United States Patent [19]

De Vries et al.

[11] 3,918,931

[45] Nov. 11, 1975

[54]	MANUFA	N-PRECIPITATION PROCESS FOR CTURING CUBIC BORON ABRASIVE TOOLS
[75]	Inventors:	Robert C. De Vries, Burnt Hills; James F. Fleischer, Scotia. both of N.Y.
[73]	Assignee:	General Electric Company, Schenectady, N.Y.
[22]	Filed:	Dec. 17, 1973
[21]	Appl. No.:	425,201
[51]	Int. Cl. ²	
[56]		References Cited
	UNIT	ED STATES PATENTS
2.947.	617 8/196	0 Wentorf 51/307

3.212.852	10/1965	Bundy
3,743,489	7/1973	Wentorf et al
3.768,972	10/1973	Taylor et al

Primary Examiner—Donald J. Arnold Attorney, Agent, or Firm—Charles T. Watts; Joseph T. Cohen; Jerome C. Squillaro

[57] ABSTRACT

Hexagonal boron nitride (HBN) is converted to cubic boron nitride (CBN) within a transition metal alloy solvent system containing a small percentage of aluminum. Precipitous drops in the conversion of HBN to CBN occur as the ratio of the weight of HBN to the weight of metal in the initial mixture increases beyond some maximum yield ratio that may be routinely determined for each alloy. An abrasive body is produced in which the binder for the CBN gains is the metal alloy solvent itself, e.g., a superalloy.

13 Claims, No Drawings

SOLUTION-PRECIPITATION PROCESS FOR MANUFACTURING CUBIC BORON NITRIDE ABRASIVE TOOLS

BACKGROUND OF THE INVENTION

The method of converting hexagonal boron nitride (HBN) to cubic boron nitride (CBN) employing at least one catalyst selected from the class consisting of ¹⁰ alkali metals, alkaline earth metals, lead, antimony, tin and nitrides of these metals is described in U.S. Pat. No. 2,947,617 — Wentorf, Jr. This patent is incorporated by reference.

The use of Fe₃Al and certain silver-cadmium alloys as ¹⁵ catalysts in the conversion of HBN to CBN has been described in "Synthesis of Cubic Boron Nitride" by Saito et al. (Yogyo-Kyokai Shi, Vol. 78, No. 893).

The use of aluminum alloys of cobalt, nickel and manganese as catalysts for the conversion of HBN to 20 the CBN form at high pressure and high temperature is disclosed in U.S. patent application Ser. No. 351,338 — Wentorf, Jr. et al. (incorporated by reference), filed Apr. 16, 1973 and assigned to the assignee of the instant invention.

The term "minimum composition" is that alloy composition for a given alloy system at which extensive solid solution is obtained at the lowest temperature.

The term "room temperature" is intended to mean a temperature in the 70°-75°F range. "Quenching" 30 means instituting a rapid drop in temperature. With the apparatus employed herein a temperature drop of about 1500°C/minute can be achieved by simply turning of the power to the reaction vessel with the pressure still applied.

DESCRIPTION OF THE INVENTION

This invention is an improvement over the invention in the Wentorf, Jr. et al. application. The product produced from the process of this invention is a solid abrasive transition metal-aluminum alloy matrix body consisting of small well-formed CBN crystals distributed uniformly through the metal binder phase. Conversion of HBN to CBN as high as 93 percent have been achieved. These capabilities depend upon the discoveries (not disclosed in Wentorf, Jr. et al.) that:

- a. at pressures and temperatures at which CBN is the stable phase, HBN dissolves quickly in a number of alloy systems made up of a small amount of aluminum together with at least two metals from the 50group consisting of chromium, manganese, iron cobalt and nickel; the alloy system becomes supersaturated with respect to CBN and the CBN precipitates; b. when the weight percent of HBN to be used in the HBN/alloy mixture is properly selected 55 within the 10-50 weight percent (w/o) HBN range, the maximum CBN yield for that given operating temperature and specific alloy can be obtained; the optimum w/o HBN is routinely determinable for the particular alloy to be employed and this deter- 60 mination should be made, because remarkably steep drops in yields have been unexpectedly encountered in each instance, when increasing amounts of HBN are employed, the peak value being encountered in the aforementioned w/o 65
- c. the operating temperature should be the lowest temperature at which all of the alloy will be melted

at the operating pressure whereby maximum liquid formation of the alloy will be made available, because yields of CBN appear to decrease with increasing temperature, and

d. by utilizing all component materials (HBN, preformed alloy or individual alloy components) in powder form, well mixed to produce fairly uniform distribution, the CBN crystals produced are wellformed, more equiaxed with individual face development and free of gross defects.

