

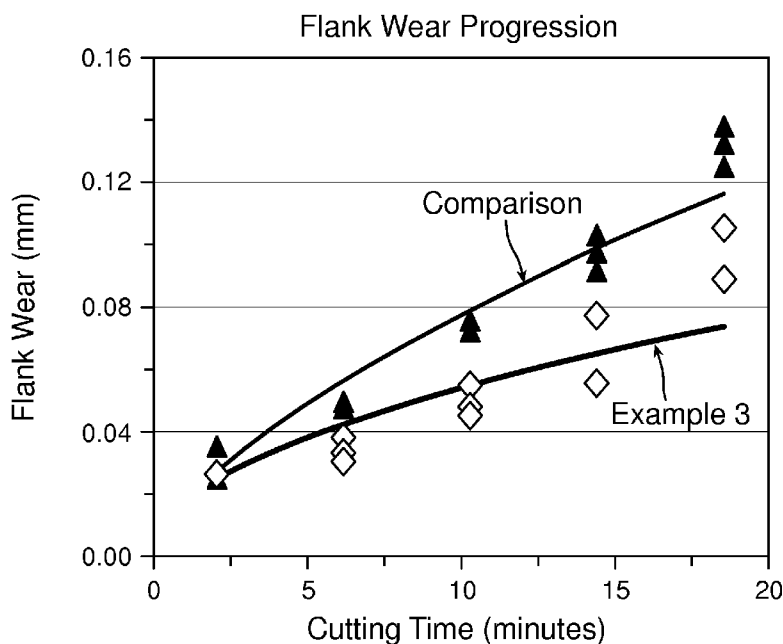


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(57) Abstract: A method and composition of a sintered superhard compact is provided. The sintered superhard compact body may comprise superhard particles and a binder phase. The binder phase may bond the superhard particles together. The binder phase comprises tungsten and cobalt. The ratio of tungsten to cobalt is between 1 and 2 and sum of W and Co in the sintered superhard compact is in a range of from about 2 to about 20 percent by weight.

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SINTERED SUPERHARD COMPACT FOR CUTTING TOOL APPLICATIONS AND
METHOD OF ITS PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority of provisional application, No. 61/653,779, filed 5/31/2012. The application is related to co-pending application, titled "CUTTING TOOLS MADE FROM STRESS FREE CBN COMPOSITE MATERIAL AND METHOD OF PRODUCTION", which claims priority of provisional application No. 61/653,699, filed on May 31, 2012. The application is further related to co-pending application, titled "Method of making a cBN material", which claims priority of provisional application No. 61/653,686, filed on May 31, 2012.

TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY

[0002] The present disclosure relates to a sintered superhard material made from powdered composition suitable for use in the manufacture of superhard abrasive compacts, and specifically to a sintered body containing cubic boron nitride (cBN) which may be used in cutting tools for hard part turning applications with enhanced toughness and good consistency.

[0003] Polycrystalline cubic boron nitride (PcBN), diamond and diamond composite materials are commonly used to provide a superhard cutting surface for cutting tools such as those used in metal machining.

[0004] It is generally accepted that such described materials suffer from more or less brittle behavior, that is, the materials exhibit undesirable random breakages in toughness demanding operations, such as intermittent machining of hardened steel. This brittleness entails partly as a result of the binder phase being ceramic, but is also due to imperfect dispersion of cBN particles and tungsten carbide mill debris. Imperfect dispersion leads to mechanically weak parts, or defects, in the material.

[0005] Therefore, there is a need for homogeneous and consistent dispersion in the material in order to produce a superhard compact for hard part machining having superior toughness characteristics to be used in toughness demanding operations, in particular in intermittent hard part turning, or milling.

SUMMARY

[0006] In one embodiment, a sintered superhard compact body may comprise superhard particles; and a binder phase bonding the superhard particles together, wherein the weight percent ratio of W/Co in the sintered compact falls between 1.0 and 2.0, and sum of weight percent of W and Co in the sintered compact is in a range from about 2 to about 20.

[0007] In another embodiment, a sintered superhard compact body may comprise superhard particles; and a binder phase bonding the superhard particles together, wherein the binder phase comprises tungsten and cobalt derived from milling debris, wherein the binder phase comprises stoichiometric or substoichiometric carbides, nitrides, oxides, or sums thereof from aluminum, titanium or other transition metals of group IV, V, or VI in the periodic table of elements.

[0008] In yet another embodiment, a method of making a superhard compact may comprise steps of providing milling bodies; milling a powder mixture of superhard powder and a binder material, and fluids with the milling bodies; and incorporating W and Co from the milling bodies into the superhard compact.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The foregoing summary, as well as the following detailed description of the embodiments, will be better understood when read in conjunction with the appended drawings. It should be understood that the embodiments depicted are not limited to the precise arrangements and instrumentalities shown.

[0010] FIG. 1 is a backscattered scanning electron micrograph (BSE) image of a microstructure of a sintered superhard compact body made from a roll mill using cemented carbide milling bodies;

[0011] FIG. 2 is a backscattered scanning electron micrograph (BSE) image of a microstructure of a sintered superhard compact body made from a roll mill using cermet milling bodies;

[0012] FIG. 3 is a backscattered scanning electron micrograph (BSE) image of a microstructure of a sintered superhard compact body made from an attritor mill using cermet milling bodies according to an embodiment;

[0013] FIG 4 is a graph of flank wear progression for a cutting tool made from materials milled by an attritor mill with cermet milling bodies, compared with a commercial grade;

[0014] FIG 5 is a graph of crater wear progression for a cutting tool made from materials milled by an attritor mill with cermet milling bodies, compared with a commercial grade; and

[0015] FIG 6 is a graph of toughness test result for a cutting tool made from materials milled by an attritor mill with cermet milling bodies, compared with a commercial grade.

