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Characterization of diamond obtained by shock compression of carbon black

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Summary — Morphology and structure of cubic diamond found in a product of shock compression of carbon black were examined with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron diffraction (ED), and atomic force microscopy (AFM).

diamond / carbon black / shock compression / characterization

Résumé — Caractérisation du diamant obtenu par compression de choc du noir de charbon. *La morphologie et la structure du diamant cubique obtenu par compression de choc du noir de charbon ont été examinées par diffraction aux rayons X (XRD), microscopie à balayage électronique (SEM), microscopie à transmission électronique (TEM), diffraction électronique (ED) et microscopie à force électronique (AFM).*

diamant / noir de charbon / compression par choc / caractérisation

Introduction

Since the discovery in 1797 that diamond is a crystalline form of carbon, many attempts have been made to synthesize diamond from various carbonaceous materials [1]. The first synthesis of diamond was achieved by Bundy, Hall, Strong and Wentorf [2] in 1955. They used high static pressures and high temperatures to attain a region of the phase diagram where diamond is the thermodynamically stable form, and used molten-metal solvent catalysts to transform graphite into diamond. The non-catalytic synthesis of diamond needs higher static pressures [3, 4]. Dynamic compression of graphite by shock loading is another way to produce diamond. In 1961, De Carli and Jamieson [5] announced the presence of diamond in samples of explosively shocked graphite. In addition to these techniques using high pressures and high temperatures, the synthesis of polycrystalline diamond films and diamond-like carbon by chemical vapor deposition at low pressure has been rapidly developed in recent decades [6]. In our case, diamond was obtained under dynamic compression by means of explosives, with carbon black as the starting material. Kurdyumov et al have reported the synthesis of such product [7]. Some results of characterization studies of diamond obtained by this procedure are presented in this article.

Experimental section

Diamond-containing products were generated by shock compression of carbon black/additive mixtures placed in a steel container surrounded by explosive 'composite B'. The shock wave pressure was about 30 GPa. Determination of the temperature during the shock is rather difficult but it can be estimated in the range of 1 500–3 000 K [8]. The additive used as heat-sink material was chemically inert to carbon black. The retained samples were completely additive free.

The products were characterized by several methods including X-ray diffraction (XRD), electron diffraction (ED), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). ED patterns and transmission electron micrographs were obtained with a CM 200-Philips electronic microscope. X-ray phase analysis was performed with a STOE STADI-P diffractometer using the Cu$K\alpha 1$ ($\lambda = 1.5406$ Å) within a 20–120° (2θ) range.

The morphology of the products was observed by SEM and AFM. The SEM images were obtained with a XL 30-Philips microscope. The AFM instruments used were the Nanoscope II and III (Digital Inc, Santa Barbara, USA). The Nanoscope III was operated with the 'taping mode' function giving fewer particle morphology artefacts than the 'contact mode'. Two kinds of cantilever were also tested for their chemical nature and geometrical form of the tips: one consisted of Si_3N_4 (NanoProbes^{TM}; triangular legs; elastic constant ~0.58 N/m) with a pyramidal form (cone angle ~70°), the other of silicon monocrystals with a 20° cone angle (Taping^{TM}). For AFM observations the diamond powder

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was either compressed or deposited on a cleaved mica surface from an aqueous suspension.

Results and discussion

Starting material

П 803 carbon black (Russian name) was used as starting material, with the following main characteristics: impurity <0.5% and specific surface area of 18 m^2/g. Figure 1a shows some aggregates of spherical particles of carbon black with typical morphology. The corresponding electron diffraction pattern (fig 1b) exhibits broad (002) and (10) reflections, indicating the turbostratic structure. The reflection (11) was not observed. The *d*-spacing obtained from the electron diffraction rings $d_{002} = 3.5$ Å and $d_{10} = 2.1$ Å are less precise than those obtained with the X-ray diffraction pattern (fig 2) on the same sample $d_{002} = 3.57$ Å and $d_{10} = 2.11$ Å. The carbon black primary particles are roughly 40–50 nm in diameter (fig 1a).

