ of (3.33) for spherical deformation.

Figure 2 shows pressure and shear stress predicted by the model for spherical deformation. Also shown for comparison is the response for hydrostatic compression.
using (3.1), with \( B_{i0} \) and \( s \) corresponding to experiment [12,13]. Comparing the present model results for spherical deformation, the polar polytype is stiffer than the CCC polytype (i.e., larger pressure at a given \( V/V_0 \)). The experimental hydrostat is in reasonable agreement with predicted pressures under spherical compression, and maximum shear stress predicted by the model for spherical compression [\( \tau \) of (3.19)] is much smaller than pressure for compression ratios of interest in this work (\( V/V_0 > 0.75 \)), lending justification for assumption (3.27).

Figure 3 shows axial Cauchy stress for uniaxial strain loading described in Section 3.3. Stresses shown are computed using (3.25), with a single crystal compressed along its a-axis ([\( \bar{2}210 \)]) or c-axis ([\( 0001 \)]). Results in Figure 3a are for both polytypes with \( \xi = 1 \); the polar polytype is stiffer for compression along either axis. Results in Figure 3b are for the CCC polytype with variable \( \xi \); differences in axial response for compression along a particular axis for different values of \( \xi \) are noticeable only for moderate compressions, i.e., \( V/V_0 < 0.95 \). The response for uniaxial compression along the b-axis ([\( \bar{1}2 \bar{1}0 \)]) was also computed; results are nearly the same as those for a-axis compression and are not shown.

### 3.5. Stability

For a trigonal crystal belonging to Laue group RI, elastic stability condition (2.67) reduces to the three inequalities [18]

\[
\begin{align*}
C_{11}\lambda_0 - |C_{12}|\lambda_0 &> 0, \\
C_{33}\lambda_0(C_{11}\lambda_0 + C_{12}\lambda_0) - 2C_{13}^2\lambda_0 &> 0, \\
C_{44}\lambda_0(C_{11}\lambda_0 - C_{12}\lambda_0) - 2C_{14}^2\lambda_0 &> 0.
\end{align*}
\]

(3.34)

For boron carbide single crystals with second-order elastic constants listed in Table 2, these conditions are satisfied; the minimum eigenvalue of \([C_{ij}\lambda_0]\) is \( \lambda_0 = 127 \text{ GPa} \) for the CCC polytype and \( \lambda_0 = 150 \text{ GPa} \) for the polar polytype.

At all states other than the stress-free reference state, tangent moduli of Section 2.2 differ, and hence have different minimum eigenvalues associated with stability criteria listed in (2.65). Loading programs described in Sections 3.2 and 3.3,
i.e., spherical and uniaxial compression, involve symmetric deformation gradients, and hence criteria (2.65), which do not address rotations, are always valid. Shown in Figure 4 is the ratio $\lambda / \lambda_0$, where $\lambda$ corresponds to the minimum eigenvalue of $6 \times 6$ symmetric tangent stiffness matrices $[C_{ab\beta}]$, $[A_{ab\beta}]$, $[D_{ab\beta}]$, and $[B_{ab\beta}]$ entering respective stability criteria (2.42), (2.49), (2.53), and (2.60). For each increment in applied compressive strain, eigenvalues of each stiffness matrix are computed numerically using Jacobi’s method [43].

For all criteria, elastic stability decreases with decreasing volume (i.e., with increasing pressure), since minimum eigenvalues of each stiffness matrix decrease monotonically with decreasing $V/V_0$. Recall from Section 2.2 that the onset of instability corresponds to a vanishing eigenvalue of the tangent stiffness, i.e., $\lambda / \lambda_0 = 0$. For the three loading programs of Figure 4, boron carbide is the least stable for compression along the c-axis (Figure 4c) and the most stable for compression along the a-axis (Figure 4b). The bend in each $\lambda$-curve in Figure 4b corresponds to a change in critical eigenmode.

The following ranking of stability criteria typically holds for cases examined in this work, i.e., for boron carbide single crystals subjected to spherical and uniaxial compression:

$$B \, \text{stable} \Rightarrow D \, \text{stable} \Leftrightarrow A \, \text{stable} \Rightarrow C \, \text{stable}. \quad (3.35)$$

Figure 4. Minimum eigenvalue ratio versus volume ratio for both polytypes and $\xi = 1$: (a) spherical compression; (b) a-axis uniaxial compression; (c) c-axis uniaxial compression.
Conversely,

\[
\text{C unstable } \Rightarrow \text{ A unstable } \Leftrightarrow \text{ D unstable } \Rightarrow \text{ B unstable.}
\]  \hspace{1cm} (3.36)

In other words, for a given program of compressive loading, instability will usually occur first (i.e., at the largest volume ratio \( J/V_0 = V/V_0 \)) for the B criterion, and will usually occur last (i.e., at the smallest value of \( J/V_0 \)) according to the C criterion.

