2014

Strain-induced phase transformation under compression in a diamond anvil cell: Simulations of a sample and gasket

Biao Feng
Iowa State University, biaofeng@iastate.edu

Valery I. Levitas
Iowa State University, vlevitas@iastate.edu

Yanzhang Ma
Texas Tech University

Follow this and additional works at: http://lib.dr.iastate.edu/aere_pubs

Part of the Aerospace Engineering Commons, Materials Science and Engineering Commons, and the Mechanical Engineering Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/aere_pubs/39. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Strain-induced phase transformation under compression in a diamond anvil cell: Simulations of a sample and gasket

Abstract
Combined high pressure phase transformations (PTs) and plastic flow in a sample within a gasket compressed in diamond anvil cell (DAC) are studied for the first time using finite element method. The key point is that phase transformations are modelled as strain-induced, which involves a completely different kinetic description than for traditional pressure-induced PTs. The model takes into account, contact sliding with Coulomb and plastic friction at the boundaries between the sample, gasket, and anvil. A comprehensive computational study of the effects of the kinetic parameter, ratio of the yield strengths of high and low-pressure phases and the gasket, sample radius, and initial thickness on the PTs and plastic flow is performed. A new sliding mechanism at the contact line between the sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Strain-controlled kinetics explains why experimentally determined phase transformation pressure and kinetics (concentration of high pressure phase vs. pressure) differ for different geometries and properties of the gasket and the sample: they provide different plastic strain, which was not measured. Utilization of the gasket changes radial plastic flow toward the center of a sample, which leads to high quasi-homogeneous pressure for some geometries. For transformation to a stronger high pressure phase, plastic strain and concentration of a high-pressure phase are also quasi-homogeneous. This allowed us to suggest a method of determining strain-controlled kinetics from experimentation, which is not possible for weaker and equal-strength high-pressure phases and cases without a gasket. Some experimental phenomena are reproduced and interpreted. Developed methods and obtained results represent essential progress toward the understanding of PTs under compression in the DAC. This will allow one optimal design of experiments and conditions for synthesis of new high pressure phases.

Disciplines
Aerospace Engineering | Materials Science and Engineering | Mechanical Engineering

Comments
Strain-induced phase transformation under compression in a diamond anvil cell: Simulations of a sample and gasket

Biao Feng,1 Valery I. Levitas2,a) and Yanzhang Ma3
1Department of Aerospace Engineering, Iowa State University, Ames, Iowa 50011, USA
2Departments of Aerospace Engineering, Mechanical Engineering, and Material Science and Engineering, Iowa State University, Ames, Iowa 50011, USA
3Department of Mechanical Engineering, Texas Tech University, Lubbock, Texas 79409, USA

(Received 25 March 2014; accepted 14 April 2014; published online 24 April 2014)

Combined high pressure phase transformations (PTs) and plastic flow in a sample within a gasket compressed in diamond anvil cell (DAC) are studied for the first time using finite element method. The key point is that phase transformations are modelled as strain-induced, which involves a completely different kinetic description than for traditional pressure-induced PTs. The model takes into account, contact sliding with Coulomb and plastic friction at the boundaries between the sample, gasket, and anvil. A comprehensive computational study of the effects of the kinetic parameter, ratio of the yield strengths of high and low-pressure phases and the gasket, sample radius, and initial thickness on the PTs and plastic flow is performed. A new sliding mechanism at the contact line between the sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Strain-controlled kinetics explains why experimentally determined phase transformation pressure and kinetics (concentration of high pressure phase vs. pressure) differ for different geometries and properties of the gasket and the sample: they provide different plastic strain, which was not measured. Utilization of the gasket changes radial plastic flow toward the center of a sample, which leads to high quasi-homogeneous pressure for some geometries. For transformation to a stronger high pressure phase, plastic strain and concentration of a high-pressure phase are also quasi-homogeneous. This allowed us to suggest a method of determining strain-controlled kinetics from experimentation, which is not possible for weaker and equal-strength high-pressure phases and cases without a gasket. Some experimental phenomena are reproduced and interpreted. Developed methods and obtained results represent essential progress toward the understanding of PTs under compression in the DAC. This will allow one optimal design of experiments and conditions for synthesis of new high pressure phases.

© 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4873460]

I. INTRODUCTION

A diamond anvil cell (DAC) is a powerful and primary tool to generate high pressure and in-situ study the material physical behavior and phase transformations (PTs) to high pressure phases, by using advanced diagnostics, such as Raman, x-ray, and optical techniques.1–5 In some cases, the material under study is compressed between two diamond anvils without any external support,6–8 i.e., the external part of the sample serves as a gasket for the internal part, which is under high pressure. However, in most cases,9–14 the sample is placed inside of a deformable gasket made of a material with different strength. If achieving maximum possible pressure in a reasonably large volume is the goal, the gasket is made of the strongest possible materials, such as T301 stainless steel,13 rhenium,10,15 and even diamond powder.16 If the goal is just to avoid an intense flow of powder sample at the initial stage of compression, a weak gasket could be made of polymer, paper, or cardboard. Utilization of the gasket, in particular, allows one: (1) Performing experiments under hydrostatic conditions by filling gasket hole with fluid, in which sample is placed. (2) Performing experiments under reduced nonhydrostatic (deviatoric) stresses by filling the gasket hole with media with low yield strength (e.g., neon, argon, mixture of methanol and ethanol, cesium iodide,17 and sodium chloride17,18), in which the sample is placed. (3) Reducing plastic flow in a sample from the center and causing flow to the center, thus increasing pressure level. (4) Reducing radial pressure gradients and even producing an almost homogeneous pressure distribution.19,20 This allows one to perform a quantitative study of phase transformations and achieve complete phase transformation in a sample. This also reduces the probability of fracture of an anvil, because without the gasket, pressure grows at the center above the level required for transformation, or grows at the center after completing phase transformation in the central region during transformation at the periphery. Detailed discussions of the effect of a gasket can also be found in Refs. 11, 21, and 22.

Within a liquid, the sample is subjected to hydrostatic loading and undergoes pressure-induced phase transformations. Without hydrostatic media, or above the solidification pressure for transmitting media, the sample is under nonhydrostatic stresses or stress tensor. Moreover, if there is an irreversible reduction in the sample thickness, significant plastic straining in the sample may drastically affect phase

[a)Author to whom correspondence should be addressed. Electronic mail: vlevitas@iastate.edu.
transformation through changing their mechanism, as it was recognized in Refs. 23 and 24. For pressure-induced or stress-tensor-induced phase transformations below the yield strength of the material, a high pressure phase nucleates at pre-existing defects, e.g., dislocations that represent pressure and stress concentrators. In contrast, plastic strain-induced PTs under high pressure occur by nucleation at new defects, which are continuously generated during plastic deformation. Thus, dislocations as the main kind of defects are generated and densely piled up against grain boundaries or other obstacles during plastic flow, which creates a strong concentrator of the stress tensor and may lead to an obvious reduction of threshold pressure for PTs. For example, the rhombohedral-to-cubic boron nitride (rB:N-to-cBN) transformation under compression without hydrostatic media starts at 5.6 GPa, while it takes place at 55 GPa under hydrostatic conditions. A corresponding analytical model and much more detailed finite element simulations are developed to elucidate strain-induced nucleation at dislocation pile ups. The best way to study strain-induced PTs and the effect of plastic strain on thermodynamics and kinetics of PTs is to utilize combined compression and torsion loading in a rotational diamond anvil cell. However, there is no fundamental difference between strain-induced PTs under plastic compression in traditional DAC and under pressure and shear in rotational DAC in terms of mechanism, thermodynamics, and kinetics. The only difference is in the pressure-plastic strain loading path: while in rotational DAC one can increase plastic strain at constant pressure, in traditional DAC both pressure and plastic strain grow during compression of a sample, and the effect of plastic strain on PT thermodynamics and kinetics is not as easy to separate.

