Stability of Carbon Nitride Materials at High Pressure and Temperature

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High-pressure and -temperature techniques are commonly used to probe dense and hard solid phases,[1,2] although their use in the synthesis of potentially ultrahard carbon nitride materials has been relatively unexplored. Herein, we report the first mapping of the pressure−temperature−composition diagram for a prototypical sp^2-bonded amorphous carbon nitride material. Experiments were carried out using piston−cylinder and multianvil presses at pressures up to 20 GPa and temperatures up to 2000 °C. These studies demonstrate that the carbon nitride material undergoes an irreversible decomposition into carbon and molecular nitrogen at a well-defined temperature that increases monotonically with pressure: 550 °C at 3 GPa to 750 °C at 20 GPa. The kinetic and thermodynamic implications of these results to a potential high-pressure synthesis of carbon nitride solids containing sp^3-bonded carbon are discussed.

There is currently significant experimental[3−9] and theoretical[10−12] interest in the synthesis and properties of carbon nitride materials due in part to the early prediction that a solid with the β-Si_3N_4 structure β-C_3N_4 would have a hardness comparable to diamond.[10] To date, the majority of experimental studies have centered on low-pressure film growth.[3−6] While these studies have led to syntheses of carbon nitride materials with a wide range of compositions, including a well-defined C_2N phase with some diamond-like properties,[4a] the local C bonding in all materials evaluated is predominantly sp^2 that is typical of low-density, graphitic structures.[3] The uniform tetrahedral, sp^3 C bonding expected for pure β-C_3N_4 or other high-density phases has not yet been achieved in low-pressure studies.

High-pressure and -temperature techniques represent an alternative approach to the synthesis of sp^3-bonded carbon nitride in analogy to the synthesis of diamond.[13] Indeed, recent theoretical studies have suggested that ultrahard carbon nitride phases with sp^3 carbon bonding should exhibit greater stability at high pressure.[11c,12] However, it is not known whether the kinetic barriers to the formation of a sp^3-bonded carbon nitride phase can be overcome at temperatures below the point that a sp^2-bonded precursor decomposes into carbon and N_2. Such decomposition has been observed in previous work,[7−9,14] although the temperature−pressure decomposition boundaries needed for rational synthesis have not been determined. Early studies of hexamethylenetetramine and diphenylamine at 2000 °C and 15 GPa led to the production of black, graphitic solids that apparently arose from decomposition and nitrogen loss.[14] More recently, paracyanogen (C_1N_1) heated at 725 °C and 0.3 GPa was found to decompose completely into carbon and molecular nitrogen,[15] and tetracyanoethylene (C_6N_4) was also reported to lose nitrogen upon reaction at 0.3, 5, and 16 GPa.[7,8] In addition, shock wave processing of carbon−nitrogen polymers at peak pressures in excess of 60 GPa and at high peak temperatures yielded only diamond (and presumably molecular nitrogen).[9] This latter very high pressure study highlights the need to map the pressure−temperature decomposition line of carbon nitrides if a sp^3-bonded phase is to be achieved.

We have systematically mapped the composition of the prototypical carbon nitride precursor material paracyanogen (pCN) as a function of pressure and temperature. pCN represents an ideal model since it (1) can be prepared in pure form and large quantities, (2) has a composition close to that expected for the hypothetical C_3N_4 phase, and (3) has sp^2 C bonding typical of carbon nitride materials studied previously.[15−18] pCN was prepared by the pyrolysis of $Hg(CN)_2$ in sealed quartz tubes at 460 °C for 24 h.[19,20] Rutherford backscattering spectroscopy demonstrated that the C:N ratio in the product was 1:1 and that there was <0.02 atomic % mercury contamination. High-pressure and -temperature studies of this pCN precursor material were performed in a Boyd and England type piston cylinder apparatus (3 GPa) and a Walker type multianvil press (10−20 GPa) using procedures described previously.[2,21] The composition of samples reacted at specific pressure−temperature conditions was measured using an electron microprobe (Cameca MBX).