Two criteria are equivalent in Figure 4:

\[ \text{D (un)stable } \Leftrightarrow \text{ A (un)stable.} \hspace{1cm} (3.37) \]

Since \( d^2U_A = J d^2U_D \) and \( J > 0 \), \( \lambda_A = \lambda_D(=0) \) at \( E^* \), though at other applied strains, minimum eigenvalues of \([A_{ijkl}]\) and \([D_{ijkl}]\) may differ. For similar reasons, the C criterion applied with either of \( \bar{C}_{ijkl} \) or \( \hat{C}_{ijkl} \) (i.e., tangent stiffness in terms of Green strain measured from the stress free reference state or the current state) will indicate the same critical strain \( E^* \) at the onset of instability.

Figure 5 shows minimum eigenvalue ratio \( \lambda/\lambda_0 \) versus pressure (for spherical compression) or axial stress (for uniaxial compression) for C and B instability criteria of (2.43) and (2.61), respectively. The polar polytype is more stable than the CCC polytype at any given pressure or stress, for both C (Figure 5a) and B (Figure 5b) criteria. In particular, from Figure 5b, according to the B criterion, instability of the...
CCC polytype occurs at a critical axial stress of 21 GPa for c-axis compression and a critical pressure of 32 GPa for spherical compression. Analogous values for the polar polytype are 41 and 63 GPa, respectively. Figure 5c demonstrates that stability of either polytype is relatively insensitive to \( \xi \).

Table 5 lists critical eigenmodes (i.e., normalized directions of incremental strain) \( d_{1a}^* \) corresponding to instability conditions \( \lambda/\lambda_0 = 0 \) for C and B instability criteria of (2.43) and (2.61). In Table 5, \( J^* \) is the value of \( V/V_0 \) at instability and \( \sigma^* \) is the corresponding pressure (for spherical compression) or axial stress (for uniaxial compression). Recall from Section 2.2 that for C instability, \( d_{1a}^* = dE_{1a}^* \); for B instability, \( d_{1a}^* = dE_{1a}^* \). Eigenmode \( d_{1a}^* \) is associated with a null eigenvalue \( \lambda \) of \([C_{\alpha\beta}]\) or \([B_{\alpha\beta}]\) and is of unit length, i.e., \( d_{1a}^* d_{1a} = 1 \). For spherical compression, by far the largest critical eigenmode component in relative magnitude is \( d_{1a}^* \), which correlates with a loss of tangent stiffness \( C_{44} \) or \( B_{44} \). For c-axis compression, by far the largest critical eigenmode component is \( d_{1a}^* \), which correlates with a loss of tangent stiffness \( C_{355} \) or \( B_{355} \). Thus the mode of instability is similar for spherical and c-axis compression, since \( C_{44} = C_{55} \) and \( C_{344} = C_{355} \) for a trigonal crystal with \( 3m \) symmetry. Note also that for these two loading modes, the eigenmode is deviatoric (i.e., a shearing mode) since \( d_{1a}^* + d_{2a}^* + d_{3a}^* \approx 0 \). For a-axis compression, the largest (in magnitude) critical components are \( d_{1a}^* \) and \( d_{2a}^* \), corresponding to a decrease in stiffness components different to \( C_{44} \) or \( C_{55} \), and the critical eigenmode is not deviatoric.

### 4. Boron carbide: polycrystal response

#### 4.1. Homogenized variables

Let a polycrystalline material element of total volume \( V_0 \) consist of \( N \) grains (i.e., single crystals) each of equal reference volume. Let \( (\cdot)_g \) correspond to a field
variable associated with grain $g$. The average of a generic quantity is defined as

$$\langle \cdot \rangle = V_0^{-1} \int_{V_0} \cdot dV_0 = \frac{1}{N} \sum_{g=1}^{N} \langle \cdot \rangle_g. \quad (4.1)$$

