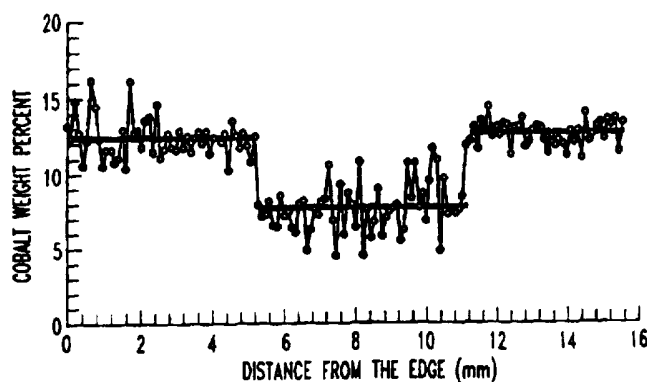




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(21) International Application Number: <b>PCT/US95/14042</b> (22) International Filing Date: <b>30 October 1995 (30.10.95)</b> (30) Priority Data: 08/363,172                      23 December 1994 (23.12.94) <b>US</b> (71) Applicant: <b>KENNAMETAL INC. [US/US]; P.O. Box 231, Latrobe, PA 15650 (US).</b> (72) Inventors: <b>MASSA, Ted, R.; 53 Orchard Drive, Latrobe, PA 15650 (US). VAN KIRK, John, S.; 3727 Windover Road, Murrys ville, PA 15668 (US). CONLEY, Edward, V.; 10187 Lavonne Drive, North Huntingdon, PA 15642 (US).</b> (74) Agents: <b>ANTOLIN, Stanislav et al.; Kennametal Inc., P.O. Box 231, Latrobe, PA 15650 (US).</b>			(81) Designated States: <b>AU, CN, JP, PL, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  <b>Published</b> <i>With international search report.</i>

(54) Title: COMPOSITE CERMET ARTICLES AND METHOD OF MAKING



## (57) Abstract

Methods for making, methods for using and articles comprising cermets, preferably cemented carbides and more preferably tungsten carbide, having at least two regions exhibiting at least one property that differs are discussed. Preferably, the cermets further exhibit uniform or controlled wear to impart a self-sharpening character to an article. The multiple-region cermets are particularly useful in wear applications. The cermets are manufactured by juxtaposing and densifying at least two powder blends having different properties (e.g., differential carbide grain size or differential carbide chemistry or differential binder content or differential binder chemistry or any combination of the preceding). Preferably, a first region of the cermet comprises a first ceramic component having a relatively coarse grain size and a prescribed binder content and a second region, juxtaposing or adjoining the first region, comprises a second ceramic component, preferably carbide(s), having a grain size less than the grain size of the first region, a second binder content greater than the binder content of the first region or both. These articles have an extended useful life relative to the useful life of monolithic cermets in such applications as, for example, wear. The multiple region cermets of the present invention may be used with articles comprising tools for materials manipulation or removal including, for example, mining, construction, agricultural, and metal removal applications.

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**COMPOSITE CERMET ARTICLES**  
**AND METHOD OF MAKING**

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**BACKGROUND**

Cermet is a term used to describe a monolithic material composed of a ceramic component and a binder component. The ceramic component comprises a nonmetallic compound or a metalloid. The ceramic component may or may not be interconnected in two or three dimensions. The binder component comprises a metal or alloy and is generally interconnected in three dimensions. The binder component cements the ceramic component together to form the monolithic material. Each monolithic cermet's properties are derived from the interplay of the characteristics of the ceramic component and the characteristics of the binder component.

A cermet family may be defined as a monolithic cermet consisting of specified ceramic component combined with a specified binder component. Tungsten carbide cemented together by a cobalt alloy is an example of a family (WC-Co family, a cemented carbide). The properties of a cermet family may be tailored, for example, by adjusting an amount, a characteristic feature, or an amount and a characteristic feature of each component separately or together. However, an improvement of one material

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property invariably decreases another. When, for example, in the WC-Co family resistance to wear is improved, the resistance to breakage decreases. Thus, in the design of monolithic cemented carbides there is  
5 a never ending cycle that includes the improvement of one material property at the expense of another.

Despite this, monolithic cemented carbides are used in equipment subject to aggressive wear, impact, or both. However, rather than build the entire  
10 equipment from monolithic cemented carbides, only selected portions of the equipment comprise the monolithic cemented carbide. These portions experience the aggressive wear, impact, or both. In some equipment the cemented carbide portion has a specified  
15 profile that should be sustained to maintain the maximum efficiency of the equipment. As the specified profile changes, the equipment's efficiency decreases. If the equipment is used for cutting a work piece, the fraction of the usable removed sections of the work  
20 piece decreases as the profile of the cemented carbide deviates from the specified profile.

For example, as the specified profiles of cemented carbide cutting tips used in conjunction with a continuous coal mining machine change, once sharp  
25 cemented carbide cutting tips transform into cemented carbide blunt tips pounding on a coal seam to create dust, fine coal, and noise rather than desirable coarse coal. During this transformation, power supplied by a motor driving the continuous mining machine must also  
30 be increased. One solution to the loss of a specified profile includes removing the equipment from use and reprofiling the cemented carbide-- this is costly due to the loss of productive use of the equipment during reprofiling. Another solution involves scrapping the  
35 used cemented carbide portion and inserting a new cemented carbide -- this too is costly due to the loss of productive use of the equipment during refitting and

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the scrapped cemented carbide. If these cemented carbides could be made to sustain their specified profiles, for example, by self sharpening, economic and technical gains would result.

5           A solution to the endless cycle of adjusting one property of a monolithic cermet at the expense of another is to combine several monolithic cermets to form a multiple region cermet article. The resources (i.e., both time and money) of many individuals and  
10 companies throughout the world have been directed to the development of multiple region cemented carbide articles. The amount of resources directed to the development effort is demonstrated by the number of publications, US and foreign patents, and foreign  
15 patent publications on the subject. Some of the many US and foreign patents, and foreign patent publications include: US Patent Nos. 2,888,247; 3,909,895; 4,194,790; 4,359,355; 4,427,098; 4,722,405; 4,743,515; 4,820,482; 4,854,405; 5,074,623; 5,333,520; and  
20 5,335,738; and foreign patent publication nos. DE-A-3 519 101; GB-A 806 406; EPA-O 111 600; DE-A-3 005 684; DE-A-3 519 738; FR-A-2 343 885; GB-A-1 115 908; GB-A-2 017 153; and EP-A-0 542 704. Despite the amount of resources dedicated, no  
25 satisfactory multiple region cemented carbide article is commercially available nor for that matter, currently exists. Further, there is no satisfactory methods for making multiple region cemented carbide articles. Furthermore, there are no satisfactory  
30 monolithic self-sharpening cemented carbide articles let alone multiple region cemented carbide articles. Moreover, there are no satisfactory methods for making multiple region cemented carbide articles that are further self-sharpening.