When the properties (e.g., toughness, hardness, etc.) of the alloy binder are to be optimized, the specific composition of the transition metal alloy will be selected from the phase diagram for the alloy system. Otherwise, for convenience, the composition of the transition metal alloy is selected by choosing the binary or ternary eutectic or the minimum composition of the given alloy system. Once the specific combination has been selected, a small amount (less than 5 percent) of aluminum is added thereto. The aluminum can be added as aluminum metal, AlN or Al₄C₃. When the eutectic or minimum compositions for the given alloy system can be used, maximum liquid formation can be obtained at the lowest temperature and this, in turn, helps 25 in maximizing the yield of CBN. The percentage of HBN converted to CBN is a function of the alloy, the pressure-temperature conditions and the initial amount of HBN.

The metals listed hereinabove for the alloy formation are used, because they do not form such stable nitrides and borides as will reduce the availability of nitrogen and boron atom at the CBN-metal interface or significantly reduce (by dissolution) the amount of CBN.

The method of this invention comprises the following 35 steps:

- 1. mixing HBN powder with a powdered metallic phase to produce a homogeneous mixture, the atomic content of said metallic phase consisting essentially of aluminum atoms, atoms of a metal selected from the group consisting of chromium and manganese, and atoms of at least one metal selected from the group consisting of iron, cobalt and nickel, the weight percent of HBN in said mixture, being in the range of from about 10 to about 50 weight percent;
- pressing said mixture into some predetermined shape;
- 3. simultaneously subjecting said mixture to an operating temperature and operating pressure within the stability region of CBN defined by the use of the selected metallic phase, the operating temperature being high enough to render molten all of the metallic phase, the period of time of simultaneous temperature and pressure application being sufficient to permit dissolution of all of the HBN in the molten metallic phase and the precipitation of CBN crystals therefrom;
- quenching the resulting CBN/alloy system to about room temperature while maintaining the operating pressure;
- 5. reducing the pressure to atmospheric pressure and
- recovering the preshaped abrasive body consisting essentially of CBN crystals distributed in a transition metal-aluminum alloy matrix.

The minimum pressure for the conversion of HBN to CBN has been found to be about 45-47 kb regardless of the specific metallic phase (unalloyed mix or preformed alloy) employed, but the minimum temperature

3

varies. Thus, once a metallic phase formulation has been selected it is preferable to determine the Pressure-Temperature Stability Region for CBN for that given formulation. A representative P-T phase diagram for boron nitride showing the CBN-stable and HBN-stable regions is shown in FIG. 1 of the Wentorf patent. Such a phase diagram is routinely determinable for a given metallic phase formulation by one skilled in the high temperature-high pressure art.

In order to determine the w/o HBN for maximum conversion to CBN for the specific metallic phase the above method steps were repeated using a number of different weight percentages of HBN. The CBN produced in each abrasive body was recoverd by acid dissolution of the alloy portion. If the chromium content of the alloy was low, aqua regia or dilute hydrochloric acid was used. If the chromium content was high, solutions of H₂SO₄-H₃PO₄ acids were used.

As may be seen from the data set forth below, the percentage yield of CBN increases sharply with increasing w/o of HBN in the mixture, reaches a peak and then falls off in a very steep drop in percent yield that was not expected and is not understood. In principle a continued increase or a leveling off in yield would have been expected. This peaking out and sharp decrease in CBN yield occurs in the 10-50 w/o HBN range regardless of the alloy solvent.

Table I below shows the percent yield of CBN obtained as a function of increasing w/o of HBN in the mixture. In the various runs the powders for yielding the alloy composition (46 w/o Fe, 32 w/o Ni, 21 w/o Cr and 1 w/o Al) and HBN powder were mixed and pressed into a cylindrical shape in a mold and were then subjected to temperatures in the 1440°-1460°C range and pressures in the 50-55 kb range. After lowering the temperature and pressure, a cylindrical abrasive body (CBN grains in an alloy binder) was removed from the reaction vessel remains. The metal was dissolved away in acid and the remaining CBN was weighed.