In experiments under nonhydrostatic conditions in DAC, PT is characterized by pressure for initiation of transformation (e.g., Refs. 8, 12, and 18) and, in rear cases, for completing PT, and the pressure-concentration of high pressure phase curve. Results for the same materials differ essentially in different papers. In some cases, the reason is specified, e.g., transmitting media with different yield strength (degree of nonhydrostaticity). In most cases without transmitting media, the reasons for discrepancy are not clear. However, if one would consider PT as strain-induced rather than pressure-induced, the difference is caused by different plastic strain, which was not measured. Different geometric parameters and elastoplastic properties of the gasket and sample lead to different plastic strains and, consequently, transformation pressure and pressure-concentration of high pressure phase curves. Thus, experimental results do not characterize thermodynamic and kinetics of a sample material but represent complex behavior of the sample-gasket (and, at very high pressure, anvil) system. This is also the reason that the threshold pressure for PTs under non-hydrostatic condition differs for different types of high-pressure apparatuses, due to distinct degrees of plastic flows. For example, when different gaskets and high-pressure apparatuses are utilized, PT of the highly ordered hexagonal BN to wBN are found at 9.6 GPa, 10 GPa, and 12.5 GPa, respectively.

Thus, there is clear necessity to consider phase transformations under compression of a sample in a gasket as strain-induced rather than pressure-induced. Note that pressure-induced PTs in DAC have been modelled in Refs. 31 and 32 using theory developed in Refs. 33 and 34 and finite element method (FEM) algorithm in Refs. 35 and 36, which are very much different from the current paper. Since plastic strain field in a sample is not measured directly, the only way to gain understanding and develop combined experimental and theoretical methods of characterization is to develop corresponding models and perform simulations. In comparison with pressure-induced PTs, strain-induced ones are not just terminologically different, but require completely different thermodynamic and kinetic descriptions, as well as experimental characterization. Nanoscale models and mechanisms of strain-induced PTs at dislocations generated during plastic flow are presented in Refs. 23 and 25. Based on the understanding gained at the nanoscale, a microscale theory is developed. In this theory, strain-induced PTs are described (characterized) by a pressure-dependent, strain-controlled (instead of time-controlled) kinetic equation (see Eq. (8)), for concentration of the high-pressure phase \( c \), which depends on four main parameters: (1) kinetic parameter \( k \), which scales the rate of PTs, (2) the minimum pressure \( p_r^c \), below which direct strain-induced PT does not take place, (3) the maximum pressure \( p_x^c \), above which reverse strain-induced PT cannot occur, and (4) the ratio of yield strengths of low \( (\sigma_y) \) and high-pressure \( (\sigma_y) \) phases. This is an equation which ideally should be found from experiments. However, it was not done before because there is only one paper where the distribution of concentration of high-pressure phase along the contact surface diamond-sample was measured and plastic strain distribution was not measured in literature at all. That is why the simulation of strain-induced PTs in DAC and rotational DAC have been performed for generic material and the effect of the four material parameters above have been elucidated. Simulations first have been performed with complete adhesion between sample and diamond and then with allowing for contact sliding and it was demonstrated that contact sliding significantly affects all fields and should be included. However, all these papers are devoted to sample without gasket. It is known from experiments that pressure distribution, and character and intensity of plastic flow with and without the gasket are completely different. That is why in the current paper, we will study for the first time strain-induced PTs in a sample within a gasket. This is computationally a more complex problem, because it contains one more contact surface between sample and gasket and, more importantly, contact line between sample, gasket, and anvil. This introduces additional nonlinearities and often causes divergence of the iterative procedure.

In this paper, strain-induced PTs under compression of a sample in DAC including a gasket are modeled and simulated. A coupled problem is solved using FEM for PT and mechanics with large plastic flow and contact sliding at all three contact surfaces, which thus leads to high complexity in simulations. The combined effect of the following parameters on phase transformation kinetics and heterogeneity of
the pressure, concentration of high pressure phase, and accumulated plastic strain fields in the sample has been studied: kinetic parameter \( k \), which scales the rate of PTs; the ratio of yield strengths \( \sigma_{y2}/\sigma_{y1} \) of phases; ratio of the yield strength of gasket and sample \( \sigma_g/\sigma_s \); and relative radius and height of a sample. A gasket with essentially higher strength than a sample could fundamentally change direction and heterogeneity of plastic flow and contact friction, causing a more homogeneous pressure field, which would change PT kinetics. It was demonstrated that any pressure \( p \)-concentration \( c \) of high pressure phase curve is not related directly to PT kinetics but represents the behavior of a sample-gasket system, which determines the pressure – plastic strain loading curve. That explains why gaskets with different strength and geometric parameters change pressure for initiation and completion of PT and the entire \( p-c \) curve. In particular, the growth of pressure required to continue and complete PT is not a necessity or a fundamental property of the PT. It is just consequence that in DAC plastic straining creating nucleation sites cannot be produced without pressure increase. If such a straining would be produced at constant pressure, like in rotational DAC, PT could occur at much lower pressure (see Refs. 19, 20, and 26–29).

Many of obtained results are essentially different from previous results\(^3\)\(^6\)\(^–\)\(^4\)\(^1\) for DAC without a gasket or even have opposite trends. Utilization of a gasket changes radial plastic flow toward center of a sample, which leads for some geometries to high quasi-homogeneous pressure. For transformation to a stronger high-pressure phase, plastic strain and concentration of high pressure phase are also quasi-homogeneous. This allows us to suggest a method of determination of strain-controlled kinetics from experiments. This is not possible for a weaker or equal-strength high-pressure phase and case without a gasket, for which a completely transformed high pressure phase near the sample-anvil boundary is separated from almost an untransformed low pressure phase by a very sharp interface. A new sliding mechanism at the contact line between sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Some experimental phenomena are reproduced and interpreted.

II. PROBLEM FORMULATION
A. Geometry and boundary conditions

A scheme of DAC subjected to an axial compressive force \( P \) is shown in Fig. 1(a). Due to symmetries of the load and geometry, a quarter of DAC is taken into consideration. In Fig. 1(b), a quarter of an initial undeformed sample (the rectangle \( abcde \)) is encapsulated into the gasket’s hole and they contact along the cylindrical surface \( bc \). The initial thickness of the sample and gasket inner side is \( H_0 \); the thickness of a gasket at the periphery is \( H_1 + H_0(H_1 = m \cdot H_0) \); sample radius \( ab \) is \( R_s = n \cdot H_0 \), and the radius of flat surface of a diamond anvil is \( R = 5H_1 = 5m \cdot H_0 \). Effects of gasket size on \( p-c \) curve is not related directly to PT kinetics but represents the behavior of a sample-gasket system, which determines the pressure – plastic strain loading curve. That explains why gaskets with different strength and geometric parameters change pressure for initiation and completion of PT and the entire \( p-c \) curve. In particular, the growth of pressure required to continue and complete PT is not a necessity or a fundamental property of the PT. It is just consequence that in DAC plastic straining creating nucleation sites cannot be produced without pressure increase. If such a straining would be produced at constant pressure, like in rotational DAC, PT could occur at much lower pressure (see Refs. 19, 20, and 26–29).

Many of obtained results are essentially different from previous results\(^3\)\(^6\)\(^–\)\(^4\)\(^1\) for DAC without a gasket or even have opposite trends. Utilization of a gasket changes radial plastic flow toward center of a sample, which leads for some geometries to high quasi-homogeneous pressure. For transformation to a stronger high-pressure phase, plastic strain and concentration of high pressure phase are also quasi-homogeneous. This allows us to suggest a method of determination of strain-controlled kinetics from experiments. This is not possible for a weaker or equal-strength high-pressure phase and case without a gasket, for which a completely transformed high pressure phase near the sample-anvil boundary is separated from almost an untransformed low pressure phase by a very sharp interface. A new sliding mechanism at the contact line between sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Some experimental phenomena are reproduced and interpreted.

