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High-Purity, Fine-Particle Boron Nitride Powder Synthesis at -75° to 750° C

By Rustu S. Kalyoncu

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	μm	micrometer
°C	degree Celsius	m^2/g	square meter per gram
g	gram	pct	percent
g/cm^3	gram per cubic centimeter	ppm	part per million
h	hour	psi	pound per square inch
mL/min	milliliter per minute		

HIGH-PURITY, FINE-PARTICLE BORON NITRIDE POWDER SYNTHESIS AT -75° TO 750° C

By Rustu S. Kalyoncu[1]

ABSTRACT

Nonoxide ceramics with improved high-temperature properties could substitute for high-temperature alloys and reduce the Nation's dependence on imports of Cr, Co, Ni, and Mn. To meet this objective, the Bureau of Mines conducted research to synthesize ultrafine reactive boron nitride (BN) powders.

BN powders were prepared at temperatures ranging from -75° to 750° C. Low-temperature reactions (-75° to 200° C) between boron halides and N compounds led to formation of elemento-organic compounds that were thermally decomposed to ultrafine (approximately 100- to 150-Å particle size) reactive BN powders.

BN powders were also prepared through the reaction of a low-melting inorganic B compound (boric acid, borax) with an organic N compound (carbimide and thiocarbimide) in N_2 and/or ammonia (NH_3) atmospheres at temperatures between 500° and 750° C.

INTRODUCTION

There has been increasing interest in structural materials that can withstand severe conditions of temperature, pressure, and environment and can substitute for high-temperature alloys that require imported critical materials such as Cr, Co, Ni, and Mn.

Nonoxide ceramic materials, such as nitrides, carbides, and borides, are extremely hard and exhibit high mechanical strength and erosion, oxidation, corrosion, and thermal shock resistance at elevated temperatures. Silicon nitride ceramics, for example, show great promise for use as structural components in gas turbine and diesel engines. The nonoxide ceramic, BN, is not wetted by molten Fe, Al, Cu, brass, Ni, or Zn and therefore has excellent corrosion resistance to these melts. It withstands rapid heating and quenching at 1,500° C and has a thermal conductivity comparable with that of stainless steel. These characteristics make BN indispensable in many applications such as crucibles for metal evaporation, corrosion-resistant jigs, transistor heat sinks, nuclear reactor control rods, and neutron absorbers.

In support of its mission of conserving the Nation's mineral resources by identifying materials with improved performance, the Bureau of Mines initiated research on novel methods of producing ultrafine reactive BN powders.

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[1] Ceramic engineer, Tuscaloosa Research Center, Bureau of Mines, University, AL.

BACKGROUND

Extensive literature, published during recent years, identifies three general methods of fine-particle preparation (1):[2] (1) solution techniques, (2) vapor-phase techniques, and (3) salt decomposition techniques. Solution techniques, also referred to as "chemical" preparation (2), offer the advantages of ease of preparation, good control of composition, and homogeneity. Among the solution techniques a number of terms, such as "codecomposition" (3), "evaporative decomposition from solutions" (EDS) (4-5), "citrate process" (6), and "alkoxide process" (7) are frequently encountered.

Vapor-phase techniques are receiving more and more attention, due mostly to interest in high-performance structural ceramics such as SiC and Si_3N_4. These techniques lead to unaggregated powders. Among the techniques in this category are all plasma methods (8-9) and others involving gaseous reactants.

Decomposition of precursor salts (e.g., oxalates) has been employed in the preparation of fine-powder carbides (10-11).

BN powders have been prepared by the reaction of boron oxides and borates with ammonium chloride (NH_4Cl) in N_2 and NH_3 atmospheres (12). In certain reactions, in order to increase the reaction rates in the solid state, that is, to effectively increase the reaction surface areas, inert fillers such as $CaCO_3$ and calcium phosphates have also been employed (13). Ammonium salts other than NH_4Cl have also been used in BN synthesis. Ammonium thiocyanate, for example, resulted in much higher reaction rates with boric acid in the BN synthesis (14).

Among the less conventional laboratory techniques reported for the preparation of nonoxide ceramic powders are the reaction of compounds (such as silanes, boranes, and halides) containing the desired cations in super-high-frequency discharge plasma (15), chemical vapor deposition techniques (16-22), and the use of laser energy (23). Similar reactions have also been studied employing conventional high-temperature furnaces at 1,500° to 1,900° C (24-27).

