

Formation of metastable phases of carbon during rapid cooling of graphite

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A graphite-to-diamond transition has been observed experimentally during the rapid cooling of polycrystalline graphite that has been heated by means of an infrared laser. The results are explained both by a "freezing" of the structure and also by stresses that appear in a graphite single crystal upon rapid cooling.

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A direct, solid-phase conversion of graphite into a diamond at high static pressures was accomplished by Vereshchagin *et al.*¹ and at high dynamic pressures by De Carly and Jamieson.² At the same time it is known³ that metastable and frozen states can form at high cooling rates (up to 10^7 – 10^8 K/sec) of the condensed phases. The goal of our work was to investigate the phase transformations of graphite, which had been heated to high temperatures, during rapid cooling. To accomplish this, we heated spectroscopically pure graphite to temperatures of about 3000 K by using the focused radiation of an infrared laser, followed by cooling with liquid nitrogen.

A thin layer, in which phase transformations were anticipated, was removed from the graphite samples that had been heated and cooled. The material collected in this manner in dozens of experiments was subjected to a selective gasification in the air plasma of a glow discharge. In this method⁴ only the graphite is gasified, since the specific rate of diamond gasification is five to six orders of magnitude lower than the graphite gasification rate. Graphite samples, which had been heated to the same temperature but had been cooled slowly in air, were gasified at the same time. The latter samples were completely gasified after 10 hours, but about 2% (0.4 mg) of white powder remained of the sample that had been quenched rapidly. This residue was examined in a transmission microscope. It was established that the powder consists of individual particles ranging in size from 100 Å to fractions of a micron. The structure of these particles was investigated by the transmission electron-diffraction method. The formation of diamond, lonsdaleite, and alpha and beta carbines was established from the diffraction patterns. All the particles gave a single-crystal diffraction pattern. We note that particles of lonsdaleite and beta carbine were encountered much more rarely in the diffraction studies than diamond and alpha carbine. The higher the heating temperature, the more frequently the diamond particles appear. Conversely, as the maximum heating temperature is lowered, the alpha-carbine particles appear more frequently.

Spectroscopically pure graphite consists of small graphite crystals. For a direct conversion of graphite into a diamond the structure of the graphite particles must be single-crystal in nature. Thus, a diamond is difficult to synthesize from carbon black and vitreous carbon, which have no ordered graphite structure, even with the use of

catalysts at high pressures and temperatures (the region of thermodynamic stability for a diamond). This is due to the necessity of a complete rearrangement of the structure of these materials and to breaking the bond between the carbon atoms. Conversely, it is easier to transform well structured graphite into a diamond, since we need only to crimp the bonds in the plane of the graphite rings and to bring the base planes closer together; this is accomplished quite easily by means of an external pressure. In our experiments, therefore, it is also desirable to have graphite particles with a perfect structure.

We should call attention to the high degree of anisotropy of the graphite particles. The thermal diffusivity in the direction of the base planes (in the x direction) is almost three orders of magnitude higher than that in the transverse direction (z direction). Therefore, a sufficiently small graphite particle is cooled primarily because of the heat conductivity in the x direction.

Since the thermal expansion coefficients are $\alpha_z \gg \alpha_x$ at a temperature above 670 K, whereas $\alpha_x < 0$ at lower temperatures, we can see that the graphite single crystal is compressed initially in the x direction, and then it expands in this direction. This produces a thermal stress. A compression wave is transmitted through a graphite particle in the x direction. This may contribute to a crimping of the plane of the graphite ring. We also note that the amplitude of the atomic vibrations at high temperatures is quite large in the x plane. At 2500 K it is equal to⁵ 0.17 Å, which is greater than the difference in the bond lengths between the carbon atoms in a diamond (1.54 Å) and graphite (1.42 Å). The bonds that are characteristic of the metastable phases can be kept the same length by rapid quenching.

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