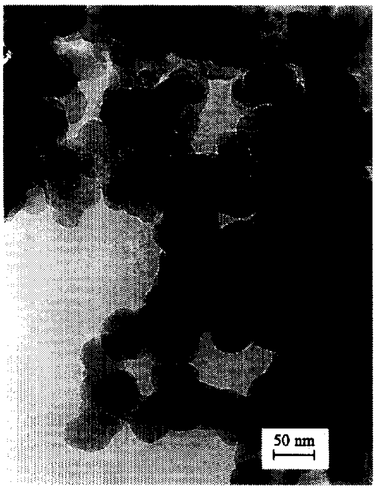

Fig 1. (a) Transmission electron micrograph of carbon black used as starting material. The spherical particles are roughly 40–50 nm in diameter;

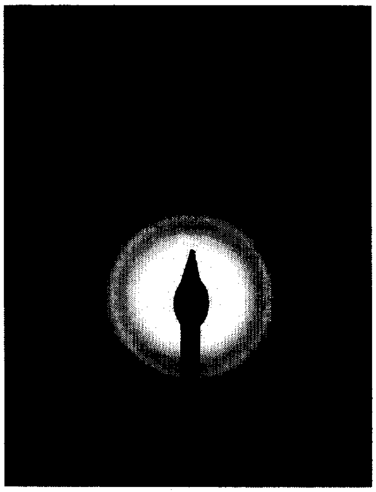

Fig 1. (b) typical electron diffraction pattern of the starting carbon black powder.

Products of shock compression

The product appears macroscopically as a gray powder, but under the optical microscope some isolated black colored particles are visible. The X-ray diffraction pattern of the shocked powder can be indexed as a mixture of cubic diamond and carbon phase with a series of intermediate structures between normal carbon black and graphitized carbon black (fig 3). Indeed, the calculated interplanar spacings, 2.060, 1.260 and 1.075 Å, correspond respectively to the reported values of the (111_d), (220_d), and (331_d) peaks of diamond. Examination of the spectra before and after compression of carbon black displays the following features: the intensity of the peak (002) of carbon black is considerably reduced and the peak (10) is overlapped by the sharper (111_d) peak. Furthermore, the (220_d) and (311_d) peaks are rather intense. The electron diffraction pattern (EDP) (fig 4) of a selected diamond region displays rings with many discrete spots which are indicative of polycrystalline material with randomly oriented units. Analysis of the EDP permits us to obtain two other d_{hkl} values, $d_{400} = 0.89$ Å and $d_{331} = 0.82$ Å, corresponding to diamond.

Scanning electron micrographs imparted interesting information about the morphology of the diamond-containing powder produced from carbon black. While the distribution in size and morphology was homogeneous for the starting material (see fig 1a), figures 5a, b and c represent widely different forms of carbon in the product of the shock compression. Because the powder product contained grains of very different density (graphite and diamond), we proceeded as follows to separate roughly both phases: the powder was dispersed in water and the half top of the suspension was removed almost immediately. We repeated the same procedure with the remaining suspension to be sure of observing the high-density particles (fig 5b, c). The lower density carbon phase (fig 5a) was found to contain rounded particles similar to the starting material but with some much bigger particles. Figure 5b shows an aggregate of high-density material with many holes, which may be indicative of a transition step in the crystal growth. In figure 5c the observed particle, about 10 μm in width and at least 30 μm in length, appears to be in a more advanced step of formation than the material in figure 5b. Indeed no holes are visible and growth seems to have gone to completion. Particle edges are well defined and the particle size is much bigger than in the starting material. This large increase in particle size may be consistent with a reconstructive mechanism in the carbon black–diamond transition, in contrast to martensitic diffusionless transformation of graphite with ordered three-dimensional structure [9].

The heterogeneous phase composition of the shocked carbon product, observed by TEM, is shown in figure 6. At least four types of particle morphology are visible in figure 6a: (A) layered flakes with straight edges and homogeneous thickness; (B) ultra-fine particles of much smaller size than the starting carbon black (compare with fig 1a); (C) round particle phase with a size similar