For a field that is uniform over all grains, $\langle \cdot \rangle = \cdot$. Consider a homogeneous deformation gradient field $F$ applied to all grains:

$$F(X, t) = F(t) = \langle F \rangle = F_g (\forall g \in V_0). \quad (4.2)$$

This loading program is the simplest prescribed condition that can be applied for a model polycrystal and corresponds to a Voigt assumption in the context of micromechanics [11] since strain and rotation are uniform. Such an assumption has been used frequently for modeling the homogenized response of ceramic and metallic polycrystals at high strain rates or under severe confinement [33, 44]. It follows from (4.2) that all relevant kinematic variables are also homogeneous, e.g.,

$$\langle E \rangle = E, \quad \langle J \rangle = J = V/V_0. \quad (4.3)$$

Each single crystal of the aggregate may possess an arbitrary lattice orientation (i.e., a different set of three Euler angles). Because crystals are anisotropic, stresses differ among crystals subjected to the same deformation gradient field. The average second Piola–Kirchhoff stress is computed from (4.1) as

$$\langle S(X, t) \rangle = V_0^{-1} \int_{V_0} S dV_0 = \frac{1}{N} \sum_{g=1}^{N} S_g. \quad (4.4)$$

Average Cauchy stress, average Cauchy pressure, and average maximum shear stress then follow from (4.3) as

$$\langle \sigma \rangle = \langle J^{-1} F S F^T \rangle = J^{-1} F \langle S \rangle F^T, \quad (4.5)$$

$$\langle p \rangle = -\frac{1}{3J} F_{ij} F_{ij} \langle S_{ij} \rangle, \quad \langle \tau \rangle = \frac{1}{2} \langle \sigma_1 - \sigma_3 \rangle. \quad (4.6)$$

In particular, for uniaxial strain loading in the $X_1$ direction via $F_{11} = F$, average axial stress is, from (3.22), (3.24), and (3.25),

$$\langle \sigma_{11} \rangle = \frac{F}{2} \left( F^2 - 1 \right) \left[ C_{111111} + \frac{1}{4} (F^2 - 1) C_{11111111} \right]. \quad (4.7)$$

4.2. Failure model

Define the stability indicator function

$$\chi(X, t) = \chi_g(X)(t) = \begin{cases} 0 & \text{for } \lambda_g^z/\lambda_0 > 0 \\ 1 & \text{for } \lambda_g^z/\lambda_0 \leq 0. \end{cases} \quad (4.8)$$

Initial minimum eigenvalue $\lambda_0$ is identical for all grains of a given polytype and depends only on second-order elastic constants. Critical eigenvalue $\lambda_g^*$ is the
minimum eigenvalue of tangent modulus \( C, B \), etc., corresponding to a particular stability criterion and varies with deformation among each grain. Under compressive loading, upon attainment of an instability condition demarcated by \( \lambda^*_g / \lambda_0 \leq 0 \), crystal \( g \) is assumed to have failed via amorphization, shear localization, or fracture, and is thereafter unable to support deviatoric stress.

According to this failure model, when applied compressive strain \( \mathbf{E}^* \) (or applied volume ratio \( J^* \)) is reached at a given time \( t \) during a given loading program, a superimposed perturbation in direction \( \mathbf{d} \) would correspond to an unstable mode since resistance to such a perturbation from the stress increment associated with the imposed instability criterion – e.g., \( S \) for \( C \) instability, \( P \) for \( A \) instability, or \( \sigma \) for \( B \) instability – would be negligible. The material would thus be free to deform instantaneously in such an “unstable direction” by a large strain, suggesting strain localization if the displacement field remains continuous or indicating fracture if displacement discontinuities arise. In a real crystalline solid, such a perturbation could be intensified by a preexisting heterogeneity, e.g., a grain or twin boundary, stacking fault, dislocation, inclusion, or pore. In particular, local shear deformation associated with pore collapse can be significant and has been suggested as a possible contributor to instability-driven failure in boron carbide under shock compression [17].

Effective Cauchy stress \( \sigma \) for the polycrystalline aggregate is computed from averaging contributions of total (deviatoric + spherical) Cauchy stress from stable crystals with spherical contributions from unstable/failed crystals:

\[
\bar{\sigma}(t) = V_0^{-1} \int_{V_0} [1 - \chi(X, t)] \sigma(X, t) dV_0 - V_0^{-1} \int_{V_0} \chi(X, t) p(X, t) 1 dV_0
\]

\[
= \frac{1}{N} \sum_{g=1}^{N} [(1 - \chi_g) \sigma_g - \chi_g p_g 1].
\]  \( 4.9 \)

Effective pressure and effective shear stress are defined, respectively, as

\[
\bar{p} = -\frac{1}{3} \bar{\sigma}_{kk}, \quad \bar{\tau} = \frac{1}{2} (\bar{\sigma}_1 - \bar{\sigma}_3).
\]  \( 4.10 \)

