Chapter 7: Suggested technical applications of carbyne materials

7.1 DIAMOND SYNTHESIS FROM CARBYNE

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Abstract - Linear carbon allotropes (carbynes) with 1D-sp κ-hybridization were found to transform readily into diamond at comparatively weak dynamic pressures below 5 GPa without external thermal activation. The mechanism involved may be based on shock-induced close interaction of the initially weakly van der Waals-type bonded carbon chains to permit overlap of wave functions of neighbouring chains and generation of coupled π-π* bonding states. Further increasing interaction is expressed through 3D-cross linking by σ-bond formation of periodically arranged carbon chains with either kinks or screw symmetry axes.

1. Introduction

The transformation of the 2D-planar sp2 graphitic carbon structure into the 3D sp3 diamond network with chair-type carbon ring arrangement is energetically difficult to achieve since it involves a change in the first coordination sphere of the carbon atoms as well as in the type of the chemical bonds. Hence high static or dynamic pressures and temperatures are required. At very high static (isotropic) pressures (>80 GPa) rhombohedral graphite may transform to diamond without any thermal or catalytic activation [1]. However, high temperatures and addition of solvents for carbon such as nickel or iron will accelerate the transformation rates and provide substantially lower equilibrium pressures [2].

On the other hand, the transformation of graphite to diamond involving shock waves has been studied for over thirty years and large-scale industrial production of such diamonds is now being undertaken in several countries. Competing hypotheses about the mechanism of shock transformation include ultrafast annealing of a glassy carbon phase created by total destruction of the crystal lattice of graphite [3-5], martensitic shear transformation of 3R-graphite [6-8], dislocation reactions [5,9], carbon self-diffusion [10] and a complex solid-vapour-liquid-solid mechanism [11]. Here we will report on other plausible mechanisms involving linear sp-hybridized carbon clusters, i.e. carbynes and carbynoid structures as precursor phases.

'Carbynes' by definition are "systems consisting only of (straight [13] or kinked [12]) carbon chains held together by van der Waals forces to form a crystal"[14].
Theoretically, linear carbon chains with conjugated triple (polyyne-type) and/or cumulated double (polycumulene-type) intrachain bonds are assembled in a hexagonal array without any chemical bonds between the chains ('pencil-in-box' model). In real samples, however, cross-linking with various periodicities as well as kinks will always occur resulting in a layered lattice arrangement. Hence the definition above can be extended by stating that carbynes are "partially cross-linked three-dimensional polymer(s) having a more or less regular (layered) crystalline structure and (are) predominantly composed of extensive fragments of linearly polymerised carbon"[14]. In the spirit of this, graphite and diamond, respectively are limiting conformations of network and chain structures that are regularly periodically cross-linked by three(graphite)- and four(diamond)-function branching points. Indeed, the graphite plane can be viewed as composed of 2D-cross linked polyyne [15] or polycumulene [16] chains whereas the diamond structure consists of a 3D-array of an equal number of screw axes of opposite chirality, i.e. of helically twisted carbon chains [17].

Based on the (tentative) carbon phase diagram developed by Whittaker (cp. Fig. 4) carbynes should transform to diamond at comparatively weak (shock) pressures without external thermal activation. If the assumption is correct that diamond formation can proceed at such weak pressures through a low energy rearrangement of 1D sp-hybridized carbon chains than the deliberate addition of carbynes to graphite or even using more or less pure carbyne as precursor material should lower substantially the energy barrier required to attain 3D sp³-hybridization.

2. Experimental Methods

2.1 MATERIALS

A variety of methods have been developed in the past to synthesize carbynes including oxidative dehydropolycondensation of acetylene [18], condensation of carbon vapour obtained by sublimation of graphite by a laser beam [19], argon ion sputtering [20] or an electrical current [21], chemical dehydrohalogenation of stereospecifically chlorinated polyacetylene [22] or poly(vinylidene fluoride) [23], and eximer laser-induced dehydrochlorination of chlorinated poly(vinylchloride) [24]. Other potential routes to carbynes were proposed recently involving pyrolysis or photolysis of 3,4-dichloro-3-cyclobutene-1,2-dione adducts [25]. A comprehensive review of carbyne syntheses was given recently by Kudryavtsev et al [26]. For additional details the reader is referred to Chapter 3 of this treatise.

To obtain the carbyne samples used in the present investigation a procedure similar to the Shirakawa method [22] was adopted [27] since the trans-elimination of HCl should result in only polyyne- but not in polycumulene-type chain segments. The latter are thought to be less useful for low energy transformation routes. Poly(vinylidene chloride) (PVDC) was dehydrochlorinated with DBU (1,8-diazabicyclo[5,4,0]undec-7-ene). The solvent for PVDC was N,N-dimethylacetamide (DMAC). A 10% (2.1 molar) solution of DBU was slowly added to a 1% (1 molar) solution of PVDC (Asahi