Production of complex nitride powder has been studied by the nitridation of metal halides ($SiCl_4$, BCl_3) in an N plasma (15). Chemical vapor deposition techniques have also been used to prepare thin films of BN, Si_3N_4, and TiN (8-12). Extremely fine, uniform Si_3N_4 and SiC powders have been synthesized from SiH_4, NH_3, and C_2H_4 gas-phase reactants heated by a CO_2 laser (23). Nitrides of Si, B, and Ti have also been prepared by the reaction of their halides with ammonia or ammonia salts at high temperatures (24-27).

No mention of preparing BN from halides of B with the reaction of ammonia salts or ammonia in the liquid phase has been made in the literature. In view of this finding, research efforts included a study of obtaining ultrafine BN powders from the reactions of halides with NH_4Cl and NH_3 in the liquid phase.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

REACTIONS BETWEEN 500° AND 750° C

Two different approaches were evaluated for the synthesis of fine BN powders. The first was the reaction between an inorganic B compound and an organic N compound between 500° and 750° C in an NH_3 atmosphere. For this a high-temperature controlled-atmosphere furnace was used. Inorganic B compounds used included boric oxide (B_2O_3), boric acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$), and anhydrous sodium tetraborate ($Na_2B_4O_7$). Carbimide ($NH_2 \cdot CO \cdot NH_2$) and thiocarbimide ($NH_2 \cdot SO \cdot NH_2$) were used as N_2 sources. The powdered reactants were mixed in stoichiometric proportions and placed in the furnace. The furnace chamber was evacuated and purged with NH_3 gas before the temperature was raised. Experiments ran from 4 to 24 h at 500° to 750° C.

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[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

REACTIONS BETWEEN -75° AND 200° C

The second approach involved the synthesis of BN through reactions between various N and B compounds leading to the formation of possible elemento-organic compounds as intermediate precursor species, the decomposition of which might lead to BN formation. Such compounds included NH_3, boron halides (principally boron trichloride, BCl_3), ammonium chloride (NH_4Cl), and sodium borohydride ($NaBH_4$).

For the second approach, material preparation and handling procedures were performed in a dry-box system, a simplified schematic of which is shown in figure 1. The atmosphere in the box was maintained by a VAC Dri-train[3] unit capable of generating an inert gas atmosphere containing less than 1 ppm O_2 and/or moisture. This high-purity inert atmosphere was obtained by circulating the gas in a closed system going through a purifying chamber equipped with molecular sieves to trap O_2 and moisture. Figure 2 shows the dry-box assembly. Reactions were carried out in the experimental unit (fig. 3) consisting of a three-necked, 500-mL glass reaction vessel and a small vacuum system with cold traps.

Three systems were studied. They included ammonia-boron halide, ammonium salt-boron halide, and ammonium salt-metal borohydride reactions.