For imposed strains small enough such that all grains are stable, \( \bar{\sigma} = \langle \sigma \rangle \) is the total stress. For imposed strains severe enough that all grains are unstable, \( \bar{\sigma} = -\langle p \rangle 1 \) reduces to a hydrostat and \( \bar{\tau} = 0 \). For uniaxial strain loading, these definitions of effective stress provide for a loss of shear strength upon attainment of instability, amorphization, and subsequent localization or fracture that have been hypothesized to occur in shock compression of boron carbide [14–17]. Validity of the failure model represented mathematically by (4.8–4.10) is examined in the context of experimental data in Section 4.3.

4.3. Model predictions

A polycrystalline aggregate consisting of equal fractions of CBC (polar) and CCC polytypes is considered. The aggregate contains 1000 grains of each polytype, with each grain assigned a unique set of three random Euler angles describing its initial
lattice orientation. Prescription of \( N = 2 \times 1000 \) was sufficient to ensure that model predictions of interest are insensitive to the random grain distribution in orientation space. With the orientation prescribed, second- and third-order elastic constants are rotated from the crystallographic frame described in Section 3.1 to initial frames of reference using standard transformation formulae for fourth- and sixth-order contravariant tensors [11].

Shown in Figure 6a are predictions of the polycrystal model for axial stress \( \bar{\sigma}_{11} \) of (4.9), pressure \( \bar{p} \) of (4.10), and shear stress \( \bar{\tau} \) of (4.10), where (4.8) is defined using B instability criterion (2.61). Also shown in Figure 6a are the experimental hydrostat \( \{ B_0 = 240 \text{ GPa}, s = 0.914 \text{ [14]} \text{ in (3.1)} \} \) and axial and shear stresses reported for shock compression of boron carbide polycrystals [16]. The model developed in the present work provides an accurate depiction of axial stress for \( 1 \geq V/V_0 \geq 0.88 \), corresponding to stress range \( 0 \leq \bar{\sigma}_{11} \leq 40 \text{ GPa} \). The model provides an accurate depiction of shear stresses slightly beyond the predicted point of first instability, i.e., for \( 1 \geq V/V_0 \geq 0.95 \).

The onset of instability predicted by the model occurs at \( V/V_0 \approx 0.96 \), corresponding to an axial stress of \( \approx 18 \text{ GPa} \). This prediction is in general agreement with other experimental and theoretical studies. Plate impact experiments have revealed a loss of shear stress or strength at shock pressures above \( \approx 18 \text{ GPa} \) [14,15,17], an axial stress level which corresponds roughly to the Hugoniot Elastic Limit (HEL). First principles predictions suggest that boron carbide loses stability under uniaxial c-axis compression at axial stresses around 20 GPa [7].

Two limitations of the present model are also apparent in Figure 6a. First, shear stress at larger compressions (\( V/V_0 \approx 0.95 \)) is over-predicted by the model relative to experimental data [16]. This suggests that the failure model of Section 4.2 provides an insufficient representation of the polycrystal shear response after some grains have become unstable. A likely explanation for the loss of shear stress in experiments at large compression is that one or a few grains become elastically unstable, undergo localized deformation, and fracture soon thereafter, presumably on cleavage planes (e.g., \{110\} planes of boron carbide [7]). Fracture and subsequent crack propagation
are not addressed in the simple rule-of-mixtures failure model of Section 4.2, which permits all elastically stable grains to maintain their full deviatoric stress even when neighboring grains become unstable and fail.

A second possible limitation of the polycrystal model developed herein is the discrepancy between the predicted pressure and the hydrostat in Figure 6a: at large compressions, the Cauchy pressure predicted for uniaxial strain compression becomes significantly smaller than that for hydrostatic compression. As shown in Appendix A, this discrepancy is an artifact of all elasticity models based on a polynomial series expansion of Green’s strain measure. In particular, as shown in Appendix A, when third- and higher-order elastic constants are omitted, the pressure predicted under spherical compression always exceeds that predicted under uniaxial compression to the same volume ratio \( V/V_0 \), even for an isotropic material.

An alternative nonlinear elastic formulation, e.g., along the lines of a neo-Hookean model incorporating \( J \) explicitly in the strain energy potential [20], would be required to alleviate this difference. Such a model does not apparently exist in exact form for anisotropic crystals of trigonal symmetry; only the invariants entering (2.40) seem to be known [37].

