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Chemistry

MASTER

**PREPARATION OF HIGH-PURITY BORON
NITRIDE POWDER**

C. R. Schmitt
R. K. Edwards

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** **Contract W-7405 eng 26**

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Nuclear Division

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ABSTRACT

Laboratory studies were made on the preparation of high-purity boron nitride powder by the reaction of a mixture of boric oxide and tricalcium orthophosphate with ammonia at 900° C. Many experimental parameters were studied, namely: reaction temperature, time at the reaction temperature, purity and dryness of gaseous ammonia, chemical removal of the calcium filler compound by dilute hydrochloric acid treatment, purification of boron nitride product by removal of unreacted boric oxide by alcohol extraction, low-temperature steam volatilization, and renitridation at 1,400° C.

Nitrogen analysis of laboratory-prepared boron nitride powder showed that 98.4 percent of the theoretical nitrogen content of boron nitride was obtained, and X-ray diffraction analysis identified hexagonal boron nitride as the major constituent with no other detectable intermediate or minor constituents. Various types of laboratory-prepared and commercial boron nitride powders were also characterized by electron photomicrographs.

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SUMMARY

A study was conducted on the preparation of high-purity boron nitride powder by the reaction of a mixture of a boron compound (B_2O_3 or H_3BO_3) and a calcium filler compound ($CaCO_3$ or $Ca_3(PO_4)_2$) with gaseous ammonia at $900^\circ C$. Paste formulations and procedures were developed for making 1/4 or 1/2-inch-diameter shreds of a mixture of boric oxide and the tricalcium phosphate filler compound that would be suitable for nitriding experiments, and an experimental apparatus was assembled for studying the parameters involved in the nitriding of these shreds at $900^\circ C$.

Experimental nitridation runs at $900^\circ C$ showed that a high oxygen content was still prevalent in the boron nitride product after hydrochloric acid and methyl alcohol purification treatments to remove the calcium filler compound and any unreacted boric oxide, despite the fact that calcium and silicon compounds (potential sources of high oxygen) were reduced to low levels. This fact indicated the presence of an alcohol-insoluble compound (intermediate B-O-N).

Removal of moisture from cylinder ammonia gas was studied by passing the gas through fixed beds of various solid drying agents. The best methods found for drying ammonia gas consisted of passing the gas through a bed of anhydrous calcium oxide powder or potassium hydroxide pellets. A modified federal specification test method (Method 0-A-445a) was investigated for analyzing the purity of compressed anhydrous ammonia and was shown to be satisfactory.

A study was made on the effect of particle size on the efficiency of removing the calcium filler compound from the $900^\circ C$ -nitridated boron nitride product powder by dilute hydrochloric acid treatment. The data showed that good calcium and phosphate removal was realized by a single dilute hydrochloric acid treatment if the nitridated boron nitride product was ground to less than a 200-mesh powder.

Hygroscopicity and drying studies were made on several commercial boron nitride powders containing various amounts of boric oxide. The rate of moisture pickup upon exposure to a controlled 75 percent relative humidity atmosphere was proportional to the boric oxide content. One sample of high-purity boron nitride (>99.5% BN) showed no measurable weight gain after an exposure of 160 minutes. Drying studies showed that extremely long drying periods in an oven at $100^\circ C$ were required for two grades of boron nitride powder containing 0.6 and 8.0 percent boric oxide.

Renitridation, at $1,400^\circ C$, of the boron nitride prepared at $900^\circ C$, using a hold time of 16 hours, resulted in a high-purity product which analyzed 55.5 percent nitrogen, compared to a theoretical nitrogen content of 56.4 percent. This result indicated that the intermediate conversion compound postulated for the $900^\circ C$ boron nitride product (B-O-N) can be eliminated by a subsequent renitridation treatment with

ammonia at 1,400° C. X-ray diffraction analysis identified hexagonal boron nitride as the major constituent with no other detectable intermediate or minor constituents. Electron photomicrographs of various types of laboratory-prepared and commercial boron nitride powders were also made.

INTRODUCTION

Pure boron nitride is a white powder consisting of 43.6 percent boron and 56.4 percent nitrogen. The usual crystalline form of boron nitride is hexagonal and it is sometimes called "white graphite". Like graphite, it has a greasy feel and possesses good lubricating properties. It is considered to be the most attractive nitride for high-temperature structural applications because it is very inert chemically and offers good oxidation resistance.

Boron nitride is also similar to graphite in that it has mechanical and thermal properties which vary widely depending on the orientation of the particles. It offers the advantages of low density, a low dielectric constant, shows good corrosion and thermal shock resistance, is readily machinable, is a good conductor of heat, and is an excellent electrical insulator. Its outstanding dielectric properties have also proved it to be useful in low-temperature electronic applications.

Boron nitride has been hot pressed to good density and strength, but pressable grades of commercial boron nitride have always required the presence of oxygen (usually present as boric oxide in amounts ranging from 1 to 20 percent) to form a strong, dense engineering material.

A previous study by Ingles and Popper⁽¹⁾ of the hot-pressing characteristics of different boron nitride powders in graphite dies showed that pure boron nitride prepared at 1,800° C in nitrogen could not be hot pressed to a density greater than 1.22 gms/cc. Additions of boric oxide raised the density to 2.06 gms/cc, but caused the material to be unstable when exposed to water or alcohol.

Ingles and Popper⁽¹⁾ have described a method for preparing a hot-pressable boron nitride by the reaction between a mixture of boric oxide and a calcium filler compound with ammonia at 900° C. This method produces 80 - 90 percent pure boron nitride and is obtained in a 75 - 85 percent yield. Some additional experimental work on this method of preparation was reported by Taylor.⁽²⁾ Although the boron nitride produced by this method is claimed to contain no free oxide, it does form the oxide when heated above 1,200° C. Since this method of preparation is convenient and economical and has been used as a commercial production method,⁽³⁾ the synthesis of ultra-high-purity boron nitride by this general method was selected for further study. Many experimental parameters needed to be studied, namely: reaction temperature, time at the reaction temperature, purity and degree of dryness of ammonia, gaseous ammonia flow rates, chemical removal of the calcium filler compound by dilute acid treatment, purification of the boron nitride product formed at 900° C by removal of unreacted boric oxide by alcohol extraction and low-temperature steam volatilization, and renitridation treatment at 900° C or higher temperatures.

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PREPARATION AND PROPERTIES OF THE POWDER

RAW MATERIALS AND PREPARATION OF SHREDS

High-purity raw materials were obtained for the preparation of boron nitride powder by the reaction of ammonia with a mixture of a boron compound and a calcium filler compound at 900° C. These compounds (boric oxide, impalpable boric acid, calcium carbonate, and a hydrated calcium phosphate, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ —called hydroxyapatite) were characterized with regard to particle size distribution, free-flow density, and tap density. Results are reported in Table 1. Spark-source mass spectrographic analysis results, showing the chemical purity of these compounds, are given in Tables 2 and 3.

Table 1
CHARACTERIZATION OF BORON AND CALCIUM FILLER COMPOUNDS
USED FOR THE PREPARATION OF BORON NITRIDE

Compound	Vendor	Density (gms/ml)		Particle Size Distribution ^(1,2)		
		Free Flow	Tap	90% (μ)	50% (μ)	10% (μ)
B_2O_3	American Potash and Chemical Corporation, Trona Division; New York, New York	0.89	1.10	(3)	(3)	(3)
H_3BO_3	Mallinckrodt Chemical Company; St. Louis, Missouri	0.57	0.78	41.9	9.7	3.4
CaCO_3	J. T. Baker Chemical Company; Phillipsburg, New Jersey	0.36	0.80	20.0	9.7	3.4
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	J. T. Baker Chemical Company; Phillipsburg, New Jersey	0.19	0.36	8.8	3.7	1.5

(1) Particle diameters were interpolated at the 10, 50, and 90 weight percent levels from the distribution curves obtained with a Sharples Micromerograph.

(2) Weight percent less than the indicated diameters.

(3) Boric oxide powder was too coarse for Micromerograph analysis. Sieve analysis showed 0.6% at +50 mesh, 36.6% at +50 -100 mesh, 24.1% at -100 +140 mesh, 17.1% at -140 +200 mesh, 14.2% at -200 +325 mesh, and 7.4% at -325 mesh.

As shown in Table 2, the spark-source mass spectrographic analysis of the technical-grade boric oxide used showed an unusually high purity (ie, ~99.97% boric oxide) with regard to extraneous metallic elements. Thus, it is indicated that the major "impurity" in technical-grade boric oxide is probably water of crystallization which should not have any detrimental effect on the nitridation reaction to boron nitride.

Procedures were developed for making 1/4-inch-diameter shreds of a mixture of the boron and calcium filler compounds that would be suitable for nitriding experiments. Using boric oxide and calcium carbonate as the filler compounds in a 5:3 weight ratio, good-quality shreds were made by drying a paste containing 10 milliliters of water per 8 grams of powder at 80° C. Quality of the paste and dried 1/4-inch-diameter shreds made with various formulations [B_2O_3 - CaCO_3 , B_2O_3 - $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, H_3BO_3 - CaCO_3 , and H_3BO_3 - $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$] is reported in Table 4.