35           Some of the resources (i.e., both time and money) have been expended for "thought experiments" and merely present wishes -- in that they fail to teach the

methods making such multiple region cemented carbide articles.

Other resources have been spent developing complicated methods. Some methods included the pre-engineering starting ingredients, green body geometry or both. For example, the starting ingredients used to make a multiple region cemented carbide article are independently formed as distinct green bodies. Sometimes, the independently formed green bodies are also independently sintered and ,sometimes after grinding, assembled, for example, by soldering, brazing or shrink fitting to form a multiple region cemented carbide article. Other times, independently formed green bodies are assembled and then sintered. The different combinations of the same ingredients that comprise the independently formed green bodies respond to sintering differently. Each combination of ingredients shrinks uniquely. Each combination of ingredients responds uniquely to a sintering temperature, time, atmosphere, or any combination of the preceding. Only the complex pre-engineering of forming dies and, thus, greenbody dimensions allows assembly followed by sintering. To allow the pre-engineering, an extensive data base containing the ingredients response to different temperatures, times, atmospheres, or any combination of the preceding is required. The building and maintaining of such a data base are cost prohibitive. To avoid those costs, elaborate process control equipment might be used. This too is expensive. Further, when using elaborate process control equipment, minor deviations from prescribed processing parameters rather than yielding useful multiple region cemented carbide articles -- yield scrap.

Still other resources have been expended on laborious methods for forming multiple region cemented carbide articles. For example, substoichiometric

monolithic cemented carbide articles are initially sintered. Their compositions are deficient with respect to carbon and thus the cemented carbides contain eta-phase. The monolithic cemented carbide articles are then subjected to a carburizing environment that reacts to eliminate the eta-phase from a periphery of each article. These methods, in addition to the pre-engineering of the ingredients, require intermediate processing steps and carburizing equipment. Furthermore, the resultant multiple region cemented carbide articles offer only minimal benefits since once the carburized peripheral region wears away, their usefulness ceases.

For the foregoing reasons, there exists a need for multiple region cemented carbides that can be inexpensively manufactured. Further, there exists a need for multiple region cermet articles that can be inexpensively manufactured. Furthermore, there exists a need for multiple region cemented carbide articles that are further self-sharpening and can be inexpensively manufactured. Moreover, there exists a need for multiple region cermet articles that are further self-sharpening and can be inexpensively manufactured.

## SUMMARY

The present invention relates to articles comprising cermets, preferably cemented carbides, having at least two regions exhibiting at least one different property. The present invention is further related to the methods of using these unique and novel articles. Also, the present invention relates to the methods of making these unique and novel articles.

The present invention satisfies a long-felt need in the cermet art for improved cermet material systems by providing articles having at least two regions having at least one property that differs and

preferably further exhibiting uniform or controlled wear to impart self-sharpening characteristics on the article when used as a tool. Such multiple-region articles are particularly useful in wear applications.

5 An example includes cermet articles having at least one leading edge or portion that exhibits wear resistance and an adjacent region that exhibits less wear resistance. A further advantage of the combination of the at least two regions includes a uniform or

10 controlled wear of such articles and thus extending the cermets useful life since this unique characteristic imparts the retention of, for example, cutting ability of the article when used as a cutting element of a tool as the article is consumed during an operation.

15 The present invention provides a method for making the present articles by recognizing the solution to the problems encounter in making multiple-region articles. Historically, attempts at making multiple-region articles failed due to defects (e.g., green body

20 cracking during sintering) arising during the articles' densification. Thus, the articles of the present invention are manufactured by methods that capitalized on the synergistic effects of processing parameters (e.g., differential carbide grain size or differential

25 carbide chemistry or differential binder content or differential binder chemistry or any combination of the preceding) to achieve unique and novel multiple region articles. These articles have an extended useful life relative to the useful life of prior art articles in

30 such applications as, for example, wear.

The unique and novel articles of the present invention comprise at least two regions, and may comprise multiple regions. A first region comprises a first ceramic component, preferably carbide(s), having

35 a relatively coarse grain size and a prescribed binder content. A second region of the article, juxtaposing or adjoining the first region, comprises a second



ceramic component, preferably carbide(s), having a grain size less than the grain size of the first region or a second binder content greater than the binder content of the first region or both. The first region  
5 of the present articles may be more wear resistant than the second region.

In an embodiment of the present invention, at least one property of each of the at least two regions is tailored by varying the ceramic component grain size  
10 or the ceramic component chemistry or the binder content or the binder chemistry or any combination of the preceding. The at least one property may include any of density, color, appearance, reactivity, electrical conductivity, strength, fracture toughness,  
15 elastic modulus, shear modulus, hardness, thermal conductivity, coefficient of thermal expansion, specific heat, magnetic susceptibility, coefficient of friction, wear resistance, impact resistance, chemical resistance, etc., or any combination of the preceding.

In an embodiment of the present invention, the amount of the at least two regions may be varied. For example, the thickness of the first region relative to the thickness of the second region may vary from the first region comprising a coating on the second region  
20 to the second region comprising a coating on the first region. Naturally, the first region and second region may exist in substantially equal proportions.

In an embodiment of the present invention, the juxtaposition of the first region and the second region may exist as a planar interface or a curved  
30 interface or a complex interface or any combination of the preceding. Furthermore, the first region may either totally envelop or be enveloped by the second region.