II. PROBLEM FORMULATION
A. Geometry and boundary conditions

A scheme of DAC subjected to an axial compressive force \( P \) is shown in Fig. 1(a). Due to symmetries of the load and geometry, a quarter of DAC is taken into consideration. In Fig. 1(b), a quarter of an initial undeformed sample (the rectangle \( abcde \)) is encapsulated into the gasket’s hole and they contact along the cylindrical surface \( bc \). The initial thickness of the sample and gasket inner side is \( H_0 \); the thickness of a gasket at the periphery is \( H_1 + H_0(H_1 = m \cdot H_0) \); sample radius \( ab \) is \( R_s = n \cdot H_0 \), and the radius of flat surface of a diamond anvil is \( R = 5H_1 = 5m \cdot H_0 \). Effects of gasket size on \( p-c \) curve is not related directly to PT kinetics but represents the behavior of a sample-gasket system, which determines the pressure – plastic strain loading curve. That explains why gaskets with different strength and geometric parameters change pressure for initiation and completion of PT and the entire \( p-c \) curve. In particular, the growth of pressure required to continue and complete PT is not a necessity or a fundamental property of the PT. It is just consequence that in DAC plastic straining creating nucleation sites cannot be produced without pressure increase. If such a straining would be produced at constant pressure, like in rotational DAC, PT could occur at much lower pressure (see Refs. 19, 20, and 26–29).

Many of obtained results are essentially different from previous results\(^3\)\(^6\)\(^–\)\(^4\)\(^1\) for DAC without a gasket or even have opposite trends. Utilization of a gasket changes radial plastic flow toward center of a sample, which leads for some geometries to high quasi-homogeneous pressure. For transformation to a stronger high-pressure phase, plastic strain and concentration of high pressure phase are also quasi-homogeneous. This allows us to suggest a method of determination of strain-controlled kinetics from experiments. This is not possible for a weaker or equal-strength high-pressure phase and case without a gasket, for which a completely transformed high pressure phase near the sample-anvil boundary is separated from almost an untransformed low pressure phase by a very sharp interface. A new sliding mechanism at the contact line between sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Some experimental phenomena are reproduced and interpreted.

II. PROBLEM FORMULATION
A. Geometry and boundary conditions

A scheme of DAC subjected to an axial compressive force \( P \) is shown in Fig. 1(a). Due to symmetries of the load and geometry, a quarter of DAC is taken into consideration. In Fig. 1(b), a quarter of an initial undeformed sample (the rectangle \( abcde \)) is encapsulated into the gasket’s hole and they contact along the cylindrical surface \( bc \). The initial thickness of the sample and gasket inner side is \( H_0 \); the thickness of a gasket at the periphery is \( H_1 + H_0(H_1 = m \cdot H_0) \); sample radius \( ab \) is \( R_s = n \cdot H_0 \), and the radius of flat surface of a diamond anvil is \( R = 5H_1 = 5m \cdot H_0 \). Effects of gasket size on \( p-c \) curve is not related directly to PT kinetics but represents the behavior of a sample-gasket system, which determines the pressure – plastic strain loading curve. That explains why gaskets with different strength and geometric parameters change pressure for initiation and completion of PT and the entire \( p-c \) curve. In particular, the growth of pressure required to continue and complete PT is not a necessity or a fundamental property of the PT. It is just consequence that in DAC plastic straining creating nucleation sites cannot be produced without pressure increase. If such a straining would be produced at constant pressure, like in rotational DAC, PT could occur at much lower pressure (see Refs. 19, 20, and 26–29).

Many of obtained results are essentially different from previous results\(^3\)\(^6\)\(^–\)\(^4\)\(^1\) for DAC without a gasket or even have opposite trends. Utilization of a gasket changes radial plastic flow toward center of a sample, which leads for some geometries to high quasi-homogeneous pressure. For transformation to a stronger high-pressure phase, plastic strain and concentration of high pressure phase are also quasi-homogeneous. This allows us to suggest a method of determination of strain-controlled kinetics from experiments. This is not possible for a weaker or equal-strength high-pressure phase and case without a gasket, for which a completely transformed high pressure phase near the sample-anvil boundary is separated from almost an untransformed low pressure phase by a very sharp interface. A new sliding mechanism at the contact line between sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Some experimental phenomena are reproduced and interpreted.

II. PROBLEM FORMULATION
A. Geometry and boundary conditions

A scheme of DAC subjected to an axial compressive force \( P \) is shown in Fig. 1(a). Due to symmetries of the load and geometry, a quarter of DAC is taken into consideration. In Fig. 1(b), a quarter of an initial undeformed sample (the rectangle \( abcde \)) is encapsulated into the gasket’s hole and they contact along the cylindrical surface \( bc \). The initial thickness of the sample and gasket inner side is \( H_0 \); the thickness of a gasket at the periphery is \( H_1 + H_0(H_1 = m \cdot H_0) \); sample radius \( ab \) is \( R_s = n \cdot H_0 \), and the radius of flat surface of a diamond anvil is \( R = 5H_1 = 5m \cdot H_0 \). Effects of gasket size on \( p-c \) curve is not related directly to PT kinetics but represents the behavior of a sample-gasket system, which determines the pressure – plastic strain loading curve. That explains why gaskets with different strength and geometric parameters change pressure for initiation and completion of PT and the entire \( p-c \) curve. In particular, the growth of pressure required to continue and complete PT is not a necessity or a fundamental property of the PT. It is just consequence that in DAC plastic straining creating nucleation sites cannot be produced without pressure increase. If such a straining would be produced at constant pressure, like in rotational DAC, PT could occur at much lower pressure (see Refs. 19, 20, and 26–29).

Many of obtained results are essentially different from previous results\(^3\)\(^6\)\(^–\)\(^4\)\(^1\) for DAC without a gasket or even have opposite trends. Utilization of a gasket changes radial plastic flow toward center of a sample, which leads for some geometries to high quasi-homogeneous pressure. For transformation to a stronger high-pressure phase, plastic strain and concentration of high pressure phase are also quasi-homogeneous. This allows us to suggest a method of determination of strain-controlled kinetics from experiments. This is not possible for a weaker or equal-strength high-pressure phase and case without a gasket, for which a completely transformed high pressure phase near the sample-anvil boundary is separated from almost an untransformed low pressure phase by a very sharp interface. A new sliding mechanism at the contact line between sample, gasket, and anvil called extrusion-based pseudoslip is revealed, which plays an important part in producing high pressure. Some experimental phenomena are reproduced and interpreted.
Due to symmetry, the radial shear stress $\tau_r = 0$ and the axial displacement $u_z = 0$ on the symmetry plane $z = 0$.

Surfaces of the gasket which are not in contact with the diamond anvil or sample are stress-free.

**B. Material model**

Similar to Refs. 38–44, the simplest isotropic, perfectly plastic model for the sample and also for the gasket will be utilized to obtain the generic solutions. The deformation of a material is described by the position vector of the particle in the deformed state $r = r(r_0, t)$, as a function of its position $r_0$ in the initial (undeformed) configuration and time $t$. The multiplicative decomposition of the deformation gradient, $F = \partial r/\partial r_0 = V_e \cdot F_t \cdot F_p$ into symmetric elastic stretch tensor $V_e$, transformational $F_t$, and plastic $F_p$ contributions, is accepted. While elastic and transformational strains are assumed (i.e., $e_t = V_e - I$ and $e_r = V_r - I$, where $I$ is the second-rank unit tensor), plastic strains and material rotations are large. Since the gasket material does not undergo phase transformation, $F_t = I$. The justification of the applicability of this perfectly plastic and isotropic model independent of the deformation history could be found in Ref. 45 for various materials (e.g., rocks, powder, metals) starting with accumulated plastic strain $q > 0.6 \div 1$, and under monotonous loading. In addition, for simplification, diamond anvils are assumed to be a rigid body in this paper, which is reasonable when small elastic strain assumption in the sample and gasket is made (but large plastic deformation and sliding are allowed). A total system of equations for the problem of coupled strain-induced PT and mechanics with plastic flow in a sample is utilized in the simulations as follows:

Decomposing the deformation rate $d = (F \cdot F^{-1}) \dot{s}$ into elastic (subscript $e$), transformation (subscript $t$), and plastic (subscript $p$) components

$$d = \dot{\varepsilon}_e + \dot{\nu} I + d_p.$$  

Hooke’s law for deviatoric and volumetric parts of the Cauchy stress $T$

$$s = 2Gdev \varepsilon_e; \quad p = -\frac{\sigma_{yy} + \sigma_{zz} + \sigma_{xx}}{3} = -K\varepsilon_0. \quad (2)$$

Transformation volumetric strain

$$e_t = \tilde{e}_t c.$$  

von Mises yield condition for two-phase mixture

$$\sigma_t = \frac{3}{2} : s : s \leq \sigma_y;$$  

$$\sigma_y = \begin{cases} (1 - c)\sigma_{y1} + c\sigma_{y2} & \text{for sample} \\ \sigma_{yg} & \text{for gasket}. \end{cases} \quad (4)$$

Plastic flow rule in the elastic region

$$\sigma_t < \sigma_y \rightarrow d_p = 0,$$  

in the plastic region

$$\sigma_t = \sigma_y \rightarrow d_p = \dot{\lambda} s; \quad \lambda \geq 0. \quad (6)$$

Equilibrium equation

$$\nabla : T = 0.$$  

Here, $c$ is concentration of high-pressure phase; the accumulated plastic strain $q$ is defined by $q = (2/3d_p : d_p)^{1/2}$; $p_\nu = p - p'_{\nu}/p_{\nu} P$ and $p_r = p - p'_{\nu}/p_{\nu} P$ are dimensionless characteristic pressures, which are used for direct and reverse PTs; $p'_{\nu}$ and $p'_{r}$ are the pressures at which direct and reverse PTs occur under hydrostatic loading, respectively; $H$ is the Heaviside step function; subscript $s$ means the symmetric part of tensor; $\varepsilon_e$ and $\tilde{\rho}$ is the objective Jaumann time derivative of the elastic strain and deviatoric stress; $\tilde{\varepsilon}_e$ and $\tilde{\nu}$ are the elastic volumetric strain and transformation volumetric strain for complete PT; $K$ and $G$ are the bulk and shear moduli, respectively; $\sigma_t$ is the stress intensity or effective stress. Parameter $\lambda$ is iteratively updated by satisfaction of the yield condition (4); and subscript $y$, $y_1$, and $y_2$ are for the yield strength for the sample with concentration $0 \leq c \leq 1$, $c = 0$, and $c = 1$, respectively.

For gasket material, which does not undergo phase transformations, Eqs. (3) and (8) are irrelevant; in Eq. (1) $\tilde{\nu} = 0$; in Eqs. (4)-(6) $c$ is irrelevant and the yield strength $\sigma_y$ is equal to the yield strength of a gasket $\sigma_{yg}$.

**C. Friction model**

This section focuses on the introduction of the friction model between sample and diamond or between sample and gasket. Due to axial symmetry, the direction of relative sliding is known (to within its sign); it is along the curve ABCD between diamond and sample and gasket, and along the curve BE between sample and gasket, without circumferential component. The contact behavior between diamond and gasket is similar and even simpler due to an absence of strength changes in materials. In standard Coulomb friction, the slippage on the contact surface initiates only when friction stress $\tau$ arrives at the critical friction stress $\tau_{crit} = \mu n$ where $n$ is normal contact stress. While standard Coulomb friction is reasonable in the elastic state, once friction stress on the contact surface reaches the yield strength in shear $\tau_y = \sigma_y/\sqrt{3}$ (von Mises yield condition (4) is used here) in plastic state, slipping can occur even if $\tau < \mu n$. As a consequence, the standard Coulomb friction could be modified by redefining the critical friction stress as $\tau_{crit} = \min(\mu n, \tau_y)$, and conditions of sliding and cohesion are separated when friction stress $\tau$ reaches this value. In principle, the critical friction stress for the contact pair between sample and gasket should be defined as $\tau_{crit} = \min(\mu n, \tau_y, \tau_{yg})$, where $\tau_{yg}$ is the yield strength in
shear for gasket. The gasket with higher yield strength than sample is utilized in most cases to produce high pressure. Therefore, we accept \( \tau_{\text{crit}} = \min(\mu \sigma_n, \tau_y) \). Theoretically, such a definition of the critical friction stress, along with sliding rule, is sufficient for a solution of the contact problem. However, in numerical simulations, the sudden change of contact conditions between cohesion and slip may result in divergence of results, especially for the large sliding problem with complex contact conditions (e.g., at point B in Fig. 1(d), where there are three different contact pairs). A penalty method is utilized to make the contact conditions continuous, in which cohesion condition will be substituted with a small elastic reversible slippage \( u^e \). While penalty method is a mathematical regularization, this elastic slip could be also physically interpreted as elastic deformation of asperities of the thin contact layer. In addition, the elastic slip \( u^e \) should be constrained in the small range to obtain an accurate solution, for example, the specified maximum elastic relative slip \( u_{\text{crit}} \) equals 0.5% of average element length for fine-meshing models. Note that there are more than 25 finite elements in the current simulations within half of the thickness of a sample along the z-axis.

One could introduce the magnitude of elastic slip by the simplest linear relation with shear stress \( \tau \), \( \tau = k_e u^e \), where \( k_e \) is elastic slip stiffness. The magnitude of \( k_e \) could be defined by the condition that sliding starts when elastic slip \( u^e \) reaches the prescribed critical value \( u_{\text{crit}} \). Then one obtains \( \tau_{\text{crit}} = k_e u_{\text{crit}} \) and \( k_e = \tau_{\text{crit}} / u_{\text{crit}} \). Consequently, \( k_e \) linearly varies with the normal stress \( \sigma_n \) or the yield strength in shear \( \tau_y \). Coupling between PTs and sliding occurs because \( \tau_y \) for the sample is not a constant but depends on concentrations and yield strengths of phases by relation: \( \tau_y = (1 - c) \tau_{y1} + c \tau_{y2} \). The complete system of equations for contact pairs is summarized below, and to some extent it is similar to that for elastoplasticity theory.

Decomposing contact relative displacement \( u^c \) into elastic (reversible) and sliding (irreversible) parts

\[
    u^c = u^e + u^s.
\]

Yield strength in shear

\[
    \tau_y = \begin{cases} 
    (1 - c) \tau_{y1} + c \tau_{y2} & \text{for sample} \\
    \tau_{yg} & \text{for gasket}. 
    \end{cases}
\]

Critical friction shear stress

\[
    \tau_{\text{crit}} = \min(\tau_y, \mu \sigma_n). \tag{11}
\]

Rule for elastic contact displacement

\[
    \begin{align*}
    u^e &= \frac{\tau - \mu \sigma_n}{\tau_y} & \text{if} \quad \mu \sigma_n > \tau_y \\
    u^e &= \frac{\tau - \mu \sigma_n}{\mu \sigma_n} & \text{if} \quad \mu \sigma_n \leq \tau_y. 
    \end{align*} \tag{12}
\]

Sliding rule below critical shear stress

\[
    |\tau| < \tau_{\text{crit}} \Rightarrow \dot{u}^s = 0. \tag{13}
\]

D. Numerical procedure

To solve pressure-dependent strain-controlled kinetic Eq. (8), ABAQUS user subroutines USDFLD and HETVAL are implemented, in which concentration \( c \) is modeled by temperature and transformation strain is treated as thermal strain. Further, the coupled mechanics and PT problem is simulated by a coupled thermo-plasticity problem.

For contact pairs between sample and gasket or between sample and diamond anvil, the critical friction stress is defined as \( \tau_{\text{crit}} = \min(\mu \sigma_n, \tau_y(c)) \) and yield strength in shear \( \tau_y(c) \) is not constant but depends on concentration \( c \) and yield strengths of phases. That is the reason why the contact problem could not be solved by the standard procedure in ABAQUS and the user subroutine FRIC should be utilized to consider Eqs. (12)–(14). For a particular case, when high- and low-pressure phases have the same yield strengths \( (\tau_y(c) = \tau_{y1}) \), yield strength in shear is independent of concentration and becomes a constant. In this case, the contact problem could be also solved by standard procedure without using the subroutine FRIC, which could be utilized to confirm the consistency of results obtained with FRIC and the standard procedure. For the contact pair between diamond anvil and gasket, standard procedure in ABAQUS can be utilized as well.