Shown in Figure 6b are model predictions of \( \overline{\sigma}_{11} \) and \( \overline{\tau} \) for various choices \( \xi = 1/2, 1, 2 \) in (3.33). The onset of B instability occurs at \( V/V_0 \approx 0.96 \) irrespective of the value of \( \xi \). Furthermore, axial and shear stresses do not vary appreciably with \( \xi \) for \( V/V_0 \geq 0.88 \).

Shown in Figure 7 are predicted unstable volume fractions of each of the CCC and polar polytypes for uniaxial compression of the same polycrystal containing 1000 randomly oriented grains of each polytype obtained using the most (B) and least (C) stringent instability measures. The most favorably oriented grains of the CCC polytype become unstable at axial stresses of \( \approx 18 \)–\( 20 \) GPa, while those of the polar polytype become unstable at axial stresses of \( \approx 32 \)–\( 36 \) GPa. The onset of instability marked on the shear stress curves in Figure 6 correlates with elastic
instability of grains of the CCC polytype whose [0001] directions (i.e., c-axes) align closely with the direction of compression, and can be associated with softening of incremental stiffness component $B_{44}$ or $B_{55}$.

Recall that equal volume fractions of each polytype have been assumed, which follows theoretical predictions indicating that polar CBC and CCC are the most abundant polytypes in boron carbide because they have the lowest Gibbs free energy (though the free energy of CCC may slightly exceed that of CBC [6]). Presence of other polytypes of varying percentages is likely among experimental samples; inclusion of different polytypes or different volume fractions would lead to different model predictions for average stresses due to the variation of elastic moduli among polytypes (Table 2).

5. Discussion

The anisotropic single crystal energy potential developed in the present work uses the Green strain measure with elastic constants of orders two and three. Second-order elastic constants have been obtained from theory for two polytypes of boron carbide [9,41]. Third-order elastic constants have been estimated following the procedure and assumptions of Section 3.4 since the 14 individual third-order constants have not been measured experimentally or predicted using first principles.

The third-order nonlinear elastic model developed here successfully captures theoretical variations [9] of tangent elastic moduli $\tilde{C}_{\alpha\beta}$ with pressure up to 80 GPa, as shown in Figure 1. Future plate impact experiments on single crystals, or atomic simulations of non-hydrostatic stress states imposed on a periodic boron carbide unit cell, could provide definitive values of third-order constants or variations in tangent moduli under moderate to large non-spherical deformations, thereby resolving indeterminancy of the present model and eliminating the need for assumptions made in Section 3.4. Such new experiments or simulations would also enable a check of the validity of third-order elasticity theory; should the general theory prove inadequate for representing the uniaxial response of single crystals along certain directions, elastic constants of order four (or possibly even higher) may be needed at very high pressures. It is noted that $\xi$, which accounts for indeterminacy of ratio $C_{133}/C_{333}$, does not affect model predictions for spherical compression, has a very minor effect on predictions of stress and elastic stability for uniaxial compression along the principal a- and c-axes (Figures 3b and 5c), and has a negligible effect on the polycrystal response for $V/V_0 \approx 0.87$ (Figure 6b).

Four different criteria have been evaluated for elastic stability of boron carbide single crystals subjected to spherical compression and uniaxial compression. Each criterion corresponds to a positive (for stability) or zero (for onset of instability) eigenvalue of a different 6 x 6 tangent stiffness matrix defined in Section 2.2. For the present material and loading conditions, the most critical criterion corresponds to a null eigenvalue of $[B_{\alpha\beta}]$, which is the symmetrized 6 x 6 matrix corresponding to incremental modulus tensor $B$. Fourth-order tensor $B$ is derived as the mapping, to the current configuration, of an exact, fully nonlinear representation of the derivative $Z = \partial \sigma(E)/\partial E$ given in (2.29).
First principles simulations of hydrostatic compression [6] have demonstrated that transformation of the CCC polytype of boron carbide into amorphous bands of segregated boron and graphite has a negative energy barrier at pressures in excess of ≈6 GPa, whereas the polar polytype (CCC) is metastable to a hydrostatic pressure of at least 40 GPa. Amorphization occurs in narrow bands of thickness 2–3 nm on (113) and (213) planes [5,6]. More recent first principles calculations [7] for the CBC (polar) polytype have demonstrated stability to hydrostatic pressure of 60 GPa, but instability occurs at stresses of 18.9–22.8 GPa for uniaxial straining along the c-axis (i.e., along the C-B-C chain). Accompanying instability, a ≈4% volume reduction is observed, along with buckling of the C-B-C chain. At even larger axial stresses, on the order of 40 GPa, cross-linking of the boron atom of the C-B-C chain occurs as this atom forms new covalent bonds with neighboring atoms in an icosahedron at a rhombohedral vertex. It has been suggested that upon subsequent decompression, amorphization and fracture take place because this cross-linked structure is unstable at lower pressures.