TABLE I

	Yield (%)	Time (min)	HBN w/o	HBN (gms)	Metal (gms)
 4	12	120	1.4	0.025	1.764
	26	71 .	2.9	0.050	1.67
	48	120	6.4	0.100	1.470
	59	80	10.6	0.150	1.270
	70	120	15.64	0.200	1.080
	83	80	22.2	0.250	0.876
5	25	80	25.0	0.270	0.804
,	9.3	77	30.5	0.300	0.684
	11.8	120	57.2	0.400	0.300

Table II shows changes occurring in CBN yield as the w/o HBN in the mixture was varied. As above, powders were combined to yield the requisite alloy (39.2 w/o Ni, 58.8 w/o Mn and 2.0 w/o Al) in situ. Preparation and shaping of the mixture to be converted to the abrasive body and determination of CBN yield were as described above. The conversion was conducted at 52.5 60 kb and 1450°C.

TABLE II

Metal (gms)	HBN (gms)	HBN (w/o)	Time (min)	Yield (%)	— 65
1.470	0.100	6.4	60	31.0	
1.074	0.200	15.6	60	88.5	
0.684	0.300	30.5	60	91.0	
0.486	0.350	42.0	60	79.4	

TABLE II-continued

Metal	HBN	H BN	Time	Yield
(gms)	(gms)	(w/o)	(min)	(%)
0.294	0.400	57.0	60	

Table III and Table IV are derived from data obtained as in Tables I and II, the metal alloy composition for Table III was 49 w/o Ni, 49 w/o Cr and 2 w/o Al and the metal alloy composition for Table IV was 8 w/o Fe, 43 w/o Ni, 47 w/o Cr and 2 w/o Al. The operating temperatures were 1450°C and the operating pressures were 52.5 kb.

TABLE III

Metal (gms)	HBN (gms)	HBN (w/o)	Time (min)	Yield (%)
1.470	0.100	6.4	60	15.2
1.0725	0.200	15.7	60	53.8
0.684	0.300	30.5	60	62.5
0.486	0.350	41.9	60	70.2
0.294	0.400	57.6	60	34.1
0.096	0.450	82.4	60	2.1

TABLE IV

	etal ms)	HBN (gms)	HBN (w/o)	Time (min)	Yield (%)
1.6	5276	0.060	3.56	50	0
1.4	1679	0.100	6.4	42	16
1.2	2728	0.150	10.5	73	38.8
1.0	781	0.200	15.7	77	57.0
0.8	3811	0.250	22.1	77	67.5
0.6	5834	0.300	30.5	70	82.5
0.4	1916	0.350	41.6	60	93.0
0.3	390	0.375	49.0	60	72.0
0.2	2878	0.400	58.2	73	55.1

Data for Table V was obtained as described hereinabove. The metal alloy resulting from the powders was 39.2 w/o Fe, 58.8 w/o Mn and 2.0 w/o Al. Operating conditions were 52.5 kb and 1450°C.

TABLE V

Metal (gms)	HBN (gms)	HBN (w/o)	Time (min)	Yield (%)
1.470	0.100	6.4	60	53.8
1.074	0.200	15.6	60	82.0
0.684	0.300	30.5	60	85.9
0.588	0.325	35.6	60	90.6
0.486	0.350	42.0	60	13.6
0.294	0.400	57.0	60	6.4

One preferred form of a high pressure, high temperature apparatus in which the method of the instant invention may be practiced is the subject of U.S. Pat. No. 2,941,248 - Hall (incorporated by reference) and is well-known in the art as the "belt apparatus." Essentially, the apparatus includes a pair of cemented tungsten carbide punches in opposed relationship to each other disposed on opposite sides of an intermediate belt or die member, and are aligned with a hole through the die member having tapered sides. The space between the punches and the wall of the hole accommodates a pair of gasket/insulating assemblies, which in turn sur-5 round a reaction vessel. The gasket/insulating assemblies are typically made of thermally insulating, electrically non-conducting pyrophyllite and include means by which electrical energy may be controllably applied

5

to the system to provide the requisite heating of the reaction vessel.

Preferably, with the exception of the heater, which is usually made of graphite, the reaction vessel parts to be employed in the conduct of this method should be 5 made of sodium chloride, although other materials such as talc, potassium chloride, etc., as described in U.S. Pat. No. 3,030,662 — Strong, incorporated by reference, may be employed. Techniques for calibration of the device for pressure and temperature are well es- 10 tablished in the literature.

The product of this process is a solid body recovered in some preselected form and consisting of small wellformed CBN crystals distributed uniformly through a metal binder phase. The volume percent of abrasive 15 grain present therein may be readily made as high as about 55 percent by volume of the abrasive body. Some small amount of boron nitride remains in solution in the metallic phase accounting for the small differential between the HBN present in the original mixture and the 20 amount of CBN recovered when the metal phase has been dissolved away to determine the CBN content.