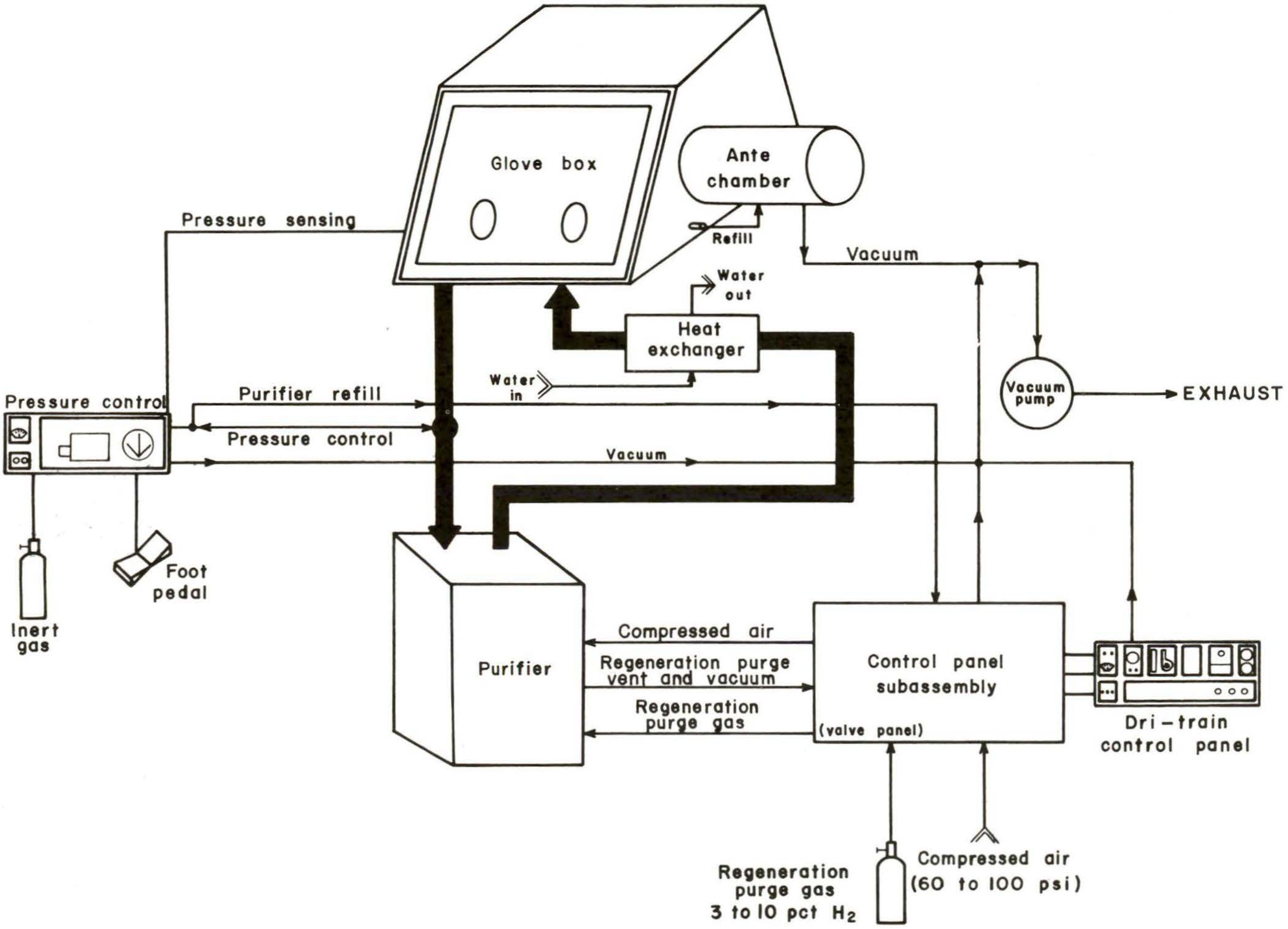

FIGURE 1. - Simplified schematic of Dri-train equipment.

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[3] Reference to specific products does not imply endorsement by the Bureau of Mines.

