UDC 661.65:661.55;539.22-620.18

Oxygen and structure transformations of h-BN in focal zone of an optical furnace

L. L. Sartinska, V. A. Tinkov[*], A. A. Frolov

[*]Kurdyumov Institute for Metal Physics of NASU, Kiev, Ukraine

In this contribution the recent results on a synthesis of the new structures of boron nitride are presented. Light-induced catalyst-free heating of fine-grained graphite-like h-BN powders was performed in the flow of dried and purified nitrogen in an optical furnace. The new structures of boron nitride were obtained. Scanning electron microscopy JSM-6490 supplemented with combined Energy Dispersive X-ray Spectroscopy (EDS) and Electron Backscatter Diffraction (EBSD) provided information about structures, phase and element transformation of fine-grained graphite-like h-BN powders. The coarse structures, thread-like nanostructures (whiskers or dendritic structures) and new morphologies were formed due to the interaction of BN plume with nitrogen ambient on the surface of the heated compacted h-BN samples. Complicated structure and element composition of the whiskers which were formed on the surface of heated samples of compacted h-BN powders were studied by scanning electron microscopy (SEM). X-ray Diffraction (XRD) study demonstrates presence of amorphous phase, pure boron of different modifications and boron nitride of different phase compositions on the surface of these substrates. The process of the synthesis, formation and growth of the nanostructures in an optical furnace was analyzed and understood. A role of oxygen in formation and growth mechanism of BN whiskers was proposed.

Introduction

Boron nitride (BN) has attracted considerable interest over the past decade as a technologically important material, possessing at the same time an interesting combination of physical and chemical properties. BN occurs in several structures ranging from the sp^2-bonded hexagonal BN (h-BN) or sp^3-bonded cubic BN (c-BN) to nanotube or fullarene structures [1, 2].

Boron nitride has a great potential in nanotechnology. Nanotubes of BN can be produced and have a structure similar to that of carbon nanotubes, however the properties are very different: whereas carbon nanotubes can be metallic or semiconducting depending on the rolling direction and radius, a BN nanotube is an electrical insulator with a wide band gap of ~5,5 eV (same as in diamond), which is almost independent of tube chirality and morphology. Similar to other BN forms, BN nanotubes are more thermally and chemically stable than carbon nanotubes which favors them for applications.

Understanding the structure transformation mechanism of boron nitride is of great fundamental and technological interest as point structure transformations play a critical role in the growth of this material and are crucial for the final electronic structure and mechanical properties of BN [3]. In general, the exposure of the BN surface to the energetic light beam, to the bombardment by energetic ions or other particles can give rise to substantial changes within the volume of the material. Among them, local densification or melting, compressive stress or production of point defects are shown to play the dominant role in properties of the final material [4—6]. Molecular nitrogen,

© L. L. Sartinska , V. A. Tinkov, A. A. Frolov, 2009

N_2, may also form easily N–N bonds in BN during ion-bombardment as N atoms [7, 8].

High-temperature methods for structure and phase transformations of boron nitride and carbon all involve sublimating in a reduced atmosphere or rare (inert) gases, brought to temperatures above 3200 ^{o}C and condensing the resulting vapor under a high temperature gradient. What differences the various processes is the method used for sublimating. This can be an electric arc formed between two electrodes, an ablation induced by a pulsed laser or a vaporization induced by a solar or a continuous laser beam.

The solar method, which can be compared with continuous laser vaporization, uses a solar furnace to focus the sunlight on a target and vaporize one. Under clear-sky conditions, temperatures of around 3000 ^{o}C can be reached at the 2 kW set-up of the solar station.

As an optical furnace can be used instead of solar furnace of the same power capacity in any season of year it is important also to research effect of heating in an optical furnace in nitrogen flow on the structure, morphology and phase transformation of BN powders, to analyze the process of formation and growth of nanostructures and to understand the role of an oxygen in the process of structure transformations of pure graphite-like boron nitride to whiskers.