In the dimensionless form, except for friction shear stress normalized by the yield strength in shear \( \tau_{y1} \), all stress-related parameters (e.g., pressure \( p \) and parameter \( p^c_0 \)) are normalized by \( \sigma_{y1} \); the dimensionless compressive force \( F \) is the axial force \( P \) normalized by the product of \( \sigma_{y1} \) and the undeformed contact area (which is equal to the area of the surface of revolution produced by complete revolution of the curve abcd in Fig. 1(b) about the z-axis). The related material parameters as follows: \( p^c_0 = 33.75 \), \( p^c_1 = -1 \), \( p^c_2 = 6.75 \), \( p^c_3 = 6.375 \), Young modulus \( E = 162.5 \), Poisson’s ratio \( v = 0.3 \), volumetric transformation strain for direct PT \( \varepsilon_t = -0.1 \), and \( k = 6 \) if there is no special note. In addition, the yield strength for the gasket \( \sigma_{yg} = 3\sigma_{y1} \) is utilized in the major parts of this paper. A high value of \( p^c_0 \) and a low value of \( p^c_3 \), which will not be reached in our simulations means that pressure-induced phase transformations are excluded.

III. SIMULATION RESULTS FOR COUPLED PLASTIC FLOW AND PHASE TRANSFORMATION

Strain-induced PT coupled with plastic flow under high pressure in a sample within a gasket will be discussed. As stated in Refs. 38–41, the strength of high-pressure phase strongly influences the kinetics of PT and plastic flow in a traditional diamond anvil cell. Similarly, in this section, the cases with equal-strength, weaker, and stronger high-pressure phases will be investigated by assuming \( \sigma_{y2}/\sigma_{y1} = 1, 0.3, 3 \), respectively. In addition, the kinetic parameter \( k \) in Eq. (8)
determines the rate of PT and will also be studied. In Fig. 1(b) m = 1, n = 2 and the gasket yield strength $\sigma_{yg} = 3\sigma_{y1}$ are used throughout this entire section; the effects of gasket strength and sizes will be investigated in detail in Sec. IV. To understand the effects of PT on the plastic flow and pressure, the model without PT will be utilized for comparison.

A. Equal-strength phases

For equal strengths between high- and low-pressure phases ($\sigma_{y2} = \sigma_{y1}$), Fig. 2(a) shows that the PT in the sample propagates from the contact surface to the symmetry plane, and from the periphery to the center, and that the fully transformed sample is obtained without large reduction of sample thickness, which are completely different from the results in DAC without the gasket. In the previous simulations, the PT progresses from the center to the periphery. Due to the absence of the gasket, there is a large pressure gradient and maximum pressure is located at the center of a sample, which intensifies the PT kinetics.

Such a difference in the PT propagation directions in comparison with previous results is caused by obvious distinctions in the distributions of accumulated plastic strain and pressure (see in the Figs. 2(b) and 2(c)), which determine PT kinetics. One can note that accumulated plastic strain is larger at the periphery and on the contact surface than the center and symmetry plane, respectively. Larger accumulated plastic strain intensifies the PT kinetics. Before the pressure distribution in Fig. 2(c) is discussed, we first consider a simpler case without PT in the sample. Fig. 3(a) shows that the maximum pressure is located at the center and pressure gradually reduces from the center to the periphery. Friction shear stress in Fig. 4(a) at the contact surface of the gasket reaches the yield strength in shear, which is three times of the shear yield strength of a sample. The gasket with high yield strength greatly reduces radial flow in a sample, and pressure could reach a very high value in the sample before thickness significantly decreases. This is in fact one of the reasons for utilization of a gasket in order to produce very high pressure in relatively low strength materials. Friction stress in the entire sample and gasket in Fig. 4(a) does not change the direction because material flows from the center to the periphery under a rising loading. When PT is taken into account, in contrast to previous results in the traditional DAC without a gasket, pressure is quite homogeneous and high in the entire sample (see Figs. 2(c) and 3(b)). Before PT, pressure monotonously reduces from the center to the periphery (Fig. 3(a)). With the increase in the applied force $F$ from 9.22 to 13.29, PT occurs and the concentration of the high-pressure phase grows. Homogeneous and high pressure provides a large driving force for fast PT kinetics in the entire sample. Fast volume reduction due to PTs causes material flow from the periphery to the center. This is opposite to the case without PT and induces the change of shear stress direction. The decreasing pressure with increasing radius in Fig. 3(a) changes into an increasing one in the sample at $F \leq 12.43$ in Fig. 3(b). This is qualitatively consistent with the well-known from the metal forming simplified equilibrium equation

$$\frac{dp}{dr} = -2r\tau_{s},$$

Since radial flow is limited and radial and axial deformation is approximately homogeneous, shear deformation makes the main contribution to the heterogeneity of the accumulated plastic strain and concentration of the high-pressure phase. Shear stress at the center and on the symmetry plane is zero and increases to its maximum in value at the

![FIG. 2. Distributions of (a) concentration of high-pressure phase $c$, (b) accumulated plastic strain $q$, (c) pressure $p$, and (d) radial displacement $u_r$ (normalized by a half thickness of undeformed sample $H_0/2$) in the sample for $\sigma_{y2} = \sigma_{y1}$. The increasing dimensionless axial compressive force $F$ is (1) 9.22, (2) 10.85, (3) 11.13, (4) 12.43, and (5) 13.29.](image)

![FIG. 3. Distribution of pressure $p$ at the contact surface for (a) the model without PTs and (b) with PT for $\sigma_{y2} = \sigma_{y1}$. The dimensionless axial force $F$ is (1) 9.22, (2) 10.85, (3) 11.13, (4) 12.43, and (5) 13.29.](image)

![FIG. 4. Distribution of the friction stress $\tau$ at the contact surface for the models (a) without PT and (b) with PT for $\sigma_{y2} = \sigma_{y1}$. The dimensionless axial force $F$ is (1) 9.22, (2) 10.85, (3) 11.13, (4) 12.43, and (5) 13.29.](image)
periphery and contact surface, which causes larger plastic shear strain at the periphery and contact surface (Figs. 2(b) and 4(b)). According to kinetic Eq. (8), high pressure (much above minimum pressure $p_d^I = 6.75$) and moderate plastic strain intensify PT kinetics and further plastic flow to the center due to volume reduction during PT, which surpasses the flow to the periphery due to compression. Note that when $F$ changes from 10.85 to 11.13, pressure in the sample even drops due to intense transformation and volume reduction. Without a gasket, the flow to the center could not be found in Ref. 40 at all and a very slight flow to the center in a small central region was found for faster kinetics in Refs. 38, 39, and 41. High pressure in the entire sample and limited radial flow due to gasket make it possible to obtain a fully transformed sample without a large reduction of sample thickness. This was not the case in a DAC without a gasket, where pressure in the periphery is too small to activate nucleation of a high-pressure phase and thickness always reduced significantly to cause large enough plastic straining. Due to a rather homogenous distribution of pressure in the sample, heterogeneous distribution of plastic strain becomes the only player to determine heterogeneity of high pressure phase concentration in the sample. Since at $F = 12.43$ PT almost completes, at $F = 13.29$ pressure at the center becomes slightly larger than at the periphery (Fig. 3(b)), because the flow from the center to the periphery starts. Indeed, shear stress in the major region of a sample becomes positive at $F = 13.29$ (Fig. 4(b)). Still, the total radial displacement is negative (see Fig. 2(d)) because of previous larger flow to the center during PTs.

