

## HIGH PRESSURE MECHANOCHEMISTRY: CONCEPTUAL MULTISCALE THEORY AND INTERPRETATION OF EXPERIMENTS

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*Summary* A simple multiscale (nano-, micro- and macro-) continuum thermodynamic theory for strain-induced phase transitions (PTs) and chemical reactions (CRs), as well as closed form solutions were developed which explain a number of mechanochemical phenomena. The results enabled the development of new methods for control of PTs and CRs under plastic deformation, some of which have experimental confirmations.

### Experimental Phenomena

Mechanochemistry studies the plastic strain-induced structural changes (SCs) that include PTs and CRs. After compression of the materials in Bridgman or diamond anvils, a very high pressure is produced in the center of the specimen, which leads to a number of PTs and CRs. It is known, from numerous experiments (Bridgman, Vereschagin, Blank, Zharov, Enikolopyan) summarized in [1] that the addition of plastic shear leads to findings that have both fundamental and applied importance. In particular, superposition of plastic shear, due to the rotation of an anvil, and high pressure in rotational diamond anvil cell (RDAC) leads to

- (a) a significant (by a factor of 3-5) reduction of SC pressure and pressure hysteresis,
- (b) an appearance of new phases, which were not obtained without additional shear,
- (c) a substitution of a reversible SC by an irreversible SC,
- (d) strain-controlled kinetics,
- (e) nanostructured phases, and
- (f) pressure self-multiplication effect, i.e. pressure growth in the transforming region under a fixed compressive force (despite the volume decrease due to SC).

Despite the basic and applied importance, there has not been any theory describing thermodynamic and kinetic coupling between plasticity and SCs and any one of the above experimental effects. In this paper, a first multiscale continuum thermodynamic theory was developed which explains the above phenomena. Thus enabling the development of new characterization methods of SCs under plastic deformation as well as methods for controlling SCs.

The developed theory consists of: (a) thermodynamic criterion for SC, (b) extremum principle for determination of geometry of transformed region (in the case of nucleation) and other unknown parameters (e.g. volume fraction of martensitic variants and orientation of interface between them) and (c) a kinetic equation for transformation time (in the case of nucleation) or interface velocity [1,2]. Finite strains and rotations were taken into account. This theory was applied at nano- and microscales.

### Nanoscale approach

At the nanoscale, the primary reason for the above phenomena is related to the generation of new defects during plastic flow, which produce strong stress concentration and serve as new nucleation sites. A model of nucleation at the tip of dislocation pile-up was developed. Geometric parameters and orientation of nucleus were determined. It was further demonstrated that shear stress can lead to substitution of thermally activated nucleation with barrierless nucleation and significantly reduce SC pressure for direct SC, as well as increase SC pressure for reverse SC. Barrierless nucleation explains the strain-controlled rather than time-controlled kinetics. Indeed, the prescribed strain increment generates defects with barrierless, i.e. very fast, nucleation and growth of the product phase up to the size where stress concentration is reduced and cannot drive the interface further. For the observation time of 1 s, this looks like instantaneous SC. As straining stops, no new defects and nuclei appear, and the growth of the existing nuclei is thermodynamically impossible. This explains also a nanosize of grains. As the contribution of the stress concentration to the driving force for SC is finite, there exists a lowest possible pressure below which strain-induced SC is impossible. Dislocation pile-ups generate both compressive and tensile pressure, which are of the same magnitude. Consequently, they simultaneously promote both direct and reverse SC in different regions. All of these results were conceptually incorporated into the microscale model. For the thermally activated regime, it was obtained that shear strain does not change significantly SC pressure, but accelerate SC kinetics, in accordance with experimental observations.