DETAILED DESCRIPTION

[0016] An embodiment provides a sintered superhard compact body with a defined weight percent ratio of W/Co and its manufacturing method. The superhard particles may be selected from a group of cubic boron nitride, diamond, and diamond composite materials. The composition of starting material used in producing the polycrystalline cBN compact comprises cBN and a binder phase, in powder or particular form. The binder phase may at least partially melt and react with cBN and

form bonding by reaction sintering during high pressure and high temperature (HPHT) sintering.

[0017] An embodiment may improve the toughness of a cBN material with an increased wear resistance and a reduction of variability of tool life for a given application area. A superhard sintered compact and a method for its production that provides significantly improved microstructural homogeneity and better toughness than other superhard sintered compacts.

[0018] Embodiments use milling bodies, such as cermet milling bodies. Cermet milling bodies may be made from a raw material powder blend which comprises 18% hexagonal close-packed (HCP) WC by weight, 16% HCP Co, and balanced face centered cubic (FCC) TiCN. After sintering, the cermet milling bodies may contain W in a range from 15% to 20%, which may be dissolved in (FCC) (Ti, W) (C, N). The cermet material may also contain up to 15% cobalt, which, in turn, may contain up to 12% dissolved tungsten.

[0019] Dispersion of cBN particles is mainly accomplished during the milling step. Milling, in general, as a means of comminution and dispersion, is well known in the art. Commonly used milling techniques in grinding ceramic powder include conventional ball mills, tumbling ball mills, planetary ball mills, attritor mills, and agitated ball mills. In conventional ball milling, the energy input is determined by the size and density of the milling media, the diameter of the milling pot and the speed of rotation. Since the method requires that the balls tumble, rotational speeds, and therefore energy are limited. Conventional ball milling is well suited for milling powders with low to medium particle strength. Typically, conventional ball milling is used where powders are to be milled to a final particle size around 1 micron or more.

[0020] In planetary ball milling, the planetary motion of the milling pots allows acceleration up to 20 times the gravitational acceleration. When dense milling bodies are used, this allows for substantially more energy in milling compared to conventional ball milling. This technique is well suited for comminution with particles of moderate strength, with final particle sizes of around 1 micron.

[0021] Attritor mills on the other hand consist of an enclosed grinding chamber with an agitator that rotates at high speeds in either a vertical or horizontal configuration. Milling bodies are typically in the size ranging from 0.2 to 15 mm and, where comminution is the objective, milling media typically are high density cemented carbide. The high rotational speeds of the agitator, coupled with high density, small diameter milling bodies, provide high energy. Furthermore, the high energy in attritor mill results in high shear in the slurry, which provides for very successful co-dispersion, or blending of powders. Attritor mill typically achieves finer particles and better homogeneity of materials in the sintered compact than the other methods mentioned.

[0022] An embodiment may use attritor or other mills with milling bodies made from cemented carbide hard metal, also known as WC/Co hard metal, containing 85-90% HCP WC, and 7-15% Co. In some embodiments, the desirable form of milling debris may allow for a longer milling time and improved dispersion. As used herein, the term "milling debris" refers to any materials produced from milling bodies or the linings of a mill due to the friction between abrasive particles, milling bodies and linings. The dispersion of the different phases during milling is critical. The maximum possible dispersion is limited in prior art, by the fact that the cemented carbide milling bodies wear and produce milling debris containing high WC content. This may cause an increased WC content in the PcBN blend with extended milling time. This is tolerable to some degrees; however, it may cause considerable deterioration of the material properties if the WC content becomes too high. Therefore, because cemented carbide has much higher W content than cermet, the tolerable milling time for cemented carbide milling bodies is much lower than that for cermet milling bodies, which greatly restricts the level of dispersion that can be achieved through milling using cemented carbide milling bodies.

[0023] In other embodiments, cermet hard metal milling bodies may comprise a composition of (Ti,W)(C,N). The composition may be beneficial to add as a part of the final blank composition. Even in these other embodiments, W and/or Co containing raw materials may be added to achieve the desired final material

composition. In one embodiment, the tungsten and cobalt are from milling debris. By using the cermet milling bodies, a more favorable form of milling debris may be formed, where the milling debris is actually a part of the raw material blend. The advantage of using cermet milling debris as raw material is that the mill debris contains (Ti,W)(C,N) and Co with the right proportion of W/Co and they are always together. During a pre-sintering process or early stage of HPHT sintering, the W in the (Ti,W)(C,N) is reduced to metallic W, which dissolves in molten Co during HPHT sintering. Therefore, molten Co may help distribute W uniformly around particles and helps increase homogeneity of the reactions between Co, W, and Al with cBN and binder phase particles. After HPHT sintering, at least some of the Co and W have reacted and formed ceramic phases.

