

Plasmachemical nitridation of boron precursors

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The aim of the present work is to introduce two possible methods of preparation of the boron nitride (BN) by means of plasmachemical techniques. The first method is based on capacitively coupled RF discharge at low pressure and the second one on plasma torch operating at atmospheric pressure. The product in the form of powder was analysed by X-ray diffraction and infrared absorption spectroscopy. We found that the products contained both crystalline forms of BN (hexagonal and cubic). The content of amorphous phase depended on the experimental conditions.

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1 Introduction

The boron nitride is an advanced ceramics with outstanding physical and chemical properties, especially the high resistivity together with a high thermal conductivity. It is often used in the metallurgy due to its inertness to metal and glass melts and its high thermal stability (up to 2700°C). Hexagonal phase of BN (h-BN) is very soft ($H_V < 0.35$ GPa) and easily machinable. The cubic phase (c-BN) is extremely hard (50 GPa) and can be used for wear protection of cutting tools.

Due to the lack of a melting point, the bulk BN must be prepared by sintering. The temperature of this process depends on temperature at which the BN powder was prepared: lower temperature for nitridation of the precursors corresponds to a lower temperature of sintering process. Consequently, lowering the temperature of nitridation can be very advantageous for industrial use.

As many chemical reactions can run at lower temperatures in the plasma reactors than in classical conditions, we tried to prepare BN powder from boron containing precursors using nitrogen plasma.

2 Experimental setups

We have used two different reactor setups for plasmachemical preparation of BN powder.

In the first arrangement, the capacitively coupled discharge was generated inside the quartz tube (i.d. 40 mm, length 900 mm) between two symmetric electrodes.

The RF generator operated at the frequency of 13.56 MHz with the power output of 400 W. The flow rate of nitrogen was 50 sccm, which corresponds to total pressure 130 Pa. Reactor could be heated up to 600°C (Fig. 1). Boric acid (H_3BO_3) and urea ($(\text{NH}_2)_2\text{CO}$) were used as the precursor for preparation of the boron nitride.

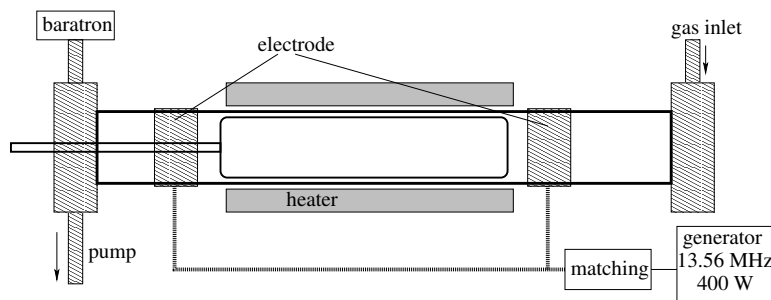


Fig. 1. Experimental setup 1 (low pressure RF discharge).

The second setup used an unipolar plasma torch operating at atmospheric pressure. It was powered by 2450 MHz, 1 kW generator through circulator, waveguide-coaxial transition and matching. Trimethylborate prepared from boric acid and methanol was dried by sulphuric acid and inserted into the flow of working gas (1.0 slm of argon and 1.8 slm of nitrogen). Plasma column was produced at the top of a hollow central electrode of the coaxial line (Fig. 2). The torch burned in a quartz tube with the inner diameter of 40 mm to prevent contact with air. Product of the reaction in the form of a fine powder was filtered out from effluent gases.

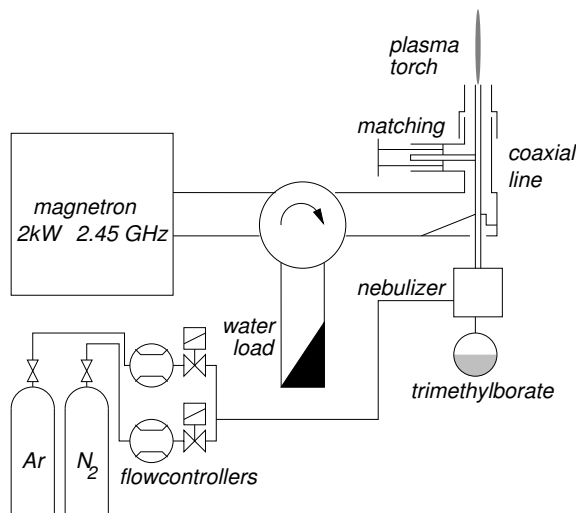


Fig. 2. Experimental setup 2 (atmospheric plasma torch).