Abrasive bodies produced by the practice of this invention have been utilized to grind sapphire, silicon carbide, cemented tungsten carbide, steel and quartz. 25 For convenience in brazing, these abrasive bodies have also been formed as composites having a layer on one surface thereof of the solvent-binder alloy employed. This metal surface has been successfully brazed into a volving machinery. Such composites may be advantageously brazed into saw blades and coring tools. Further, since the metal solvent-binder is acid soluble, the abrasive grain at the surface of the abrasive tool may be readily exposed by dipping the tool in a dilute acid solu-

This method is particularly advantageous because the matrix for the completed tool serves as the solvent from which the CBN crystals appear to be precipitated. The ure/temperature conditions. This preparation of the CBN crystals by precipitation from a metallic solvent that remains as the binder promotes excellent metal-tograin contact (no weak intermediate phases) resulting in superior bonding between the binder and each abra- 45 sive crystal. The ability to use a number of transition metals for the conduct of the conversion of HBN to CBN enables the selection of many alloy systems from among the superalloys and stainless steels. Superalloy binders for CBN grains. Conduct of the method of the instant invention for the preparation of abrasive bodies in which the binder is a superalloy composition is encompassed within the best mode of this invention as described hereinbelow.

DESCRIPTION OF THE PREFERRED **EMBODIMENT**

High melting alloy systems that have been effectively employed in the practice of this invention are the iron- 60 nickel-chromium-aluminum system; the nickel-chromium-aluminum system and the nickel-manganesealuminum system.

The amount of aluminum employed will preferably be less than 5 w/o in the aforementioned alloy systems 65 and as such will not seriously affect the eutectic or minimum melting compositions for the systems. Thus, the minimum melting composition for the iron-nickel-

chromium-aluminum alloy system is about 1315°C (at 1 atmosphere); the minimum melting composition for the nickel-chormium-aluminum system is about 1345°C (at 1 atmosphere) and the minimum melting composition of the nickel-manganese-aluminum system is about 1010°C (at I atmosphere).

Specific combinations of the metals set forth above have been successfully employed for the preparation of abrasive bodies. Once the pressure was applied to the reaction vessel the temperature thereof was raised to the desired value in a period of from 1 to 4 minutes and was held at the operating temperature. Quenching to room temperature was accomplished with the pressure applied to the system.

EXAMPLE 1

0.282 gms of HBN and 0.396 gms of metal (58.8 w/o Mn, 39.2 w/o Ni and 2.0 w/o Al) were mixed and pressed into a pellet about 0.250 inch high \times 0.250 inches diameter. HBN constituted about 42 w/o of the (metal plus HBN) mixture. A separate disc (0.060 inch deep) of metal alloy powder only was placed against the BN-metal pellet and both were simultaneously exposed to 52.5 kb and 1450°C for 30 minutes. CBN grains precipitated in the pellet and the metal alloy disc became firmly bonded together and bonded to the abrasive-containing portion. This metal alloy "pad" was silver-soldered to a steel cup having a $rac{1}{18} imes 1$ inch holder for mounting of the abrasive body for use in re- 30 shaft attached thereto to produce an abrasive tool. The abrasive grains were exposed (i.e., the wheel was "opened") by etching the surface for 3 minutes in aqua regia. This tool when mounted in a rotating machine such as a drill easily ground a steel file, a sapphire sin-35 gle crystal on both basal and prism planes, a SiC block, a piece of tungsten carbide, and a piece of talc.

EXAMPLE 2

Two CBN cylinders with attached metal alloy pad of HBN is rapidly soluble therein at the operating press- 40 the type described in Example 1 were made simultaneously by using an inert separator of NaCl, which was in contact with the metal alloy pad for each pellet. The conditions for synthesis were 52.5 kb and 1450°C applied for 45 minutes. A metal alloy pad was found to be securely fastened to each abrasive-containing portion by this process.

EXAMPLE 3

A mixture of metal and HBN and CBN was made and matrices, in particular, provide very tough solvent- 50 pressed into three separate cylinders about 0.25 inch in diameter. The mixture composition was

> 0.240 gms CBN 0.060 gms HBN 0.4824 gms Fe — (46 w/o) 0.336 gms Ni - (32 w/o)0.2208 gms Cr — (21 w/o) 0.01053 gms Al - (1 w/o).

The three pellets were placed (one above the other and in contact) in a high pressure cell and subjected to 55 kb and 1450°C for 60 minutes. Upon removal from the cell the three pellets had sintered together and had cemented the CBN grains (both original and as precipitated) to form a single cylinder 0.262 inch high and about 0.250 inch in diameter. Metallographic examination of a polished section of this specimen shows good wetting of the CBN grains.