While the present nonlinear elastic model is unable to depict details of atomic structural rearrangements, the present model does demonstrate qualitative agreement with some trends mentioned above. For spherical or uniaxial c-axis deformation of either polytype, critical eigenmodes associated with B and C criteria listed in Table 5 suggest that the crystal becomes unstable with respect to strain increments $d\eta_4$ and $d\eta_5$, i.e., relative shearing of (0001) planes, as $C_{44} \approx C_{55}$ and $B_{44} \approx B_{55}$ decrease with increasing compression along [0001]. This model feature is in general agreement with atomic theory, since a loss of shear stiffness on (0001) planes would enable easy relative motion of atoms in the C-B-C or C-C-C chains, facilitating the aforementioned buckling instability [7]. The relatively greater elastic stability of the polar polytype relative to the CCC polytype (Figures 4 and 5 and Table 5) under axial and spherical compression is in qualitative agreement with the same trend reported for hydrostatic compression [6,9].

Attainment of a zero eigenvalue associated with loss of tangent stiffness, while indicative of elastic instability from the viewpoint of continuum elasticity theory, is neither a sufficient nor necessary condition for a structural transformation to occur at the atomic scale. However, when a critical eigenmode is of deviatoric (shear) nature, then elasticity theory suggests that localized deformation in the form of slip or a shear band is a likely possibility. Structural collapse or amorphization might be expected to occur in such a band, as reported in boron carbide [5], since interatomic forces associated with incremental shearing resistance would be negligible, and such (negligible) forces would be unable to maintain atomic positions corresponding to an elastically deformed crystal structure.

The nonlinear elastic analysis of the present work suggests that instability as a precursor to failure may initiate in favorably oriented boron carbide grains at around 4% volumetric compression, which correlates in a homogeneously deforming polycrystal with average compressive stress on the order of the experimental HEL. Certain physics associated with the shock process occurring in plate impact and ballistic experiments are omitted in the analysis, as are details of failure mechanisms that have been suggested to accompany or follow instability [5].

Quasi-static diamond anvil cell compression experiments incorporating $B_4C$ powder as the Pressure Transmitting Medium (PTM) [7] revealed amorphization
upon unloading from what was deemed non-hydrostatic loading; shear bands of amorphized material were found in recovered cleavage fragments. Amorphization was not observed during pressurization with B\textsubscript{4}C powder or with NaCl powder used as the PTM, the latter corresponding to hydrostatic conditions. Dynamic indentation experiments revealed substantial amorphous shear zones in recovered samples; quasi-static indentation experiments at the same load demonstrated less evidence for amorphization [8]. Dynamic experiments are often idealized as adiabatic, quasi-static as isothermal. The present study considers stability dependent only on current strain state, does not account for strain history, strain rate, or temperature effects, and is therefore unable to distinguish among different behaviors in loading/unloading or at low/high rates of loading. Traditional DFT studies at 0 K are likewise unable to account for rate and temperature, though path dependence (bond formation and breaking) can be addressed [6,7]. The present analysis has shown that unstable modes are associated with shear strain perturbations \(\mathrm{d}n_4\) and \(\mathrm{d}n_5\) in Table 5) related to bifurcations off the primary compressive loading path. At high rates or temperatures, such perturbations needed to trigger localization might be supplied by stress wave interactions or lattice vibrations, whereas during quasi-static compression, crystals may likewise be intrinsically elastically unstable (\(\det[B_{ij}]\leq 0\)) but might not fail by localization if sufficient shear perturbations are not available. Recent analysis [45] suggests elastic strain energy may dominate kinetic energy (the latter associated with strain rate) as the source fueling adiabatic shear in brittle solids such as boron carbide. It has also been noted that locally adiabatic (i.e., fast) conditions associated with failure are possible in globally quasi-static tests. Local catastrophic failure has been suggested as descriptive of wave structures observed in shock compression [46] but not definitively established [45].

Post-mortem inspection of recovered material from impact or indentation does not enable determination of whether amorphization occurs during compression or during stress release. Dynamic hardness is reportedly smaller than static hardness [8] for the same indentation load, which suggests, but does not prove, that structural collapse and related damage take place during compression. DFT [6,7] predicts that cross-linking or segregation may be energetically favorable during compression, depending on polytype.