While there is a very sharp, approximately horizontal boundary between fully transformed and almost nontransformed regions, pressure at this interface is significantly higher than $p_d^I$. This is in contrast to compression without a gasket when pressure is close to $p_d^I$ at the diffuse interface between fully transformed and nontransformed regions.38–41 The reason of this difference is because of large plastic strains in Refs. 38–41, which initiates PT just above $p_d^I$, and small and localized plastic straining here.

As it was suggested in Ref. 20, quasi-homogeneous pressure distribution simplifies the significantly quantitative study of the PT kinetics. It also eliminates the misinterpretation of minimum transformation pressure related to radial flow of the material transformed at high pressure but convectively moved to low pressure regions. Some simplified methods to choose parameters of a gasket to ensure quasi-homogeneous pressure and their experimental confirmation for PT from hexagonal to wurtzitic BN have been presented in Ref. 20. Current work suggests a much more precise tool for design of experiments with a quasi-homogeneous pressure distribution. Still, due to heterogeneity of plastic strain and concentration of high-pressure phase in the form of fully transformed and almost nontransformed regions divided by a relatively sharp interface, the extraction of material parameters in kinetic Eq. (8) is not easy. One needs to eliminate these heterogeneities as well, which is probably possible by computational design of an optimal sample-gasket system utilizing current model and numerical approach.

### B. Weaker high-pressure phase

We will discuss PT and plastic flow in a sample with weaker high-pressure phase ($\sigma_{g2} = 0.3\sigma_{g1}$), under a rising compressive force $F$. Due to high-pressure phase with low strength, material softening during PT induces instabilities, which do not occur for equal-strength and stronger high-pressure phases.

Fig. 5(a) shows the distribution on the concentration $c$ of high-pressure phase in the sample during the growth of compressive force $F$. PT starts at the contact surface of the periphery and propagates towards the symmetry plane and the center of sample. When the axial compressive force reaches $F = 9.33$, transformation is almost completed within a very thin contact layer, while it practically does not occur in the rest of the sample. This is consistent with experimental observation for the transformation from semiconducting Si I to weaker metallic II under compression in diamond anvil.46 Such a correspondence with experiments also confirms that strain-induced rather than pressure or stress-induced PT occurs in Ref. 46, because pressure is practically homogeneous in the sample and shear stresses are very small in comparison with pressure. To some extent, this phenomenon was reproduced in our previous model40 without the gasket. However, it was based on a cohesion model and caused artificial strain localization near the contact surface. In Refs. 38, 39, and 41, PT always started in the center rather than at the contact surface. Plastic flow in the whole sample towards the central region of the sample due to compressive transformation volumetric strain (see Fig. 5) is more pronounced than for the cases with equal-strength and stronger high-pressure phase. Such a flow of material towards the center of the sample during PT was experimentally found for weaker high-pressure phase of ZnSe.28 Generally, the plastic flow and PT behavior is quite similar for the cases of weaker and equal-strength high-pressure phase. However, there are some

![FIG. 5. Distributions of (a) concentration of high-pressure phase $c$, (b) accumulated plastic strain $q$, (c) pressure $p$, and (d) radial displacement $u_r$ (normalized by a half thickness of original sample $H_0/2$) in the sample for $\sigma_{g2} = 0.3\sigma_{g1}$. The dimensionless axial force $F$ is (1) 8.59, (2) 9.33, (3) 9.69, (4) 10.3, and (5) 12.21.](image-url)
differences. Thus, at $F = 9.69$ in Fig. 5, there is a curved band of localized plastic strain and completely transformed high-pressure phase connecting symmetry plane and high pressure phase near the contact surface PT. It is caused by material instability due to materials softening during phase transformation. However, the material instability is not as strong as the one in models without a gasket\textsuperscript{38–41} because plastic flow in a sample is confined by a stronger gasket. There are no strong oscillations in pressure (Fig. 6) and shear stress (Fig. 7) at the contact surface like for the case without a gasket.\textsuperscript{38–41} As it was mentioned in Refs. 38–41, strong strain and transformation localizations, and oscillation of stresses create significant problems in extracting kinetic Eq. (8) from results of experiments for weaker high-pressure phase. With a strong gasket, the extraction of kinetic information from experiments for a weaker high-pressure phase is not more complicated than for equal-strength high-pressure phase.

An interesting mechanism, a sliding of a sample and gasket along the diamond, is revealed at point b (Fig. 1(b)), where all three materials are in contact. For the sample, contact shear stress reaches critical value $\tau_{s2}$ (after PT is completed at this point) and sliding toward the center is possible (see Fig. 5). However, friction stress at the inner side of the gasket does not reach the critical value $\tau_{g2} = 3\tau_{s1}$ and sliding of gasket is forbidden. Then the gasket material at the boundary between the gasket and sample slides up (with respect to sample), extrudes, and produces a new contact surface with an anvil (see Fig. 8). Such an extrusion allows the sample to slide toward the center while satisfying the cohesion condition at the preexisting and new surfaces between gasket and anvil. We called this sliding mechanism “extrusion-based pseudoslip.” The revealing of this mechanism also confirms the accuracy of the algorithm and the solution of the contact problem for contact of three materials.

C. Stronger high-pressure phase

For stronger high-pressure phase ($\sigma_{s2} = 3\sigma_{s1}$), results in Figs. 9–11 are very different in comparison with the previous two cases with equal-strength and weaker high-pressure phases. Hardening due to phase transformation leads to reduced plastic flow with increasing concentration $c$ and delocalization of phase transformation. That is why plastic deformation and transformation occur much more homogeneously within the sample without formation and propagation of a completely transformed region. Pressure during transformation is quasi-homogeneous as well. It grows faster in comparison with the previous two cases due to a larger yield strength, which is why plastic strain required for complete transformation is smaller. Since the strength of a gasket and transforming sample is becoming comparable, material flow to the center due to PT reduces in comparison with the previous two cases. Based on friction shear stress distribution (Fig. 11), the material at the exterior of the sample starts to flow to the periphery at $F = 13.17$, when transformation is almost complete. Further compression is equivalent to the compression of a sample without a gasket (because the strength of the sample and gasket is almost the same and the volume reduction due to a small increment in $c$ is small), which leads to a flow from the center.

![Fig. 6. Distribution of pressure $p$ at the contact surface for $\sigma_{s2} = 0.3\sigma_{s1}$. The dimensionless axial force $F$ is (1) 8.59, (2) 9.33, (3) 9.69, (4) 10.3, and (5) 12.21.](image)

![Fig. 7. Distribution of friction stress $\tau$ at the contact surface for $\sigma_{s2} = 0.3\sigma_{s1}$. The dimensionless axial force $F$ is (1) 8.59, (2) 9.33, (3) 9.69, (4) 10.3, and (5) 12.21.](image)

![Fig. 8. Extrusion-based pseudoslip as the mechanism of sliding at the contact line (line GBL) between sample (left to the curve BE), gasket (right to the curve BE), and anvil (line GBL) during compression. Initially, points B of the sample and K of the gasket coincide. The evolution of geometry of two layers of finite elements along the contact surface (BE) in Fig. 1(d) during compression. Point L of gasket does not slide along the anvil because the sliding condition for it is not met, while sliding condition for points of the sample is satisfied. Sample sliding with respect to the anvil is possible because of the sliding of the gasket material along the sample and its extrusion, which produces a new gasket-anvil contact surface (BK).](image)
an increase in the shear friction stress and the pressure gradient, and consequently pressure heterogeneity and maximum pressure at the center.