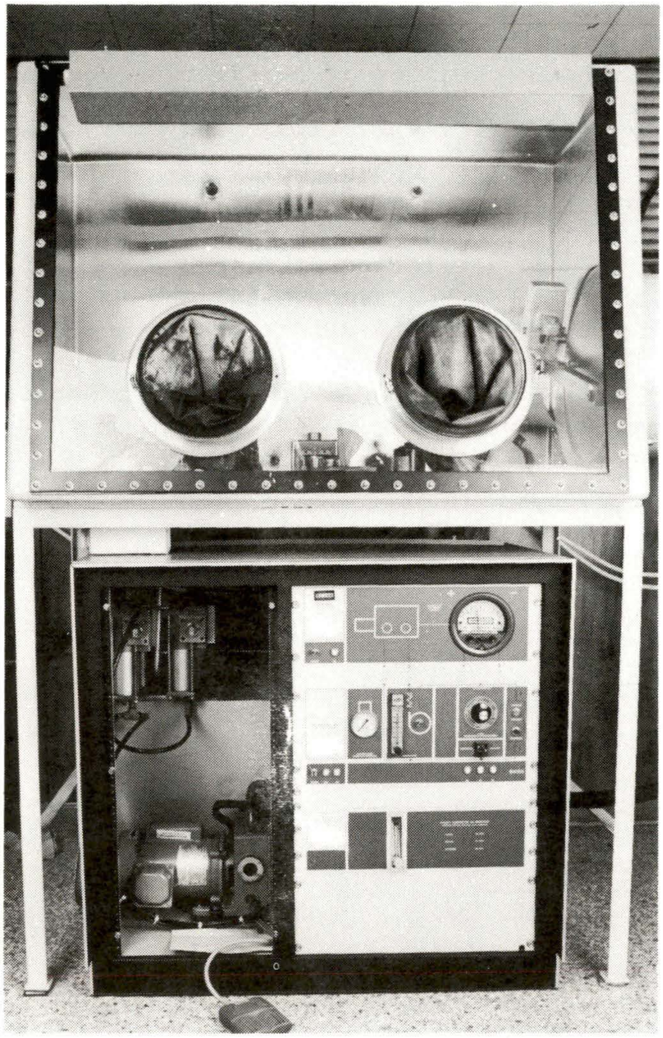

FIGURE 2. - Glove box and Dri-train equipment.

Ammonia-Boron Halide Reactions

Prior to introduction of reactants to the three-necked reaction vessel, the system was evacuated to a nominal vacuum, then flushed with dry NH_3 gas. The reaction vessel was then cooled in a Dry Ice-acetone bath, while the system continued to be flushed with excess dry NH_3 gas. During this cooling process, the dry NH_3 gas, introduced to the vessel through the inlet tube affixed to one side neck of the flask, condensed in the flask. After liquid NH_3 had accumulated in the flask, the second reaction component, BCl_3, was introduced to the vessel through the other side neck of the flask. The rate of BCl_3 gas flow into the system was maintained at 20 mL/min.

Ammonium Salt-Boron Halide Reactions

In this system NH_4Cl was refluxed with a benzene solution of BCl_3 using a three-necked flask that had been provided with a water-cooled reflux condenser connected to two cold traps of Dry Ice-acetone and liquid N_2, respectively. A dry N_2 atmosphere was maintained over the reaction medium in the flask through the second neck.

About 15 g (0.25 mol) NH_4Cl and 200 mL of freshly distilled dry benzene were placed in the reaction vessel. A cylinder of BCl_3 was connected to the inlet tube of one of the side necks. The contents of the flask were heated to a reflux temperature of 200° C while the reaction medium was agitated with a magnetic stirrer. BCl_3 was bubbled through at a rate of 20 mL/min.

Ammonium Salt-Metal Borohydride Reactions

The apparatus and procedure employed in the study of reactions between ammonium salts and metal borohydride were identical to those used in the previously described reaction between ammonium salt and boron halide in an organic solvent.

Approximately 10 g (0.25 mol) $NaBH_4$ and 12 g (0.25 mol) NH_4Cl were placed in the three-necked reaction flask. Then 200 mL of freshly distilled dry benzene was added to the flask under a flow of dry N_2 with the flask attached to a vacuum line, and care was taken to prevent air and moisture from entering the system. The reaction vessel was heated in a mineral oil bath at 170° to 180° C, and the reaction mixture was stirred vigorously with a magnetic stirrer. After a 14-h reaction time the solvent was removed by vacuum at 80° C and the remaining dry-solid residue was heated to 300° C under vacuum for several hours.

