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Growth of polycrystalline diamond

Polycrystalline diamond is currently under intense investigation for its application to cutting tools [1]. Natural polycrystalline diamonds such as ballas and carbonado are rarer forms of diamond found only at a limited number of mines. Synthesis of polycrystalline diamond is, therefore, interesting both from the engineering stand point and for the study of the origin of natural polycrystalline diamond.

Ballas is a form of diamond with globular shape in which the crystallites are arranged radially. It has probably grown from its centre to the surface [2]. Ballas-like diamond was synthesized by Kalashnikov *et al.* [3]. The synthesizing condition, however, was not described.

Carbonado is an aggregate of randomly oriented small diamond crystals [4] and carbonado-type diamond has been prepared by sintering and other methods [5–8].

In this letter we report on the growth features of polycrystalline diamond formed under high pressure and high temperature in the presence of group VIII metals, especially cobalt. Shock-synthesized diamond powder (0 to 2 μm grade obtained from DuPont Co Ltd) was used as the starting material. Natural and catalytically synthesized diamond powder of different sources and particle size distribution were also tried, but no distinct tendency to agglomeration or growth of diamond particles was observed.

High temperature and pressure experiments were carried out using a belt apparatus. The sample assembly is shown schematically in Fig. 1a. The diamond powder was charged around a rod of a catalyst metal placed at the centre of the cell. In all runs pressure was first applied and then temperature. The samples were maintained at 70 kbar and 1600° C for 5 min. Temperature was then lowered by turning off the electric power to the heater before releasing the pressure.

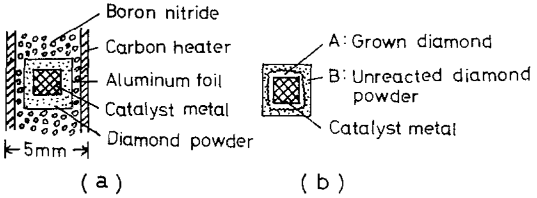

Figure 1 Sample assembly (a) before and (b) after high temperature and pressure experiments.

After the run the appearance of the sample portion was changed as shown in Fig. 1b. The diamond specimens were observed to be distinctly separated into two layers, A and B (Fig. 1b). Using X-ray diffraction, the inner layer A was found to consist of diamond and the catalyst metal. Growth and agglomeration of crystals were observed in this layer as will be described below. No significant change was observed in the outer layer B except for partial graphitization.

The growth features were examined by scanning electron microscopy (SEM). The catalyst metal in the specimens was removed by a hot mixture of HNO_3 and HCl prior to SEM observation. Figs. 2 to 5 show typical growth features of the inner layer A, obtained from the system of the shock-synthesized diamond and cobalt.

The reacted layer A of about 0.2 mm thick was again separated into three zones C, D and E by its texture. The cross-sectional view of the reacted region is shown in Fig. 2. Zone C is the boundary with the catalyst metal and zone E the outermost zone of the reacted diamond layer.

The grown single crystals having a definite shape and form were observed at the zone C. The zone D consisted of loosely packed aggregates of diamond of about 1 μm as shown in Fig. 3. The orientation of the crystals in this region was random. Some of the crystals showed the same well-defined morphology as that of single crystals. Agglomeration

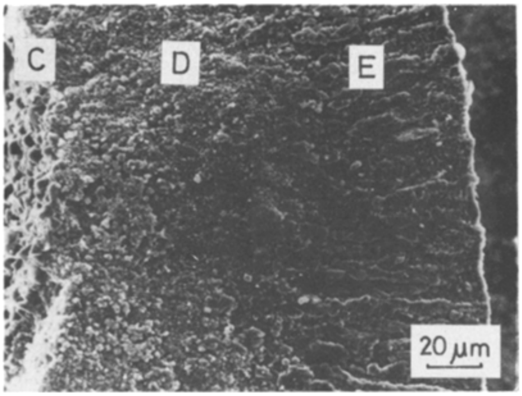

Figure 2 Scanning electron micrograph of the cross-section of the reacted layer A.

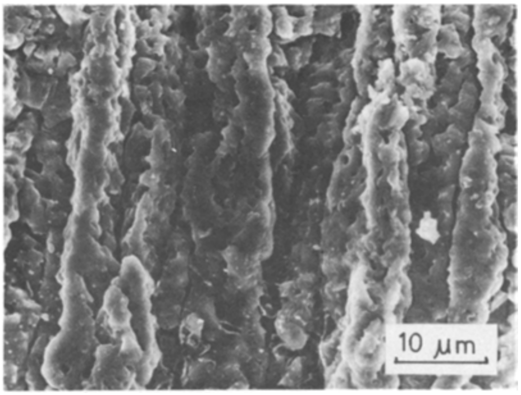

Figure 4 Enlarged photograph of zone E.

