Thermomechanical approach to the modeling of HP–HT material processing

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Abstract. The mathematical models, algorithms and software for finite element simulations both superhard materials spontaneous synthesis in high pressure apparatus, and martensitic phase transformation of material at compression in diamond anvil cell have been developed. The phase transformation processes in the reaction volume of high pressure apparatus for diamond synthesis and in the sample of polycrystalline potassium chloride when deformed in the diamond anvil cell have been numerically simulated.

1. Introduction
In this study we demonstrate the possibility of applying methods of continuum mechanics for computer modeling and simulation of material processing at high pressure and temperature (HP–HT). This thermomechanical approach allows us to simulate both the processes of spontaneous synthesis of superhard materials in high pressure apparatuses (HPA), and processes of phase transformations in diamond anvil cells (DAC). This results in determination of the fields of thermodynamic parameters in the transformation zone. The present numerical technique is used to optimize the existing technologies of the HP–HT synthesis of materials and to develop new ones.

2. Modeling the diamond spontaneous synthesis in HPA
Spontaneous crystallization of diamond particles results from joint action of several physico-mechanical processes, namely, resistance heating, heat transfer, thermoelastoplastic deformation and phase transition. Prior to heating, the reaction cell contains a compressed (up to 4–5 GPa) powder mixture of graphite and fine particles of carbon solvent alloy. Then, the cell is heated by passing the electric current. During heating, the stress field inside HPA is evolving and, after a certain pressure and temperature level was reached, carbon in the reaction volume undergoes phase transition. The diamond crystals begin to grow in the metal melt on carbon clusters being the crystallization centres.

Two-level theoretical model of the diamond spontaneous crystallization in HPA has been developed [1]. At the macro level, the model describes the coupled processes of resistance heating, heat transfer, thermoelastoplastic deformation and graphite-to-diamond phase transition at the reaction volume scale. At the diamond grain (micro) level, it describes the thermoelastic fields and conditions of phase transitions in the local diamond–metal melt–graphite system.
The thermomechanical state of the HPA in the process of diamond crystallization is described by the following closed system of coupled equations of continuum mechanics:

- steady-state current conduction,
- transient heat conduction,
- plasticity theory,
- graphite-to-diamond phase transition criterion,
- kinetic equation of the graphite-to-diamond phase transition,
- equations of thermoelasticity for the micro level.

By applying the methods of continuum thermomechanics and computer simulation, the temperature, stress and mass fraction fields in the reaction volume of HPA and in the local diamond–melt–graphite system under diamond synthesis conditions have been determined. The calculated variation in the configuration of the crystallization zones of diamonds of various habits in the reaction volume of recessed anvil-type HPA as the heating current power $W$ increases from 2.10 to 2.74 kW is given in figure 1. It has been found that diamonds start to crystallize in the central part of the reaction volume. In a rather small volume of the crystallization zone, diamonds of the cubic and cubooctahedral habits crystallize simultaneously. This fact is due to the high temperature gradient in the region under study. With increase in the $W$ the boundary of the diamond crystallization zone shifts towards both the centre and the periphery of the reaction volume. When $W = 2.33$ kW (figure 1b), an additional crystallization zone of octahedral diamonds develops and the whole morphological series of diamond crystals (from a cube to an octahedron) is observed. With further increase in $W$ when its value exceeds 2.48 kW (figure 1d), the crystallization zone starts to narrow and shifts from the centre to the periphery of the reaction volume. With $W \geq 3$ kW $p$ and $T$ parameters in the reaction volume are beyond the diamond thermodynamic stability region and crystallization does not occur.

The above calculation data have reliable qualitative and quantitative experimental verifications. Firstly, at the optimal pressure the temperature conditions required for diamond crystallization are not arranged in the whole of the reaction volume. Secondly, the volume of the diamond crystallization zone (all other things being the same) depends on the heating current power whose optimal value coincides with the calculated value of 2.5 kW. Diamond synthesis at this heating current power offers the greatest amount of single crystals mostly of cubooctahedral habit with well-developed faces.

![Figure 1. Variation of the crystallization zones of diamonds of various habits in the reaction volume of HPA.](image-url)
3. Numerical simulation of the B1 → B2 phase transformation in a potassium chloride sample when deformed in a gasket of DAC

Phase transformations (PT) in crystalline materials when deformed in DAC with the use of gaskets and without a pressure medium have an “instantaneous” nature and are accompanied by an abrupt change of the volume and all physico-mechanical properties of the material. Such PT are classified as martensitic diffusionless or as polymorphous first-order ones. At a PT the crystalline lattice of the new phase forms through the ordered displacement of atoms of the initial phase and the relative displacements of neighbouring atoms are small as compared to the atomic spacing. A high nucleation rate of the new phase crystals is defined by a small deformation, low energy barrier for the uniform PT as compared to the bond energy in a crystal, the ordered structure, and a high mobility of the phase boundaries. With some deviation from the equilibrium state, the excess energy required for the nucleation of the new phase crystals becomes comparable with the energy of defects presented in the initial phase, and the nucleation of martensitic crystals occurs at a higher rate.