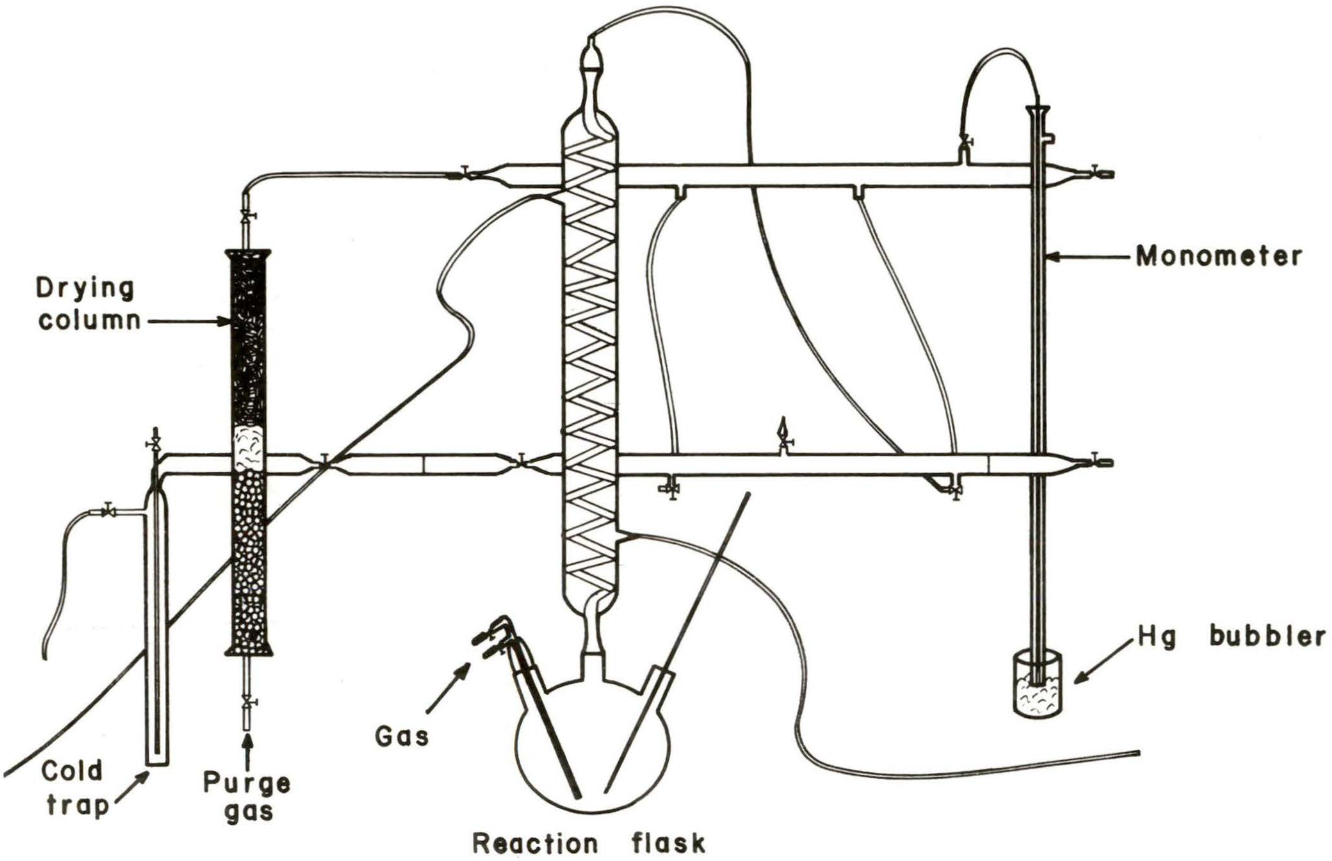

FIGURE 3. - Schematic of reaction apparatus.

RESULTS AND DISCUSSION

REACTIONS BETWEEN 500° AND 750° C

Efforts to synthesize BN from boric acid, boric oxide, and anhydrous sodium borate with carbimide in N_2 and NH_3 atmospheres are summarized in table 1.

Reactions of boric acid and boric oxide with carbimide at 500° C resulted in amorphous reaction products identified as borate glass with minute quantities of N_2 incorporated in its structure. At higher temperatures (750° C) and in an NH_3

TABLE 1. - Inorganic-organic reactions in BN synthesis

Reactants in NH_3 atmosphere	Temp, °C	Reaction time, h	Reaction products	Observations
Boric acid or boric oxide....	500	24	Borate glass........	No sign of BN formation.
Boric acid or boric oxide + inert filler.	500	24	...do...............	Do.
Do........................	750	24	Borate glass + small amount of BN.	Very low-yield BN formation.
Boric acid or boric oxide + carbimide.	750	24	Borate glass + appreciable BN.	None.
Borax anhydride + carbimide..	750	4	BN + byproducts.....	BN yield >50 pct.
Borax + carbimide...........	750	4	...do...............	BN yield ~75 pct.
Borax + thiocarbimide.......	750	4	...do...............	BN yield >90 pct.

