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Nanometric onion-like hollow spheres in laser synthesized boron nitride ultrafine powder

sphères creuses nanométriques en forme d'oignon observées dans des poudres-laser de nitrure de bore

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La pyrolyse laser de mélanges $\text{BCl}_3\text{-NH}_3$ conduit à des poudres nanométriques de nitrure de bore turbostratique qui se transforme progressivement en nitrure de bore hexagonal après traitement thermique sous azote à 1650°C . Par microscopie électronique par transmission, on a observé pour la première fois sur la poudre brute de synthèse et sur la poudre traitée thermiquement des structures qui rappellent celles rencontrées récemment pour le carbone, notamment la configuration creuse en forme d'oignons mais à une échelle beaucoup plus petite que pour le carbone.

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NANOMETRIC ONIONLIKE HOLLOW SPHERES IN LASER SYNTHESIZED BORON NITRIDE ULTRAFINE POWDER

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1. INTRODUCTION

Observations of new structures of carbon such as fullerenes, onions, nanotubes have been the object of numerous publications. These structures are related to the occurrence of the sp^2 -bonding coordination. Boron and nitrogen which stand on each side of carbon lead to isoelectronic configuration of boron-nitride. So, similarly to carbon, BN exists in different crystallographic structures: hexagonal, diamond cubic. In the following, we present TEM observations of ultra-fine BN powders elaborated by an innovative method: laser pyrolysis. The resulting microstructures in the as received state and after thermal treatment show small nanometric scale configurations close to the ones met with carbon .

2. ELABORATION METHOD

2.1 Laser synthesis

The two reagents, BCl_3 and NH_3 which have absorption bands near the emission line of the CO_2 laser (10.6 μm), are introduced separately in the laser beam. An additional argon flux carry along the resulting powder which is collected in a pumped chamber at a rate of about 30 g/h. The specific surface of the product is as high as about 150 m^2/g .

2.2 Thermal treatment

Powders are heated under nitrogen atmosphere up to 1650°C during one hour.

3. MORPHOLOGICAL ANALYSES

TEM observations have been performed with a Philips CM20 twin. Samples are prepared from powder sonically dispersed in acetone and deposited on a grid-supported carbon film.

In the initial state the powder presents small spheres (50-100 nm in diameter) with a light core inside (Fig.1) analogous to the one reported by Hamilton et al (1993). When tilting the sample with large angle amplitude (± 40 deg) views present the very same aspect. This excludes the disc geometry. Thereby this morphology is attributed to hollow spheres where matter is limited to a shell. On high resolution images, the outer side of the shell shows a structure identical to the one of so-called glassy carbon with interplanar distances of 0.35 nm. Diffraction patterns show diffused rings corresponding to the reflections : 002, 100 and 110.

After heating at 1650°C, the general microstructure shows less dense components. Two new types of morphology are present. The first consists of rod like shape structures : 10-20 nm

wide, 20-50 nm long. High resolution images show planes parallel to the axis of the rod ending at their extremity as half-circles (Fig. 2). The lattice image disappears after a few degrees tilt along the rod axis. This agrees with the hypothesis of square rod precipitates limited on a surface by (001) planes. Such arrangement can be compared to the folded graphite sheets observed by Ugarte (1992).

The second type of simple morphology presents a polygonal aspect (50 nm in diameter) (Fig. 3). After tilting, we observe the same shape: it means that this configuration corresponds to a polyhedron limited by a 5 nm thick shell. Lattice imaging of the shell reveals the turbostratic structure of BN (Fig. 4). This structure is an hollowed configuration of the onions observed by Ugarte (1992). Larger hollow spheres (1.5 μm) have been reported by Lindquist et al (1991) but to our knowledge. It is the first time that small scale spheres are observed.

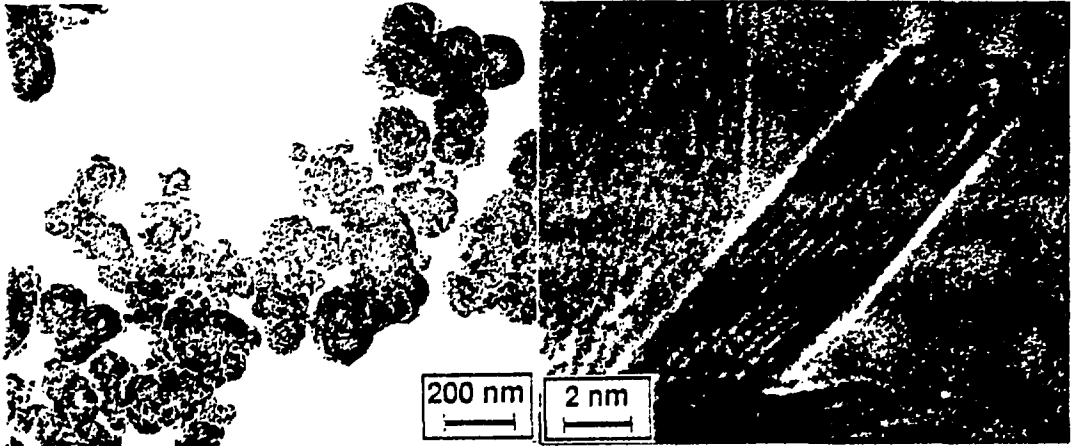


Fig. 1 : Microstructure of the as elaborated state

Fig. 2 : Rods after heating at 1650°C

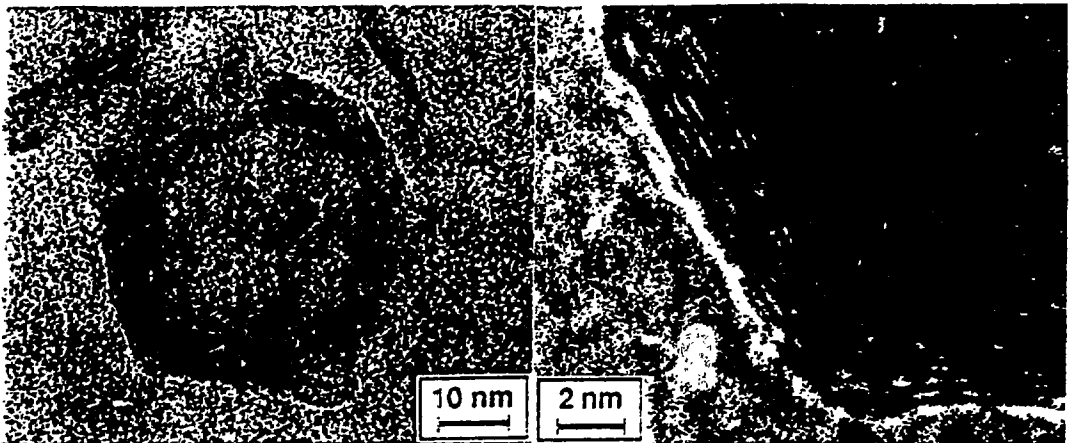


Fig. 3 : Hollow sphere after heating at 1650°C

Fig. 4 : Detail of Fig. 3

- Hamilton E. J. M., Doian S. E., Mann C. M., Coijjn H. O., McDonald C. A., Shore S.G. (1993) *Science* 260, 659-661
 Lindquist D. A., Kodas T. T., Smith D. M., Xiu K., Hietala S. L., Parne R. T. (1991) *J. Am. Ceram. Soc.* 74, 3126-28
 Ugarte D. (1992) *Chem. Phys. Letters* 198, 596-602