[0024] Similar to this concept, it is also possible to crush sintered cermet solids into powder and blend it together with cBN and ceramic binder phase materials to achieve the same effect. On the contrary, if the PCBN blend is milled with cemented carbide milling bodies, W from the mill debris will be too much to be dissolved in Co. Even though with added Co powder in the blend, W and Co particles are not always adjacent to each other. Therefore, there are often large W or WC particles sitting in the microstructure, which may not be desirable for the machining application.

[0025] In one embodiment, superhard particles may comprise 31 wt% cBN, wherein the binder phase includes 5 wt% Al, 32 wt% $Ti(C_{0.6}N_{0.4})$, 32 wt% substoichiometric $TiN_{0.72}$. The materials are milled by using cermet bodies in an attritor mill giving an addition of 3.1 +/- 1 wt% W and 2.2 +/-1 wt% Co from the milling bodies

[0026] In one embodiment, a ratio of tungsten to cobalt may be in a range of 1.0 to 2.0. In another embodiment, a ratio of tungsten to cobalt may be in a range of 1.0 to 1.8. In yet another embodiment, a ratio of tungsten to cobalt may be in a range of 1.0-1.5.

[0027] PCBN based materials for hard part turning typically comprise sintered bodies having a volume share in the range of 35 to 85 vol. % cBN particles, and a

ceramic binder phase which comprises carbides, nitrides, oxides, or sums thereof of aluminum, titanium or any other transition metal group IV, V, or VI in the periodic table of elements. The cBN based material is sintered in a high pressure, high temperature (HPHT) process. Phase transitions during the HPHT process result in generating new phases, such as, borides, nitrides and carbonitrides, for example. Small amounts of inevitable contaminants may be present in these materials, which may be generated in certain process steps, such as, milling, which gives rise to tungsten and cobalt content originating in the milling bodies.

[0028] In an embodiment of a process to make a superhard compact, raw superhard materials, such as cBN, may be blended by a milling process with fluids and ceramic materials which comprises stoichiometric or substoichiometric carbides, nitrides, oxides, or sums thereof from aluminum, titanium or other transition metals of group IV, V, or VI in the periodic table of elements. An embodiment may further include steps of preparing granules from a mixture of superhard powders, ceramic powders, organic binder materials, and fluids; pre-compacting the granules to form a soft green part of defined shape; heating the soft green part in a vacuum furnace to form a hard green part; inserting one or more the hard green parts in a container. An embodiment may further include steps of sintering the hard greens in the container in a pressure cell at a predetermined pressure and temperature; removing the container from the pressure cell to reveal the superhard compact.

[0029] PCBN may be typically made by HPHT sintering of a powder blend of cBN, ceramic phase and aluminum or aluminum compound, and may be often formed in the shape of a large PCBN disc or "blank". In addition, two phases attributable to the cBN and binder phase material may be selected from a group of Al_2O_3 , TiB_2 , AlN , for example. And at least one boride containing W, Co, or W-Co alloy phases may be detected by an X-Ray Diffraction (XRD), such as WB_2 , Co_2B , or CoW_2B_2 . In some embodiments, the W phase is not detected in the blank.

[0030] The PCBN blank may also be made from HPHT sintering of pre-compacted hard green discs. In addition to cBN and added binder phase material,

such hard greens have intermediary phases that may include Al_3Ti , Ti_2AlN , W , CoAl , AlB_2 that are produced in the pre-sintering step.

[0031] Example 1

[0032] Example A. Powders of cBN (39% by weight), substoichiometric TiN (ssTiN) (56% by weight) and Al (5% by weight) were milled in a roll mill with cemented carbide milling bodies in isopropyl alcohol for 2 hours. The slurry was then dried in an oven in air to remove the alcohol. Then the powder was dispersed in ethanol (99.6% pure), which was mixed with a polyethylene glycol (PEG) solution. The slurry was then spray dried into spherical granules, which is pre-compacted into round discs. The discs were fired in hydrogen at about 400 °C and then pre-sintered at 900 °C in vacuum. After pre-sintering, the hard green discs were loaded in a cell and HPHT sintered at temperature around 1300 to 1450 °C with pressure of at least 2 GPa.

[0033] Example B. Powders of cBN (39% by weight), ssTiN (56% by weight) and Al (5% by weight) were milled in a roll mill with cermet milling bodies. ssTiN and Al powders were milled in ethanol (99.6% pure) for 15 hours, and then cBN powders were added to the slurry and milled for another 10 hours. Then the slurry was mixed with a PEG solution after milling. The following spray drying, pre-compaction, pre-sintering and HPHT processes were the same as described in Example A.

[0034] Example C. Powders of cBN (39% by weight), ssTiN (27% by weight), TiCN (28% by weight), and Al (6% by weight) were milled together in ethanol in an attritor mill with cermet milling bodies for 3 hours. The cermet milling bodies had the composition of (weight%): W 17.36, Co 17.47, Ti 50.65, N 4.84, and C 9.83. The slurry was mixed with a PEG solution after milling. The following spray drying, pre-compaction, pre-sintering and HPHT processes were the same as described in Example A.

[0035] Table 1 shows the W and Co contents by X-Ray Fluorescence (XRF) and the calculated W/Co ratios and sum of W and Co contents of Examples A, B and C.