Due to quasi-homogeneous distributions of pressure, plastic strain, and concentration of high-pressure phase, this case is the easiest one from the point of view of the extraction of kinetic properties from experiments. Thus, averaged over sample (or central part of sample) pressure, plastic strain, and concentration of high pressure phase, determined both experimentally and in simulations, can be utilized for the determination of the kinetic equation of the type of Eq. (8). This will be discussed below. Since at the symmetry axis material undergoes uniaxial compression without shear and material rotation, all tensors in the multiplicative decomposition of the deformation gradient \( F = V_e \cdot F_t \cdot F_p \) are coaxial, i.e., have the same principal axes, one of which is the \( z \)-axis and the two others are in the plane orthogonal to the \( z \)-axis. Then, multiplicative decomposition transforms into an additive decomposition of the logarithmic strains

\[
\sigma_{12} = 3\sigma_{y1}
\]

FIG. 10. Distribution of pressure \( p \) on the contact surface for \( \sigma_{12} = 3\sigma_{y1} \). The dimensionless axial force \( F \) is (1) 9.42, (2) 12.35, (3) 13.17, (4) 14.4, and (5) 15.47.

\[
\ln F = \ln V_e + \ln F_t + \ln F_p.
\]  

(15)

Because for uniaxial compression the integration of the equation \( \dot{q} = (2/3d_p : d_p)^{1/2} \) shows that \( q \) is equal to the negative logarithmic plastic strain along compression axes, along the \( z \)-axis, Eq. (15) simplifies to

\[
\ln H/H_0 = \ln(1 + e_{cz}) + \ln(1 + 1/3e_{cz}) - q,
\]  

(16)

where \( e_{cz} \) is the elastic strain along \( z \) axis. Indeed, for fixed principle axes of plastic deformation gradient \( F_p \), \( d_p = F_p : F_p^{-1} = \frac{d}{dt} \ln F_p \). Plastic incompressibility condition \( \ln F_{pz} + 2n\ln F_p = 0 \) results in \( d_{pz} = -1/2d_{pz} \), and \( q = (1/2(d_{pz}^2 + 2d_{pz}^2))^{1/2} = |d_{pz}| = |d_{pz}|\ln F_{pz} = -\frac{d}{dt}\ln F_{pz} \), which leads to \( q = -\ln F_{pz} \).

Pressure can be routinely measured using fluorescence of ruby particles. Concentration \( c \) is measured using relative intensities of x-ray diffraction peaks. Thickness of the sample \( H \) under load can be measured using a special pre-calibrated sensor. [47]

D. Effects of kinetic parameter \( k \)

In addition to the ratio of the yield strength of phases in a sample, the kinetic parameter \( k \) in Eq. (8) also has strong effect on PT and plastic flows. In this section, the effects from \( k \) will be investigated by comparing results of \( k = 6 \) and \( k = 30 \) for equal yield strengths between phases. As shown in Fig. 12, with growth of \( k \) from 6 to 30, the rate of PT increases at the initial stage of loading \( F < 11.3 \). At initial loading, the sample volume reduces much faster during fast PT for \( k = 30 \), which leads to lower pressure than that for \( k = 6 \) and negative mechnochemical feedback. As a result, there are not essential differences in concentration of high pressure phase for \( F = 12.43 \) and PT for both \( k = 6 \) and 30 are completed at almost same load \( F \). Initially, flow to the center is more pronounced for \( k = 30 \) than \( k = 6 \), which is determined by faster volume reduction during PT. In addition, faster kinetics leads to the formation of vertical strain
and PT localization zones, like for \( k = 6 \) and a smaller yield strength of the high-pressure phase. Pressure is quite homogeneous in the sample for both cases.

IV. EFFECTS OF GASKET/SAMPLE PARAMETERS

In Sec. III, we found that the strain-induced PT and plastic flow under compression of a sample with a gasket are much different from those in a DAC without gasket.38–41 In this section, the effects of a gasket/sample will further be investigated in detail in three aspects: relative sample radius, gasket/sample thickness, and gasket strength. A sample with equal-strength phases \((\sigma_{y2} = \sigma_{y1})\) will be analyzed.

A. Effects of relative sample radius

A gasket with higher yield strength (e.g., here \( \sigma_{y2} = 3\sigma_{y1} \)) could effectively impede the flow of the sample to the periphery and reduce heterogeneity of all parameters along the radial direction. This effect decreases with the increase of the relative sample radius \( S = R_i/R \) and the reduction of the relative gasket length \( G = 1-S \), because the total friction force between anvil and gasket reduces with a decreasing contact area. Fig. 13 shows the distributions of the concentration of high-pressure phase \( c \) and pressure \( p \) in the sample for relative sample radii \( S = 0.4 \) and \( S = 0.7 \) under a rising axial force \( F \). As it follows from Figs. 13 and 14, because of smaller yield strength, the thickness of a longer sample reduces much faster with increasing force than of a shorter sample. This induces larger plastic deformation (both due to axial strain and shear strain due to friction) and leads to faster PT kinetics for a longer sample. As can be seen in Figs. 13(a) and 13(b), approximately 80% of the material completely transforms into high-pressure phase at \( F = 9.22 \) in the sample with \( S = 0.7 \), while PT just starts at the contact surface of the shorter sample with \( S = 0.4 \).

Also, maximum pressure required for almost complete transformation in the entire sample is significantly larger for the shorter sample. For \( S = 0.9 \), a completely transformed sample could not be obtained anymore, because the sample material flows outside of the flat anvil region, where the pressure is low. The developed simulation technique could be utilized for finding the optimal parameter \( S \) for different objectives. One can formulate the following possible objectives: (a) creating homogeneous pressure distribution to simplify extraction of kinetic material parameters from experiments; (b) to obtain a detectable amount of high-pressure phase at lowest pressure, which is important for the search for new phases while avoiding fracture of an anvil; (c) to obtain the maximum amount of high-pressure phase at the lowest maximum pressure, which is important for technological application, and others. The requirement of minimum pressure can be substituted with a stricter requirement of a lack of fracture of anvils based on strength criterion.48,49

Fig. 15 shows variations of concentration of high-pressure phase \( c_0 \) and accumulated plastic strain \( q_0 \) averaged over a deformed sample thickness at the \( z \)-axis \((r = 0)\) versus pressure \( p \) on the contact surface at the symmetry axis \( z \). The reason for focusing on these parameters is that \( c_0 \) and \( p \) can be directly measured and plastic strain at the \( z \)-axis for relatively small \( S \)
can be calculated based on a reduction in thickness (which can be measured) and measured $c_0$ and $p$ (see Sec. VI). One could note that for the same pressure, the rate of PT with a longer sample is faster than for a shorter one due to larger plastic deformation during initially faster thickness reduction (Fig. 15). For the shorter sample, when force exceeds 11 (Fig. 14), a very fast reduction in thickness occurs, which causes a sharp increase in plastic strain, concentrations, and corresponding pressure drops (Fig. 15) due to volume reduction. After this, the pressure grows up to 25 to complete PT for the shorter sample in comparison with 18 for the longer sample.

PT starts at different pressures for different $S$. Thus, if initiation of PT is accepted as a detection of $c_0 = 0.025$, then it starts at $p \approx 8.23$ for the longer sample and at $p \approx 8.89$ for the shorter sample. This is one possible explanation for different transformation pressure observed in experiments with different gaskets.\(^{12,30}\)

B. Effects of sample relative initial thickness

In this section we will discuss the effects of the sample initial thickness on the deformation and transformation processes. From Fig. 16, one can note that the geometry of the sample exterior in the deformed configuration is different for thin and thick samples. While for $H_0/R = 0.2$ sliding to the periphery at the contact surface of a sample is well visible, for $H_0/R = 0.3$ sliding at the contact surface of a sample is practically absent but radial flow intensifies away from the contact surface and is maximal at the symmetry plane. Figs. 16(a) and 16(b) show that for the same axial force $F$ the PT progress is slightly faster in a thinner sample (except at the periphery), which is caused by both higher pressure and larger accumulated plastic strain. However, the PT propagates much faster in the small periphery region of a thicker sample, because of higher pressure and larger plastic deformation (Fig. 16). Since the volume at the periphery is much larger than the volume at the center, the average concentrations $c$ over the entire sample for both cases in Fig. 17 are surprisingly very close. It could be seen in Fig. 16 that pressure is very heterogeneous for both cases, but for a larger thickness the pressure heterogeneity in the radial direction is obviously smaller. Fig. 17 presents that averaged over sample accumulated plastic strain is slightly larger for the thinner sample, which is caused by a slightly faster reduction in relative thickness. Note that the total axial displacement for the thicker sample is larger but $h/H_0$ is smaller. Although for the same axial force $F$ an averaged PT kinetics is faster and accumulated plastic strain is larger in Fig. 16 at the center of a thinner sample, Fig. 18 shows that at the center, for the same pressure, concentration of the high-pressure phase and accumulated plastic strain are almost the same.