Seven distinct samples were pressurized to 3 GPa and then annealed for 3 h at 400, 500, 550, 600, 650, 700, or 800 °C. The nitrogen composition of these samples determined by microprobe was 50, 50, 47, 22, 12, 7, and 9 ± 2 atomic %, respectively. The large loss of nitrogen above 550 °C indicates that this temperature represents the upper stability point for pCN at 3 GPa. Above this temperature gas release was evident when the sample capsules were opened, and furthermore, the remain-

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(20) $Hg(CN)_2$ (12 g) sealed inside a quartz ampule (2 cm i.d. × 11 cm) was placed in a high-pressure bomb and pressurized to 50 atm (298 K). The temperature was raised to 460 °C at a rate of 70 °C/h and held at 460 °C for 24 h. The black product was suspended in acetone and decanted from heavy precipitates (∼1.5 g). Traces of Hg were removed by heating in *vacuo* at 400 °C. The final product (∼0.7 g) had a composition of $CNO_{0.06}P_{0.005}Ca_{0.004}Hg_{0.0004}$. IR spectra obtained from our product were essentially identical to that published previously.[15] *Caution: paracyanogen decomposes to cyanogen gas upon ambient pressure heating at 695 °C.*

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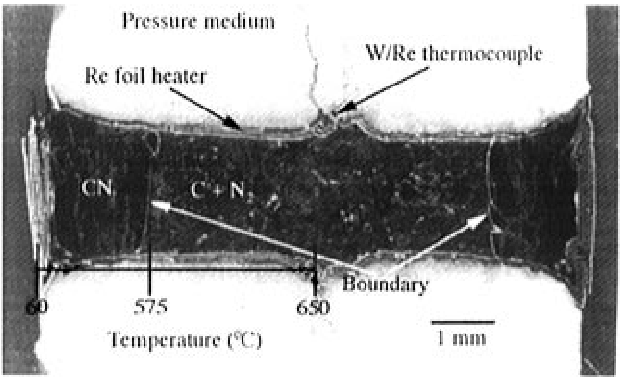

Figure 1. Optical micrograph of a pCN sample annealed 5 h at 10 GPa.

ing carbon phase had an open structure with pore sizes >1 μm. Analysis of the recovered sample mass from the experiment performed at 650 °C (1.6 mg, final; 3.8 mg, starting) shows that at least 77% of the carbon remained after decomposition. These observations are consistent with release of primarily N_2 upon pCN decomposition. Loss of N_2 is consistent with previous experiments carried out at 0.3 GPa and 750 °C,[15] although the stability−decomposition point was not determined in this latter work. It is also important to note that some of the nitrogen detected by the microprobe in samples annealed above the decomposition temperature is likely to be trapped N_2 gas,[22] and this (trapped N_2) must be considered in any analysis of structure and/or decomposition kinetics at high pressures.

We have also characterized the decomposition temperature of pCN at significantly higher pressures using the multianvil press. In most experiments, thermal shielding was omitted to establish a thermal gradient across the sample and thereby determine the decomposition point for a given pressure in a single run.[2] An optical micrograph of a sample annealed at 10 GPa with a center temperature of 650 °C exhibits two optically distinct sample regions separated by a sharp boundary (Figure 1). The nitrogen composition in regions closest to the (cooler) ends is 50%, while immediately across the boundary in the optically distinct region the composition drops to 15% nitrogen. The large drop in nitrogen composition across this boundary shows that there is a relatively well-defined decomposition point for pCN and that this precursor does not gradually lose nitrogen with increasing temperature. The data from these experiments is summarized in Figure 2.[23]

In general, our results show that the pCN decomposition temperature increases with increasing pressure; for 10.0, 15.7, and 20.0 GPa these temperatures are 575, 700, and 750 ± 20 °C, respectively. Within the region of this quasi phase diagram (Figure 2) where pCN is stable, we find that the density increases from 1.6 g/cm^3 at ambient pressure to 2.1 g/cm^3 at 10−20 GPa. Because the observed maximum density is close to that of graphite (2.25 g/cm^3) and much lower than diamond (3.51 g/cm^3), it is likely that the carbon in pCN retains sp^2 hybridization at pressures at least up to 20 GPa. Preliminary X-ray diffraction studies of our samples show that at pressures up to 10 GPa the pCN remains amorphous and decomposes to an amorphous carbon. At 15 GPa and above, however, weak crystal diffraction was observed from the 50% nitrogen phase.[24] Above the decomposition line ($P \geq 15$ GPa), we detected microcrystalline graphite as a carbon product ($d = 3.32$ Å (002), 2.08 Å (101), 1.67 Å (004), and 1.22 Å (110)).