Entropy production may be significant during shock compression, especially at stress levels intense enough to compress pores, activate dislocations and twins, and generate frictional sliding between microcrack facets. This creates locally heterogeneous strain and temperature conditions where instability, localization, and further inelasticity and failure mechanisms likely become more probable relative to the homogeneous isentropic elastic regime considered herein. Since the total second variation of internal (or Helmholtz free) energy involves both strain and entropy (or temperature) variations [30] for non-ideal thermodynamic loading paths, a stability analysis incorporating bounds on state-dependent thermoelastic properties (thermal expansion, specific heat, etc.) in addition to elastic stiffness may be warranted. Dislocations and twins, while likely present, are thought to be scarce and immobile [5,7]. Should such defects contribute significantly to deformation, elastic–plastic instability analysis [47] would become prudent.

The polycrystal model developed and exercised in Section 4 captures experimental axial stress for compressions to \(V/V_0\approx 0.88\), and experimental shear stress up
into the regime of instability at $V/V_0 \approx 0.95$, as shown in Figure 6a. The loss of shear strength as predicted by the model initiates at $\approx 5\%$ compression, corresponding to an axial stress of about 20 GPa, in general agreement with plate impact [14–17] and ballistic [5] experiments. The polycrystal failure model of Section 4.2 presumably overestimates shear stress at higher impact pressures (i.e., at $V/V_0 \approx 0.95$) because grain interactions and fracture are not addressed. The elastic instability model could be implemented in mesoscale simulations wherein grain geometries and discrete fracture surfaces are resolved explicitly, as has been done previously for shock compression of other polycrystals [48,49]. Results obtained from such an approach should be reported in the future.

6. Conclusions

A nonlinear elasticity model has been developed and analyzed for trigonal ceramic crystals of boron carbide. The model, which relies on elastic constants of up to order three, accounts for theoretically predicted variations in elastic stiffness with increasing pressure. Results and analysis provide new insight into the high pressure behavior of boron carbide single- and polycrystals. Elastic instability associated with a reduction in tangent modulus coefficient $C_{44}/C_{25}$ is represented for spherical compression and uniaxial compression along the c-axis, with loading by the latter yielding instability at lower pressure.

Predictions of a polycrystal representation of the model provide close agreement with data from plate impact experiments for axial stresses at up to 40 GPa impact pressure and for shear stresses at up to 20 GPa impact pressure. The onset of instability in favorably oriented crystals occurs at impact pressures of 18–20 GPa, corresponding approximately to the experimental HEL. Various instability criteria linked with vanishing eigenvalues of different stiffness matrices have been analyzed for spherical and uniaxial compression; the most stringent criterion ("B criterion") for stability corresponds to the tangent stiffness representing the variation of Cauchy stress with incremental strain, derived in this work without use of linear approximations of the deformation gradient and its determinant. The present work represents, to the author’s knowledge, the first analysis and application of classical elastic stability criteria employing a third-order, nonlinear elastic strain energy potential for single crystals.

References

Philosophical Magazine


Appendix A. Pressure for spherical and uniaxial strain compression

Consider a solid with cubic or isotropic symmetry and vanishing elastic constants of orders three and higher. Let second-order elastic constants be related by

\[ \frac{C_{16}}{C_{11}} = \frac{C_{12}}{C_{44}} \]  

(A1)

Stability constraints (2.67) lead to the requirements [30]

\[ C_{11} - C_{12} > 0, \quad C_{11} - C_{12} > 0, \quad C_{44} > 0. \]  

(A2)

The first two of these inequalities can be combined into bounds on \( \zeta \):

\[ -1/2 < \zeta < 1. \]  

(A3)

For spherical compression described in Section 3.2, pressure is computed explicitly in terms of volume ratio \( J = V/V_0, C_{11}|_0, \) and \( \zeta \) as

\[ p|_J = -\frac{1}{6} J^{-1/3} (J^{2/3} - 1)[3(1 + 2\zeta)]C_{11}|_0. \]  

(A4)

For uniaxial strain compression as described in Section 3.3 along any one of the principal (cubic) axes, pressure is computed analytically as

\[ p|_F = -\frac{1}{6} J^{-1} (J^2 - 1)(J^2 + 2\zeta)C_{11}|_0. \]  

(A5)

As shown in Figure A1, the ratio of these Cauchy pressures

\[ \frac{p|_F}{p|_J} = \frac{1}{(3J^{2/3}) (J^{2/3} - 1)} \left( \frac{J^2 - 1}{1 + 2\zeta} \right) \]  

(A6)

is less than unity for \( V/V_0 < 1 \). This at least partially explains the lower pressure predicted for boron carbide single crystals in uniaxial compression relative to that for spherical compression for the same value of \( J \) (e.g., as in Figure 6a), since from Table 2, \( C_{12}|_0/C_{11}|_0 < 1/4 \) and \( C_{13}|_0/C_{33}|_0 < 1/7 \) with \( C_{11}|_0 \approx C_{33}|_0 \).