atmosphere with reaction times of 24 h or longer, formation of BN was observed. This reaction, however, was low yielding, probably owing to the decreased reactive surface area of the boric anhydride upon melting at 450° C. To increase the yield, the effective surface area of the boric acid was increased by the addition of tricalcium phosphate ($Ca_3(PO_4)_2$) as an inert filler. This resulted in BN yields as high as 75 pct for reaction times of 24 h. The synthesis process may be represented by the following reaction:

$$B_2O_3 + NH_2{\cdot}CO{\cdot}NH_2 \xrightarrow{750^\circ\ C} 2BN + CO_2 + 2H_2O. \qquad (1)$$

When borax and carbimide were used as reactants in an NH_3 atmosphere, BN formation proceeded much faster than in the boric acid-carbimide system. The reaction could be represented by--

$$Na_2B_4O_7{\cdot}10H_2O + 2NH_2{\cdot}CO{\cdot}NH_2 \xrightarrow{750^\circ\ C} 4BN + Na_2O + 2CO_2 + 14H_2O. \qquad (2)$$

Reaction products obtained were washed in dilute HCl, and the insoluble portion was filtered out. X-ray diffraction (XRD) analysis of the filtered powder indicated that it was amorphous. Heat treatment of this material at 1,400° C in an N_2 atmosphere for several hours resulted in crystalline BN powder based on XRD patterns. The BN yield of reaction 2 was as high as 95 pct of expected theoretical value. It appears that dehydration of borax at temperatures (200° to 400° C) below the reaction temperature results in a spongelike anhydrous borax with a very high surface area. This, along with the decomposition of the carbimide to produce additional NH_3 gas of high reactivity, results in higher BN yields.

The same reaction run in an N_2 atmosphere resulted in lower yields. The higher yields produced in an NH_3 atmosphere compared to an N_2 atmosphere may be due to the higher reactivity of N_2 produced by NH_3 decomposition at 450° C. The H_2 produced as a result of NH_3 decomposition might also have a catalytic effect on the reaction, resulting in higher yields.

The use of thiocarbimide (NH_2SONH_2) as the organic N_2 source further increased the reaction rate, as evidenced by the shorter time required for the reaction to reach completion. In the reaction with thiocarbimide, sodium sulfides were produced as potential reaction byproducts, which may further decompose at about the reaction temperature of 750° C. This decomposition process at the BN-formation temperature results in spongelike high-surface-area material, thus accelerating the reaction rates.

REACTIONS BETWEEN -75° AND 200° C

Ammonia-Boron Halide Reactions

Once the reactants (NH_3 and BCl_3) are introduced into the three-neck reaction flask, reaction starts immediately, as evidenced by formation of a white powder around the walls of the reaction flask. This reaction is allowed to continue for 2 to 3 h. At the end of such time the excess liquid NH_3 remaining in the flask is removed by vacuum, the white powdered reaction product is isolated and dried at room temperature. The following two reactions appear to take place either concurrently or consecutively:

$$6NH_3\ (\text{liquid}) + BCl_3\ (\text{liquid}) \xrightarrow{-75^\circ\ C} B(NH_2)_3 + 3NH_4Cl, \qquad (3)$$

$$3NH_3\ (\text{liquid}) + 3BCl_3 \xrightarrow{-75^\circ\ C} Cl_3{\cdot}B_3{\cdot}N_3{\cdot}H_3 + 6HCl. \qquad .(4)$$

The intermediate reaction products, elemento-organic BN compounds, that may be formed in these reactions have not been isolated and identified. The general chemistry of these systems, however, suggests the formation of such compounds and the precipitation of BN as a result of their carbothermic decomposition.

An attractive feature of these reactions appears to be their general applicability to the preparation of other nitrides, such as AlN, TiN, and Si_3N_4. Future efforts should be directed toward a study of the reaction mechanisms through the isolation and characterization of the intermediate precursor compounds. Understanding these reactions would help determine the feasibility of the formation of other nitride compounds at low temperatures.

XRD analysis of the dried material identified the presence of NH_4Cl in reaction 3; detection of HCl fumes through the mercury bubbler in the reaction set confirmed reaction 4.