To summarize, for the same force and pressure, PT progress is practically independent of the thickness $H_0/R$ of a sample. This means that the volume of transformed phase is larger for larger initial thickness. Pressure heterogeneity is smaller for larger thickness as well.
C. Effects of gasket strength

The effects of gasket strength on PT and plastic flow will be studied by comparing results for gaskets with yield strengths $\sigma_{yg} = 3\sigma_{s1}$ and $\sigma_{yg} = 2\sigma_{s1}$. With the reduction of gasket strength, the reduction in sample thickness and radial material flows are intensified (Fig. 19). At $F = 11.09$ in Figs. 19(b) and 19(d), the sample points reach the anvil radius $R$. This means that pressure at the periphery is low and the material does not transform completely. The sample with a weaker gasket has much larger accumulated plastic strain, which intensifies PT kinetics. At the initial loading, higher pressure close to the center is another reason for faster PT rate for the case with a weaker gasket. Therefore, some reduction of the yield strength of the gasket intensifies PT kinetics due to larger plastic deformation, but it increases the heterogeneity of pressure (Fig. 19). Fig. 20 presents that at the initial loading averaged over sample concentration of high pressure phase is larger for a weaker gasket, due to larger plastic strain during faster thickness reduction. At the late stage of loading, PT is uncompleted only at the periphery (Figs. 19(a) and 19(b)), and averaged concentration over the sample increases more slowly for a weaker gasket (Fig. 20), due to lower pressure in the periphery. At the center of a sample, for the same pressure at the contact surface, Fig. 21 shows that PT progress is slightly more pronounced for the case with a weaker gasket, due to larger accumulated plastic strain during faster reduction of thickness.

V. POSSIBILITY OF EXPERIMENTAL DETERMINATION OF KINETIC EQUATION FOR PHASE TRANSFORMATIONS TO STRONGER HIGH PRESSURE PHASE

Here, we will discuss how to apply obtained results for experimental determination of kinetic equation of the type of Eq. (8). As it was discussed in Sec. III, for the high pressure phase with lower and equal yield strengths than for low-pressure phase, we do not currently see a simple way to determine kinetic equation. This is because the solution for concentration has a form of localized high-pressure and low-pressure phases separated by a quite narrow interface, which makes it difficult to determine intermediate values of concentration $c$. However, for a stronger high-pressure phase, all fields (pressure, concentration, and plastic strains) are quasi-homogeneous at least near the center of a sample and can be determined without direct measurement of the plastic strain.
To simplify the procedure and eliminate strain hardening of phases (i.e., dependence of the yield strength on accumulated plastic strain \( q \)), the sample material should be initially strongly plastically deformed to \( q > 1 \). This can be done by compression, extrusion, rolling, ball milling, and other methods of plastic deformation. Then constant or pressure-dependent yield strength of phases \( \sigma_{y,1} \) and \( \sigma_{y,2} \) can be determined by compression of a sample without a gasket (or with a gasket but \( R_f < R \)) by measuring pressure distribution and sample thickness \( H \) for single-phase samples, i.e., before and after complete phase transformation (see Ref. 45).

There are some different methods (see, e.g., Ref. 50).

Since at the symmetry axis the material undergoes uniaxial compression without shear and material rotation, Eqs. (15) and (16) are valid.

Pressure can be routinely measured using fluorescence of ruby particles. Concentration \( c \) is measured using relative intensities of \( x \) ray diffraction peaks. \(^{19,20}\) Thickness of the sample \( H \) under load can be measured using a special pre-calibrated sensor. \(^{47,50}\) Pressures at which direct \( p_d \) and reverse \( p_0 \) PTs occur under hydrostatic loading can be determined using standard methods.

Stress state at the symmetry axis is characterized by three principle stresses \( \sigma_1, \sigma_2, \sigma_3 \), which gives mean stress \( \sigma_0 = \frac{-p}{3} + \frac{2\sigma_r}{3} \) and deviatoric stresses \( s_1 = \sigma_2 - \sigma_0 = 2(\sigma_1 - \sigma_0)/3 \) and \( s_2 = \sigma_0 - \sigma_0 = (\sigma_1 - \sigma_2)/3 \). The stress intensity \( \sigma_t = \sqrt{2(\sigma_1^2 + \sigma_2^2)} = \sigma_1 - \sigma_2 = \sigma_2 - \sigma_3 \). Thus, knowledge of \( \sigma_0 \) and pressure \( p \) allows one to define stresses \( \sigma_1 \) and \( \sigma_2 \), and then with the help of elasticity rule Eq. (2). Then all parameters for the determination of accumulated plastic strain in Eq. (16) are known. In such a way, for each loading step, one can determine \( p, c, q \) and thus have all the parameters in the kinetic Eq. (8). By varying initial thickness and relative radius of the sample and gasket material, one can obtain various combinations of pressure and plastic strains and corresponding transformation kinetics. One can check correctness of Eq. (8) and if accuracy is not sufficient, determine more precise kinetic equation and find rationale for it.

VI. CONCLUDING REMARKS

In this paper, an advanced modeling approach for high-pressure phase transformations in a sample within a gasket compressed in the DAC is developed. The key point is that under such conditions, phase transformations are treated as the plastic strain-induced ones rather than pressure-induced transformations. This is not just a terminological difference. Strain-induced PTs have completely different mechanisms and thermodynamic and kinetic description. In particular, a strain-controlled and pressure-dependent kinetic Eq. (8) is utilized in the model. Other points that ensure an adequate modeling are: a description of coupled PTs and plastic flow under large strains and allowing for contact sliding with combined Coulomb and plastic friction at the boundaries between sample, gasket, and anvil. The latter allowed us to reveal new sliding mechanism at the contact line between sample, gasket, and anvil. When the sliding condition along the boundary with the diamond is met for the sample but not for gasket, the sample still can slide without producing a gap between the sample and gasket. Gasket material at the boundary with the sample slips along the sample and extrudes to the diamond-gasket boundary, producing a new surface area. This mechanism was called extrusion-based pseudoslip and it is very important for providing the possibility of sample flow toward the center and producing high quasi-homogeneous pressure. Obtained results demonstrate that experimentally obtained pressure for initiation and completion of PT and the entire \( p-c \) curve do not represent fundamental properties of phase transformation but rather deformation and transformation behavior of the sample/gasket system. That is why pressure for initiation and completion of PT and the entire \( p-c \) curve vary in different works that use different geometric parameters and gasket materials, as well as different high-pressure apparatuses. Consequently, plastic strain is a primary parameter, which should be measured, along with pressure and concentration of high-pressure phase. One of the most important results consists of the suggested method to extract full kinetic information (including plastic strain) from experiments for stronger high-pressure phase, which was not possible without the gasket. If realized in practice, it will completely change the characterization of high-pressure phase transformation and lead to the possibility of characterizing material transformation behavior rather than mechanical and transformational behavior of a sample/gasket/anvil system. It is still impossible for a material with weaker and equal-strength high-pressure phase. For such materials, completely transformed high-pressure phase appears at the diamond-sample boundary (which corresponds to experiment in Ref. 46) and propagates toward the symmetry axis without large regions with intermediate values of \( c \). We hope that superposition of torsion will create a more homogeneous distribution of all parameters in the sample, which will allow us to formulate methods of experimental determination of the strain-controlled kinetic equation. This will be studied in future works. The obtained model and results are also beneficial to design high pressure experiments for different purposes, including producing the highest possible and quasi-homogeneous pressure without breaking the diamond.

ACKNOWLEDGMENTS

The support of the Army Research Office (W911NF-12-1-0340) managed by Dr. David Stepp, Defense Advanced Research Projects Agency (W31P4Q-13-1-0010) managed by Dr. Judah Goldwasser, and Iowa State University is gratefully acknowledged.