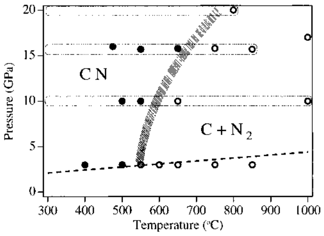

Figure 2. Stability phase diagram for pCN. Circles correspond to the center sample temperature in individual experimental runs: (●) pCN samples that did not decompose; (○) samples that decomposed in the central (hot) region. Because there is a temperature gradient across the samples (Figure 1), the decomposition region could be mapped from experiments carried out to the right of this region. Dotted boxes around points at 10−20 GPa correspond to regions where the composition was mapped using the estimated thermal gradient. The dashed line corresponds to the graphite/diamond phase boundary.

There are several important implications of these results. This work demonstrates that there is a well-defined decomposition line for the prototypical carbon nitride precursor pCN. Significantly, this line falls at moderate temperatures up to the 20 GPa pressures examined. For these pressures, it is apparent that the barrier leading to N_2 formation is lower than the carbon sp^2 to sp^3 transformation essential for conversion to ultrahard carbon nitride. The formation of N_2 is a local event with a large thermodynamic driving force and is expected to be essentially irreversible. Hence, we believe that kinetics are likely to play a dominant role in the synthesis of sp^3-bonded carbon nitrides. In this regard it is encouraging that the decomposition line has a positive slope (i.e., the barrier to N_2 elimination is increasing with pressure).[25] Hence, higher pressures and temperatures may lead to a successful sp^2 to sp^3 transformation with the following caveats: (1) well-controlled temperatures, which are accessible through resistive or furnace heating, are required to avoid precursor decomposition and (2) composition analyses of microcrystalline phases are essential to avoid misassignment of products.

In addition, the identification of crystalline graphite in the decomposition products is significant since it occurs in a region of the carbon phase diagram where diamond is stable. This observation further supports our suggestion that kinetics dominate even at the high-pressure and -temperature conditions of our experiments. The pCN precursor, with sp^2 carbon bonding, clearly favors the formation of sp^2-hybridized carbon in graphite (despite being thermodynamically unfavored) versus that of sp^3-hybridized carbon of diamond. Interestingly, high-pressure and -temperature studies (15 GPa and 2000 °C) of fused ring aromatics also found that graphite products were favored over diamond.[14] These observations suggest that simply going to higher pressure and temperature with pCN-like precursors may not be the best approach to sp^3-bonded carbon nitride. Hence, we believe that it will be important to explore other precursors that minimize the barrier to formation of sp^3 carbon in carbon nitrides. This may be achieved by using a material with a significant amount of sp^3 carbon in the precursor, such as found in carbon nitride films grown by pulsed laser ablation.[4a−c] Alternatively, it may be possible, as in high-pressure diamond synthesis, to exploit a catalyst[13] to lower the barrier to the formation of sp^3-bonded carbon nitride.

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(23) The center sample compositions corresponding to the data points plotted in Figure 2 are the following (pressure (GPa)/temperature (°C)/% nitrogen): 10/500/50; 10/550/50; 10/650/12; 10/200/1; 16/475/50; 15.7/550/50; 15.8/650/48; 15.8/750/13; 15.7/850/11; 17/1000/5; 20/800/12. For each experiment, the nitrogen composition was mapped across the sample with ∼10 μm resolution; dotted boxes correspond to temperature regions where the composition was mapped. Within the decomposition region, the nitrogen composition may vary 5−10%.

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(25) The barrier pressure dependence will depend on decomposition mechanism. In pCN and similar precursors that contain N═C bonds,[15−18] we speculate that the bond distortion necessary for elimination of N_2 becomes increasingly difficult in dense structures.