

## Graphitization of Carbon under High Pressure

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The density of carbon increases or the molar volume of carbon decreases as amorphous carbon transforms to graphite. This means that pressure favors graphitization thermodynamically.

Noda and Matsuoka (1959) obtained well-crystallized graphite having the same  $c_0$ -spacing as natural graphite by solidifying molten carbon in argon atmosphere of 110 ~ 160 atm. However, Bundy (1963) reported that the  $c_0$ -spacing of graphite crystals, solidified from melt under 19 and 78 kbar, did not changed practically from that of original artificial graphite. Noda and Tanaka (1962) heat-treated carbon black based rod in the medium of alumina powder under several kilobars and obtained graphite crystals having the  $c_0$ -spacing of 6.708 Å with heat treatment above 2400°C. Ubbelohde et al (1963) hot-pressed pyrolytic graphite disks by applying a uniaxial pressure of about 400-500 kg/cm<sup>2</sup> in the c-axis direction to the disks during heating to temperatures around 2800°C and obtained graphite with density and other physical properties indistinguishable from those of natural graphite. Noda and Kato (1965) heat-treated polyvinylchloride coke and pitch coke based carbon under 10 kbar, and found that the graphitization proceeded very rapidly around 1500°C to the extent which could be attained with the heat treatment around 3000°C under the normal pressure. Glassy carbon, which is a typical hard carbon and is unable to be graphitized even with the heat treatment around 3000°C under the normal pressure, could be graphitized under pressure.

In order to investigate the effect of pressure on graphitization more precisely, the time dependences of graphitization under 1, 3 and 5 kbar were investigated at several temperatures.

In the early stage of graphitization, the profile of (002) diffraction sharpened and shifted to higher angle up to around 26.0° in  $2\theta$  for CuK $\alpha$  radiation ( 3.42 Å in d-spacing ) with the increase in heat treatment temperature and in residence time. In the next, a sharp peak at 26.5° in  $2\theta$  ( 3.36 Å in d-spacing ) appeared beside the peak at 26.0°. The sharp peak at 26.5° seemed to correspond to the graphite structure of which intensity increased with further increase in heat treatment temperature and in residence time.

The appearance of composite profile in the graphitization process under pressure is phenomenally similar to the so-called 2- or 3-phase graphitization of hard carbon.

The presence of minerals such as limestone was found to accelerate the graphitization of carbon under pressure. Carbon specimens sandwiched with calcium carbonate disks began to develop the sharp graphite peak at  $26.5^\circ$  on a broad band of (002) diffraction of carbon above  $1100^\circ\text{C}$  under 3 kbar. The content of graphite part was estimated from the area under the graphite peak at  $26.5^\circ$ , separated graphically from the observed composite profile. The content increased sharply with the increase in heat treatment temperature. The sharp graphite peak appeared even with heat treatment at  $800^\circ\text{C}$  under 3 kbar in the presence of calcium hydroxide. The graphitization under pressure in the presence of minerals seemed to be related with the melting or the decomposition of minerals.

1) 3 kbar pressure,  $\text{CaCO}_3$ , Accelerated graphitization.  
 $\text{Ca(OH)}_2$   
 $\text{CaF}_2$