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ON WHISKER CRYSTALS OF DIAMOND

Whisker crystals (whiskers) are at present attracting ever increasing interest in connection with a number of their unique properties, which are close to those of ideal single crystals. The present work describes the production of whisker crystals of diamond from a carbon-containing gas medium at pressures below atmospheric on seed diamond crystals (a substrate). The possibility of a process of epitaxial growth of diamond under these conditions has been indicated in certain patents (^{1}). The principal drawback of the patented methods is the parasitic deposition of the more stable form of carbon—graphite—which blocks the surface of the growing diamond. After a certain time has elapsed, the process of diamond buildup has to be stopped and the graphite that has formed removed in one way or another. This circumstance severely limits the linear rate of diamond buildup. Thus, in the cited patents (^{1}), the linear rate was 10^{-8} cm per hour, and even the very effect of diamond buildup could be detected only owing to the enormous surface area (up to 20 m^2 per gram) of the seed diamond powders. If, however, measures are taken to prevent the deposition of graphite, conditions can be created for the growth of whisker crystals of diamond on the surface of seed diamond single crystals.

The experiments were carried out in a radiation-heating apparatus constructed on the basis of a DKSR-6000 super-high-pressure xenon lamp. The apparatus is described in detail in (^{2}). The seed diamond single crystal was fastened with rhenium needle holders and placed in the focal spot of the apparatus, the size of which was larger than the linear dimension of the substrate. The temperature of the single crystal was measured with an optical pyrometer. The surface of the seed single crystal could be observed during the experiment under a microscope. In these experiments, the formation and subsequent growth of whisker crystals of diamond were established. Their growth rate depends on temperature, pressure, and certain other parameters. Since in the focal spot the parameters of the radiant flux are substantially nonuniform, during growth of whisker crystals the conditions at their tip change considerably in comparison with the conditions on the substrate. Thus, upon formation of a whisker crystal 400 μ long, the irradiation of its base and of its tip could differ by a factor

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of two. The average growth rate of the whisker crystals was about 10 μ/hour, but in individual cases reached 50–250 μ/hour. It should be noted that this was precisely the average linear rate, and it may be assumed that it is not the maximum possible linear growth rate.

Figure 1 shows a photograph of a whisker crystal 400 μ long; Fig. 2, a photograph of a whisker crystal 170 μ long. As a rule, the thickness of a crystal did not exceed 25 μ and was usually 10–20 μ, with the longer crystals usually having a larger diameter.

Observations made of the cathodoluminescence of a whisker crystal showed that it luminesces analogously to the substrate. For more precise identification of the formations obtained, after one of the

Fig. 1. A filamentary diamond crystal 400 μ long, grown on the (110) face

Fig. 2. A filamentary diamond crystal 170 μ long, grown on the (111) face

Fig. 3. Microelectron diffraction pattern from a crushed filamentary diamond crystal

the experiments the whisker crystals were carefully separated from the substrate, crushed, and placed on an electrolytic grid in the specimen holder of an electron microscope. A microdiffraction study of the resulting whisker crystals was carried out, and from the electron-diffraction patterns (Fig. 3) the interplanar spacings were calculated, platinum being used as the standard.

$d_{\text{tab.}}$, Å	2.05	1.26	1.072	0.885	0.813	0.721
$d_{\text{calc.}}$, Å	2.07	1.24	1.068	0.920	0.825	0.740

The tabulated values of the interplanar spacings were taken from (3).

The electron-diffraction patterns indicate the single-crystal character of separate crushed pieces of the whisker crystals. In some electron-diffraction patterns

Fig. 3

Figure 3: Fig. 3

Fig. 4. Dependence of the diffusion flux $j(r)$ to the surface of a substrate through a hemispherical drop of molten metal of radius r_0

Figure 4: Fig. 4. Dependence of the diffusion flux $j(r)$ to the surface of a substrate through a hemispherical drop of molten metal of radius r_0

Kikuchi lines are clearly visible. The question of whether a diamond whisker crystal is a single monocrystal still remains open.

In some experiments it was noted that at the tips of diamond whisker crystals there are dark formations of spherical shape. This can be explained by the deposition of metallic particles on the surface of the substrate before the experiment. Therefore special experiments were carried out on the growth of diamond single-crystal whiskers beneath molten drops of metals by the VLS method (4). In this case numerous transparent whisker crystals were formed, with droplets of solidified metal at the tip. Positive results were obtained with metals that readily dissolve carbon and wet diamond: nickel, iron, and manganese, whereas in the case of drops of molten gold no formations were detected. Evidently, it may be considered that one of the possible methods of growing diamond whisker crystals is the VLS method. In this method two limiting regions of the course of the process may be distinguished: kinetic and diffusion. Increasing the pressure of the carbon-containing gas by an order of magnitude did not lead to an increase in the number of whisker crystals formed or to an increase in the rate of their linear growth. In (1) it was also noted that increasing the total pressure of the carbon-containing gas by more than two orders of magnitude does not increase the rate of diamond deposition. Similarly, dilution with hydrogen also did not affect the process. It may therefore be concluded that the growth rate of diamond whisker crystals is not determined by the diffusion of carbon atoms through the liquid drop as the slow stage of the process.

Fig. 4. Dependence of the diffusion flux $j(r)$ to the surface of a substrate through a hemispherical drop of molten metal of radius r_0

In (5) the growth of tubular whisker-like graphite formations from a carbon monoxide medium at 800° on small iron particles was observed in the absence of bulk soot formation. In this case the process was probably determined by diffusion of dissolved carbon through the drop. Calculation gives the following character of the dependence of the diffusion flux $j(r)$ through a hemispherical drop (Fig. 4): at the center the flux $j(r)$ is minimal and increases markedly toward the periphery, which leads to the formation of long tubular graphite filaments.

Diamond whisker crystals are of interest not only in themselves, but also show that epitaxial overgrowth of a diamond seed crystal at considerable rates is possible at pressures significantly lower than those on the diamond—graphite phase-equilibrium line. This can be explained by the fact that the energy of formation of a critical diamond nucleus under a metal layer, under certain conditions, is considerably less than the work of formation of a critical graphite nucleus, which in turn is connected with the difference in surface energies on the gra-

is lower than diamond—metal and graphite—metal and with the surface energy at the graphite—diamond interface.

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