In an embodiment of this invention, the articles of the invention may be used for materials manipulation or removal including, for example, mining,  
35

construction, agricultural, and metal removal applications. Some examples of agricultural applications include seed boots (see e.g., US Patent No. 5,325,799), inserts for agricultural tools (see  
5 e.g., US Patent Nos. 5,314,029 and 5,310,009), disc blades (see e.g., US Patent No. 5,297,634), stump cutters or grinders (see e.g., US Patent Nos. 5,005,622; 4,998,574; and 4,214,617), furrowing tools (see e.g., US Patent Nos. 4,360,068 and 4,216,832), and  
10 earth working tools (see e.g., US Patent Nos. 4,859,543; 4,326,592; and 3,934,654). Some examples of mining and construction applications include cutting or digging tools (see e.g., US Patent Nos. 5,324,098; 5,261,499; 5,219,209; 5,141,289; 5,131,481; 5,112,411; 5,067,262; 4,981,328; and 4,316,636), earth augers (see  
15 e.g., US Patent Nos. 5,143,163 and 4,917,196), mineral or rock drills (see e.g., US Patent Nos. 5,184,689; 5,172,775; 4,716,976; 4,603,751; 4,550,791; 4,549,615; 4,324,368; and 3,763,941), construction equipment  
20 blades (see e.g., US Patent Nos. 4,770,253; 4,715,450; and 3,888,027), rolling cutters (see e.g., US Patent Nos. 3,804,425 and 3,734,213), earth working tools (see e.g., US Patent Nos. 4,859,543; 4,542,943; and 4,194,791), comminution machines (see e.g., US Patent  
25 Nos., 4,177,956 and 3,995,782), excavation tools (see e.g., US Patent Nos. 4,346,934; 4,069,880; and 3,558,671), and other mining or construction tools (see e.g., US Patent Nos. 5,226,489; 5,184,925; 5,131,724; 4,821,819; 4,817,743; 4,674,802; 4,371,210; 4,361,197; 4,335,794; 4,083,605; 4,005,906; and 3,797,592). Some  
30 examples of materials removal applications included materials cutting or milling inserts (see e.g., US Patent Nos. 4,946,319; 4,685,844; 4,610,931; 4,340,324; 4,318,643; 4,297,058; 4,259,033; and 2,201,979 (RE 30,908)), materials cutting or milling inserts  
35 incorporating chip control features (see e.g., US Patent Nos. 5,141,367; 5,122,017; 5,166,167; 5,032,050;

4,993,893; 4,963,060; 4,957,396; 4,854,784; and  
4,834,592), and materials cutting or milling inserts  
comprising coating applied by any of chemical vapor  
deposition (CVD), pressure vapor deposition (PVD),  
5 conversion coating, etc. (see e.g., US Patent Nos.  
5,325,747; 5,266,388; 5,250,367; 5,232,318; 5,188,489;  
5,075,181; 4,984,940; and 4,610,931 (RE 34,180). The  
subject matter of all of the above patents relating to  
applications is incorporated by reference in the  
10 present application. Particularly, the articles may be  
used in wear applications where an article comprising,  
for example, a pre-selected geometry with a leading  
edge manipulates or removes materials (e.g., rock,  
wood, ore, coal, earth, road surfaces, synthetic  
15 materials, metals, alloys, composite materials (ceramic  
matrix composites (CMCs)), metal matrix composites  
(MMCs), and polymer or plastic matrix composites  
(PMCs), polymers, etc.). More particularly, the  
articles may be used in applications where it is  
20 desirable to substantially maintain a pre-selected  
geometry during the wear life of the article.

An embodiment of the present invention  
relates to the novel method of making the present novel  
and unique articles. That is, at least a first powder  
25 blend and a second powder blend are arranged in a  
prescribed manner to form a green body. If the shape  
of the green body does not correspond substantially to  
the shape of the final article, then the green body may  
be formed into a desired shape, for example, by green  
30 machining or plastically deforming or sculpting the  
green body or by any other means. The green body,  
whether or not shaped, may then be densified to form a  
cermet, preferably a cemented carbide article. If the  
densified article has not been pre-shaped or when  
35 additional shaping is desired, the densified article  
may be subjected to a grinding or other machining  
operations.

In an embodiment of the present invention, the constituents of a first powder blend and a second powder blend may be selected such that the resultant article exhibits the characteristic discussed above.

5 For example, the average particle size of the ceramic component, preferably carbide(s), of the first powder blend is relatively larger than the average particle size of the ceramic component, preferably carbide(s), of the second powder blend. Additionally, the binder

10 content of a first powder blend and a second powder blend may be substantially the same or substantially different. Furthermore, the binder chemistry or the ceramic component chemistry, preferably carbide(s) chemistry, or both may be substantially the same,

15 substantially different or vary continuously between the at least two powder blends.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional schematic of a general article 101 comprising a first region 102 and a

20 second or an at least one additional region 103 in accordance with the present invention.

Figure 2A, 2B, 2C, 2D, 2E, and 2F are examples of schematic cut away views of possible geometries of articles or portions of articles

25 encompassed by the present invention.

Figure 3A is a cross-sectional schematic of a charging configuration 301 corresponding to the methods of Example 1.

Figure 3B is a cross-sectional schematic of a

30 pressing configuration corresponding to the methods of Example 1.

Figure 3C is a cross-sectional schematic of a green body 320 made by the methods of Example 1.

Figure 4A is a photomicrograph taken at a

35 magnification of about 3.4 x of a longitudinal cross-

section through sintered articles 401 made according to the methods of Example 1.

Figures 4B, 4C, and 4D are respectively photomicrographs taken at a magnification of about 500x of an interface 417 between a first region 414 and a second region 413, a first region 414, and a second region 413 of an article made according to the methods of Example 1.

Figure 4E, 4F and 4G are respectively photomicrographs taken at a magnification of about 1,500x of an interface 417 between a first region 414 and a second region 413, a first region 414, and a second region 413 of an article made according to the methods of Example 1.

Figures 5A and 5B correspond to the results of binder concentration determinations using EDS techniques as a function of distance at two diameters of an article made according to the methods of Example 1.

Figure 6 corresponds to the results of hardness measurements at various locations (i.e., hardness distribution profile) as a longitudinal cross section of an article made according to the methods of Example 1.

Figure 7 corresponds to a schematic cut away view of a conical cutter bit 701 incorporating an article made by the methods of Example 1.

Figures 8A, 8B, and 8C correspond to tool profile comparisons of articles made according to the methods of Example 1 of the present invention (——) and the prior art (- - - - -) after use to mine 4 meters (13.1 feet) of coal as described in Example 1 and compared to the starting tool profile (·····).

Figure 9A, 9B, and 9C correspond to profile comparisons of the articles of the present invention (——) and the prior art (- - - - -) after use to mine 8 meters (26.2 feet) of coal as described in

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Example 1 and compared to the starting tool profile (.....).

#### DETAILED DESCRIPTION

Articles of the present invention are  
5 described with reference to a hypothetical article 101 depicted in Figure 1. Line A-A in Fig. 1 may represent, for example, a boundary or surface of an article, a plane of mirror symmetry, an axis of cylindrical or rotational symmetry, etc. In the  
10 following discussion, it is assumed that line A-A is a boundary. It will be apparent to an artisan skilled in the art that the following discussion may be extended to articles having complex geometry. Thus, the following discussion should not be construed as  
15 limiting but, rather, as a start point.