![Figure A1. Pressure ratio of (A6) versus volume under spherical and uniaxial compression.](image-url)
Appendix B. Stability with respect to incremental strain

Throughout this paper, strain $E$, stress $S$, and tangent modulus $C$ have been defined with respect to total deformation gradient $F$ measured from a stress free, undistorted reference state. It is instructive to consider such quantities measured from a stressed intermediate state [34]. Let $\tilde{X}_I$ represent coordinates in such a state, such that the deformation gradient obeys

$$ F = \hat{F} \tilde{F}, \quad F_{IJ} = \frac{\partial \tilde{X}_I}{\partial \tilde{X}_J} = \hat{F}_{ik} \tilde{F}_{kj}. $$

(B1)

Total Green strain from the stress free state and incremental Green strain from the intermediate state are, respectively,

$$ E_{IJ} = \frac{1}{2} \tilde{F}_{KI} (\hat{F}_{ik} \hat{F}_{jkl} - \tilde{F}_{IK} \tilde{F}_{jkl}) \tilde{F}_{LJ}, \quad \hat{E}_{MN} = \frac{1}{2} (\hat{F}_{IM} \hat{F}_{jln} - \delta_{MN}). $$

(B2)

It follows that

$$ \frac{\partial E_{IJ}(\hat{F}, \tilde{F})}{\partial \hat{E}_{MN}} \bigg|_{\tilde{F} = \text{const.}} = \frac{\partial (\hat{F}_{KI} \hat{F}_{jkl} \tilde{F}_{LJ})}{\partial (\hat{F}_{IM} \hat{F}_{jln})} \bigg|_{\tilde{F} = \text{const.}} = \frac{\hat{F}_{IM} \hat{F}_{jln}}{\tilde{F}_{KL}}. $$

(B3)

Volumes are related by

$$ J = \frac{V}{V_0} = (V/\tilde{V}) (\tilde{V}/V_0) = \det \hat{F} \det \tilde{F} = \tilde{J} \tilde{J}. $$

(B4)

Henceforward let each deformation gradient be a pure stretch (i.e., no rigid rotation) such that deformation gradients and strains are uniquely related by

$$ F = (2E + 1)^{1/2}, \quad \hat{F} = (2\hat{E} + 1)^{1/2}. $$

(B5)

Strain energy density can then be expressed as

$$ U = U[E(\hat{F}, \tilde{F})] = U(\hat{F}, \tilde{F}). $$

(B6)

Thermodynamic tension with respect to strain from the intermediate state is

$$ \hat{S}_{ij} = \frac{V_0}{V} \frac{\partial U}{\partial \hat{E}_{ij}} = \tilde{J}^{-1} \frac{\partial U}{\partial \hat{E}_{KL}} \frac{\partial \hat{E}_{KL}}{\partial \hat{E}_{ij}} = \tilde{J}^{-1} \hat{F}_{IK} \hat{F}_{jkl} S_{KL}. $$

(B7)

Cauchy stress is

$$ \hat{\sigma}_{ij} = \tilde{J}^{-1} \hat{F}_{IK} \hat{F}_{jkl} \hat{S}_{KL} = \tilde{J}^{-1} \hat{F}_{IK} \hat{F}_{jkl} S_{KL} = \sigma_{ij}. $$

(B8)

Incremental Green tangent modulus measured from the intermediate state is [34]

$$ \hat{C}_{ijkl} = \frac{V_0}{V} \frac{\partial^2 U}{\partial \hat{E}_{ij} \partial \hat{E}_{KL}} = \tilde{J}^{-1} \hat{F}_{IM} \hat{F}_{jln} \hat{F}_{kdo} \hat{F}_{LPO} C_{MNOP}. $$

(B9)

When the current configuration is identified with the stressed intermediate (i.e., reference) state, then $F = I$, $\sigma = \tilde{S}$ from (B8), $\hat{F} = F$, and (B9) produces (2.33).
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