3 Results and discussion

The solid products of our plasmachemical process were analysed by FTIR and XRD and their morphology was observed by microscope. The process itself was examined by optical emission spectroscopy and by IR absorption of effluent gases.

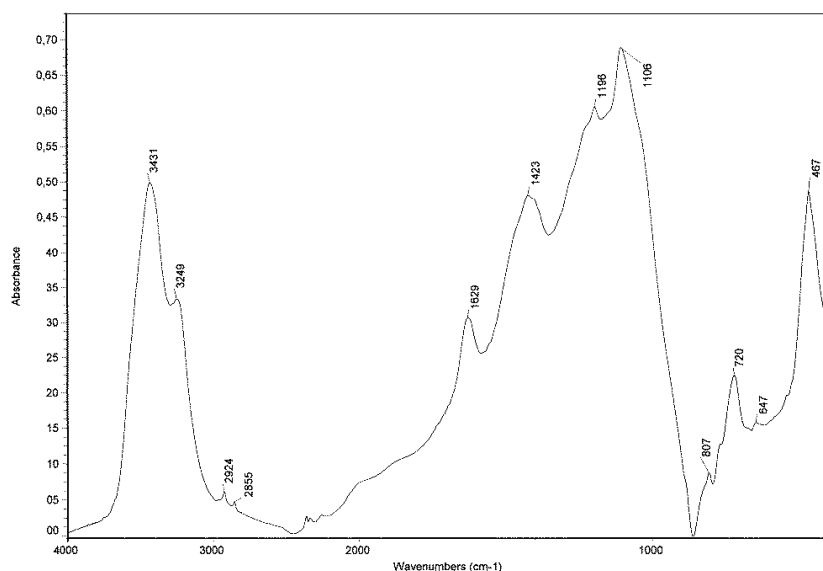


Fig. 3. FTIR spectra of BN prepared by capacitively coupled discharge. The temperature during the process was kept at 600°C

Results from infrared absorption spectroscopy on samples prepared in Apparatus 1 (low pressure discharge) are presented in Figs. 3 and 4. For sp^2 -bonded crystalline h-BN or amorphous BN, there are two characteristic peaks at about 1400 cm^{-1} and 800 cm^{-1} , which are associated with the in-plane (IP) B–N bond stretching vibration and the out-of-plane (OOP) B–N–B bending vibration, respectively [2]. On the other hand, c-BN with sp^3 hybridization has an infrared active TO mode around 1100 cm^{-1} . Other peaks about 3400 cm^{-1} and 1600 cm^{-1} are present due to hydroxyl group OH [3].

In FTIR spectra taken on the samples prepared in Apparatus 2 (microwave torch) show typical peaks for both h-BN and c-BN. However, the bands typical for boron oxide (B_2O_3) are present too. Sample in Fig. 5 was prepared at a higher input power and therefore the temperature was also higher. Here, the BN/ B_2O_3 ratio is higher, as predicted by thermodynamic calculation (Table 1). For sample prepared at lower temperature Fig. 6, there is more boron oxide than boron nitride. The fact that temperature was not sufficient for BN preparation is also supported by high content of CO_2 in comparison to CO in effluent gases (as determined by FTIR absorption) and by presence of pyrolytic carbon in product.