In reference to Figure 1, article 101 has a first region 102 adjoining and integral with a second or at least one additional region 103. It will be understood by an artisan skilled in the art that  
20 multiple regions may be included in an article of the present invention. Interface 104 defines the boundary of the adjoining at least two regions. In a preferred embodiment, interface 104 is autogeneously formed. Article 101 may further comprise a leading surface 105  
25 defined by at least a portion of the material of the first region 102 and a recessed surface 106 defined by at least a portion of the material of the second or at least one additional region 103.

Compositionally, the materials comprising the  
30 at least two regions comprise cermets. Such cermets comprise at least one of boride(s), carbide(s), nitride(s), oxide(s), silicide(s), their mixtures, their solutions or any combination of the proceeding. The metal of the at least one of boride(s), carbide(s),  
35 nitride(s), oxide(s), or silicide(s) include one or

more metals from International Union of Pure and Applied Chemistry (IUPAC) groups 2, 3 (including lanthanides and actinides), 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14. Preferably, the cermets comprise  
5 carbide(s), their mixtures, their solutions or any combination of the proceeding. The metal of the carbide comprises one or more metals from IUPAC groups 3 (including lanthanides and actinides), 4, 5, and 6; more preferably one or more of Ti, Zr, Hf, V, Nb, Ta,  
10 Cr, Mo and W; and even more preferably, tungsten. The cermet binder for the at least two regions comprise metals, glasses or ceramics (i.e., any material that forms or assists in forming a liquid phase during liquid phase sintering). Preferably, the binder  
15 comprises one or more metals from IUPAC groups 8, 9 and 10; preferably, one or more of iron, nickel, cobalt, their mixtures, and their alloys; and more preferably, cobalt or cobalt alloys such as cobalt-tungsten alloys. Binders comprise single metals, mixtures of metals,  
20 alloys of metals or any combination of the preceding.

Dimensionally, the size of the ceramic component, preferably carbide(s), of the at least two regions may range in size from submicrometer to about 420 micrometers or greater. Submicrometer includes  
25 ultrafine structured and nanostructured materials. Nanostructured materials have structural features ranging from about 1 nanometer to about 300 nanometers or more. The average grain size of the ceramic component, preferably carbide(s), in the first region  
30 is greater than the average grain size of the ceramic component, preferably carbide(s), in the second region.

In a preferred embodiment, the grain size of the ceramic component, preferably carbide(s) and more preferably, tungsten carbides, of the first region  
35 ranges from about submicrometer to about 30 micrometers or greater with possibly a scattering of grain sizes measuring, generally, in the order of about 40

micrometers. Preferably, the grain size of the ceramic component of the first region ranges from about 0.5 micrometer to about 30 micrometers or greater with possibly a scattering of grain sizes measuring, generally, in the order of about 40 micrometers, while the average grain size ranges from about 0.5 micrometers to about 12 micrometers; preferably, from about 3 micrometers to about 10 micrometers; and more preferably, from about 5 micrometers to about 8 micrometers. Likewise, the grain size of the ceramic component of the second region ranges from about submicrometer to 30 micrometers or greater with possibly a scattering of grain sizes measuring, generally, in the order of about 40 micrometers. Preferably, the grain size of the ceramic component of the second region ranges from about 0.5 micrometer to about 30 micrometers or greater with possibly a scattering of grain sizes measuring, generally, in the order of about 40 micrometers, while the average grain size ranges from about 0.5 micrometer to about 8 micrometers; preferably, from about 1 micrometer to about 5 micrometers; and more preferably, from about 2 micrometers to about 5 micrometers.

In general, the ceramic component grain size and the binder content may be correlated to the mean free path of the binder by quantitative metallographic techniques such as those described in "Metallography, Principles and Practice" by George F. Vander Voort (copyrighted in 1984 by McGraw Hill Book Company, New York, NY). Other methods for determining the hard component grain size included visual comparison and classification techniques such as those discussed in ASTM designation: B 390-92 entitled "Standard Practice for Evaluating Apparent Grain Size and Distribution of Cemented Tungsten Carbide," approved January 1992 by the American Society for Testing and Materials, Philadelphia, PA. The results of these methods provide



apparent grain size and apparent grain size distributions.

In a preferred embodiment relating to ferromagnetic binders, the average grain size of the ceramic component, preferably carbide and more preferably tungsten carbide, may be correlated to the weight percent binder ( $X_b$ ), the theoretical density ( $\rho_{th}$ , grams per cubic centimeter) and the coercive force ( $H_c$ , kiloampere-turn per meter (kA/m)) of a homogeneous region of a sintered article as described by R. Porat and J. Malek in an article entitled "Binder Mean-Free-Path Determination in Cemented Carbide by Coercive Force and Material Composition," published in the proceedings of the Third International Conference of the Science of Hard Materials, Nassau, the Bahamas, November 9-13, 1986, by Elsevier Applied Science and edited by V. K. Sarin. For a cobalt bound tungsten carbide article, the calculated average grain size,  $d$  micrometers, of the tungsten carbide is given by equation 1,

$$d = 0.3 \left[ \frac{80}{H_c} \right]^{(164.822/X_b \rho_{th})^{1/3}} \quad (1)$$

In a preferred embodiment, the ratio of the average grain size of the ceramic component of the first region to that of the second region ranges from about 1.5 to about 12 and, preferably ranges from about 1.5 to about 3.

In a preferred embodiment, the binder content of the first region comprises, by weight, from about 2 percent to about 25 percent or more; preferably, from about 5 percent to about 10 percent; and more preferably, from about 5.5 percent to about 8 percent. Likewise, the binder content of the at least one additional region ranges, by weight, from about 2 percent to about 25 percent and preferably, from about 8 percent to about 15 percent. The binder content of

the second region is greater than that of the first region.

In a preferred embodiment, the combination of carbide grain size and binder content may be correlated to a binder mean free path size,  $\lambda$ , as discussed generally by Vander Voort and particularly for ferromagnetic materials by Porat and Malek. The binder mean free path ( $\lambda$  micrometers) in an article having a ferromagnetic metallic binder is a function of the weight percent binder ( $X_b$ ), coercive force ( $H_c$ , kiloampere-turn per meter (kA/m), and the theoretical density ( $\rho_{th}$ , grams per cubic centimeter) of a homogeneous region of the densified article. For a cobalt bound tungsten carbide article, the mean free path,  $\lambda$ , of the cobalt binder is given by the equation 2,

$$\lambda = \frac{0.3X_{co}\rho_{th}}{890 - X_{co}\rho_{th}} \left( \frac{80}{H_c} \right)^{(164.822/X_{co}\rho_{th})^{1/3}} \quad (2)$$

In a preferred embodiment, the binder mean free path size in the first region ranges from about 0.5 micrometers to about 2.5 micrometers, and preferably comprises about 0.8 micrometers while the mean free path size of the at least one additional region ranges from about 0.5 micrometers to about 1.5 micrometers.