Table 2
SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSIS OF BORON COMPOUNDS
(ppm by Weight)

Element	B ₂ O ₃	H ₃ BO ₃	Element	B ₂ O ₃	H ₃ BO ₃	Element	B ₂ O ₃	H ₃ BO ₃
Al	0.66	10.1	Hg	< 2.1	< 0.82	Rh	< 0.30	< 0.13
As	< 0.20	0.90	Ho	< 0.46	< 0.21	Ru	< 1.0	< 0.40
Au	< 0.54	< 0.69	I	< 0.35	< 0.46	S	2.2	140
B	Matrix	Matrix	In	< 0.33	< 0.15	Sb	< 0.30	8.0
Ba	< 0.53	< 4.6	Ir	< 0.88	< 0.71	Sc	0.37	< 0.17
Be	73.7	37.8	K	85.6	3.6	Se	1.3	< 6.7
Bi	< 0.60	< 0.78	La	< 0.37	< 0.50	Si	59.4	78.8
Br	1.3	< 0.13	Lu	< 0.50	< 0.19	Sm	< 1.5	< 0.71
Ca	8.5	36.8	Mg	1.6	< 0.78	Sn	< 1.0	< 0.02
Cd	< 1.1	3.8	Mn	< 0.02	0.67	Sr	< 0.29	< 0.44
Ce	< 0.44	< 6.7	Mo	< 1.0	< 1.7	Tb	< 0.44	< 0.19
Co	0.15	0.21	Na	14.5	7.1	Te	< 1	< 0.44
Cr	16.0	78.8	Nb	< 1.3	< 0.10	Th	< 0.64	< 0.02
Cs	< 0.35	< 0.50	Nd	< 1.6	< 0.74	Ti	4.4	7.1
Cu	0.24	115.5	Ni	0.24	0.08	Tl	< 0.90	< 0.36
Dy	< 1.6	< 0.69	Os	< 1.5	< 0.57	Tm	< 0.44	< 0.21
Er	< 1.4	< 0.63	P	4.2	< 0.19	U	< 0.66	< 0.17
Eu	< 0.80	< 0.34	Pb	< 1.0	< 1.5	V	0.02	0.63
F	0.53	-	Pd	< 0.30	< 0.48	W	< 1.5	< 0.71
Fe	< 0.02	10.7	Pr	< 0.35	< 0.17	Y	< 0.24	< 0.36
Ga	2.9	< 0.65	Pt	< 2.5	< 0.69	Yb	< 1.8	< 0.67
Gd	< 2.0	< 0.86	Rb	< 0.33	< 0.15	Zn	< 0.02	48.9
Ge	1.6	< 0.23	Re	< 0.85	< 0.36	Zr	0.88	< 0.21
Hf	< 2.0	< 0.80						

Table 3
SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSIS OF CALCIUM FILLER COMPOUNDS
(ppm by Weight)

Element	CaCO ₃	Ca ₁₀ (OH) ₂ (PO ₄) ₆	Element	CaCO ₃	Ca ₁₀ (OH) ₂ (PO ₄) ₆	Element	CaCO ₃	Ca ₁₀ (OH) ₂ (PO ₄) ₆
Al	0.60	1.5	Hg	< 0.55	< 2.8	Rh	0.30	0.44
As	0.14	0.32	Ho	< 0.46	< 0.71	Ru	0.88	1.4
Au	< 0.18	< 0.85	I	0.35	< 0.55	S	20	31
B	366	570	In	0.34	0.50	Sb	0.47	< 0.46
Ba	< 0.53	< 0.83	Ir	< 0.28	< 1.3	Sc	0.12	< 0.18
Be	2.5	39.0	K	2.0	3.0	Se	2.8	4.6
Bi	< 0.20	< 1.4	La	< 0.38	< 0.60	Si	166	253
Br	0.38	0.70	Lu	< 0.49	< 0.78	Sm	< 1.6	< 2.5
Ca	Matrix	Matrix	Mg	30.0	10.0	Sn	3.7	6.0
Cd	2.2	3.0	Mn	1.0	0.90	Sr	35.0	54.5
Ce	< 0.43	< 0.67	Mo	2.8	4.4	Tb	< 0.44	< 0.69
Co	< 0.01	< 0.34	Na	4.9	7.6	Te	5.0	< 1.6
Cr	17.0	25	Nb	0.25	0.39	Th	< 0.16	< 0.83
Cs	< 0.37	< 0.58	Nd	< 1.7	< 2.5	Ti	0.96	25
Cu	17.0	< 0.23	Ni	2.2	11.5	Tl	< 0.27	< 1.2
Dy	< 1.6	< 2.5	Os	< 0.43	< 2.0	Tm	< 0.47	< 0.70
Er	< 1.4	< 2.2	P	1.4	Matrix	U	< 0.22	< 0.34
Eu	< 0.80	< 1.2	Pb	< 0.24	< 1.2	V	< 0.01	< 0.02
F	0.80	8.3	Pd	1.3	2.0	W	< 0.55	22.5
Fe	166	83	Pr	< 0.39	< 0.60	Y	0.25	0.37
Ga	0.30	0.51	Pt	< 0.53	< 2.5	Yb	< 1.5	< 2.3
Gd	2.0	< 3.0	Rb	0.32	0.50	Zn	1.8	< 1.2
Ge	2.7	4.0	Re	< 0.27	< 1.3	Zr	0.76	3.5
Hf	< 1.8	< 2.8						

Table 4
QUALITY OF PASTE AND DRIED 1/4-INCH-DIAMETER SHREDS MADE WITH VARIOUS BORON
AND CALCIUM FILLER COMPOUND FORMULATIONS

Material ⁽¹⁾	Batch ⁽¹⁾										
	1	2	3	4	5	6	7	8	9	10	11
$B_2O_3/CaCO_3$ (wt ratio)	5:3	5:3	5:3	5:3	4:4	4:4	4:4				
Water (mls/8 gms mix)	6	8	10 ⁽²⁾	12	6	8 ⁽²⁾	10				
Paste Quality	Dry	Moist	Good	Soupy	Dry	Good ⁽²⁾	Soupy				
Shred Quality	Powdery	Partially Good ⁽³⁾	Good ⁽²⁾	-	Powdery	Good	-				
$B_2O_3/Ca_{10}(OH)_2(PO_4)_6$ (wt ratio)	5:3	5:3	5:3	5:3	5:3	5:3	4:4	4:4	4:4	4:4	4:4
Water (mls/8 gms mix)	6	8	10	12	14	16 ⁽²⁾	6	8	10	12	14 ⁽²⁾
Paste Quality	Dry	Dry	Moist	Moist	Good	Good	Dry	Dry	Slightly Dry	Moist	Good ⁽²⁾
Shred Quality	Powdery	Powdery	Slightly Powdery	Stiff	Stiff	Good ⁽²⁾	Powdery	Powdery	Partially Good ⁽³⁾	Partially Good ⁽³⁾	Good ⁽²⁾
$H_3BO_3/CaCO_3$ (wt ratio)	5:3	5:3	5:3	4:4	4:4	4:4					
Water (mls/8 gms mix)	4	5 ⁽²⁾	7	2	2 ⁽²⁾	4					
Paste Quality	Dry	Good ⁽²⁾	Soupy	Dry	Good ⁽²⁾	Soupy					
Shred Quality	Powdery	Good ⁽²⁾	-	Powdery	Good ⁽²⁾	-					
$H_3BO_3/Ca_{10}(OH)_2(PO_4)_6$ (wt ratio)	5:3	5:3	5:3	5:3	4:4	4:4	4:4	4:4			
Water (mls/8 gms mix)	3	5	7 ⁽²⁾	9	4	6	8 ⁽²⁾	10			
Paste Quality	Dry	Dry	Good ⁽²⁾	Soupy	Dry	Slightly Dry	Good ⁽²⁾	Soupy			
Shred Quality	Powdery	Powdery	Good ⁽²⁾	-	Powdery	Powdery	Good ⁽²⁾	-			

(1) Used 360-gram batches of mixed boron compound/calcium compound powder in a 22-centimeter-diameter glazed porcelain evaporating dish. Shreds were dried at 80° C.

(2) Denotes best paste/shred formulation.

(3) One half of the batch gave shreds and one half crumbled to powder.

As shown in Table 4, a good quality paste and good 1/4-inch shreds were made when using boric oxide with calcium carbonate as the filler compound (4:4 weight ratio) and 8 milliliters of water for every 8 grams of mixed powder. When using a 5:3 weight ratio of the two compounds, 10 milliliters of water per 8 grams of mixed powder were needed to form good-quality paste and shreds. This larger amount of water was as expected because of the higher amount of the highly exothermic boric oxide component in this mix.

The boric oxide was dry mixed in a stainless steel twin-shell blender, and the mixture made into a stiff paste by the rapid addition of demineralized water with stirring. Shreds 1/4 inch in diameter and of various lengths were made by pressing the stiff paste through a four-mesh sieve. The resulting small agglomerates of material were then dried at 80° C.