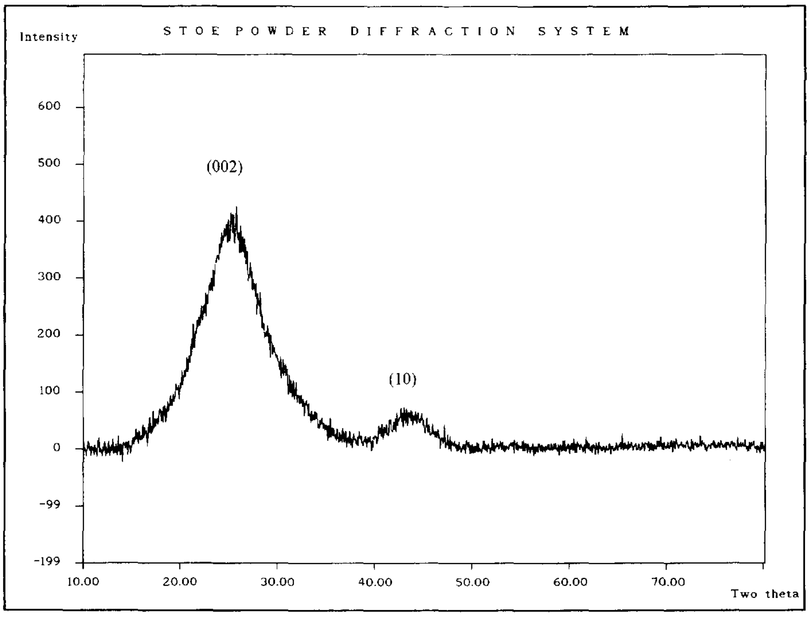

Fig 2. X-ray diffraction pattern of the starting material after background correction.

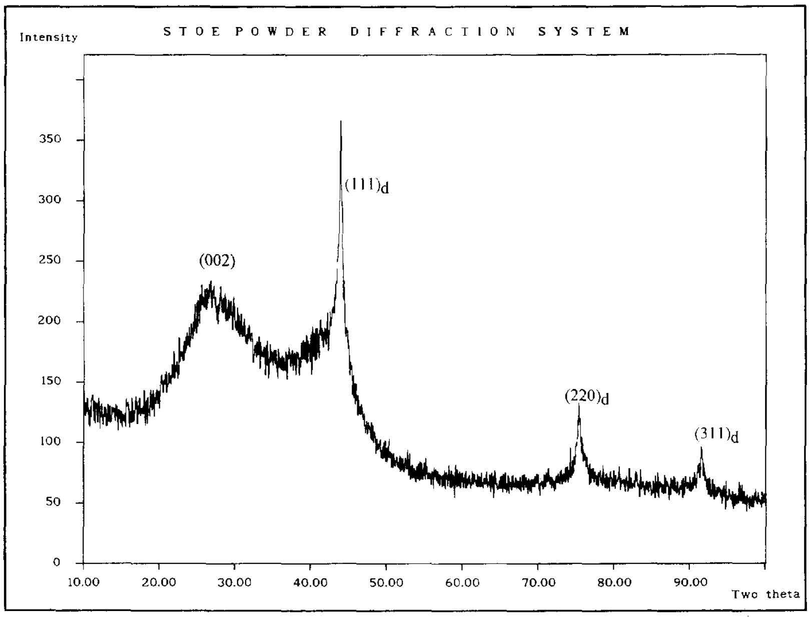

Fig 3. X-ray diffraction pattern of the diamond explosively shock-synthesized.

to that of starting black; and (D) a particle with a well-defined shape. Another particle with a similar shape to (D) is presented in figure 6b, where we can see clearly the facets and steps. Another carbon structure was observed in the product of shock compression (fig 6c). This structure is similar to that observed in the case of graphitized carbon black after thermal treatment (2 700 °C) [10]. The interplanar spacing is around 3.6 Å. Because of the high pressure and high temperature conditions obtained during the shock compression, the graphite-like structure may be formed either directly in the shock wave or by a reverse diamond–graphite transition in the post-shock stage. This problem has been discussed by others [11] and in practice some additives are sometimes added as quenching agents to prevent the diamond–graphite transformation [12, 13].

Since the product of compression was simply separated from the additive by washing, it still contained up to 30% carbon black, some diamond and an amorphous intermediate carbon phase. Kurdyumov's group has worked on product without residual carbon black, which means that the recovered sample was washed not only of the additive but also of carbon black. Such products have been investigated in reference [7]. A mixture of

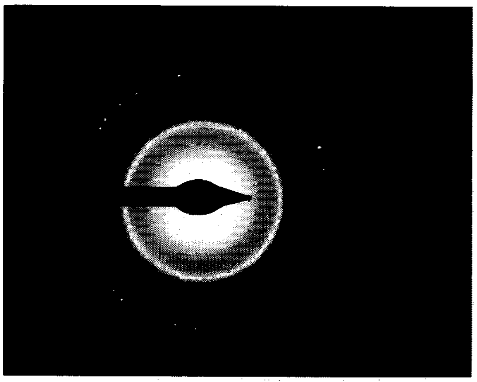

Fig 4. Electron diffraction pattern of recovered diamond. Spotty ring pattern from shocked carbon black.