The solid geometric shape of an article may be simple or complex or any combination of both. Solid geometric shapes include cubic, parallelepiped, pyramidal, frustum of a pyramid, cylinder, hollow cylinder, cone, frustum of a cone, sphere (including zones, segments and sectors of a sphere and a sphere with cylindrical or conical bores), torus, sliced cylinder, ungula, barrel, prismoid, ellipsoid and combinations thereof. Likewise, cross-sections of such articles may be simple or complex or combinations of

both. Such shapes may include polygons (e.g., squares, rectangles, parallelograms, trapezium, triangles, pentagons, hexagons, etc.), circles, annulus, ellipses and combinations thereof. Figures 2A, 2B, 2C, 2D, 2E and 2F illustrate combinations of a first region 210, a second region 211 and in some case a third region 212 (Fig. 2D) incorporated in various solid geometries. These figures are cut-away sections of the articles or portions of articles (conical cap or conical hybrid or scarifier conical in Fig. 2A; compact in Fig. 2B; grader or scraper or plow blade in Fig. 2C; roof bit borer in Fig. 2D; cutting insert for chip forming machining of materials in Fig. 2E; and conical plug or insert in Fig. 2F) and further demonstrate a leading edge or surface 207, and an outer surface 208.

Again, with reference to Figure 1, the interface 104 defining the boundary between the first region 102 and the second region 103 may divide the article 101 in a symmetric manner or an asymmetric manner or may only partially divide the article 101. In this manner, the ratios of the volume of the first region 102 and the at least one additional region 103 may be varied to engineer the most optimum bulk properties for the article 101. In a preferred embodiment, the ratio of the volume of the first region 102 to the volume of the second region 103 ranges from about 0.25 to about 4; preferably, from about 0.33 to about 2.0; and more preferably, from about 0.4 to about 2.

The novel articles of the present invention are formed by providing a first powder blend and a second or at least one additional powder blend. It will be apparent to artisan in the art that multiple powder blends may be provided. Each powder blend comprises at least one ceramic component, at least one binder, at least one lube (an organic or inorganic material that facilitates the consolidations or

agglomeration of the at least one ceramic component and at least one binder), and optionally, at least one surfactant. Methods for preparing each powder blend may include, for example, milling with rods or cycloids followed by mixing and then drying in a sigma-blade type dryer or spray dryer. In any case, each powder blend is prepared by a means that is compatible with the consolidation or densification means or both when both are employed.

10           A first powder blend having a pre-selected ceramic component, preferably carbide(s), grain size or grain size distribution and at least one additional powder blend having a finer ceramic component, preferably carbide(s), grain size or grain size  
15           distribution are provided. The at least two powder blends are at least partially juxtaposed. The at least partial juxtaposition provides or facilitates the formation of the novel articles having at least two regions having at least one different property after  
20           consolidation and densification by, for example, sintering.

          A first powder blend comprises a ceramic component, preferably carbide(s), having a coarse particle size relative to the at least one additional  
25           powder blend. Particle sizes may range from about submicrometer to about 420 micrometers or greater; preferably, grain sizes range from about submicrometer to about 30 micrometers or greater with possibly a scattering of particle sizes measuring, generally, in  
30           the order of about 40 micrometers. Submicrometer includes ultrafine structured and nanostructured materials. Nanostructured materials have structural features ranging from about 1 nanometer to about 100 nanometers or more. Preferably, the particle size of  
35           the ceramic component of the first powder blend ranges from about 0.5 micrometer to about 30 micrometers or greater with possibly a scattering of grain sizes

measuring, generally, in the order of about 40 micrometers, while the average particle size may range from about 0.5 micrometers to about 12 micrometers; preferably, from about 3 micrometers to about 10 micrometers; and more preferably, from about 5 micrometers to about 8 micrometers.

The ceramic component of a first powder blend may comprise boride(s), carbide(s), nitride(s), oxide(s), silicide(s), their mixtures, their solutions or any combinations of the preceding. The metal of the boride(s), carbide(s), nitride(s), oxide(s) or silicide(s) comprises one or more metals from IUPAC groups 2, 3 (including lanthanides and actinides), 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14. Preferably the ceramic component comprises carbide(s), their mixtures, or any combination of the preceding. The metal of the carbide comprise one or more metals from IUPAC groups 3 (including lanthanides and actinides), 4, 5, and 6; more preferably one or more of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; and even more preferably tungsten.

A binder of a first powder blend may comprise any material that is compatible with the formation process and does not adversely affect the performance of the article for its intended application. Such materials include metals, ceramics, glasses, or any combination of the preceding including mixtures, solutions, and alloys. Examples of metals suitable for use as binders include one or more metals of IUPAC groups 8, 9 and 10; preferably, one or more of Fe, Co, Ni, their mixtures, their alloys and combinations thereof; and more preferably, cobalt or cobalt alloys such as cobalt-tungsten alloys. A metal binder may include powder metal mixtures or alloy powder or both.

A binder amount of a first powder blend is pre-selected to tailor the properties, for example, to provide sufficient wear resistance of the resultant first region of an article for its intended use. It

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has been discovered that the pre-selected binder content may range, by weight, from about 2 percent to about 25 percent or more; more preferably, from about 5 percent to about 15 percent; even more preferably, from about 9 percent to about 10 percent.

A binder in a first powder blend may be any size that facilitates the formation of an article of the present invention. Suitable sizes have an average particle size less than about 5 micrometers; preferably, less than about 2.5 micrometers; and more preferably, less than about 1.8 micrometers.

One constraint on the second powder blend is that the average particle size of the ceramic component is less or smaller than the average particle size of the ceramic component of the first powder blend. As with the first powder blend, the particle size of the ceramic component, preferably carbide(s), may range from about submicrometer to about 420 micrometers or greater. Submicrometer includes ultrafine structured and nanostructured materials. Nanostructured materials have structural features ranging from about 1 nanometer to about 100 nanometers or more. Preferred particle sizes range from about submicrometer to about 30 micrometers, with possibly a scattering of particle sizes measuring, generally, in the order of about 40 micrometers. Preferably, the particle size of the ceramic component of the second powder blend ranges from about one micrometer to about 30 micrometers or greater with possibly a scattering of grain sizes measuring, generally, in the order of about 40 micrometers. Unlike the first powder blend, the average grain size of the ceramic component of the second powder blend, preferably carbide(s) and more preferably tungsten carbide, may range from about 0.5 micrometer to about 8 micrometers; preferably, from about 1 micrometer to about 5 micrometers; and more preferably, from about 2 to about 5 micrometers.