The aim of this study was to investigate the kinetics of the B1 → B2 martensitic PT in KCl crystals when deformed in DAC at a constant temperature. To study the regularities of the PT progress in materials deformed in DAC a finite element procedure [2] has been developed. The procedure is based on the thermomechanical theory of PT in inelastic materials, the thermodynamically justified criterion for the PT in elastoplastic materials and extreme principle for the determination of all unknown parameters [3].

Potassium chloride is one of the well characterized alkali–halide crystals. In KCl crystals under the external action (pressure, temperature) one can observe the PT from the B1 stable low-pressure phase, which has the structure of NaCl type, to the B2 metastable high-pressure phase with the structure of CsCl type. The PT is accompanied by an abrupt decrease in the volume (volumetric strain of about 12%) and variation of physico-mechanical properties.

The process of the compression of a polycrystalline KCl sample placed into a stainless steel gasket in a DAC at room temperature has been considered. The following assumptions were taken:

- diamond anvils and the B2 phase of KCl (after the PT) deform elastically, while a deformable gasket from a stainless steel and the B1 phase deform elastoplastically;
- elastic properties of the B1 and B2 phases of KCl are equal;
- at the constant temperature and a specified external loading a PT with a volumetric phase deformation of –0.12 occurs in the sample material;
- phase boundary is coherent, i.e. the displacements at the boundary are continuous;
- the PT pressure was taken to be 1.96 GPa.

The compression of a KCl sample in a DAC has been simulated step-by-step. At each step of loading a certain value of the anvil axial displacement was set and the distribution of fields of displacements, deformations, and stresses in the region under study was calculated.

The analysis shows that starting from the first step of loading the sample deforms plastically, the maximum value of the accumulated plastic strain at the 18th step of loading (the latter step without the PT) reaches 1.5%. The distribution of accumulated plastic strain over the sample volume is characterized by a considerable nonuniformity. The pressure and the volumetric strain distribution at the first steps of loading are also of the nonuniform nature. At the further loading, regions of the highest values of these parameters are considerably widened in the direction to the sample symmetry plane, their distribution becomes less nonuniform and by the 18th step the gradients of the pressure and volumetric strain variations become negligible. At the 19th step the small volumes of the material, for which the PT conditions start to be fulfilled, appear in the sample.

The PT in FE 496 brings about a substantial redistribution of physico-mechanical fields: in the cases of plastic and volumetric strains, the local redistribution takes place in some neighbourhood of this element, but for the pressure and the work integral, the redistribution occurs in the whole volume of the sample. A decrease in the pressure and integral force applied to the anvils is observed. A check of the fulfilment of the PT conditions after that PT has shown that the further progress of the transformation is possible only after an increase in the force applied to the anvils. After the 20th
loading step, the PT conditions start to be fulfilled for FE 495 and 486. A nucleus of the new phase forms. However, in the subsequent loading in parallel with the existing B2 phase nucleus growth, the formation of a new nucleus is observed (figure 2). Such behaviour of the sample is caused by the local redistribution of stress and strain tensors components in the elastoplastically deforming B1 phase of the sample. Because of the plastic relaxation of stresses, the formation of a new nucleus becomes more preferable than the growth of the old one. The PT process runs in the direction of the force loading, and is characterized by a considerable nonuniformity of the local stresses and strains distribution, which facilitates the PT. At the initial stage of the PT these changes are local in nature, but as the new phase concentration exceeded 5%, the disturbance caused by the element, in which the PT has occurred, becomes essential, produces considerable stress and strain concentrations and contributes to the PT in the sample.

**Figure 2.** Stages of the B1 $\rightarrow$ B2 phase transformation in the polycrystalline KCl sample: diamond, stainless steel, B1 KCl phase, B2 KCl phase.

Figure 3 gives the photo of the KCl sample made when studying the regularities of the material straining in DAC. The distribution of the B1 and B2 phases in the sample agrees with the calculated one (figure 2). The calculated and experimental pressure dependences of the B2 phase concentration and the normalized volume of the polycrystalline KCl sample are shown on figures 4 and 5. Some disagreement of the data on the concentration stems from the fact that in the experiment the PT started at 2.09 ± 0.03 GPa and terminated at 2.82 ± 0.10 GPa, while in the calculation the pressure of the PT onset was 1.96 GPa. In addition, in the experiment the sample was loaded by stages with a holding time at the constant pressure for several min in the course of the PT, while in the calculation after an increase of loading, a decrease in the pressure in the sample during the PT was allowed.

**Figure 3.** PT in KCl sample when deformed in a DAC.  
**Figure 4.** Pressure dependence of the B2 phase concentration in the KCl sample: (1) calculated data, (2) experiment.  
**Figure 5.** Pressure dependence of the normalized volume $V(p)/V(0)$ of the KCl sample in loading and PT: (1) calculated data, (2) experiment.

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