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Abstract

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PHYSICS

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ON THE QUESTION OF THE MECHANISM OF THE POLYMORPHIC TRANSFORMATION OF GRAPHITE INTO DIAMOND

At present, both abroad ($^{1-3}$) and in the USSR, the synthesis of diamond from graphite at high pressures and temperatures has been successfully achieved. Transformations of this kind have been obtained in the region of thermodynamic stability of diamond on the P–T diagram graphite—diamond.

The diagram has been calculated more than once (^{4,5}), but for a long time it proved impossible to obtain the transformation of graphite into diamond; the reverse transition of diamond into graphite, as is well known, is obtained rather easily. Studies of the reverse transition of diamond into graphite were first carried out at pressures up to 30 kbar by Bridgman (^{6}). This question was the subject of a paper by Grenville-Wells (^{7}) and later a paper by Titova and Futerendler (^{8}). In particular, in the latter work it was experimentally found that, under short-term exposure of diamond (together with a pyrope concentrate) to pressure and temperature, the maximum blackening on the graphite ring (0002) corresponds to the [111] direction of diamond.

Thus it was shown that, in the reverse transition of diamond into graphite, the hexagonal planes of graphite are arranged parallel to the (111) planes of diamond. Pictures of this kind had been observed earlier by Grenville-Wells. As indicated above, the transformation of graphite into diamond at high pressures and temperatures could not be achieved under static conditions until sufficiently reliable apparatus had been constructed that made it possible to work in the region of thermodynamic stability of diamond.

On the other hand, Jamieson et al. (^{9}) obtained the transformation of graphite into diamond in a shock wave. However, if one takes into account that, at the high temperature developing during shock compression along the Hugoniot adiabat, destruction of the graphite lattice and reconstruction of the diamond

Fig. 4. Arrangement of atoms along two crystallographic directions in graphite (a) and diamond (b)

Figure 1: Fig. 4. Arrangement of atoms along two crystallographic directions in graphite (a) and diamond (b)

lattice can occur, then experiments of this kind cannot establish the mechanism of rearrangement of the graphite lattice into diamond.

Lonsdale, Milledge, and Nève ([12]), proceeding from structural considerations, proposed a mechanism for the polymorphic transformation of graphite into diamond by means of a simple transformation of the graphite lattice.

Some researchers ([10,11]) have recently come to the conclusion that the formation of diamond from graphite at high pressures and temperatures with the aid of a metal catalyst apparently occurs by dissolution of carbon in the molten metal catalyst, followed by crystallization of diamond from the metal. It is thus evident that, in this case, a complete rupture of the bonds in the graphite lattice is assumed during its dissolution, and then the formation of a new phase during crystallization of graphite from the molten metal. Thus, up to the present time, this question has not been theoretically clarified, which led us to the necessity of carrying out an investigation. The most suitable material would be a single crystal of graphite; however, obtaining such single crystals is extremely difficult. It proved possible to circumvent this difficulty by using pyrolytic graphite. It could be assumed that the use of pyrographite as the starting material with the applica-

by the use of metal catalysts, provides a suitable starting material possessing a sufficiently pronounced anisotropy of the individual graphite crystals, so that the planes (0001) in the hexagonal graphite lattice are directed, for all crystals, to one side.

The sample of pyrographite at our disposal was examined by X-ray diffraction. The X-ray diffraction pattern showed that the maximum angle of deviation of the normals to the plane (0001) of graphite from a definite direction was no more than 25° (Fig. 1).

Fig. 4. Arrangement of atoms along two crystallographic directions in graphite (**a**) and diamond (**b**)

It seemed of interest to carry out experiments on obtaining diamonds from pyrolytic graphite at high pressures and high temperatures in order to determine whether diamonds would grow that were likewise strictly oriented with their principal crystallographic axes, or whether intergrowths of randomly oriented crystals would be obtained. The experiment on the formation of diamond from this graphite sample, repeated several times in the presence of a catalyst, led to the formation of synthetic diamonds with a strongly pronounced texture (Figs. 2 and 3).

From their examination it was possible to conclude that pressure contributes to a decrease in the angle of divergence between the individual crystals of such a textured sample, and if in the graphite crystals this angle was about 25°, then for the synthetic diamonds it did not exceed 4°. On the other hand, photographs and X-ray diffraction patterns obtained from diamond samples clearly indicate that, if the [0001] direction of graphite was parallel to the axis of the high-pressure chamber, then the synthetic diamonds formed in this case from pyrolytic graphite grow in a quite definite manner, being oriented so that the [111] direction of diamond is perpendicular to the graphite plane (0001), which leads to the following mechanism of diamond formation from the graphite lattice.

The graphite lattice in the region of thermodynamic stability of diamond, in the presence of a metal catalyst, is rearranged into the diamond lattice not by dissolution of carbon in the metal catalyst, but by direct reconstruction of the graphite lattice into the diamond lattice. This is confirmed both by the experimental material set out above and by consideration of two models of the graphite and diamond lattices. Consequently, the mechanism of transforma-

Fig. 1. Lauegram of a pyrolytic graphite specimen

Fig. 2. Octahedral planes of an artificial diamond obtained from pyrolytic graphite. The (0001) planes of pyrolytic graphite are parallel to the octahedral planes of diamond (70×). In the lower left corner of the photograph is the surface of pyrolytic graphite (10×)

Fig. 3. Typical intergrowth and twinning of crystals of artificial diamonds obtained from pyrolytic graphite (60×)

···may be such that, under the influence of high pressure, the distances between carbon atoms in the graphite lattice along the direction [0001] decrease.

The atoms of the catalyst metal, diffusing into the graphite mass, apparently facilitate deformation of the graphite lattice and the establishment of "diamond" bonds. In this process the arrangement of the carbon atoms in the layer changes relative to one another: the initially planar net ceases to be such, and atoms that in graphite belonged to a definite layer are now located alternately above and below one another (with respect to the established direction [0001]).

If one considers the projections of the models of the space lattices of graphite and diamond along the directions [0001] and [111], respectively, onto a plane, their configurational similarity is revealed (Fig. 4).

The decrease in the divergence of the normals to the [111] plane of diamond grown from textured graphite with the oriented direction [0001] under pressure can apparently be explained on the basis of thermodynamic considerations. It is known that a decrease in disorder in a crystal lattice leads to a decrease in its entropy. Since entropy decreases with increasing pressure, one may conclude that the mosaicity of a crystal grown under pressure can decrease.

Thus, diamond from graphite as the starting material can apparently be obtained at high pressure and temperature in the diamond-stable region by three routes. The first of these is crystallization of diamond from molten graphite without a catalyst. The second is crystallization of diamond from a solution of graphite in a molten catalyst metal. The third route is the transformation of the graphite lattice into the diamond lattice in the solid state, which was first demonstrated by the experiments described above.

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Note: Figure translations are in progress. See original paper for figures.