The ratio of the average ceramic component particle size of the first powder blend and the average ceramic component particle size of the second powder blend is selected to both facilitate the formation of an article of the present invention and optimize the performance of the resultant article. Thus, it is believed that the ratio of the average coarse particle size to the average fine particle size may range from about 1.5 to about 12, with a preferred ratio ranging from about 1.5 to about 3.

The chemistry of the ceramic component of the second or at least one additional powder blend may be substantially the same as or substantially different from the chemistry of the first powder blend. Thus, the chemistry includes all the enunciated chemistries of the first powder blend.

Likewise, the chemistry of the binder of the second powder blend may be substantially the same as or substantially different from the chemistry of the binder of the first powder blend. Thus, the chemistry includes all the enunciated chemistries of the first powder blend.

The binder content of each powder blend is selected both to facilitate formation of an article and provide optimum properties to the article for its particular application. Thus, the binder content of the first powder blend may be greater than, less than or substantially equivalent to the binder content of the second powder blend. Preferably, the binder content of the second powder blend ranges, by weight, from about zero (0) to about two (2) percentage points different from the percentage of the pre-selected binder content of the first powder blend; more preferably, about 0.5 percentage points different from the percentage of the pre-selected binder content of the first powder blend. In a more preferred embodiment, the binder content of the second powder blend is less

than that of the first powder blend. For example, if the preselected binder content of the first powder blend is by weight, about 9.5 percent, then the binder content of the second powder blend may range from about 7.5 percent to about 11.5 percent, preferably from about 9 percent to about 10 percent, more preferably from about 7.5 percent to about 9.5 percent and even more preferably from about 9 percent to about 9.5 percent.

The at least two powder blends are provided in any means that allows at least a portion of each to be at least partially juxtaposed. Such means may include, for example, pouring; injection molding; extrusion, either simultaneous or sequential extrusion; tape casting; slurry casting; slip casting; sequential compaction; co-compaction; or and any combination of the preceding. Some of these methods are discussed in US Patent Nos. 4,491,559; 4,249,955; 3,888,662; and 3,850,368, which are incorporated by reference in their entirety in the present application.

During the formation of a green body, the at least two powder blends may be maintained at least partially segregated by a providing means or by a segregation means or both. Examples of providing means may include, for example, the methods discussed above while segregation means may include a physically removable partition or a chemically removable partition or both.

A physically removable partition may be as simple as a paper or other thin barrier that is placed into a die or mold during the charging of the at least two powder blends and which is removed from the die or mold after powder blend charging and prior to powder blend densification. More sophisticated physically removable partitions may include concentric or eccentric tubes (e.g., impervious or pervious sheets, screens or meshes, whether metallic or ceramic or



polymeric or natural material, or any combination of the preceding). The shapes of physically removable partitions may be any that facilitate the segregation of the at least two powder blends.

5           A chemically removable partition includes any partition, whether in a simple or complex form or both, or pervious or impervious or combinations of both, that may be removed from or consumed by the segregated at least two powder blends by a chemical means. Such  
10 means may include leaching or pyrolysis or fugitive materials or alloying or any combination of the preceding. Chemically removable partitions facilitate the formation of articles of the present invention wherein the at least two regions, cross-sectionally as  
15 well as in regard to the solid geometry, comprise complex shapes.

          In an embodiment of the present invention, the segregated and at least partially juxtaposed at least two powder blends are densified by, for example,  
20 pressing including, for example, uniaxial, biaxial, triaxial, hydrostatic, or wet bag either at room temperature or at elevated temperature.

          In any case, whether or not consolidated, the solid geometry of the segregated and at least partially  
25 juxtaposed at least two powder blends may include: cubes, parallelepipeds, pyramids, frustum of pyramid, cylinders, hollow cylinders, cones, frustum of cones, spheres, zones of spheres, segments of spheres, sectors of spheres, spheres with cylindrical bores, spheres  
30 with conical bores, torus, sliced cylinders, ungula, barrels, prismoids, ellipsoids, and combinations of the preceding. To achieve the direct shape or combinations of shapes, the segregated and at least partially juxtaposed at least two powder blends may be formed  
35 prior to or after densification or both. Prior forming techniques may include any of the above mentioned providing means as well as green machining or

plastically deforming the green body or their combinations. Forming after densification may include grinding or any machining operations.

5 The cross-sectional profile of a green body may be simple or complex or combinations of both. Shapes include polygons such as squares, rectangles, parallelograms, trapezium, triangles, pentagons, hexagons, etc.; circles; annulus; ellipses; etc.

10 The green body comprising the segregated and at least partially juxtaposed at least two powder blends is then densified by liquid phase sintering. Densification may include any means that is compatible with making an article of the present invention. Such means include hot pressing, vacuum sintering, pressure sintering, hot isostatic pressing (HIPping), etc.  
15 These means are performed at a temperature and/or pressure sufficient to produce a substantially theoretically dense article having minimal porosity. For example, for tungsten carbide-cobalt articles, such  
20 temperatures may include temperatures ranging from about 1300°C (2372°F) to about 1650°C (3002°F); preferably, from about 1350°C (2462°F) to about 1537°C (2732°F); and more preferably, from about 1500°C (2732°F) to about 1525°C (2777°F). Densification  
25 pressures may range from about zero kPa (zero psi) to about 206,850 kPa (30,000 psi). For carbide articles, pressure sintering may be performed at from about 1,723 kPa (250 psi) to about 13,790 kPa (2000 psi) at temperatures from about 1370°C (2498°F) to about 1540°C (2804°F), while HIPping may be performed at from about  
30 58,950 kPa (10,000 psi) to about 206,850 kPa (30,000 psi) at temperatures from about 1,310°C (2390°F) to about 1430°C (2606°F).

35 Densification may be done in the absence of an atmosphere, i.e., vacuum; in an inert atmosphere, e.g., one or more gasses of IUPAC group 18; in nitrogenous atmospheres, e.g., nitrogen, forming gas

(96% nitrogen, 4% hydrogen), ammonia, etc.; in a carburizing atmosphere; or in a reducing gas mixture, e.g.,  $H_2/H_2O$ ,  $CO/CO_2$ ,  $CO/H_2/CO_2/H_2O$ , etc.; or any combination of the preceding.