Experimental

The platelet-like fine-grained powders of boron nitride (Chempur, CH070802) have been used as a initial. The origin powders are h-BN textured on 002 with impurity of B_2O_3. The diameter of platelets of boron nitride is ~0,6—1,0 μm and thickness ~0,1 μm. Detail description of origin powders and experimental procedure presented in [9—11].

A quartz chamber was used for process of sublimation of powders (fig.1). Heating of the surface of initial powders was done in a furnace of high intensity optical energy in the flow of nitrogen. An optical light source such as the three xenon light sources can produce over 2 kW of the energy concentrated in the focal zone. A diameter of the spot is 10 mm.

The optical furnace involves also three ellipsoidal reflectors. Xenon tubes are centered in the focus of every ellipsoidal reflector. The calculated value of the density of the light flux energy in the focal zone is about $E = 1{,}4 \cdot 10^4$ kW/m^2

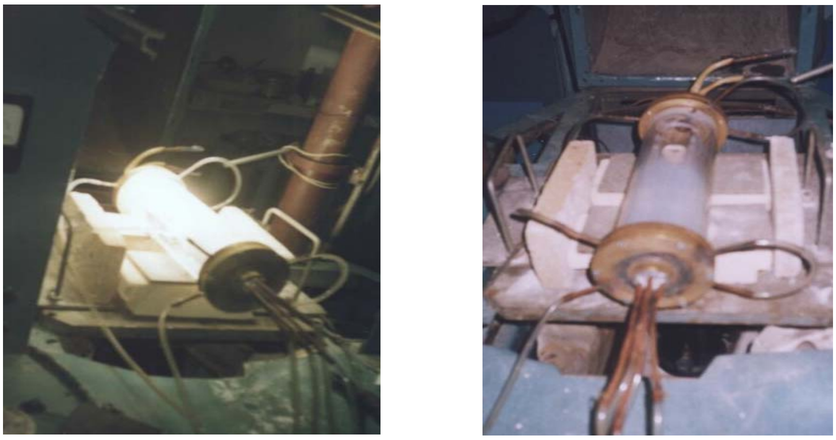

a *b*

Fig. 1. Chamber for h-B transformations: *a* — during the heating; *b* — after experiment.

if the current in the tubes is $I = 300$ A. Because of an emission spectrum of the xenon tubes is closely matched by that of the black-body radiation the calculated temperature in the focal zone is ~4000 K.

Produced compacted samples of origin h-BN powders were tablets (diameter 20 mm and thickness 10 mm). The last were placed on a copper water-cooling screen of the quartz chamber. The chamber was positioned in the centre of radiation of the three xenon emitters. Direct measurements of the temperature were not provided. However heating of h-BN was carried out at the average densities of light flux energy in focal zone of set-up $E \sim 0{,}7 \cdot 10^4$ kW/m^2. Temperature of the blackbody are matched to the xenon tube emission corresponds to ~1400 K. Time of the experiment was 60 min.

The chamber was flowed by purified and dried nitrogen. Cooper chips heated up to 500 ^{o}C purified the nitrogen from oxygen and other pollutions. Platelets of KOH made drying of nitrogen from the water.

Obtained new structures of the BN powders on the surfaces of h-BN compacted samples were examined by optical microscopy and scanning electron microscopy (JSM-6490, JEOL, Japan). The TEM study of whisker structures obtained on the surface of h-BN compacted sample was also carried out. The structure information has been supplemented by X-ray Diffraction (XRD) study (diffractometer DRON-3.0, radiation of K_{α}Cu) of phase composition.