NITRIDATION APPARATUS AND RESULTS

An experimental apparatus was assembled for studying the parameters involved in the nitriding of 1/4-inch-diameter shreds of the mixtures of boron compounds and calcium filler compound. This facility consists essentially of a 3-inch-diameter by 36-inch-long quartz tube, an 18-inch-long clamshell-type electrical resistance furnace, a 12-inch-long preheater furnace, a 0 - 1,000° C temperature controller, and a gaseous ammonia pressure regulator and flow measuring equipment. A schematic representation of the apparatus is presented in Figure 1.

Figure 1. APPARATUS FOR THE PREPARATION OF BORON NITRIDE.

The experimental nitriding apparatus shown in Figure 1 allows for a study of the major variables affecting the conversion of boric oxide to boron nitride (eg, nitriding temperature, effect of using a preheater, effect of the ammonia flow rate, and effect of cooling and purging under nitrogen). The double filter flask arrangement, shown in Figure 1, served a dual purpose: The first flask permitted the collection of condensed water formed by the reaction and also served as a siphon breaker during the cooling cycle; the second flask, containing the water bubbler, sealed the apparatus and prevented the influx of air as a contaminant.

During the nitridation run, it was found to be expedient to burn the exit gases from the reactor with a Bunsen burner. The burnable exit gases contained hydrogen, presumably formed by the cracking of ammonia at 900° C according to the equation:

It is believed that the nitrogen and hydrogen gases formed then react with the boric oxide in two stages according to the equations:

The burning of hydrogen in the exit gases was made visible as a yellow flame by the application of a few drops of sodium chloride solution to the medicine dropper tip.

Twelve nitriding runs were made at 900° C using technical-grade boric oxide with calcium carbonate as the filler compound. The runs ranged from 5 to 24 hours, and a modified Ingles and Popper⁽¹⁾ procedure was used. It was reported by Ingles and Popper⁽¹⁾ that the boric oxide nitridation reaction occurs at 800 - 1,200° C according to the equation:

A solid filler is used to prevent fusion of the boric oxide and to increase the porosity and surface area of the shreds to be reacted. Suitable fillers are tricalcium orthophosphate, hydroxyapatite, calcium carbonate, and preformed boron nitride. The calcium fillers are removed with hydrochloric acid and any unreacted boric oxide is removed by a hot alcohol treatment. The analytical results are summarized in Table 5.

The particle-size distribution of two pressable commercial boron nitride powders, and boron nitride powder made by ammonia treatment of boric oxide at 900° C, is given in Table 6. X-ray diffraction analysis of the product obtained from Run A-1 of Table 5, which represented only a five-hour reaction time, identified the product to be hexagonal boron nitride with no detectable intermediate or minor constituents after hydrochloric acid and ethyl alcohol treatments. In all subsequent runs, the same

Table 5
SUMMARY OF BORIC OXIDE NITRIDING RUNS AT 900° C
($B_2O_3/CaCO_3$ Weight Ratio = 4:4)

	Run Number											
	A-1	A-5	A-2	A-6	A-4	A-3	A-7	A-8	A-9	A-10	A-11	A-12
Reaction Time at 900° C (hrs)	5.0	7.0	12.0	18.0	19.0	24.0	5.0	7.0	5.0	5.0	12.0	18.0
NH ₃ Flow Rate (cc/min)	800	800	800	800	800	800	800	800	1,600	800	800	800
BN Product Analyses (after HCl treatment)												
Conc HCl/H ₂ O Volume Ratio = 5:18 ⁽¹⁾	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Conc HCl/H ₂ O Volume Ratio = 1:5 ⁽¹⁾	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No	No	No	No
Total Boron (%)	41.2	40.6	40.9	-	39.7	41.7	-	41.8	40.7	-	-	42.1
Free Boron (%)	0.5	1.3	0.9	-	1.7	0.8	-	1.2	2.1	-	-	1.3
Oxygen (Nitrox) (%)	4.43	5.07	6.20	-	5.52	4.02	-	7.61	7.52	-	-	5.84
Calculated B_2O_3 (%) ⁽²⁾	1.61	4.19	2.90	-	5.48	2.58	-	3.87	6.77	-	-	4.19
BN Product Analyses (after C ₂ H ₅ OH treatment)												
Total Boron (%)	42.2	41.3	41.5	40.1	41.1	42.4	42.3	42.0	40.4	40.6	42.0	41.4
Nitrogen (%)	53.0	49.4	52.2	-	51.6	51.4	50.2	49.6	48.4	49.8	50.8	49.6
Oxygen (Nitrox) (%)	0.80	4.94	5.57	5.92	5.12	-	7.19	6.84	7.48	7.74	6.46	5.61
Total B, N, and O (%)	96.0	95.64	99.27	-	97.82	-	99.69	98.44	96.28	98.14	99.26	96.61
Free Boron (%)	0.5	0.8	0.8	1.3	1.0	-	1.5	1.2	2.4	1.7	0.6	2.5
Calculated B_2O_3 (%) ⁽²⁾	1.61	2.58	2.58	4.19	3.22	-	4.82	3.87	7.73	5.48	1.93	8.06
Helium Density (gms/cc)	-	2.03	-	-	2.07	2.13	1.98	2.18	-	2.18	-	-
Loss on Drying (100° C for 2 hours, gm)	0.17	0.33 ⁽³⁾	0.32	-	0.44 ⁽³⁾	0.36 ⁽³⁾	0.26	0.28 ⁽³⁾	0.23 ⁽³⁾	0.67 ⁽³⁾	0.14 ⁽³⁾	0.20 ⁽³⁾
Loss on Drying (200° C for 2 hours, gm)	0.34	-	0.45	-	-	-	-	-	-	-	-	-
Crystallite Size (Å)	-	55	-	55	-	57	53	54	48	50	53	50
Spectrochemical Analysis												
Calcium (%)	-	1.0	-	-	1.0	0.8	-	1.0	0.8	0.8	1.5	1.0
Silicon (%)	-	0.05	-	-	0.08	0.8	-	0.01	0.02	0.02	0.04	0.06

(1) Total volume of acid used was 1,800 mls.

(2) Calculated from the free boron content: $\% B_2O_3 = \% B \times \frac{B_2O_3 (69.6)}{2B (21.6)}$.

(3) After 16 hours.

Table 6
 PARTICLE-SIZE DISTRIBUTION OF COMMERCIAL BORON NITRIDE
 AND BORON NITRIDE POWDER MADE BY AMMONIA
 TREATMENT OF BORIC OXIDE AT 900° C
 (Weight Ratio of $B_2O_3/CaCO_3 = 4:4$)

Run Number	Time (hrs)	Weight Percent of Particles Less Than or Equal to Indicated Diameter (μ)		
		90%	50%	10%
A-1	5.0	-	-	-
A-2	12.0	24.0	7.0	3.4
A-3	24.0	30.8	8.2	2.7
A-4	19.0	13.6	5.7	2.2
A-5	7.0	14.7	7.0	3.0
A-6	18.0	11.7	5.2	2.4
A-7	5.0	13.6	5.0	2.1
A-8	7.0	14.0	6.8	2.7
A-9	5.0	16.4	5.6	2.8
A-10	5.0	11.7	5.2	2.0
A-11	12.0	11.8	5.7	2.6
A-12	18.0	27.0	9.3	3.7
Commercial BN ⁽¹⁾	-	12.5	5.3	2.2
Commercial BN ⁽²⁾	-	12.2	6.4	2.3

(1) Pressable powder, Vendor A.

(2) High-purity-grade powder, Vendor B.

hexagonal boron nitride diffraction pattern was obtained, but the pattern was somewhat less intense despite the longer nitridation times used.

In as much as the data of Table 5 indicate that a relatively high oxygen content is associated with the product boron nitride powder produced, a study was made to investigate the stability of a commercial batch of pressable boron nitride powder in air at 120° C. These data are summarized in Table 7 and Figure 2. For the nitriding runs shown in Table 5, 100-gram quantities of the dried shreds were placed in two quartz boats and nitrided by heating in flowing ammonia for various reaction times. After nitriding, the shreds were ground in a mortar and pestle to pass through a 60-mesh screen and then treated with 1,800 milliliters of hydrochloric acid (5 volumes of concentrated HCl/18 volumes of H_2O) to dissolve the calcium carbonate. The material was kept in the hydrochloric acid with occasional stirring for approximately 18 hours and filtered. It was then treated with 1,800 milliliters of hydrochloric acid (1 volume of concentrated HCl/5 volumes of H_2O) for approximately three hours and filtered. The solids were rinsed well with demineralized water, dried at 120° C, and sampled for analysis. The remaining portion was refluxed with 1,000 milliliters of ethyl alcohol at 70° C for approximately four hours and filtered. After final drying at 80° C, additional analytical data were obtained. (Results are given in Tables 5 and 6.)