5                   In an effort to explain the workings of the present invention, but without wishing to be bound by any particular theory or explanation for the present invention, it appears as though when a green body is liquid phase sintered, binder from the first powder  
10 blend migrates by capillary wetting into the second powder blend or the ceramic component of the second powder blend is transported by a dissolution, diffusion, and precipitation mechanism to the first powder blend or both.

15                   With regard to the capillary migration mechanism, metal binders, particularly in carbide-cobalt systems, may wet ceramic component particles readily. The particle size difference between the first powder blend and the second powder blend  
20 translates into a corresponding difference in effective capillary size of the at least two powder blends. The effective capillary size in the second powder blend (e.g., the powder blend with the fine particle size) would be smaller and thus provide a driving force for a  
25 molten binder to migrate from the first powder blend to the second powder blend.

                  With regard to the dissolution, diffusion, and precipitation mechanism, the particle size difference of the at least two powder blends translates  
30 into a corresponding difference in effective particle surface area of the at least two powder blends. The effective surface area of the second powder blend (i.e., the fine particle powder) would be greater and thus there would be a driving force to reduce that area  
35 during densification. As a result, finer particles would then preferentially dissolve in the molten binder, diffuse to the region of the first powder

blend, and precipitate onto the coarser particles of the first powder blend.

The present invention is illustrated by the following Examples. These Examples are provided to demonstrate and clarify various aspects of the present invention. The Examples should not be construed as limiting the scope of the claimed invention.

#### EXAMPLE 1

The present Example demonstrates, among other things, a method of making an article, an article, and a method of using an article of the present invention. More particularly, the present Example demonstrates the formation of an article having a first region and a second region, the first region comprising a coarse grain size carbide material and the second region comprising a fine grain size carbide material. The juxtaposing of the first region and the second region with a predetermined exterior or surface profile in a single article facilitates its use for the removal of material, and specifically, the removal of coal in a mining operation. This Example describes the method of making the article, the characterization of the article and a description of the method of using the article.

#### METHOD OF MAKING

To make articles according to the present Example and the present invention, a granulated first powder blend and a granulated second powder blend were separately prepared. The first powder blend (depicted as 314 in Figs. 3A, 3B and 3C) comprised, by weight, about 87.76 percent macrocrystalline tungsten carbide (Kennametal Inc. Fallon, Nevada), about 9.84 percent commercially available extra fine cobalt binder, about 2.15 percent paraffin wax lubricant, and about 0.25 percent of surfactant.

A portion of the first powder blend was then sintered and the tungsten carbide average grain size, which had an observed grain size ranging from about 1 micrometer to about 25 micrometers with the possibility of scattered grains having a grain size, generally, in the order of about 40 micrometers, was calculated at about 6.7 micrometers by Equation (1) after measuring the sintered articles coercive force ( $H_C$ ) and binder content ( $X_{Co}$ ).

The second powder blend (depicted as 313 in Figs. 3A, 3B and 3C) comprised, by weight, about 88.82 percent macrocrystalline tungsten carbide (Kennametal Inc., Fallon, Nevada), about 8.78 percent commercially available cobalt binder, about 2.15 percent paraffin wax lubricant, and about 0.25 percent of a surfactant surfactant. The observed grain size of the tungsten carbide in a sintered piece ranged from about 1 to about 9 micrometers with the possibility of scattered grains having a grain size, generally, in the order of about 40 micrometers and had a calculated average grain size of about 2.8 micrometers as determined by Equation (1).

The first powder blend 314 and the second powder blend 313 were then charged into a die cavity having an about 19 mm (0.75 inch) diameter using charging configuration 301 depicted schematically in Figure 3A. Charging configuration 301 included engagement of a lower ram 303 with a side cylindrical wall of the die 302, the placement of an outer portion charging funnel 304 having a contact point 307 between the outer portion charging funnel and the die cavity, an inner portion charging funnel 308 contacting forward portion defining surface 312 via physically removable portion 310, which had a diameter measuring about 10 mm (0.39 inch), at contact point 311 of the lower ram 303. About 8.4 grams of the first powder blend 314 were poured into the inner portion charging funnel 308.

About 18.6 grams of the second powder blend 313 were charged into the outer portion charging funnel 304. After both the first powder blend 314 and the second powder blend 313 had been placed within the die cavity, the inner and the outer charging funnels were removed to form an interface 317 between the first powder blend 314 and the second powder blend 313. An upper ram 315 having a rear portion defining surface 316 was then engaged at about room temperature with the first powder blend 314 and the second powder blend 313 to a load of about 31,138 newtons (N) (7,000 pounds (lbs.)). After the load was removed, green body 320 was ejected from the die cavity and had a forward portion 321 defined by a lower ram 303 and a rear portion defined by the upper ram 315. Further, the green body 320 comprised compacted first powder blend 314 and second powder blend 313. This operation was repeated until a sufficient number (about 72) of green bodies comprising the first powder blend 314 and the second powder blend 313 had been formed. Additionally, several bodies comprised only of the first powder blend 314 and other bodies comprised only of the second powder blend 313 were formed. These bodies were used as control samples during sintering of the green bodies 320 to determine the types of changes that may occur as a result of the co-densification of a first powder blend 314 contacting a second powder blend.

Once a sufficient number of green bodies 320 had been formed, green bodies 320 and the control samples were placed in an Ultra-Temp pressure sintering furnace (Ultra-temp Corporation, Mt. Clement, Missouri). The furnace and its contents were evacuated to about five (5) torr and then raised from about room temperature to about 177°C (350°F) at a rate of about 3.3°C (6°F) per minute under vacuum; held at about 177°C (350°F) for about 15 minutes; heated from about 177°C (350°F) to about 371°C (700°F) at about 3.3°C

(6°F) per minute; held at about 371°C (700°F) for about 90 minutes; heated from about 371°C (700°F) to about 427°C (800°F) at about 1.7°C (3°F) per minute; held at about 427°C (800°F) for about 45 minutes; heated from about 427°C (800°F) to about 538°C (1000°F) at about 1.4°C per minute; held at about 538°C (1000°F) for about 12 minutes heated from about 538°C (1000°F) to about 593°C (1000°F) at about 1.4°C (2.5°F) per minute and then from about 593°C (1100°F) to about 1,121°C (2050°F) at about 4.4°C (8°F) per minute; held at about 1,121°C (2050°F) for about 30 minutes under a vacuum ranging from about 13 micrometers to about 29 micrometers; heated from about 1,121°C (2050°F) to about 1,288°C (2350°F) at about 4.4°C (8°F) per minute; held at about 1,288°C (2350°F) for about 30 minutes while argon was introduced to about 15 torr; heated from about 1,288°C (2350°F) to about 1,510°C (2750°F) at about 3.3°C (6°F) per minute while argon was introduced to about a pressure of about 5,516 kPa (800 psi); held at about 1,510°C (2750°F) for about 5 minutes; and then the power to the furnace was turned off and the furnace and its contents were allowed to cool to about room temperature at about 5.6°C (10°F) per minute.