20

7

EXAMPLE 4

Two grinding tools with a central hole to facilitate mounting were made simultaneously in a high pressure cell by treatment for 60 minutes at 52.5 kb and 1450℃. Two discs 0.140 inch high × 0.250 inch in diameter were pressed from a powder mixture of HBN (0.140 gm), Mn(0.170 gm), Fe(0.114 gm) and Al(0.006 gm). A 1/2 inch diameter hole was then drilled through the center of each disc. In the high pressure cell these holes 10 were filled with a 1/8 inch diameter NaCl plug, and the two discs were separated by a 0.030 inch salt disc. Two "doughnut-shaped" grinding tools consisting of CBN in a metal matrix were produced. Using the central hole these tools could be mounted directly on a shaft without further preparation. In actual practice the initial discs could be pressed out in the final shape before the high pressure treatment rather than having to drill the central hole.

EXAMPLE 5

The process of Example 4 was repeated except that the central hole was made 0.099 inch in diameter. Two annular grinding tools with sharp edges were simultaneously prepared. One such tool was taken as recovered from the high pressure-high temperature apparatus and was mounted on a shaft without additional preparation. The shaft was used to accommodate the tool in a small rotating machine and a piece of tool steel was ground easily therewith.

EXAMPLE 6

A metal HBN mixture was made from powders taken in the following amounts:

0.200 gms HBN 0.0865 Fe — (8 w/o) 0.405 Ni — (43 w/o) 0.505 Cr — (47 w/o)

0.0216 Al - (2 w/o)

After mixing, this material was divided into three approximately equal portions and pressed into three 45 discs. These were placed in a high pressure cell and were separated from each other with NaCl discs. After treatment at 55 kb and 1450°C for 60 minutes, the discs were removed from the cell. Well-bonded CBN was visible in each metal-BN disc, and the discs were 50 suitable for mounting for use as abrasive units as removed from the cell. The dimension of each metal-BN disc was 0.250 inch diameter × approximately 0.050

What we claim as new and desire to secure by Letters 55 process of claim 1. Patent is:

13. The preshape

inch high.

1. The method of preparing cubic boron nitride abrasive tools comprising the steps of

8

- a. mixing HBN powder with a powdered metallic phase to produce a homogeneous mixture, the atomic content of said metallic phase consisting essentially of aluminum atoms, atoms of a metal selected from the group consisting of chromium and manganese, and atoms of at least one metal selected from the group consisting of iron, cobalt and nickel, the weight per cent of HBN in said mixture, being in the range of from about 10 to about 50 weight percent;
- b. pressing said mixture into some predetermined shape:
- c. simultaneously subjecting said mixture to an operating temperature and operating pressure within the stability region of CBN defined by the use of the selected metallic phase and thereby forming a melt of the constituents of the metallic phase, the period of time of simultaneous temperature and pressure application being sufficient to permit dissolution of all of the HBN in the metallic phase melt and the precipitation of CBN crystals therefrom;
- d. cooling the resulting CBN/alloy system to about room temperature while maintaining the operating pressure:
- e. reducing the pressure to atmospheric pressure and
- f. recovering the preshaped abrasive body consisting essentially of CBN crystals distributed in a transition metal—aluminum alloy matrix.
- 2. The method of claim 1 wherein the metallic phase consists of iron, nickel, chromium and aluminum.
- 3. The method of claim 2 wherein the mixture contains from about 10 to about 22 weight percent HBN.
- 4. The method of claim 1 wherein the metallic phase consists of nickel, chromium and aluminum.
- 5. The method of claim 1 wherein the metallic phase consists of iron, manganese and aluminum.
- 6. The method of claim 5 wherein the mixture con-40 tains from about 15 to about 36 weight percent HBN.
 - 7. The method of claim 1 wherein the metallic phase consists of nickel, manganese and aluminum.
 - 8. The method of claim 7 wherein the mixture contains from about 16 to about 42 weight percent HBN.
 - 9. The method of claim 1 wherein the metallic phase consists of iron—nickel—chromium—aluminum alloy containing 46 weight percent iron, 32 weight percent nickel, 21 weight percent chromium and 1.0 weight percent aluminum.
 - 10. The method of claim 9 wherein the mixture contains about 42 weight percent HBN.
 - 11. The method of claim 1 wherein the predetermined shape is annular.
 - 12. The preshaped abrasive body prepared by the process of claim 1.
 - 13. The preshaped abrasive body produced by the process of claim 10.

60