Results and discussion

Surface observation of the heat treated compacted samples of h-BN has demonstrated the formation of the new different structures (fig. 2, 3). Process of heating in optical furnace induced by a light beam involve vaporation and sublimating in a atmosphere of nitrogen, bring to temperatures above 3000 ^{o}C and condensing the resulting vapor under a high temperature gradient. As a result, whiskers were formed at the edge of the crater on the surface of compacted samples of the initial h-BN powders. Such structures were not found in any of the other parts of chamber. It means that occur a proper temperature gradient in the compacting powder enabling vapor transporting from the lower part of the powder to the surface and the growth of filamentary structures only on the surface of compacted samples. The vapors of boron and nitrogen will re-condense and re-vaporize as they are rising and will favour the appearance of bushy whiskers and tiny droplets around crater edge during the light heating (fig. 3) if keep the proper temperature gradient in the samples.

The obtained whiskers were pure, their composition is boron and nitrogen in different proportion of components (fig. 4) that can be explained by turbulence of nitrogen flow in the centre of crater. Generally, whiskers didn't include oxygen.

The drops of different sizes have the elevated boron content and negligible quantity of oxygen (fig. 5). This can be explained by removing of nitrogen from the surface in the process of sublimating and melting of surface layer of the initial powders of h-BN.

Carefully observation of the top of the whiskers demonstrated that their structures are tangled straight sticks fully covered by melted droplets (fig. 6). It is of interest to note that element composition of the top and of the foot of whiskers includes oxygen (fig. 7). Presence of oxygen in the foot of whiskers can be explained by its availability in initial powers of h-BN and its direct lifting movement.

Fig. 2. Surface of compacted h-BN sample after heating in optical furnace.

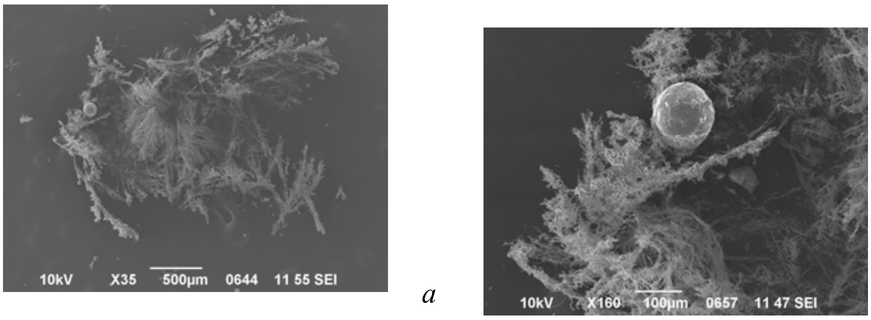


Fig. 3. Whiskers and drops formed on the surface of heated h-BN sample around a crater.