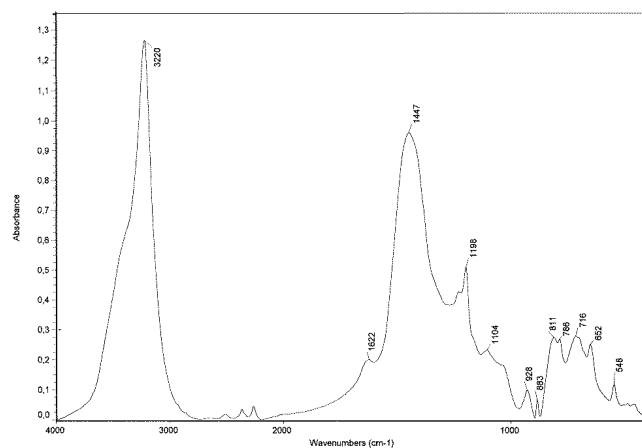


Fig. 4. FTIR spectra of BN prepared by capacitively coupled discharge without additional heating.

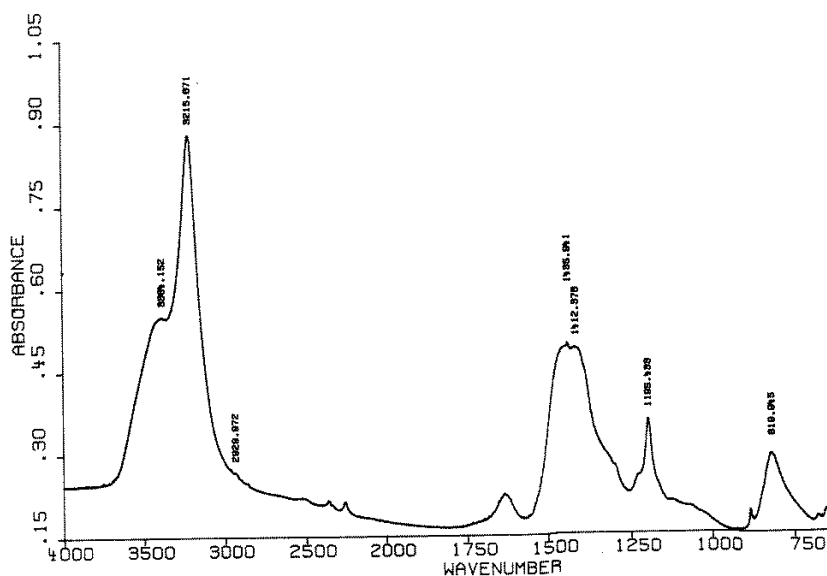


Fig. 5. FTIR spectra of BN prepared in plasma torch, power 800 W

Although the temperature in plasma channel is much higher than 1500 K necessary for successful BN preparation (see Table 1), the time of reaction was probably not sufficient due to high flow rate and relatively compact plasma core (1 mm diameter, 1 cm length). Diffusive region around a core of the torch was sufficiently long (more than 10 cm) but had considerably lower temperature. It should be noted that

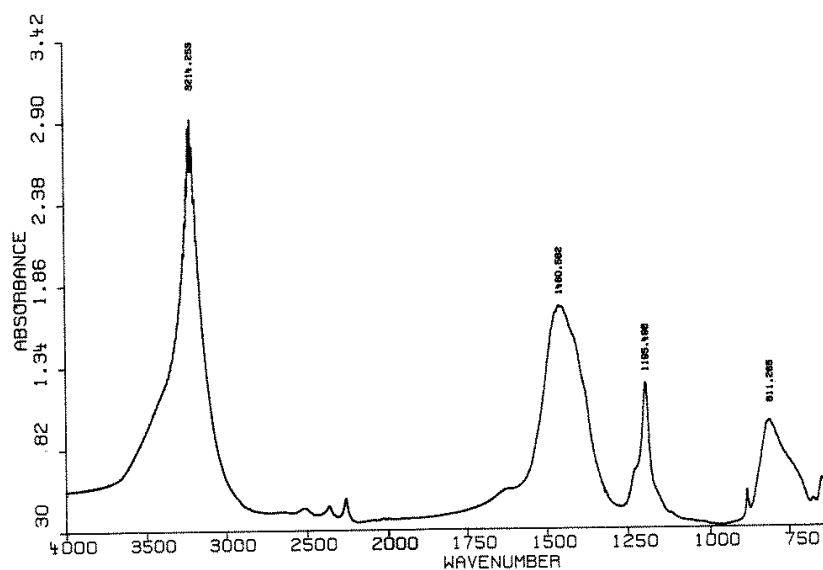


Fig. 6. FTIR spectra of BN prepared in plasma torch, power 1000 W

Table 1. Thermodynamic calculations of preferred products of reaction $(\text{CH}_3\text{O})_3\text{B}+10\text{N}_2$. Values represent mol.%. For details see [1].