All three examples had the same W level (4.2 to 4.5% by weight), but the Co level was much higher in Example C than in the other two cases. In Example B, although the powders were milled with cermet milling bodies, because the milling bodies were grinding the surface of the milling jar, which had a WC lining, WC mill debris might come from the WC lining as well as the milling bodies. Therefore, the W/Co ratio might be much higher than that from the cermet milling bodies. In Example C, the attritor milling action determined that the wearing between milling bodies was much more severe than from the mill jar. As a result, even though the attritor milling jar was made of stainless steel, there was not much mill debris from the attritor milling jar. The iron content in the final blend was only about 0.3% by weight. The mill debris in attritor milling with cermet milling bodies mainly came from the milling bodies, which resulted in the low W/Co ratio.

[0036] FIG. 1, 2 and 3 show the back scattered electronic (BSE) micrographs of examples A, B and C. FIG. 1 shows the BSE image of example A with 39 wt% cBN which was roll milled with cemented carbide milling bodies for two hours. FIG. 2 illustrates the BSE image of example B with 39 wt% cBN which was roll milled with cermet milling bodies for 25 hours. FIG. 3 illustrates the BSE image of example C with 39wt% cBN which was attritor milled with cermet milling bodies for three hours. It can be seen that with the same W level, dispersion in Example A is not very good. Dispersions in Example B and C much improved compared to Example A. It should be noted that in both Examples A and B, because of the excess W, large mill debris (white spots in the micrographs) were visible, whereas in example C, because W was dissolved in Co and uniformly distributed in the microstructure, large mill debris was scarce.

Table 1:

Example	Mill	Milling Body	Milling Time (hours)	W (wt%)	Co (wt%)	W/Co	W+Co (wt%)
A	Roll	Cemented carbide	2	4.3	0.2	21.5	4.5

B	Roll	Cermet	25	4.5	0.8	5.6	5.3
C	Attritor	Cermet	3	4.2	3.4	1.2	7.6

[0037] Example 2

[0038] Table 2 shows a number of other material blends which were milled using different milling bodies (cermet or cemented carbide) and different mills (roll mill or attritor mill). The lining of the roll mills might be stainless steel (ss) or cemented carbide (cc). All materials had a good dispersion of the constituents except for mill D, which was milled for too short duration. The W/Co ratio was the highest (over 10) in the case of milling with cemented carbide bodies, because the W/Co ratio was high in the milling body material. In the case of roll milling with cermet bodies, again because the experiments were conducted in mills with cemented carbide lining, WC mill debris from the lining in addition to the cermet milling bodies contributed to the higher overall W/Co ratio (such as over 5) than that of cermet material. The lowest W/Co ratio was achieved through attritor milling with cermet bodies, because, as explained above, majority of the milling debris came from the cermet milling bodies. It should be noted that it was possible to achieve similar low W/Co ratio through roll milling with stainless steel lining. However, it required much longer time than attritor milling to achieve the same dispersion and W level, and the iron content would be rather high due to mill debris from the milling jar.

Table 2:

Example	cBN (vol%)	Mill	Lining of Mill	Milling Body	W (wt%)	Co (wt%)	W/Co	W+Co (wt%)
D	38	attritor	Ss	cermet	3.1	2.0	1.6	5.1

E	47	roll	Cc	cemented carbide	5.9	0.5	11.8	6.4
F	47	roll	Cc	cermet	4.5	0.8	5.6	5.3
G	47	attritor	Ss	cemented carbide	2.1	0.2	10.5	2.3
H	47	attritor	Ss	cermet	3.0	2.2	1.4	5.2
I	65	roll	Ss	cemented carbide	5.8	0.5	11.6	6.3
J	65	roll	Cc	cermet	3.5	0.6	5.8	4.1
K	65	attritor	Ss	cermet	2.7	2.1	1.3	4.8
L	65	attritor	Ss	cermet	6.6	5.4	1.2	12.0

[0039] Example 3

[0040] Powders of aluminum (5 wt%), TiCN (32 wt%), ssTiN (32 wt%), and cBN (31 wt%) were milled in an attritor mill with cermet milling bodies in ethanol for 5 hours. After milling, the slurry was mixed with a PEG solution and the material was spray dried, pre-compacted, pre-sintered and HPHT sintered in the same way as described in Example 1. Then tips were Electrical Discharge Machining (EDM) cut from HPHT sintered discs and standard cutting tools were made and machining tests were conducted together with a commercial hard part turning grade, which was referred to as “comparison grade” or “Comparison” in the following text, FIG. 4, 5 and 6 and Table 4.

[0041] Table 3 shows the XRD data after pre-sintering and HPHT for Example 3. Co and W had reacted to form several different reaction products. In the material after HPHT, cBN, TiCN, Al₂O₃, and TiB₂ were detected, as expected traditionally. The new phases were some boron-containing tungsten, cobalt, or tungsten-cobalt phases, such as WB₂, Co₂B, or CoW₂B₂. Most notably, the intermediary phases after pre-sintering, such as AlB₂, Ti₂AlN, W, were not visible after HPHT. The TiN peak

detectable after pre-sintering also disappeared after HPHT due to solid state diffusion and homogenization between the TiCN/TiN binders during HPHT sintering.