The rest of the powder in the reaction products was amorphous to X-rays. After being heated in vacuum at 200° to 250° C for several hours, the powder was still amorphous to XRD. Heat treatment of the powder at 1,200° to 1,400° C for several hours resulted in BN detectable by XRD. A chemical analysis of the powder after washing in dilute HCl acid solution and filtration revealed 42.4 pct B, 53.1 pct N, and 0.7 pct O. Low O_2 content of the sample illustrates the appropriateness of the method for preparing high-chemical-purity BN compared to borax technique ($O_2 \cong 5$ pct). Surface area of BN powder prepared by this method was measured to be 80 to 100 m^2/g depending on the temperature of crystallization. Surface area and particle size of a commercially available BN powder were determined to be 10 m^2/g and 45 µm, respectively. Densities (helium pycnometer) were 2.18 to 2.21 g/cm^3.

Ammonium Salt-Boron Halide Reactions

As previously described the reaction was allowed to proceed for 8 to 12 h. The flask was then cooled to room temperature, and the organic solvent was removed by vacuum followed by heating the solid residue in vacuum to 200° to 250° C for several hours. XRD analysis of reaction product(s) showed an amorphous component and NH_4Cl. Further heat treatment of this powder at 1,200° to 1,400° C in vacuum or N_2 atmosphere resulted in BN powder detectable by XRD. A possible reaction sequence may be--

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{Benzene}]{\sim 80°\ C} Cl_3 \cdot B_3 \cdot N_3 \cdot H_3 + 9HCl, \qquad (5)$$

then, upon heating in vacuum at approximately 250° C,

$$Cl_3 \cdot B_3 \cdot N_3 \cdot H_3 \xrightarrow{\Delta} 3BN + 3HCl. \qquad (6)$$

Elemental analysis of the BN thus obtained gave 42.8 pct B, 54.1 pct N, and 2.5 pct O, which is similar to the composition of the BN powder from the ammonia-boron halide reaction and compares favorably with theoretical composition of BN (B/N = 0.79).

Surface area and density measurements gave values ranging from 80 to 110 m^2/g and 2.15 to 2.20 g/cm^3, respectively.

Ammonium Salt-Metal Borohydride Reactions

White powder formed by the NH_4Cl + $NaBH_4$ reaction was isolated upon the removal of organic solvent by vacuum and heating of the sample to 200° to 250° C under vacuum for several hours. As with the two previous reaction systems, this powder was amorphous to X-rays; only upon heat treatment at 1,200° to 1,400° C in vacuum or N_2 for several hours was BN detected by XRD analysis.

Chemical analysis of the powder showed 42.0 pct B, 52.7 pct N, and 2.3 pct O, which again compared well with the theoretical BN composition and the powder from the other two reaction systems described.

Values of 70 to 200 m^2/g and 2.15 to 2.22 g/cm^3 were obtained for the surface area and density, respectively.

In addition to surface area, density and elemental analysis attempts were made to measure the particle size by direct methods; namely, by scanning electron microscope (SEM) and X-ray line-broadening techniques.

SEM measurements indicated particle size values ranging from 0.3 to 5.0 µm. These large particle size values appear to be due to difficulties in obtaining effective dispersion of the ultrafine particles for SEM photomicrographs. X-ray line-broadening techniques yielded values between 100 to 200 Å, which compare well with the Brunauer-Emmet-Teller (BET) surface area values (approximately 150 Å).

CONCLUSIONS

Submicrometer-size BN powders can be obtained by reacting borax with carbimide in an NH_3 atmosphere at temperatures up to 800° C. It is important to keep the reaction temperatures below the melting point of reactants; otherwise, the effective reactive surface area of the borax decreases drastically upon the melting of borax, slowing the reaction rates considerably. Where the reaction temperatures exceed the melting points of the reactants, the effective surface area can be increased by using inert powders in the reaction mixtures.

Fine amorphous BN powder has also been prepared through reaction systems involving B and N compounds, such as metal borohydrides, boron halides, and NH_3, at low temperatures ranging from -75° to 200° C (in quantities of 1 to 3 g). The BN powders obtained exhibited fine particle size (100 to 150 Å) and high surface areas (70 to 200 m^2/g). In addition to very fine particle size and high surface areas, these reactions also result in powders with lower O contents (1 pct or less) than those produced by more conventional techniques.

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[4] A title enclosed in parentheses is a translation from the language in which the work was published.

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