Table 7
STABILITY OF PRESSABLE BORON NITRIDE POWDER AT 120° C

	Sample Number ⁽¹⁾							
	0-1	0-2	0-3	0-4	0-5	0-6	0-7	0-8
Gross Weight (gms)	29.5589	27.8336	21.7857	27.5520	28.3625	24.9791	28.7527	25.9515
Tare Weight (gms)	22.5117	20.2324	14.4512	20.4076	21.3538	17.3490	21.7252	18.9264
Net Weight (gms)	7.0472	7.6012	7.3345	7.1444	7.0087	7.6301	7.0275	7.0251
Gross Weight After 3 Days at 25° C (gms)	29.6935	27.9776	21.9153	27.6869	28.4833	25.1151	28.8885	26.0765
Weight Gain (gm)	0.1346	0.1440	0.1296	0.1349	0.1208	0.1360	0.1358	0.1250
Percent Weight Gain at 25° C (gms)	1.91	1.89	1.77	1.88	1.72	1.78	1.93	1.77
Time at 120° C (hrs)	4.0	4.0	8.0	8.0	24.0	24.0	48.0	48.0
Gross Weight After 120° C (gms)	29.5569	27.8274	21.7391	27.5044	28.2958	24.9299	28.6779	25.8698
Weight Loss at 120° C (gm)	0.1366	0.1502	0.1762	0.1825	0.1875	0.1852	0.2106	0.2067
Percent Weight Loss at 120° C	1.94	1.97	2.40	2.55	2.68	2.43	2.99	2.94
Average Percent Weight Loss		1.95	2.47		2.56		2.97	
Percent Free Boron	2.1	2.4	2.3	2.3	2.4	2.4	2.3	2.5
Average Percent Free Boron		2.25	2.3		2.4		2.4	
Percent Oxygen (Nitrox)	9.26	9.58	9.39	9.32	8.89	8.34	8.38	7.84
Average Percent Oxygen		9.42	9.36		8.62		8.11	
Percent Loss on Drying at 100° C for 16 Hours	0.70	0.53	0.21	0.55	0.49	0.53	0.64	0.53

(1) The pressable boron nitride powder from Vendor A.

Figure 2. STABILITY OF PRESSABLE BORON NITRIDE AT 1200° C.

It is shown in Table 5 that a high oxygen content is associated with the boron nitride made in Runs A-2 through A-12. This high oxygen content may be attributed to several factors: (1) inadequate removal of calcium carbonate from the nitrated product, as evidenced by the 0.8 to 1.5 percent calcium content shown in Table 5; (2) silicon dioxide contamination from the three-inch-diameter quartz reaction tube, as evidenced by the 0.8 percent silicon content shown for Run A-3 of Table 5; (3) agglomeration of boric oxide-calcium carbonate shreds to a diameter of greater than 1/4 inch, which would prevent effective diffusion of ammonia to the interior of the shreds; (4) oxidation of the nitrated boron nitride product during cooling after nitridation or during oven drying at 1200° C; (5) hygroscopicity of the boron nitride; (6) inadequate drying after ethyl alcohol treatment.

The stability of a batch of commercial, pressable boron nitride powder (7.7% O₂, dry basis) was studied. Four sets of duplicate samples of boron nitride powder (4.0 in² area) were exposed for 4, 8, 24, and 48 hours in air at 1200° C. Results indicate that the oxygen content decreased from 9.4 percent after 4 hours to 8.1 percent after 48 hours, and the weight loss ranged from 2.1 percent after 4 hours to 3 percent after 48 hours (see Table 7 and Figure 2). The data also indicate that the analytical method (Nitrox) for determining oxygen also measures the oxygen from any moisture picked up by the hygroscopic powder.

AMMONIA DRYING STUDIES

In an attempt to further purify a batch of boron nitride powder prepared by the reaction of boric oxide with ammonia for five hours at 900° C, the compound was renitrated with as-received commercial cylinder ammonia gas at 1,400° C for 24 hours. But,

instead of further conversion to boron nitride, it was found that a large amount of the product had degraded to a grayish-white deposit which was identified by X-ray diffraction as, primarily, silicon nitride.

A dew-point measurement of the cylinder ammonia gas (Vendor A) being used indicated that it contained approximately 630 ppm moisture. It was also indicated that some of the 900° C boron nitride product had become partially pyrohydrolyzed during the 1,400° C renitridation attempt and showed the need for predrying the cylinder ammonia gas used. Methods for determining the moisture content of cylinder ammonia gas and methods for drying the ammonia gas were therefore investigated.

The removal of moisture from cylinder ammonia gas was studied by passing the gas through fixed beds of various granular solids. It was found that the indicating-grade anhydrous calcium sulfate could not be used for drying the ammonia since cobalt chloride is used as the impregnated indicator, and the ammonia reacted highly exothermically with the chloride which disintegrated the calcium sulfate granules to a fine powder. The white, anhydrous calcium sulfate granules appeared to be unreactive with ammonia, but reproducible weight-gain data at constant ammonia flow rates could not be obtained.

The best methods found for drying cylinder ammonia gas consisted of passing the gas through a bed of anhydrous calcium oxide powder or potassium hydroxide pellets. The calcium oxide method was found to be quantitative (Table 8) in that the weight gain of the calcium oxide drying trap was found to be directly proportional to the total volume of ammonia gas flowing through the trap. The use of a potassium hydroxide drying column was also found to be effective for drying ammonia within the limits of detection of moisture in the ammonia by the calcium oxide analytical method.

A federal specification test method, Method 0-A-445a, was investigated for analyzing the purity of compressed anhydrous ammonia. Using this method, analysis of Vendor A cylinder ammonia sampled directly from the cylinder as liquid ammonia showed a liquid residue impurity content of approximately 333 ppm. The liquid residue obtained was tentatively identified by infrared analysis to be ammonium hydroxide. The federal specification residue tube apparatus used for analyzing the purity of liquid ammonia is shown in Figure 3.

Table 8
DRYING OF CYLINDER AMMONIA GAS WITH
ANHYDROUS CALCIUM OXIDE
(Vendor A, 150-Lb Cylinder)

Ammonia Flow Rate (cc/min)	Time (min)	Calcium Oxide Trap Weight (gms)		Weight Gain (gm)
		Initial	Final	
200	30	131.3588	131.3598	0.0010
200	30	131.3620	131.3630	0.0010
200	30	131.3630	131.3640	0.0010

Figure 3. FEDERAL SPECIFICATION RESIDUE TUBE APPARATUS FOR AMMONIA.

A sample of Vendor A cylinder ammonia which was removed from the cylinder as a gas and liquefied in the residue tube apparatus indicated a liquid residue impurity content of less than 167 ppm. This sample of ammonia removed from the cylinder as a gas also contained a considerably lower amount of an unidentified waxy-solid particulate impurity than the sample of ammonia removed from the same Vendor A cylinder as a liquid.

A series of drying columns containing potassium hydroxide pellets followed by a 36-inch-long column of potassium hydroxide pellets was installed to remove residual moisture and particulate impurities from the cylinder ammonia gas being used for experimental boric oxide-ammonia nitridation runs. Upon analyzing this potassium hydroxide-dried ammonia gas by the federal specification test method, no measurable moisture or particulate impurities were detected.

According to Dodd and Robinson,⁽⁴⁾ it was impossible to dry ammonia over an acidic desiccant or over calcium chloride with which it forms ammoniates. It can, however, be conveniently dried over solid caustic potash, freshly prepared calcium oxide, or sodium-sputtered glass wool.⁽⁴⁾ Since caustic potash (KOH) is conveniently supplied in stick or pellet form, which would be highly advantageous to laboratory or plant-scale drying operations involving high gas flow rates from the standpoint of low pressure drops, this method of drying was chosen for use with the boric oxide-hydroxyapatite nitridation apparatus at 900° C. The drying of ammonia gas using a vertical column of broken potassium hydroxide sticks was also reported by Overstreet and Giaque.⁽⁵⁾ Although dew-point measurements have been used for indicating the degree of dryness of dissociated ammonia gas in industry, it is believed that this method may not be reliable for measuring the moisture content of compressed ammonia gas from a cylinder because the moisture impurity is presumed to be ammonium hydroxide and a suitable correction factor would probably have to be applied. Although some quantitative analytical data on the moisture content of cylinder ammonia gas were obtained in this study by the calcium oxide and federal specification residue tube methods, the lower limits of moisture detectability by these methods will require further study.

The federal specification ammonia test method, Method 0-A-445a, has been modified to analyze gaseous ammonia by the following procedure: A 500-milliliter graduated residue tube, shown in Figure 3, was placed in a Dewar flask containing acetone and dry ice at -78° C. Gaseous ammonia was introduced into the residue tube through a 1/4-inch-diameter glass inlet tube extending to within two inches of the bottom of the tube. The residue tube acts as a cold trap, and the gaseous ammonia is liquefied until 500 milliliters are collected.

In recent determinations, the vent tube was connected to a combination vacuum and pressure gauge, and it was observed that a vacuum of approximately 15 inches of mercury was maintained in the residue tube during filling despite the use of a very high flow rate of ammonia into the tube (eg, 2,000 cc/min). This vacuum is attributed to the rapid condensation of ammonia gas. After collecting 500 cubic centimeters of liquid ammonia, the residue tube was placed in a close-fitting, empty Dewar flask; and, when the gage showed a positive pressure, a 16-inch length of rubber vent tubing was substituted for the gage. The liquid ammonia was then allowed to vaporize slowly out of the residue tube.