Table 3:

Peak	Variant M	
	HPHT	Presint.
AlB₂		5
Al₂O₃	3	
cBN	28	40
Co₂B	2	
CoW₂B₂	6	
Ti₂AlN		1
TiB₂	10	
TiCN	100	100
TiN		55
W		8
W₂B	3	

[0042] FIGS 4 and 5 show the flank wear and crater wear test results on Example 3 compared with the comparison grade. The test was conducted on 8620 steel with continuous cutting. Cutting was stopped every 2 to 4 minutes, and flank wear and crater wear were measured and recorded. It could be seen that Example 3 had similar crater wear to the comparison grade, but much lower flank wear than the comparison grade.

[0043] Table 4 shows a series of wear test by cutting 8620 steel on Example 3 compared with the comparison grade. Flank wear was measured every 4 minutes and tool life was determined based on 0.15 mm of flank wear. Different cutting

speeds (240 and 180 m/min), feeds (0.1 and 0.15 mm/rev), and depth of cut (0.1 to 0.2 mm/doc) were tested. It could be seen that in every case, Example 3 has much longer tool life than the comparison grade illustrating this material may have a potential for broad application.

Table 4:

Cutting Parameters	Example 3 (tool life, minutes)			Comparison (tool life, minutes)		
	Group 1	Group 2	Average	Group 1	Group 2	Average
240 m/min, 0.1 mm/rev., 0.1 mm doc	38.7	37.1	37.9	21.2	21.0	21.1
180 m/min., 0.15 mm/rev., 0.2 mm doc	26.5	22.9	24.7	21.0	21.4	21.2
180 m/min., 0.1 mm/rev., 0.1 mm doc	84.0		84.0	55.8		55.8

[0044] FIG. 6 shows the toughness test result on Example 3 compared with the comparison grade. The test was conducted on 52100 steel with hardness of Rc 60 to 62. Four samples of each were tested and the failing feed of each sample was recorded. Traditionally, toughness increases with cBN content. However, it could be seen that although Example 3 had much lower cBN content than the comparison grade, 38 vol% in Example 3 and 50 vol% in the comparison grade, it had the same toughness level as the comparison grade, and much better consistency. This could be attributed to the higher Co content and more uniform distribution of mill debris.

[0045] While reference has been made to specific embodiments, it is apparent that other embodiments and variations can be devised by others skilled in the art without departing from their spirit and scope. The appended claims are intended to be construed to include all such embodiments and equivalent variations.

1. A sintered superhard compact body, comprising:
superhard particles; and
a binder phase bonding the superhard particles together, wherein the binder phase comprises W and Co, wherein the weight % ratio of W/Co in the sintered superhard compact falls between 1.0 and 2.0, and sum of weight% W and Co in the sintered superhard compact is in a range of from about 2.0 to about 20.
2. The sintered superhard compact body of claim 1, wherein the superhard particles are selected from a group of cubic boron nitride, diamond, and diamond composite materials.
3. The sintered superhard compact body of previous claims 1-2, further comprises stoichiometric carbides, nitrides, oxides, or sums thereof from aluminum, titanium or other metals in transition group IV, V, and VI in Periodic Table of elements.
4. The sintered superhard compact body of previous claims 1-3, further comprises substoichiometric carbides, nitrides, oxides, or sums thereof from aluminum, titanium or other metals in transition group IV, V, and VI in Periodic Table of elements.
5. The sintered superhard compact body of previous claims 1-4, wherein a ratio of tungsten to cobalt is in a range of from 1.0 to 1.8.
6. The sintered superhard compact body of previous claims 1-5, wherein a ratio of tungsten to cobalt is in a range of from 1.0 to 1.5.
7. The sintered superhard compact body of previous claims 1-6, further comprising at least one boron containing tungsten, cobalt, or tungsten-cobalt phases as detected by X-Ray diffraction (XRD).

comprising at least one phase selected from a group of WB_2 , Co_2B , or CoW_2B_2 as detected by X-Ray diffraction (XRD).

9. The sintered superhard compact body of previous claims 1-8, wherein tungsten or tungsten carbide is not detected by X-Ray diffraction (XRD).
10. The sintered superhard compact body of previous claims 1-9, wherein the tungsten and cobalt are from milling debris of milling bodies.
11. A method of making a superhard compact, comprising:
 - providing milling bodies;
 - milling a powder mixture of superhard powder, binder materials, and fluids with the milling bodies; and
 - incorporating cobalt and tungsten from the milling bodies into the superhard compact, wherein the milling bodies are low tungsten content milling bodies.
12. The method of making a superhard compact of claim 11, further comprising preparing granules from a mixture of superhard powder blend, organic binder materials, and fluids.
13. The method of making a superhard compact of claims 11-12, further comprising pre-compacting the granules to form a soft green part of defined shape.
14. The method of making a superhard compact of claims 13, further comprising heating the soft green part in a vacuum furnace to form a hard green part.
15. The method of making a superhard compact of claims 11-14, further comprising inserting one or more the hard green parts in a container.
16. The method of making a superhard compact of claims 11-15, further comprising sintering the container in a pressure cell at a predetermined pressure and temperature.

17. The method of making a superhard compact of claims 11-16, further comprising removing the container from the pressure cell to reveal the superhard compact.
18. The method of making a superhard compact of claim 11-17, wherein the superhard powder includes a material selected from the group of cubic boron nitride, diamond, and diamond composite materials.
19. The method of making a superhard compact of claims 11-18, wherein the granules comprise a mixture of cubic boron nitride and aluminum in organic binder materials of polyethylene glycol.
20. The method of making a superhard compact of claims 11-19, wherein the powder mixture contains W and Co containing compounds to accomplish a desired composition.