### Strain-controlled kinetic equation

At the microscale, a new strain-controlled kinetic equation is derived from our thermodynamic SC criterion. It considers the possibility of direct and reverse PT and the difference in plastic strain in each phase due to the different yield stress of the phases. A stationary solution of this equation is found and analyzed. Stationary solution explains zero pressure hysteresis observed experimentally as well as the appearance of new phases, especially strong phases, which were not obtained without shear. However, zero hysteresis can be obtained at any pressure in some range and has nothing to do with phase equilibrium pressure. Phase equilibrium pressure does not appear in any equation and cannot

be obtained from experiment on strain-induced SC. Also an explanation was obtained why a nonreacting matrix with a yield stress higher (lower) than that for reagents significantly accelerates (slows down) the reactions.

### Macroscale approach

At the macroscale, mechanics of plastic flow and SC in rotating diamond anvils is modeled. A strain-controlled kinetic equation derived at the microscale was used. Sliding of an anvil with respect to material is determined. Promotion of the SC due to the rotation of the anvil is related to reduction in radial component of shear stress. This leads to the possibility of additional axial displacement, which compensates a volume decrease due to SC, increases plastic strain and pressure. If new phase has larger yield strength, pressure grows in transforming regions; this explains and quantifies a pressure self-multiplication effect observed experimentally. It was also obtained that the rotation of an anvil can lead to new phases, especially hard phases, which were not only but cannot be obtained without the rotation of the anvil. Possible reasons for appearance of small steps (regions with almost homogeneous pressure) on very heterogeneous pressure distribution are found. One of which is related to reduction of contact shear stresses due to transformation-induced plasticity for PTs or reaction-induced plasticity for CRs. However, this constant pressure is not related to any basic properties of SCs and therefore cannot be used for their characterization.

### Methods of control of structural changes

The results obtained enabled the development of new methods of control of PT and CR under plastic deformation, even without rotation of the anvils. Some of them have experimental confirmations. One of the most impressive confirmations consists of the following. For rhombohedral rBN single crystals, deforming by slip on the basal plane only, the theoretical compressive yield strength varies from infinity, for compression along the C-axis, to the minimum value when the basal plane and slip direction are at  $45^\circ$  to the compression direction. If a single crystal is compressed in a diamond anvil, in the C-direction with a small disorientation, the rotation of the C-axis will occur during plastic flow. Consequently, this rotation will lead to a reduction of the yield stress in the direction of compression (rotational softening and instability), and to a reduction of disk thickness at constant force. Indeed, the following extraordinary experimental results were obtained [3]. A highly textured rBN was compressed along the C-axis  $\pm 3^\circ$ . An abrupt irreversible martensitic rBN  $\rightarrow$  cubic cBN PT was recorded at the sample center at a pressure 5.6 GPa before the PT. The thickness of the disc in different tests decreased from 0.175-0.450 mm to 0.020-0.050 mm. In comparison, under hydrostatic loading the irreversible PT rBN  $\rightarrow$  cBN occurs at 55 GPa (Ueno et al. 92). Thus a reduction of PT pressure, by one order of magnitude has been achieved. Note that cBN is an important superhard material with hardness second to a diamond. It was concluded that a new phenomenon, namely PT induced by rotational plastic instability takes place.

### Concluding remarks

The obtained results predict the unique potential of plastic straining to produce high-strength nanostructured phases. They also suggest a new approach for characterization of strain-induced SCs. In most cases, even without the rotation of an anvil, when a high pressure experiment is performed without hydrostatic media, the specimen undergoes large plastic deformations. This is the case in experiments under megabar pressure, in particular, with solid hydrogen. PT conditions for such a case are characterized by the pressure only (like for pressure-induced SC) and are compared with or led by atomistic calculations of phase equilibrium pressure. We believe that this is conceptually wrong, and even the term "pressure-induced PT or CR" is misleading in such a situation. This is even more true for the case with rotation of an anvil. The usual way of characterization (SC pressure at prescribed rotation or shear) is not complete. Strain-induced SCs under high pressure can be completely characterized by a strain-controlled kinetic equation only. Some recent experiments in RDAC performed at the Center for Mechanochemistry will be reported [4, 5].

### References

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