CALCIUM FILLER COMPOUND REMOVAL

A study was made to determine the effect of particle size on the efficiency of removal of the calcium filler compound by dilute hydrochloric acid treatment from the 900° C-nitridated boron nitride product. The data showed that good calcium and phosphate removal can be realized by a single dilute hydrochloric acid treatment if the nitridated boron nitride product is ground to less than 200-mesh powder. Analytical results are summarized in Table 9.

Table 9
EFFECT OF PARTICLE SIZE OF NITRIDATED BORIC OXIDE-CALCIUM FILLER COMPOUND ON THE
REMOVAL OF CALCIUM AND PHOSPHORUS BY DILUTE HYDROCHLORIC ACID

	Powder Fraction				
	A	B	C	D	E
Weight of BN Product ⁽¹⁾ (gms)	5.596	20.015	20.018	20.025	11.465
Particle Size of BN Product					
Mesh Size Range	- 50 +100	-100 +200	-200 +325	-325 +500	-500
Microns	-297 +149	-149 + 74	- 74 + 44	- 44 + 30	- 30
Volume of Dilute Hydrochloric Acid ⁽²⁾ (mls)	495	1,500	1,500	1,500	860
Volume of Rinse Water (mls)	380	455	500	610	570
Total Volume (mls)	875	1,955	2,000	2,110	1,430
Analytical Results (HCl + H ₂ O)					
Gms Ca ⁺⁺ /ml	0.000850	0.001554	0.001676	0.001554	0.001228
Gms PO ₄ ⁼ /ml	0.001558	0.002423	0.002457	0.002310	0.001911
Total Ca ⁺⁺ (gms)	0.744	3.038	3.352	3.279	1.756
Total PO ₄ ⁼ (gms)	1.363	4.737	4.914	4.874	2.733
Total gms Ca ⁺⁺ /gm in BN Product	0.1329	0.1518	0.1674	0.1637	0.1532
Total gms PO ₄ ⁼ /gm in BN Product	0.2066	0.2367	0.2455	0.2434	0.2384
Oven-Dried BN Product ⁽³⁾					
Calcium (ppm)	100	50	215	33	178
76	76	84	258	50	78
Average	88	67	236	41	128
Phosphate (ppm as PO ₄ ⁼) ⁽⁵⁾	1,355	2,232	3,253	1,508	3,168
1,457	1,457	1,881	2,260	1,882	3,162
Average	1,406	2,056	2,756	1,695	3,165

(1) Composite sample of BN product from 6-hour nitridation of B₂O₃/Ca₁₀(OH)₂(PO₄)₆ at 900° C.

(2) Five volumes of 38 weight percent HCl/18 volumes of H₂O.

(3) After dilute HCl and rinse water treatment.

(4) By atomic absorption analysis after sodium carbonate fusion of BN.

(5) By colorimetric analysis after sodium carbonate fusion of BN.

In previous work by Ingles and Popper⁽¹⁾ and Taylor⁽²⁾ on the removal of the calcium phosphate filler compound, two treatments with hydrochloric acid had been required. The first treatment used hydrochloric acid at a volume ratio of five parts concentrated hydrochloric acid to 18 parts water. A second acid treatment was then applied using a volume ratio of one part concentrated hydrochloric acid to five parts water.

For the data shown in Table 9 on the effect of particle size on the efficiency of removal of the calcium filler compound [Ca₁₀(OH)₂(PO₄)₆] by dilute hydrochloric acid treatment, three batches of six-hour nitridated boric oxide-calcium filler shreds were blended together, ground in a disc mill, and sieved into five different screen-size fractions. Each powder fraction was slurried for 24 hours with dilute hydrochloric acid (5 volumes of concentrated HCl/18 volumes of H₂O), filtered, and rinsed with distilled water. As shown in Table 9, a single treatment with dilute hydrochloric was very effective in reducing the calcium and phosphate impurities to low levels (less than 250 ppm Ca) even for the relatively coarse -50 +100 mesh fraction. With regard to Table 9, it is shown that the ratio of total grams of calcium per gram of boron nitride product increases to a maximum value of 0.167 for -200 mesh boron nitride powder, thus grinding and sieving boron nitride product to -200 mesh before hydrochloric

acid treatment should be even more effective for the removal of calcium and phosphate than the coarser particle-size fractions.

In Table 9, the individual residual calcium and phosphate values shown for the final, dried boron nitride product show a considerable variation which is attributed to difficulties experienced with the previously untried sodium carbonate fusion method for solubilizing the boron nitride product.

EQUIPMENT MODIFICATIONS AND RESULTS

The following modifications were made on the boric oxide-ammonia nitridation apparatus shown in Figure 1:

1. Double drain cocks were installed on the outlet end of the quartz tube to permit draining off the water evolved from the reaction of boric oxide. This provision should reduce the hydrolysis of boron nitride in the latter stages of nitridation due to a water-saturated ammonia atmosphere at 900° C.
2. Inconel boats were substituted for quartz boats for containing the boric oxide shreds to reduce the possibility of silicon dioxide contamination.
3. The quartz reaction tube was lined with an Inconel sleeve to reduce the possibility of silicon dioxide contamination.
4. Methyl alcohol was substituted for ethyl alcohol for the final alcohol extraction treatment.

The results of four experimental nitridation runs at 900° C, using these equipment modifications, are summarized in Table 10. These data show that a high oxygen con-

Table 10
SUMMARY OF BORIC OXIDE NITRIDING RUNS AT 900° C

	Run Number			
	E-1	E-2	E-3	E-4
NH ₃ Flow Rate (cc/min)	800	900	800	800
Weight Ratio B ₂ O ₃ /Filler Compound	4:4	4:4	5:3	5:3
Filler Compound	CaCO ₃	CaCO ₃	Ca ₁₀ (OH) ₂ (PO ₄) ₆	Ca ₁₀ (OH) ₂ (PO ₄) ₆
BN Product Analysis ⁽¹⁾				
Total Boron (%)	41.5	39.2	39.7	39.5
Free Boron (%)	1.3	1.6	1.0	1.0
Oxygen (Nitrox) (%)	9.0	6.9	9.1	10.6
Hydrogen (ppm)	583	714	604	649
Nitrogen (%)	47.7	51.0	48.4	42.9
Spectrochemical				
Calcium (%)	0.6(2)	0.6(2)	< 0.005	0.008
Silicon (%)	0.04	0.01	< 0.01	< 0.01

(1) After dilute HCl and CH₃OH treatment.

(2) Relatively coarse, unscreened BN product.

tent is still prevalent in the boron nitride product after the hydrochloric acid and methyl alcohol purification treatment despite the fact that the calcium and silicon compounds (potential sources of high oxygen) were reduced to low levels.

For the boric oxide nitriding runs shown in Table 10, shreds were prepared for nitridation runs at 900° C from boric oxide and calcium phosphate mixed in a stainless steel twin-shell blender using a weight ratio of five parts boric oxide to three parts hydroxyapatite. Two-hundred-gram batches of the 5:3 powder mixture were then mixed with 400 milliliters of demineralized water. The resulting paste was loaded into a caulking gun and extruded through a 3/8-inch-diameter opening onto flat Teflon sheets. Finally, the shreds were dried in an oven at 80° C and placed in a desiccator for cooling and storage.

An alternate method of preparing shreds of uniform thickness, which was also shown to be satisfactory, consisted of loading the boric oxide-calcium filler compound-water paste into a triangularly shaped polyethylene bag and extruding it out of a 3/8 or 1/2-inch-diameter opening at one end of the bag onto flat Teflon sheets. Hand manipulation and the application of finger pressure to the back end of the paste-filled bag allowed the paste to extrude onto the Teflon sheet at a controlled rate. Leakage of the paste from the back end of the bag was prevented by using laboratory pinch clamps to hold the folded edge in position. A photograph showing the triangular polyethylene bag hand-extrusion apparatus is presented in Figure 4.

A total of fourteen additional boric oxide nitridation runs were made at 900° C using potassium hydroxide-dried ammonia gas and the new equipment modifications described previously. A summary of the experimental run conditions and analytical results is given in Table 11. Temperature profiles showing the heating and cooling cycles used for the runs under flowing ammonia gas are given by the graph of Figure 5.