1/4

FIG. 1 (PRIOR ART)

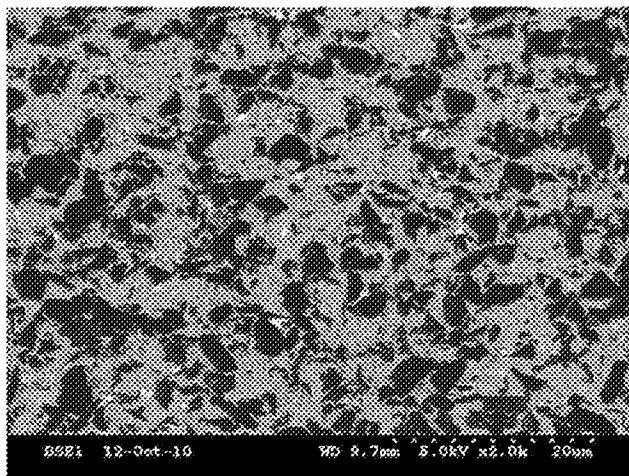


FIG. 2 (PRIOR ART)

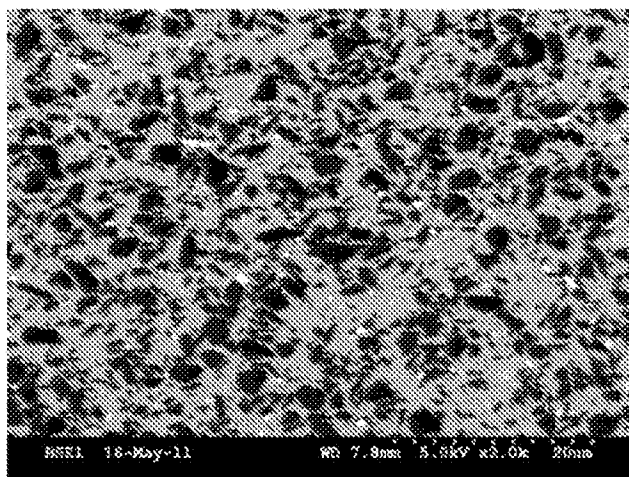


FIG. 3

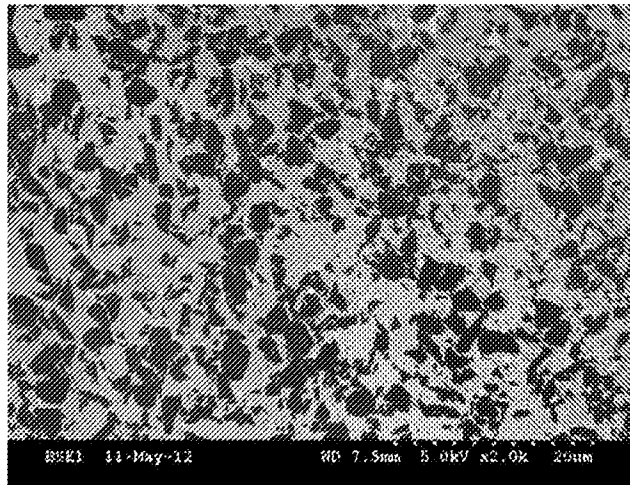
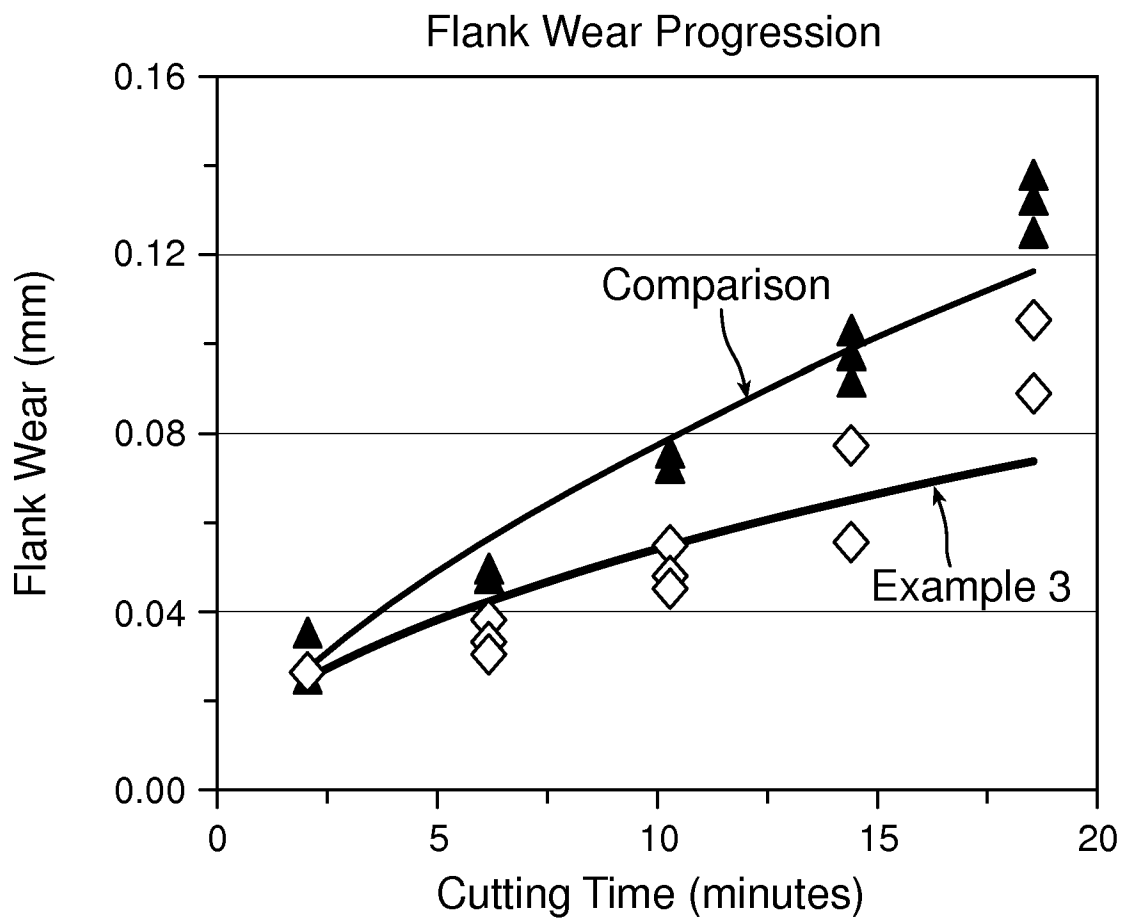