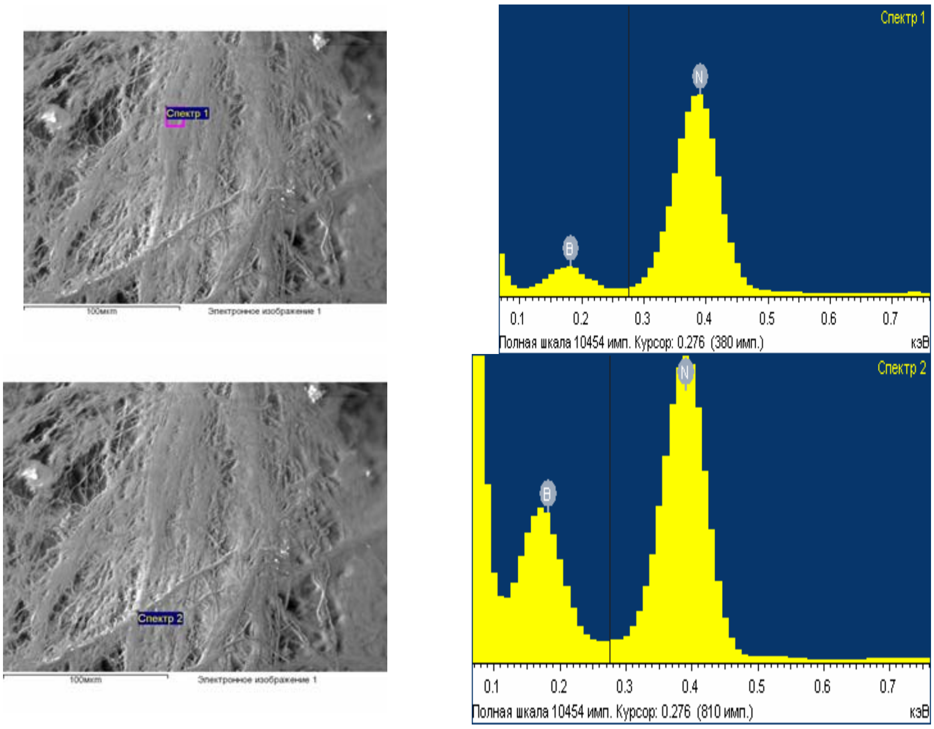


Fig. 4. Element distribution of the obtained whiskers.

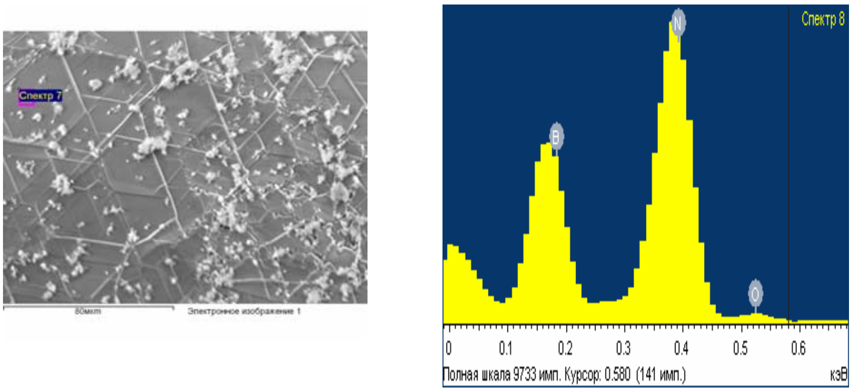


Fig. 5. Element distribution of obtained drop.

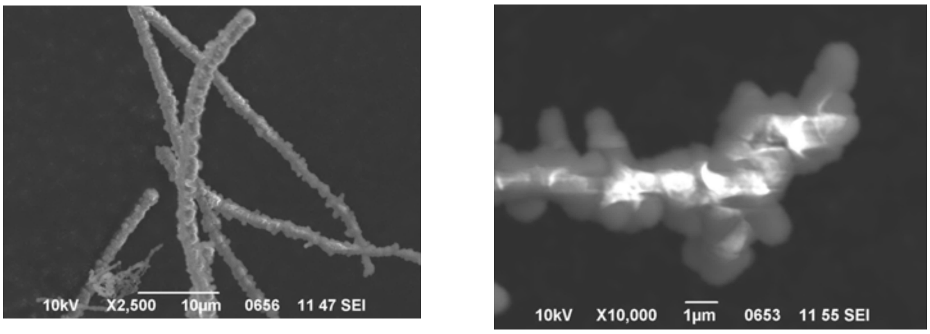
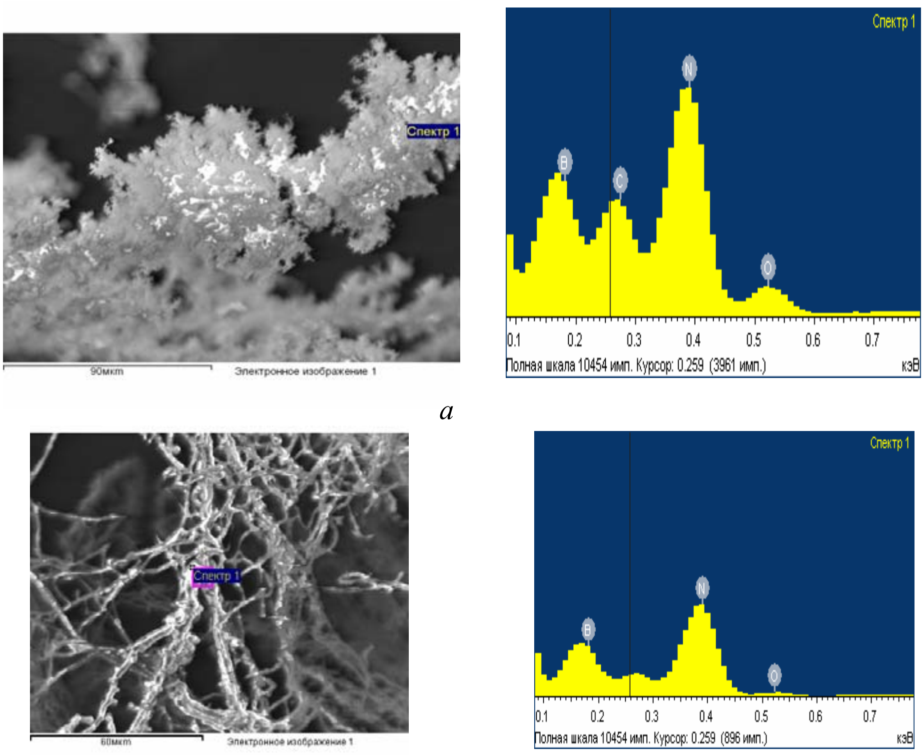