An inspection of the data in Table 11 (Runs E-15 through E-18) shows that although the oxygen content of the experimentally prepared boron nitride powders that had been hydrochloric acid treated, water rinsed, and dried was significantly high (ie, 15.0%), the associated boric oxide content of these powders, as determined by a methyl alcohol extraction procedure, is quite low (ie, 0.2 to 0.5%). This information indicates the presence of an intermediate conversion compound (B-O-N) or possibly boron nitride-coated shells of boric oxide particulates. The existence of such an intermediate compound was postulated by Ingles and Popper⁽¹⁾ and by Saunders.⁽⁶⁾

An attempt was made to study the relative positions of boron, nitrogen, and oxygen videographically on a pressed pellet of the 900° C boron nitride powder by electron microprobe analysis; but, due to the low intensities and rapid contamination from the electron beam, such analyses were invalid. According to Postma⁽⁷⁾ "A 120-micron line scan was made monitoring the intensity of boron, nitrogen, and oxygen. A boron nitride standard was utilized for the boron and nitrogen setup. The boron response was similar to the boron content of the standard. There was no significant change in the

Figure 4. POLYETHYLENE BAG PASTE-EXTRUSION APPARATUS.

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Table 11
SUMMARY OF BORIC OXIDE NITRIDING TESTS AT 900° C

	Run Number				
	E-5, 6, 7	E-8, 9	E-10, 11, 12	E-13, 14, 15	E-16, 17, 18
Reaction Time at 900° C (hrs)	6.0	5.0	8.0	16.0	24.0
NH ₃ Flow Rate (cc/min)	780	780	780	780	780
Weight Ratio B ₂ O ₃ / Filler Compound(1)	5:3	5:3	5:3	5:3	5:3
BN Product Analyses After HCl Treatment:					
Total Boron (%)	39.9	-	39.3	40.1	41.3
Free Boron (%)	3.0	-	3.7	3.1	3.3
Oxygen (%)	14.6	-	11.5	14.9	15.0
Hydrogen (ppm)	817	-	-	862	1,399
Nitrogen (%)	44.2	-	45.0	45.3	45.0
H ₂ O (Karl Fischer) (%)	1.59	-	-	1.3	1.6
B ₂ O ₃ (CH ₃ OH extraction) (%)	9.8	-	-	0.45	0.17
BN Product Analyses After HCl and CH ₃ OH Treatment:					
Total Boron (%)	-	39.3	-	39.5	40.8
Free Boron (%)	-	6.1	-	2.5	2.3
Oxygen (%)	-	13.5	-	15.7	13.7
Hydrogen (ppm)	-	954	-	807	732
Nitrogen (%)	-	44.3	-	45.3	46.5
Loss on Drying (2 hrs at 100° C)	-	0.08	-	0.16	0.5
H ₂ O (Karl Fischer) (%)	-	2.3	-	1.4	2.1

(1) Filler compound is Ca₁₀(OH)₂(PO₄)₆.

boron response across the specimen. At two points along the line scan, each approximately 6 - 8 microns wide, the nitrogen response increased more than twofold. The oxygen response varied in cycles approximately 60 microns wide, but these variations were unrelated to the nitrogen increases observed. No positional pattern between the boron, nitrogen, and oxygen was detected."

Figure 5. TEMPERATURE PROFILES OF BORIC OXIDE NITRIDATION HEATING AND COOLING CYCLES.

The effect of the reaction time at 900° C on converting boric oxide to boron nitride was studied. Results, as given in Table 12 and Figure 6, indicate that a nitridation time of approximately 14 or 16 hours is required to achieve maximum conversion to boron nitride, as based on the final shred residue weights.

Table 12
EFFECT OF REACTION TIME AT 900° C ON NITRIDATED
BORIC OXIDE-FILLER COMPOUND
SHRED RESIDUE WEIGHTS
(Initial Shred Weight = 100 gms at a 5:3 B₂O₃ to
Ca₁₀(OH)₂(PO₄)₆ Ratio)

Reaction Time (hours)	Residue Weight (grams)
5.0	74.996
5.0	71.676
Average	73.33
8.0	70.873
8.0	73.838
8.0	71.925
Average	72.21
16.0	63.840
16.0	66.743
16.0	63.653
Average	64.75
24.0	63.220
24.0	72.229
24.0	70.035
Average	68.49

A study was made to determine the degree of variation in the analytical results obtained on various particle-size fractions of 900° C nitridated boron nitride product. The results of the study are summarized in Table 13.

Figure 6. EFFECT OF THE REACTION TIME AT 900° C ON NITRIDATED BORIC OXIDE-CALCIUM FILLER COMPOUND SHREDS.

Table 13
EFFECT OF PARTICLE SIZE ON THE ANALYSIS OF 900° C NITRIDATED BORON NITRIDE PRODUCT

Component(1)	Composite Batch, -74 μ	Agglomerated Particles, +149 μ	Particle Size Fraction (microns)			
			-74 +44	-44 +30	-30 +20	-20 +10
Total Boron (%)	39.3	39.3	39.3	38.6	39.4	39.6
Free Boron (%)	3.7	4.7	4.2	4.8	3.9	4.6
Nitrogen (%)	45.0	45.5	42.3	41.1	42.6	41.4
Oxygen (Leco) (%)	11.5	15.7	15.7	16.0	17.8	16.5
B ₂ O ₃ (CH ₃ OH Extraction) (%)	-	0.06	0.06	0.39	0.16	0.10

(1) After dilute HCl treatment and H₂O rinse to remove calcium phosphate filler compound, drying, and fractionating powder on a Sonic Sifter.

The variation in the analytical results with particle size of 900° C nitridated product, as shown in Table 13, was obtained on three batches of product. Three batches of boric oxide-hydroxyapatite shreds were nitridated for eight hours at 900° C with ammonia, ground to a -200 mesh powder, treated with dilute hydrochloric acid, rinsed with water, and dried. The composited powder was blended and separated into five separate particle-size fractions ranging from 10 to 149 microns using a Sonic Sifter. (a) As shown in Table 13, no significant difference in converting to boron nitride is evident, although somewhat higher oxygen contents are associated with the finer particle-size fractions and the +140 micron agglomerated particles. As also shown in Table 13, some of the boron nitride powder had agglomerated to greater than 100 mesh (140 microns). This agglomerated fraction comprised approximately 27 percent of the total composite batch. Since the boron nitride powder used had a great tendency to agglomerate, it is believed that efficient separation of the powder into the discrete particle-size fractions shown in Table 13 may not have been realized with the Sonic Sifter used.

HYGROSCOPICITY STUDIES

As shown in Tables 5 and 11, relatively high oxygen and water contents (by Karl Fischer) are indicated for the experimentally prepared, alcohol-treated, and dried boron nitride powders. Table 11 indicates that three composite batches of experimentally prepared boron nitride powder that had been treated with hydrochloric acid, methyl alcohol, and dried still contained a high moisture content—approximately 1.4 to 2.3 percent water (by Karl Fischer). These results prompted a study of the hygroscopicity and oven-drying characteristics of various types of commercially available boron nitride powder containing various known oxygen contents. Hygroscopicity results are given by the graph of Figure 7.

(a) Manufactured by Allen-Bradley Company, Milwaukee, Wisconsin.

Figure 7. HYGROSCOPICITY OF BORIC OXIDE AND VARIOUS COMMERCIAL BORON NITRIDE POWDERS THAT WERE EXPOSED TO 75 PERCENT RELATIVE HUMIDITY.

For the hygroscopicity studies, shown in Figure 7, ten-gram samples of three commercially available boron nitride powders and one 10-gram sample of anhydrous boric oxide were exposed to a constant 75 percent relative humidity atmosphere in a desiccator containing a saturated solution of sodium chloride with excess solute. As the graph indicates, the rate of moisture pickup by the powders was highest for anhydrous boric oxide, second for Vendor A pressable boron nitride (containing $\sim 8\%$ B_2O_3), and third for Vendor A nonpressable boron nitride (containing $\sim 0.6\%$ B_2O_3). No measurable water pickup was observed for Vendor B high-purity boron nitride ($>99.5\%$ BN).

DRYING STUDIES

The drying characteristics, at 100°C , of various commercial boron nitride powders that had been equilibrated by prior exposure to a 100 percent relative humidity atmosphere for one week were also studied. Results, as summarized in Table 14, indicate that extremely long drying periods in an oven at 100°C are required for two grades of Vendor A boron nitride powders containing approximately 0.6 to 8.0 percent boric oxide.