compound	500K	1000K	1500K	2000K
BN	0	0	0.999	0.997
B_2O_3	0.49	0.49	0	0
C	1.4	1.58	0	0
CO	0.003	8	17.6	17.6
CO_2	0.69	0.37	0.004	0.001

chemical calculations were carried out under assumption of thermal equilibrium, which is not fully satisfied by torch plasma.

Fig. 7 shows results of XRD analysis of BN powder prepared without heating. The results are in good agreement with the standard powder diffraction pattern of boron nitride. The peaks at $2\Theta = 27.0^\circ, 41.8^\circ, 55.1^\circ, 76.0^\circ$ correspond to (002), (100), (103) and (110) orientations of the h-BN phase. The small peaks observed at $2\Theta = 43.6^\circ$ and 50.8° corresponds to (111) and (200) orientation of c-BN [3, 4]. Therefore the powder consists of both phases of boron nitride and is crystalline.

The XRD results of powder BN prepared in the RF discharge at temperature 600°C are presented in Fig. 8. The spectrum consists of two broad peaks with relatively low intensities. One peak is positioned between 23° and 29° and the other one between 40° and 44° . The Bragg angles of these peaks agree with Bragg angles of (002) and (100) reflection of amorphous structure of BN [4].

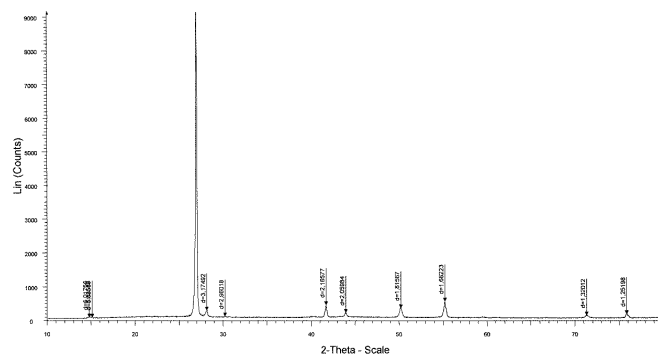


Fig. 7. XRD analysis of BN prepared by capacitively coupled discharge without heating

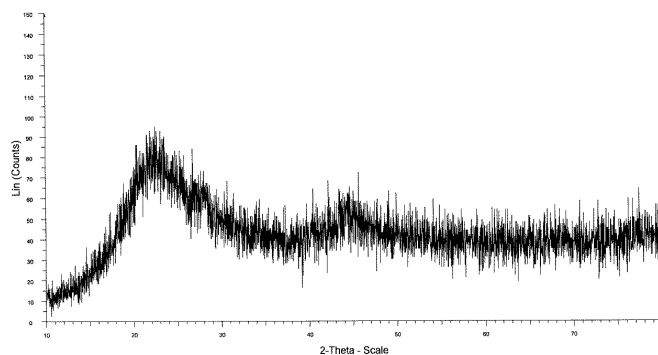


Fig. 8. XRD analysis of BN prepared by capacitively coupled discharge. The temperature during the process was raised to 600°C by additional heating

It seems that at lower temperature of preparation both crystalline phases are formed but at higher temperatures the BN became amorphous.

XRD analysis of the products, prepared in the microwave plasma torch show that the sample is amorphous. This is in agreement with a previous paragraph, because the temperature in the plasma channel was several thousands of degrees.

4 Conclusions

Plasmachemical preparation of BN is very dependent on temperature in both experimental setups. Generally we observe that for lower temperature the product is more crystalline, for higher temperatures amorphous.

Despite high temperature in microwave torch the short reaction time negatively affected the production of BN and considerable part of powder was boron oxide.

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