Fig. 6. Structure of the whiskers top.



a

b

Fig. 7. Element composition of the top and of the foot of the whiskers.

Based on above mentioned result and the principal trend of the oxygen to go up during heating from the a bottom layers of initial material it is possible to suppose that oxygen together with temperature gradients are the main driving force for the growth of whiskers.

Conclusions

Thus, heating in focal zone of an optical furnace initiates a structure transformation of h-BN in pure BN whiskers.

The lifting motion of oxygen from the bottom layers of initial material under light heating of the surface at the temperature gradient is the main driving force, which contribute to whisker formation and growth.

Acknowledgements

We acknowledge support of STCU project No. 4133.

1. *Chopra N. G., Luyken R. J., Cherrey K. et al.* // Science. — 1995. — 26. — P. 966.
2. *Goldberg D., Bando Y., Han W. et al.* // Chem. Phys. Lett. — 1999. — **308**. — P. 337.
3. *Mosuang T. E., Lowther J. E.* // Phys. Rev. B 66 (2002) 014112.
4. *Hofsдss H., Feldermann H., Eyhusen S., Ronning C.* // Ibid. B 65 (2002) 115410.
5. *Jimйnez I. et al.* // Ibid. B 55 (1997) 12025
6. *Gago R., Abendroth B., Cerdб J. I. et al.* // Ibid. B 76 (2007) 174111.
7. *Hecht J.-D., Frost F., Hirsch D. et al.* // J. Appl. Phys. 90 (2001) 6066.
8. *Petravic M., Gao Q., Llewellyn D.* // Chem. Phys. Lett. 425 (2006) 262.
9. *Frolov A. A., Andrievskaya E. P., Sartinska L. L.* // Inttrnat. conf. “Modern Materials Science: Achievements & Problems", Proc., 26—30 Sept. 2005. Kyiv, Ukraine, 174—175pp. (in Russian).
10. *Sartinska L. L., Frolov A. A., Koval' A. Yu. et al.* Transformation of fine-grained graphite boron nitride induced by concentrated light energy // Mater. Chem. and Phys. — 2008. — **109**. — P. 20—25.
11. *Frolov A. A., Sartinska L. L., Koval' A. Yu., Danilenko N. A.* Application of the optical furnace for nanosized boron nitride production // Nanomaterials. —2008. — No. 2—4. — P. 115—120. (in Russian).