For the drying studies shown in Table 14, three large dishes containing Vendor A pressable boron nitride, Vendor A nonpressable boron nitride, and Vendor B high-purity

Table 14
 DRYING OF VARIOUS COMMERCIAL BORON NITRIDE POWDERS AT 100° C

Vendor A, Pressable BN(1)			Vendor A, Nonpressable BN(1)			Vendor B, High-Purity BN(1)		
Drying Time	Weight Loss		Drying Time	Weight Loss		Drying Time	Weight Loss	
	Gram	Percent		Gram	Percent		Gram	Percent
0	-	-	0	-	-	0	-	-
1 Hr	0.4227	8.16	1 Hr	0.2108	2.09	1 Hr	0.0338	0.64
2 Hrs	0.4355	8.67	2 Hrs	0.1889	1.88	2 Hrs	0.0355	0.55
3 Hrs	0.3885	7.55	3 Hrs	0.2069	2.09	3 Hrs	0.0245	0.41
19 Hrs 5 Min	0.4868	9.73	19 Hrs 15 Min	0.2353	2.34	19 Hrs 25 Min	0.0102	0.23
						19 Hrs 25 Min	0.0377	0.71
27 Hrs	0.4965	9.92	27 Hrs 10 Min	0.2150	2.17	27 Hrs 20 Min	0.0245	0.41
45 Hrs 35 Min	0.5115	10.22	45 Hrs 15 Min	0.2308	2.29	45 Hrs 25 Min	0.0368	0.69
45 Hrs 35 Min	0.4751	9.24	45 Hrs 30 Min	0.2252	2.27	45 Hrs 25 Min	0.0269	0.45
45 Hrs 35 Min	0.5021	10.00	45 Hrs 30 Min	0.2447	2.44	45 Hrs 25 Min	0.0430	0.66
45 Hrs 35 Min	0.4878	9.42	45 Hrs 30 Min	0.2080	2.07			
140 Hrs 30 Min	0.5925	11.84	140 Hrs 15 Min	0.2310	2.33	51 Hrs 5 Min	0.0115	0.26
140 Hrs 30 Min	0.5631	10.94	140 Hrs 15 Min	0.2458	2.54	145 Hrs 5 Min	0.0115	0.26

(1) Ten grams of sample used.

boron nitride were exposed to a 100 percent relative humidity atmosphere for one week. Twelve Petri dishes (9.6 in² area) were tared, then five grams of boron nitride powder (weighed to ± 0.1 mg) were weighed in the dishes. The dishes were placed in a laboratory drying oven at 100° C. One dish of each powder was removed, cooled under a Petri-dish cover for five minutes, and weighed at intervals of one hour for the first three hours. After weighing, the dishes were returned to the oven to be removed and weighed in order at a later time. The powders remained in the oven for 140 hours. These data indicate that extremely long drying times are required at 100° C for various commercial boron nitride powders. Vendor A pressable boron nitride showed a gross weight loss of 11.4 percent and Vendor A nonpressable boron nitride a weight loss of 2.4 percent. Vendor B high-purity boron nitride had a negligible weight loss.

BORON NITRIDE STEAM PURIFICATION

Some preliminary low-temperature steam purification studies of 900° C boron nitride were made at 200 - 500° C following the method of Mercuri and Litz.⁽⁸⁾ According to this method, the removal of oxygen impurities from such refractory materials as boron nitride can be accomplished by contacting the material to be purified with a water-vapor-laden gas, or steam, at a temperature of approximately 300° C. As a result of the contact of the stream of water vapor with the boron nitride material, oxygen impurities are vaporized out of the boron nitride material and removed with the exiting gases. However, results, as summarized in Table 15, show that no reduction in the oxygen content of the boron nitride was realized, but it is suspected that oxidation

of the boron nitride may have occurred in these tests because of air inleakage to the apparatus.

Table 15
LOW-TEMPERATURE STEAM PURIFICATION OF 900° C BORON NITRIDE

	Initial 900° C BN Powder	Run Number ⁽¹⁾			
		1	2	3	4
Temperature (° C)	-	200	300	400	500
Reaction Time (hrs)	-	12.0	12.0	12.0	12.0
Total Boron (%)	40.2	40.3	39.5	38.4	39.3
Free Boron (%)	2.6	1.7	4.4	3.0	11.3
Oxygen (% O ₂)	13.83	14.57	15.64	16.38	13.68
Nitrogen (% N ₂)	42.5	43.0	39.85	41.29	41.0
H ₂ O (%) ⁽²⁾	1.0	1.4	1.0	2.7	1.8
Percent Weight Loss During Run	-	-	9.98	25.8	67.8

(1) A water-saturated argon atmosphere was used in these tests.

(2) By the Karl Fischer titration method.

The low-temperature steam purification studies were continued in an attempt to lower the oxygen content of the 900° C boron nitride by passing a flowing atmosphere of water-saturated argon over the boron nitride at temperatures of 200 - 500° C. A horizontal tube furnace was used that contained a three-inch-diameter by 32-inch-long quartz tube, with quartz boats to contain the boron nitride powder. Since the Chromel-Alumel thermocouple wire used for measuring the temperature at the quartz boats inside the reactor tube extended through the exit tubing which was exposed to the atmosphere, it is believed that back diffusion of air into the reactor probably occurred. Thus, oxidation of the 900° C boron nitride having a fine particle size (average diameter, 7.2 μ) and high surface area could have occurred at 300° C to account for the unusually high percent oxygen results obtained.

As shown in Table 15, when the temperature was increased from 300 to 500° C, an increased weight loss of the 900° C boron nitride resulted, which indicates that steam pyrohydrolysis of the boron nitride occurred as a consequence of this air inleakage.

BORON NITRIDE RENITRIDATION

An additional 24 batches of boron nitride were prepared by the reaction of boric oxide and tricalcium orthophosphate at 900° C with potassium hydroxide-dried ammonia

gas using the equipment and procedure described previously. After removing the tricalcium orthophosphate filler compound, this 900° C boron nitride material was composited by dry blending, analyzed, and used as the starting material for high-temperature renitridation studies and low-temperature steam purification studies. A summary of the renitridation data obtained at 1,320 and 1,400° C is given in Table 16. Nitrogen analysis indicates that 98.4 percent of the theoretical nitrogen content of boron nitride was obtained by this renitridation treatment.

X-ray diffraction analysis of some of the renitridated boron nitride product showed hexagonal boron nitride as the major constituent, with no other detectable intermediate or minor constituents. An X-ray diffraction pattern of the laboratory prepared hexagonal boron nitride is presented in Figure 8. The diffraction pattern obtained showed sharp and distinct lines which agreed at all interplanar spacings with the ASTM standard. A summary of the major X-ray diffraction spacings and their relative intensities for standard hexagonal boron nitride is given in Table 17.

As shown in Table 16, renitridation of the 900° C boron nitride at 1,400° C, using a hold time of 16 hours (Run 3), resulted in a high-purity product which analyzed 55.5 percent nitrogen compared to a theoretical nitrogen content of 56.4 percent nitrogen. The nitrogen content of the starting 900° C boron nitride was only 40.5 percent nitrogen. This 1,400° C renitridated boron nitride product also contained only 1.05 percent oxygen compared to 13.83 percent for the 900° C boron nitride material. These data indicate that the intermediate conversion compound that has been postulated^(1,6) for the 900° C boron nitride product can be eliminated by a subsequent renitridation treatment at 1,400° C.

SPECTROCHEMICAL PURITY

The spectrochemical purity of laboratory prepared boron nitride powders after dilute hydrochloric acid treatment and methyl alcohol extraction treatment is given in Table 18. The spectrochemical purity of a commercial grade of boron nitride powder (Vendor A pressable BN) is also listed in Table 18. These data show that the total elemental impurities (exclusive of oxygen) is 0.047 - 0.050 percent, representing a minimum purity of 99.95 percent for the laboratory prepared boron nitride powders. For comparison, the spectrographic purity of the commercial batch of boron nitride powder, shown in Table 18 (also exclusive of oxygen), was approximately 99.87%. Only three elemental impurities, calcium, nickel, and silicon, were found to be present in detectable quantities; all other elements were present in amounts less than their detectable limits.

ELECTRON MICROSCOPY

Electron photomicrographs were made of various types of laboratory prepared and commercially procured boron nitride powders at magnifications from 17,000 to 183,000X

Table 16
RENITRIDATION TREATMENT OF 900° C BORON NITRIDE WITH AMMONIA AT ELEVATED TEMPERATURES

	Initial 900° C BN Powder	Run Number						
		1	2	3	4	5	6	7
Temperature (°C)	-	1,320(1)	1,400	1,400	1,400	1,400	1,400	1,400
Reaction Time (hrs)	-	-	8	16	8	24	28	48
Total Boron (%)	40.2	42.7	42.2	43.1	42.5	42.2	44.1	41.8
Free Boron (%)	2.6	2.0	1.4	1.4	0.7	0.6	1.0	0.7
Oxygen (% O ₂)	13.83	1.77	1.83(2)	1.05	2.24(2)	1.21	2.15	2.14(3)
Nitrogen (% N ₂)	42.5	49.3	54.2	55.5	53.7	54.6	52.6	53.1
H ₂ O (%) ⁽⁴⁾	1.0	0.7	1.1	0.2	0.4	0.12	0.6	0.19
B ₂ O ₃ (%) ⁽⁵⁾	-	0.24	1.40	-	0.25	-	-	-
Percent Weight Loss During Renitridation	-	8.0	9.0	10.8	12.3	17.6	-	-

(1) Run took 20 hours to attain a temperature of 1,320° C.

(2) Tube cracked during run; some partial oxidation of the boron nitride product is possible.

(3) Supply of flowing ammonia gas failed during run; some partial oxidation of the boron nitride product is possible.

(4) By the Karl Fischer titration method.

(5) By methyl alcohol extraction.

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Figure 8. X-RAY DIFFRACTION PATTERN OF LABORATORY PREPARED HEXAGONAL BORON NITRIDE.