FIG. 4



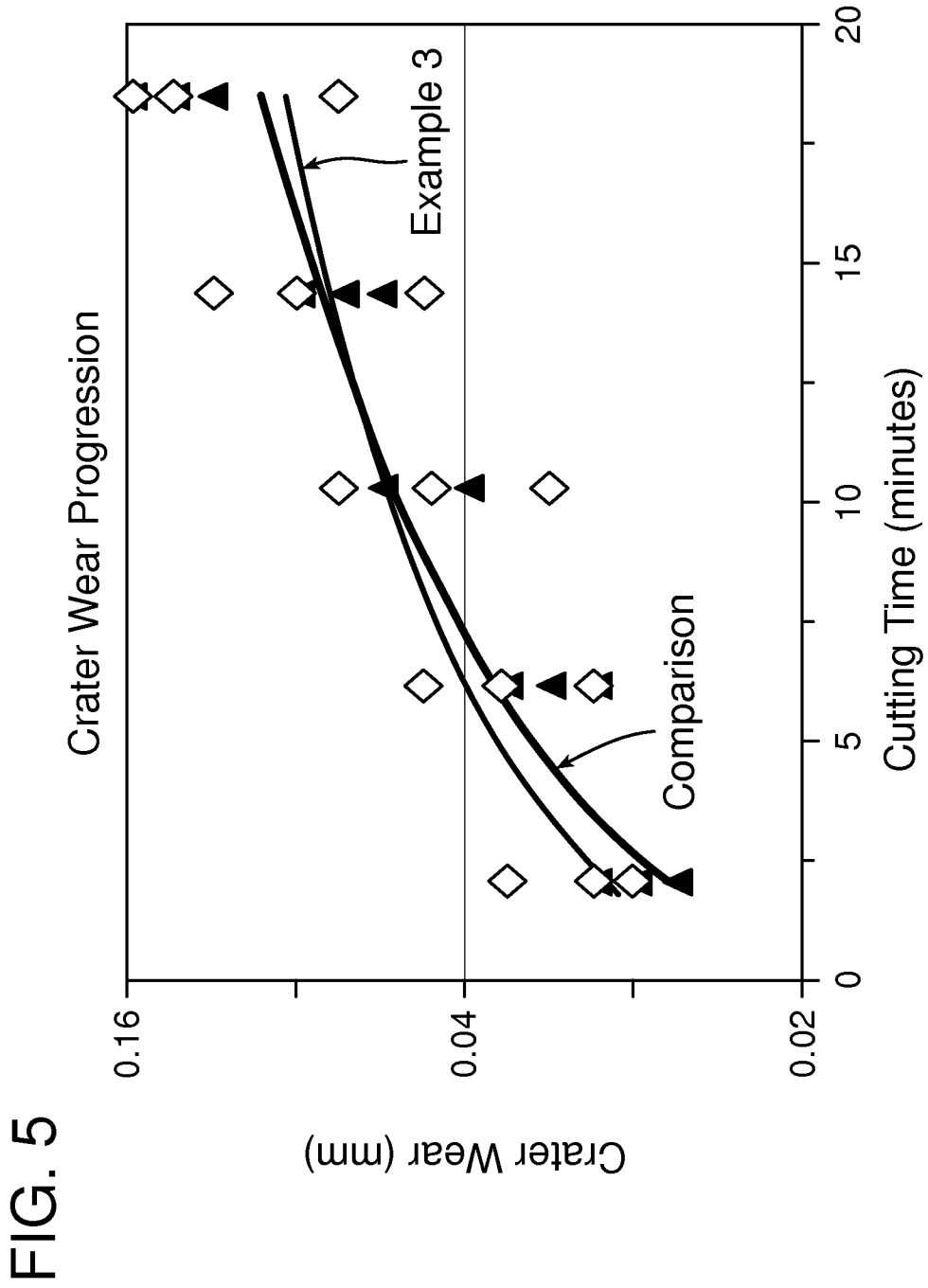
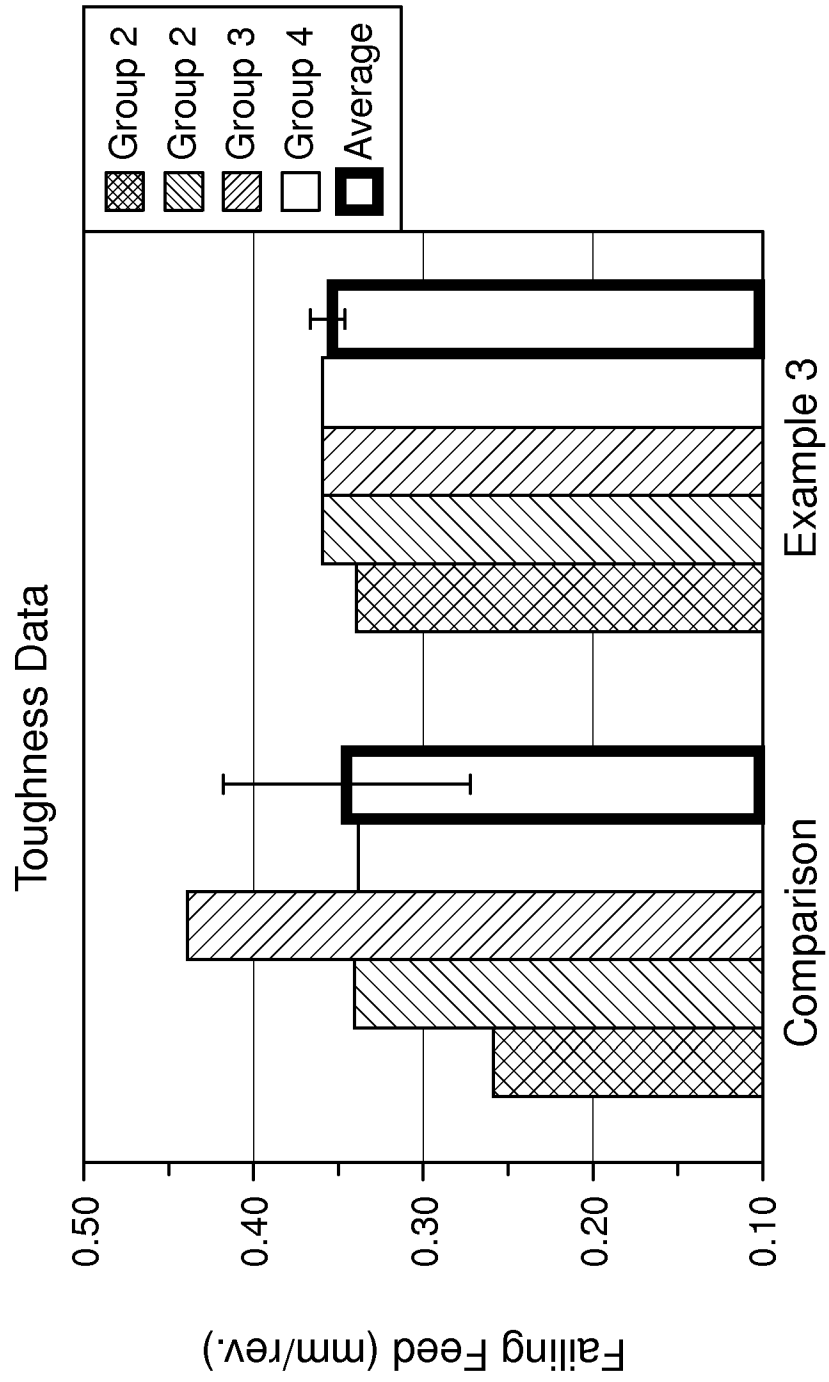