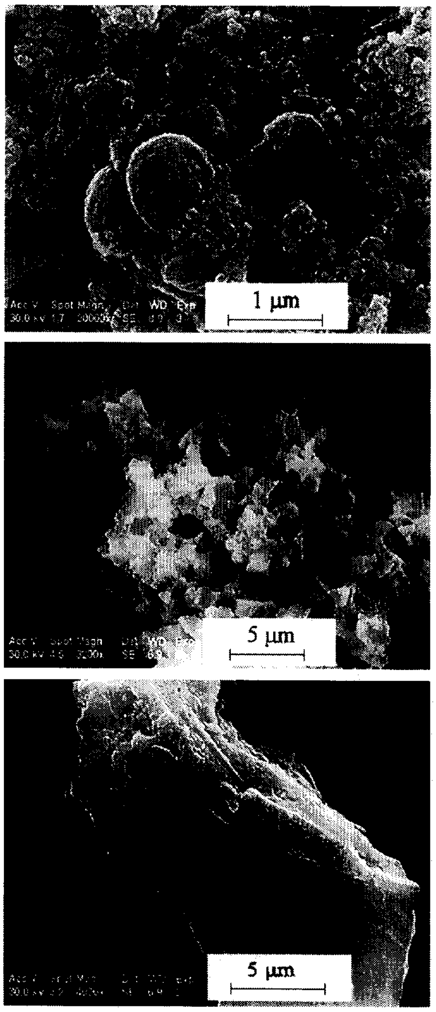

Fig 5. (a) SEM image of a low density carbon product; (b) SEM image of a high density aggregate; (c) SEM image of a high density particle.

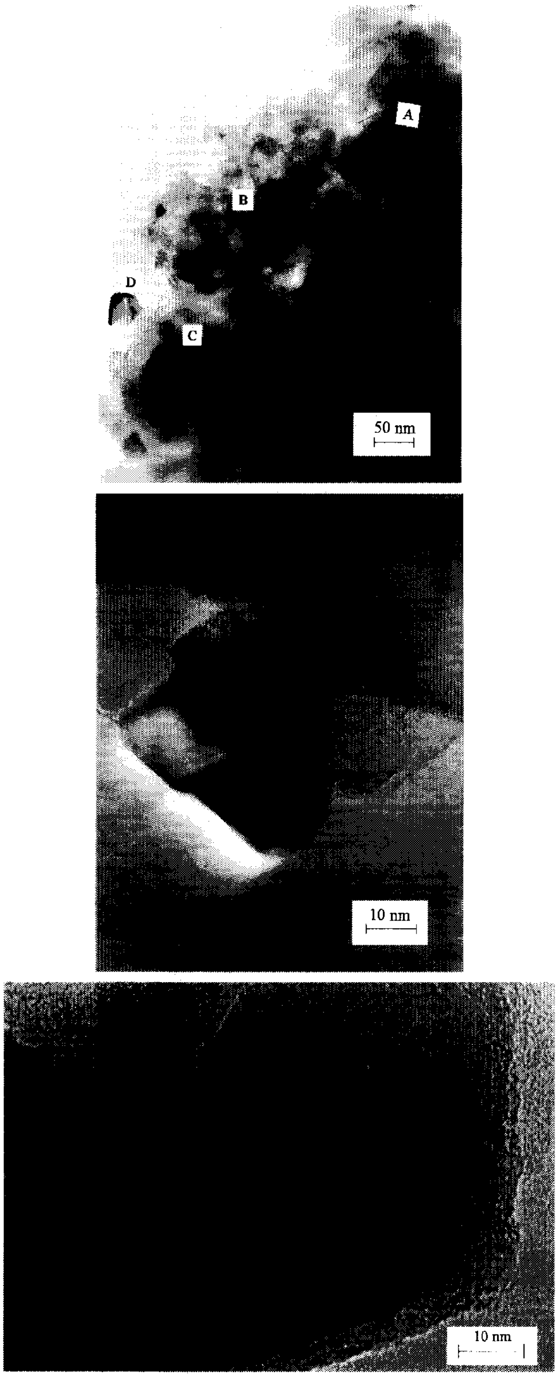

Fig 6. (a) Transmission electron micrograph at low magnification of the product of shock compression; (b) transmission electron micrograph at high magnification of a well-faceted grain of diamond with size in the range 50–100 nm; (c) transmission electron micrograph of a graphitized carbon black particle. The interlayer spacing is around 3.6 Å.