Table 17
STANDARD X-RAY DIFFRACTION SPACINGS
FOR HEXAGONAL BORON NITRIDE

d Spacings ⁽¹⁾ (angstroms)	Relative Intensity (%)
3.33	100
2.17	15
2.00	6
1.82	13
1.67	6
1.17	8
1.00	5

(1) ASTM powder diffraction file.

Table 18
SPECTROCHEMICAL ANALYSIS OF LABORATORY PREPARED AND COMMERCIAL
BORON NITRIDE POWDERS

Element	Three Batch Composite ⁽¹⁾ (%)	Batch 4 ⁽¹⁾ (%)	P-BN ⁽²⁾ (%)	Element	Three Batch Composite ⁽¹⁾ (%)	Batch 4 ⁽¹⁾ (%)	P-NB ⁽²⁾ (%)
Ag	<0.005	<0.005	<0.005	Mn	0.007	<0.005	<0.005
Al	<0.01	<0.01	0.01	Mo	<0.002	<0.002	<0.002
Au	<0.02	<0.02	<0.02	Na	<0.01	<0.01	0.015
B	Matrix	Matrix	Matrix	Nb	<0.02	<0.02	<0.02
Ba	<0.002	<0.002	<0.002	Ni	0.025	0.04	0.02
Be	<0.001	<0.0005	<0.001	P	<1	<1	<1
Bi	<0.01	<0.01	<0.01	Pb	<0.01	<0.01	<0.01
Ca	0.015	0.008	0.04	Rb	<0.15	<0.15	<0.15
Cd	<0.04	<0.04	<0.04	Sb	<0.04	<0.04	<0.04
Co	<0.005	<0.005	<0.005	Si	0.01	<0.01	0.06
Cr	<0.01	<0.01	<0.01	Sr	<0.005	<0.005	<0.005
Cs	<0.6	<0.6	<0.6	Ta	<0.15	<0.15	<0.15
Cu	<0.005	<0.005	<0.005	Th	<0.04	<0.04	<0.04
Fe	<0.02	<0.02	<0.02	Ti	<0.01	<0.01	<0.01
Hf	<0.02	<0.02	<0.02	U	<0.3	<0.3	<0.3
K	<0.04	<0.04	<0.04	V	<0.005	<0.005	<0.005
Li	<0.02	<0.02	<0.02	W	<0.08	<0.08	<0.08
Mg	<0.01	<0.01	<0.01	Zn	<0.08	<0.08	<0.08
				Zr	<0.002	<0.002	<0.002

(1) Laboratory prepared BN powder.

(2) Commercially procured, pressable BN powder.

to characterize these powders with regard to size and shape. Representative electron photomicrographs are presented in Figures 9 through 27; analytical data for the various boron nitride powders shown in the electron photomicrographs are given in Table 19.

Table 19
ANALYTICAL DATA FOR ELECTRON PHOTOMICROGRAPHS SHOWN IN FIGURES 9 THROUGH 27

Material	Percent Nitrogen	Percent Oxygen	Percent Boron	Particle Size Distribution ⁽¹⁾ (% $\leq$ Diameter)			Electron Photomicrograph Reference
				10% (μ)	50% (μ)	90% (μ)	
Laboratory Prepared, Batch A-6E ⁽²⁾	-	5.92	40.1	2.4	5.2	11.7	Figures 9, 10, 11
Laboratory Prepared, Batch A-12E ⁽²⁾	49.6	5.61	41.4	3.7	9.3	27.0	Figures 12, 13
Laboratory Prepared, Batch B-1E ⁽²⁾	49.4	8.50	40.1	3.6	7.7	18.2	Figures 14, 15
Laboratory Prepared, Batch B-2E ⁽²⁾	49.6	2.94	41.0	3.5	8.4	20.1	Figures 16, 17
Vendor A, Pressable Grade ⁽³⁾	49.0	4.71	41.2	2.2	5.3	12.5	Figures 18, 19, 20
Vendor A, Nonpressable Grade ⁽⁴⁾	55.1	0.64	42.9	3.4	6.8	25.6	Figures 21, 22
Vendor B, High-Purity Grade	-	0.50	-	2.3	6.4	12.2	Figures 23, 24
Laboratory Prepared, Renitrided at 1,400° C ⁽⁵⁾	55.5	1.05	43.1	-	-	-	Figures 25, 26, 27

(1) Particle diameters were interpolated at 10, 50, and 90 weight percent levels from the distribution curves obtained with a Sharples Micromerograph.

(2) By reaction with NH_3 at 900° C.

(3) Surface area = 16.4 m^2/gm , bulk density = 0.35 gm/cc , tap density = 0.76 gm/cc .

(4) Surface area = 8.7 m^2/gm , bulk density = 0.45 gm/cc , tap density = 0.87 gm/cc .

(5) After prior nitridation with NH_3 at 900° C.

A comparison of the electron photomicrographs of the various types of boron nitride powders indicates that those powders having a known high oxygen content show the presence of a white or gray material, presumably boric oxide or hydrated boric acid. This condition is evident by comparing Figures 18 and 19, which show a pressable grade of boron nitride containing a relatively high oxygen content (6.8% as B_2O_3), with Figures 21 through 24 which represent the nonpressable and high-purity grades of boron nitride containing a relatively low oxygen content.

The electron microscope studies were made by dispersing small amounts of boron nitride powder in a 2.5 percent solution of collodion in amyl acetate using a stainless steel spatula and a flat glass plate. The mixture was stirred to achieve homogeneity, and a drop, when placed on a water bath, formed a film which spread out. This film was picked up on 1/8-inch microscope grids and examined directly in the electron microscope. Electron photomicrographs were then taken at various magnifications.

PEM-200-7575

Figure 9. TYPICAL PARTICLE SHAPES OF BATCH A-6E LABORATORY-PREPARED BORON NITRIDE POWDER. (17,700X)

PEM-200-7577

Figure 10. TYPICAL PARTICLE SHAPES OF BATCH A-6E LABORATORY-PREPARED BORON NITRIDE POWDER. (69,000X)

PEM-200-7582

Figure 11. TYPICAL SHAPES OF BATCH A-6E LABORATORY-PREPARED BORON NITRIDE POWDER THAT WAS RECRYSTALLIZED AFTER DISPERSION IN BUTYL ALCOHOL. (69,000X)

PEM-200-7661

Figure 12. TYPICAL PARTICLE SHAPES OF BATCH A-12E LABORATORY-PREPARED BORON NITRIDE POWDER. (17,700X)

PEM-200-7660

Figure 13. TYPICAL PARTICLE SHAPES OF BATCH A-12E LABORATORY-PREPARED BORON NITRIDE POWDER. (69,000X)

PEM-200-7705

Figure 14. TYPICAL PARTICLE SHAPES OF BATCH B-1E LABORATORY-PREPARED BORON NITRIDE POWDER. (17,700X)

PEM-200-77C9

Figure 15. TYPICAL PARTICLE SHAPES OF BATCH B-1E LABORATORY-PREPARED BORON NITRIDE POWDER. (69,000X)

PEM-200-7756

Figure 16. TYPICAL PARTICLE SHAPES OF BATCH 3-2E LABORATORY-PREPARED BORON NITRIDE POWDER. (17,700X)

PEM-200-7759

Figure 17. TYPICAL PARTICLE SHAPES OF BATCH B-2E LABORATORY-PREPARED BORON NITRIDE POWDER. (69,000X)

PEM-200-7633

Figure 18. TYPICAL PARTICLE SHAPES OF VENDOR A PRESSABLE-GRADE BORON NITRIDE POWDER. (17 700X)

PEM-200-7634

Figure 19. TYPICAL PARTICLE SHAPES OF VENDOR A PRESSABLE-GRADE BORON NITRIDE POWDER. (69,000X)

PEM-200-7638

Figure 20. TYPICAL PARTICLE SHAPES OF VENDOR A PRESSABLE-GRADE BORON NITRIDE POWDER. (165,000X)

PEM-200-7752

Figure 21. TYPICAL PARTICLE SHAPES OF VENDOR A NONPRESSABLE-GRADE BORON NITRIDE POWDER. (17,700X)

PEM-200-7754

Figure 22. TYPICAL PARTICLE SHAPES OF VENDOR A NONPRESSABLE-GRADE BORON NITRIDE POWDER. (69,000X)

PEM-200-7927

Figure 23. TYPICAL PARTICLE SHAPES OF VENDOR B HIGH-PURITY GRADE BORON NITRIDE POWDER. (17,700X)

PEM-200-7928

Figure 24. TYPICAL PARTICLE SHAPES OF VENDOR B HIGH-PURITY GRADE BORON NITRIDE POWDER. (69,000X)

PEM-200-10770

Figure 25. TYPICAL PARTICLE SHAPES OF LABORATORY-PREPARED HIGH-PURITY BORON NITRIDE POWDER. (15,000X)

PEM-200-10772

Figure 26. TYPICAL PARTICLE SHAPES OF LABORATORY-PREPARED HIGH-PURITY BORON NITRIDE POWDER. (75,000X)

PEM-200-10775

Figure 27. TYPICAL PARTICLE SHAPES OF LABORATORY-PREPARED HIGH-PURITY BORON NITRIDE POWDER. (183,000X)

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