FIG. 5

FIG. 6



INTERNATIONAL SEARCH REPORT

International application No PCT/US2013/043600

A. CLASSIFICATION OF SUBJECT MATTER INV. C04B35/52 C04B35/5831 C22C26/00 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) C04B C22C				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	EP 1 184 354 A1 (SUMITOMO ELECTRIC INDUSTRIES [JP]) 6 March 2002 (2002-03-06) example 4 - in particular samples 4-11, 4-12, 4-13, 4-19 & 4-20 in Table 4 - see also table 1 -----	1-10		
X	WO 2007/049140 A2 (ELEMENT SIX PRODUCTION PTY LTD [ZA]; GOUDEMOND IAIN PATRICK [ZA]; CAN) 3 May 2007 (2007-05-03) examples -----	1,2,5,7,9,10		
Y	-----	11-20		
X	WO 2012/004294 A1 (ELEMENT SIX LTD [IE]; PERSSON STEFAN MAGNUS OLOF [SE]) 12 January 2012 (2012-01-12) examples 1 and 4 -----	1,2,5,9,10		
----- -/--				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
12 August 2013	21/08/2013			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Munro, Brian			

INTERNATIONAL SEARCH REPORT

International application No PCT/US2013/043600

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	col. 5, l.1-3; col. 6, l. 24-62; example 4 with reference to example 1; claims 1-3 -----	11-20
Y	US 4 370 149 A (HARA AKIO [JP] ET AL) 25 January 1983 (1983-01-25) examples & table 1 -----	11-20

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Information on patent family members

International application No PCT/US2013/043600

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