melting caustic potash and potassium nitrate was used to remove the remaining carbon black in the product. The global picnometrical density of the purified product is 3.14 g/cm^3. By measuring the intensity of the (311) XRD peak and the intensity of the same peak of a 100% diamond sample, the yield of diamond in volume was calculated to be about 40%. The other 60% corresponds to an 'amorphous' carbon phase with a density of 2.9 g/cm^3, a value which is intermediate between the

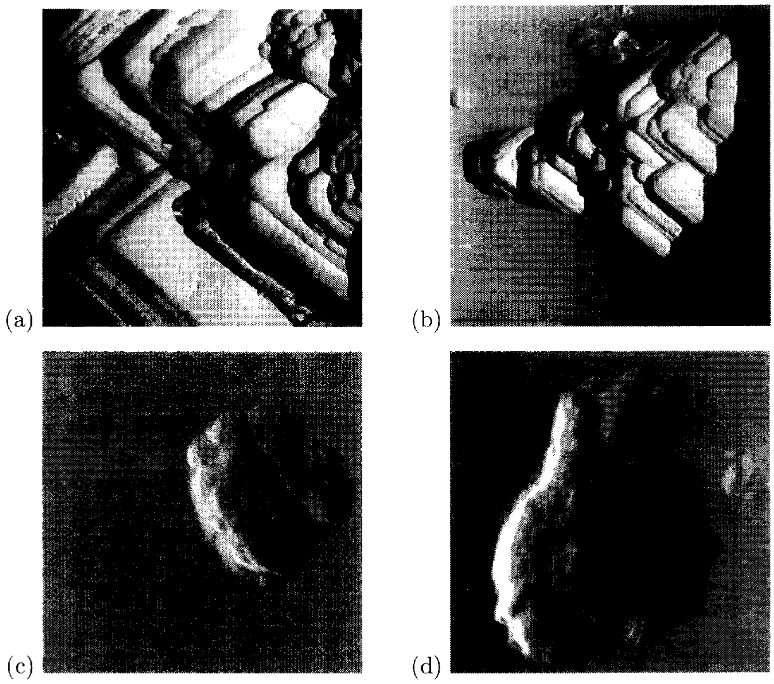

Fig 7. AFM images of the diamond particles: (a, b) 'contact mode', Si_3N_4 tip, pyramidal form, cone angle 70°; they may be an artefact: the inversed image of the extremity of the tip in contact with the diamond particles. (a: 1 800 × 1 800 nm^2; b: 1 640 × 1 640 nm^2); (c, d) 'taping mode', monocrystal silicon tip, sharp form with cone angle 20° (c: 708 × 708 nm^2; d: 720 × 720 nm^2).

initial carbon black density (1.85 g/cm^3) and that of diamond (3.51 g/cm^3). In our opinion this 'amorphous' carbon phase, with a rather high density and a high chemical inertness, could be an intermediate state in the carbon black–diamond transformation.

Our previous observation of diamond particles by AFM (Nanoscope II, contact mode, Si_3N_4 cantilever) showed some images with a typical crystal feature (fig 7a, b), very similar to some reported images of CVD diamond [14]. However, this feature was not confirmed by other techniques (eg, SEM). Subsequent study with the 'taping mode' (Nanoscope III, monocrystal silicon cantilever) showed quite different results (fig 7c, d). The size of the observed particles is 300–600 nm. These particles have irregular morphology with features similar to diamond particles of high density (fig 5c). The discrepancy between the two modes is attributed to the tip geometry and cantilever distortion. The larger cone angle of the AFM tip in 'contact mode' sometimes gives false particle images when the slope of particle is too deep. This effect is more pronounced when the tip is worn out by continuous friction against the diamond surface, as observed in our experiment and reported by others [15]. In fact, because of the hardness of the diamond powder, the tip morphology is modified during 'contact mode' analysis of the sample, and becomes dull. We also tried the silicon tip in the 'contact mode' but the image quality was not improved because of the cantilever distortion. Therefore precaution must be taken to avoid artefacts in the characterization of diamond particles by AFM.

In summary, a shock-compressed product from carbon black was characterized by several techniques that showed that diamond was produced. The shock compression is a dynamic process and thus the system varies with time and under different real-space conditions (mass, temperature, pressure, etc). The products obtained are very heterogeneous in terms of structure and particle morphology. More work must be undertaken to understand the diamond formation mechanisms under these complex conditions.

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