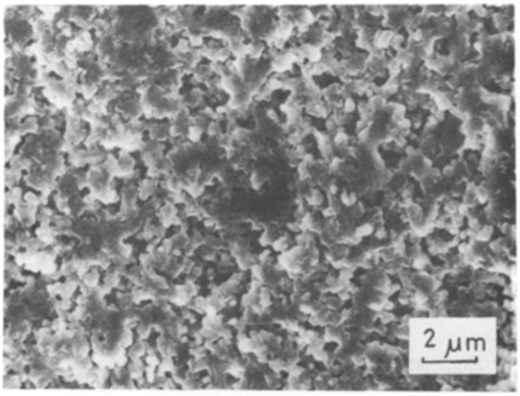

Figure 3 Enlarged photograph of zone D.

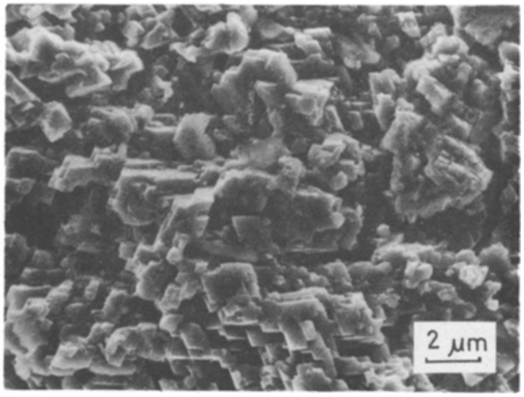

Figure 5 Outer surface of zone E.

of crystals was also observed as seen in the photograph.

The outermost zone E showed a characteristic texture consisting of radially arranged needle-like crystals. Under higher magnification, irregularly agglomerated crystals extending to the radial direction of the sample were observed as shown in Fig. 4. The needle-like agglomerates were a few microns in diameter and about 0.1 mm in length.

The bonding strength in each needle-like agglomerate is probably very high, since the zone was highly resistant to the scratching test on a sintered tungsten carbide–cobalt alloy surface.

Fig. 5 shows the structure of the outer surface of the zone E viewed along the radial direction. The surface consisted of (1 1 1) faces of 1 to 3 μm crystals. Pores and cracks were frequently observed.

Although the above descriptions are limited to the specimens reacted with cobalt, similar results were also obtained by using nickel or iron in place of cobalt.

It is interesting to note the textural similarity between the present specimens and carbonado and ballas. Zone D consists of nearly spherical or distorted octahedral small particles. This texture coincides with that of carbonado studied by Trueb and de Wys [9]. On the other hand, the texture of zone E has similar characteristics to ballas-type polycrystalline diamond in that the zone consists of radially oriented needle-like crystals as shown in Figs. 2 and 4.

From the present results, it is expected that the two typical forms of polycrystalline diamond, i.e. ballas and carbonado, may be synthesized under nearly the same P–T conditions. Probably, the two textures appear at regions with different concentrations of flux melts relative to carbonaceous materials.

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Electron microprobe analysis of niobium-based superconducting materials

In this letter we report the results of our investigations to ascertain the accuracy of electron probe composition measurements in four superconducting materials when the standards used are pure elements; as for many superconducting systems compound standards are not easily available. The transition temperature, T_c, of a superconducting A-15 compound is very sensitive to composition variations. To illustrate this, in the V–Ga system the highest T_c is found for the A-15 phase compounds V_3Ga. Although the A-15 phase extends from 22 at.% Ga to 36 at.% Ga, T_c is maximum at exactly 25 at.% Ga and falls off at either side of this composition by about ~1 K per at.% change [1]. Further, many other superconducting properties may be related to the composition, or to small additions of a third or fourth element [2]. The electron microprobe is a useful tool for the characterization of superconducting materials because it provides a convenient, non-destructive means of obtaining their composition.

The accuracy of the composition measurement is related to the use of standards and the corresponding correction procedures used. In superconducting materials a compound standard with a composition known within 1% is difficult to make. On the other hand, if elemental standards (i.e. pure metals as standards) are used it is believed that the errors could be as large as 10%. For example Sweatman and Long [3] found that the use of pure aluminium as a standard for silicate analysis could lead to errors of about 8%. These errors are essentially due to excessive matrix corrections and large wavelength shifts due to the difference in chemical composition between the unknown and the standard. Clearly there is a need to determine accurately the error involved in the use of elemental standards in taking microprobe data. We report here the results on four systems, Nb–Al, Nb–Al–Si, Nb–Pt and Nb–Ir. The procedure used was to prepare a compound by the method described below, to determine its composition with the electron microprobe using elemental standards, and to compare the results with actual weight measurements and calculations from lattice parameter data.

The Nb–Al and Nb–Al–Si samples were prepared by melting pellets pressed from carefully weighed amounts of the powders in an argon-filled arc furnace. The niobium powder was necessarily coarser to reduce the oxygen contamination. The samples were turned over and remelted three to four times to assure homogeneity. Most of the samples were subjected to high temperature (~1850° C) heat treatments.

A Debye–Scherrer photograph was taken of the material evaporated and deposited on the hearth during this melting procedure and this material was found to be entirely aluminium, as