



	Experiment title: Crystallization of cubic boron nitride from BN solutions in supercritical fluids: <i>in situ</i> studies	Experiment number: HS494
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Report:

Peculiarities of cBN formation in the BN - N₂H₄ system to 5.2 GPa and 1900 K have been studied *in situ* using energy-dispersive X-ray diffraction with synchrotron radiation at beamline ID30. The experiments have been done using a large-volume Paris-Edinburgh press. The results obtained are briefly described below.

Chemical interaction of boron and supercritical hydrazine

In the 2.5-5.2 GPa pressure range, the interaction of amorphous boron with hydrazine proceeds in the 850-1000 K temperature range and results in the formation of hexagonal boron nitride (hBN). Although practically in all the cases, the interaction occurred in the region of thermodynamic stability of cBN in the equilibrium p,T-phase diagram of boron nitride [1], the formation of cBN has not been experimentally observed, which is indicative of kinetic limitations of the cBN formation at relatively low temperatures.

It should be noted that over the whole pressure range under study, hBN formed as a result of a chemical interaction between boron and hydrazine exhibited a high degree of three-dimensional ordering ($P_3 > 0.95$),¹ which points to a significant reduction of the diffusion barriers due both to a highly exothermic reaction and to the presence of a fluid phase in the system.²

Dissolution of boron nitride in supercritical hydrazine

hBN Dissolution of both highly-ordered ($P_3 \approx 1$) graphite-like hexagonal boron nitride as well as of the hBN being formed *in situ* in the reaction of boron and hydrazine is observed only at temperatures exceeding 1100 K and is accompanied by a considerable pressure drop in the system (e.g., from 5.0 to 4.3 GPa during the formation of a saturated solution).³ The latter points to a large negative volume effect of BN dissolution which is probably due to a strong interaction between dissolved BN and hydrazine and the formation of the associated solution.

¹ ($P_3=1-\gamma$), where γ is the concentration of turbostratic stacking faults, calculated following the procedure of reference [2]

² in using conventional methods of industrial synthesis, the formation of highly ordered hBN is observed only at $T > 2000$ K [3]

³ the pressure in the experiment was evaluated based on the p-V-T EOS of hBN [4]

At low pressures the process of dissolution of hBN proceeds in a wide temperature range (1100-1400 K at 2 GPa). However, with increasing pressure, the tendency for narrowing of the temperature range of coexistence of solution and solid hBN and a pronounced increase in BN solubility are observed. Thus, at 2 GPa and 1800 K, the concentration of a saturated solution is about 60 wt.% BN, while at 5 GPa and 1800 K, the corresponding value exceeds 80 wt.%. The above peculiarities are easily explainable when the negative volume effect of BN dissolution is taken into account.

wBN Dissolution of wurtzitic boron nitride was observed only at temperatures above 1500 K, despite the fact that the wBN powder used was synthesized by shock-wave compression and characterised by a highly imperfect structure and small grit sizes.

All the above results suggest that there are strong pressure and temperature dependencies of the solubility of BN in supercritical hydrazine caused by the structure of the solution and by the nature of interaction between its components.

Crystallization of boron nitride from its solutions in supercritical hydrazine

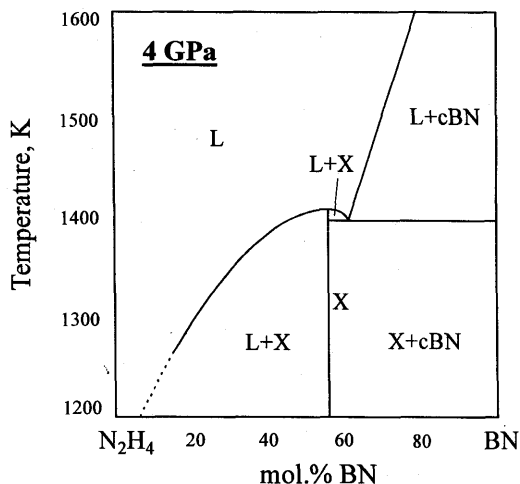
At 4.1 GPa, cooling of the solution containing 77 wt.% BN from 1460 to 1400 K is accompanied by spontaneous crystallization of cubic boron nitride. The emergence of cBN lines is accompanied by a change in the shape of the solution spectrum, in particular by the **appearance** of broad halo with a maximum at 107 keV ($d = 1.1$ Å). Further decrease of the solution temperature down to ambient does not, however, result in a significant increase in the intensities of cBN lines.

A similar change in the shape of the solution spectrum was also observed at 4 GPa and 1350 K by cooling the solution containing 28 wt.% BN. In this case, however, no formation of any crystalline phase was recorded even in cooling the solution down to room temperature.

A subsequent heating of the above mentioned $\text{BN-N}_2\text{H}_4$ mixtures **up to 1600 K** in both cases gave rise to a recovery of the characteristic shape of the solution spectrum due to dissolution of solid phase(s). This fact is an unambiguous evidence for the reversibility of the observed precipitation/dissolution processes.

The above experimental facts should be attributable to the $L \approx X + \text{cBN}$ eutectic reaction at **1360±25 K** and 4 GPa. This reaction results in crystallization of cubic boron nitride and formation of an unknown amorphous phase of the $\text{BN-N}_2\text{H}_4$ system which contains x at.% BN (phase X). In cooling solutions with BN concentrations exceeding x when the line of ultimate solubility in the diagram is intersected, the precipitation of cBN begins. On attaining the eutectic temperature the simultaneous formation of the X phase and cubic boron nitride takes place. Subsequent cooling should not result in a further increase of cBN content which is in accordance with our findings. For solutions with BN concentration below x , cooling gives rise to the formation of the X phase that coexists with the solution down to room temperature, and no BN crystallization is observed in this case. A hypothetical phase diagram of the $\text{BN-N}_2\text{H}_4$ system at 4 GPa is shown in the Figure.

At 1.7 GPa, cooling of the solution containing 70 wt.% BN from 1370 to 1335 K is accompanied by crystallization of graphite-like hexagonal boron nitride with a simultaneous formation of the X phase. That means that at low pressures the $L \approx X + \text{hBN}$ metastable eutectic equilibrium is realised, in which metastable hBN participates instead of the thermodynamically stable cubic phase. This fact is attributable to the predominant nucleation of hBN according to the Ostwald-Volmer principle.'



References

1. V.L. Solozhenko, *High Press. Res.*, **13** (1995) 199-214.
2. A.V. Kurdyumov, *Sov. Phys.-Crystallography*, **20** (1975) 969.
3. J. Thomas, N.E. Weston and T.E. O'Connor, *J. Amer. Ceram.Soc.*, **84** (1962) 4619-4622.
4. V.L. Solozhenko and T. Peun, *J. Phys. Chem. Solids*, **58** (1997) 1321.
5. A.V. Kurdyumov, V.L. Solozhenko and W.B. Zelyavski, *J. Appl. Cryst.*, **28** (1995) 540-545.

⁵ the density of hBN is lower than that of cBN by a factor of 1.5 [5], hence, its nucleation is preferable