Several of the sintered articles (now having diameters of about 15.9 mm (0.625 inch) and included tip angles,  $\phi$ , of about 75°), including sintered control samples for the sintered only first powder blend and the sintered only second powder blend, were characterized using metallography, wet chemical analysis, magnetic properties characterization, hardness, and energy dispersive x-ray analysis (EDS).

Table I sets forth the results of characterization of the first region and the second region of articles made in accordance with the present Example and the sintered control samples of the only first powder blend and only second powder blend. The

results of wet chemical analysis indicate that cobalt binder migrated from the first powder blend to the second powder blend during the densification of the green body to form the article. This migration of the cobalt binder had an effect on the hardness of the first region relative to the sintered control samples of only first powder blend and the second portion relative to the sintered only second powder blend.

Figure 4A is a photomicrograph at about 3.4 X of longitudinal cross sections of sintered article 401 having a first portion 414 contacting a second portion 413 at an interface 417. A forward region 421 corresponds to the forward region of a green body and the rear portion 422 corresponds to the rear portion of a green body. Examination of the interface 417 between the first region 414 and the at least one additional region 413 at a magnification of about 500X is shown in Figure 4B, while at a magnification of about 1500X in Figure 4E. Figures 4C and 4D are photomicrographs of a first region 414 and an second region 413 at a magnification of about 500X, while Figures 4F and 4G are photomicrographs of the first region 414 and the second region 413 at a magnification of about 1500X. The constituents of the first region 414 and the second region 413 are identified in Figures 4E, 4F and 4G and include a cobalt alloy binder 425, coarse grain tungsten carbide 426 and the fine tungsten grain carbide 427. The autogeneously formed bond line 417 is clearly seen in Figure 4E as a sudden change in tungsten carbide grain size. There is an excellent autogeneously produced metallurgical bond which is free



TABLE I

CHARACTERIZATION RESULTS OF REGIONS OF AN ARTICLE MADE IN ACCORDANCE WITH EXAMPLE 1 AND CONTROL SAMPLES								
	Results of Wet Chemical Analysis (Wt%) †				Hardness	Average Calculated Grain Size	Coercive Force, H <sub>c</sub>	Magnetic Saturation
	Co	Ta	Ti	Fe				
					Rockwell A	Microns	Oersteds <sup>‡</sup>	Percent §
PRESENT INVENTION								
First Region	5.45	0.26	0.16	0.06	0.02	87.6	76	92
	5.48	0.26	0.16	0.07	0.02			
Second Region	10.75	0.285	0.17	0.13	0.02	88.4	111	91
	10.78	0.285	0.17	0.13	0.02			
CONTROL SAMPLES								
Sintered FPB*	10.08	0.28	0.40	0.10	0.04	86.1	51 50	100 100
Sintered SPB**	9.00 9.01	0.278 0.275	0.15 0.16	0.10 0.11	0.02 0.02	89.1	124 125	91 92

\* FPB = First Powder Blend

\*\* SPB = Second Powder Blend

† Nb, Cr, &amp; V, when analyzed, were usually less than about 0.01 wt%. Balance of the material is W + C + other minor impurities.

§ 100 percent = about 160 emu per gram or 1.7 tesla or 17,000 gauss

¶ 1 oersted = 79.58 ampere-turns per meter (A/m) = 0.08 kiloampere-turns per meter (kA/m)

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of cracks and inclusions. These dense, sintered articles are also free of eta-phase and C porosity.

To quantify the cobalt distribution within the article made by the method of the present Example,

5 a mounted and polished sample was analyzed by standardless spot probe analysis using energy dispersive x-ray analysis (EDS) at two different diameters of an article. Specifically, a JSM-6400 scanning electron microscope (Model No. ISM64-3, JEOL

10 LTD, Tokyo, Japan) equipped with a LaB<sub>6</sub> cathode electron gun system and an energy dispersive x-ray system with a silicon-lithium detector (Oxford Instruments Inc., Analytical System Division, Microanalysis Group, Bucks, England) at an accelerating

15 potential of about 20 keV was used. The scanned areas measured about 125 micrometers by about 4 micrometers. Each area was scanned for equivalent time intervals (about 50 seconds live time). The step size between adjacent areas was about 0.1 mm (0.004 inch). Figures

20 5A and 5B show the results of this standardless analysis as well as the average across a region. Figure 5A corresponds to the results of a spot probe analysis done at a diameter of about 10.5 mm (0.413 inch) and shows a stepwise gradation of cobalt content

25 from the first region (average about 11.9 wt%) to the second region average to about 7.2 wt%). Likewise, Figure 5B shows the results of spot probe analysis for a diameter measuring about 15.5 mm (0.610 inch) and also suggests a stepwise gradation of cobalt content

30 from the first region (average about 12.3 wt%) to the second region (average about 7.6 wt%) of the article.

Figure 6 presents the results of a hardness profile on an article which indicate that the hardness of the first region (inner or core portion of this

35 article, Rockwell A  $\cong$  87.4-87.8) is lower than the

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hardness of the second region (outer or peripheral portion of the present article, Rockwell A  $\cong$  88.3-88.7).

#### METHOD OF USE

5                   A sufficient number of sintered articles made according to the present Example were brazed to steel bodies to form "KENNAMETAL®" U765KSA Conical Tools as schematically depicted in Figure 7 (Kennametal Inc., Latrobe, Pennsylvania) used in conjunction with  
10 "KENNAMETAL®" KB175SLSA Cutting System. The brazing of the articles was accomplished using the materials disclosed in commonly owned US Patent No. 5,324,098, issued in the name of Massa et al, on June 28, 1994, and entitled "Cutting Tool Having Tip with Lobes." The  
15 subject matter of US Patent No. 5,324,098 is incorporated by reference. Conical tool 701 is comprised of an elongated body 705 with an attached hard cutting tip 702. The elongated body 705 has an axially forward end 710 and an axially rearward end  
20 707. Between ends 710 and 707 are a radially projecting flange 704, an enlarged diameter portion 711, and a reduced diameter section 706. The axially forward end 710 comprise a socket 709 for receiving hard cutting tip 702. Hard cutting tip 705 is  
25 comprised of a first region 714 and a second region 715 at least partially autogeneously metallurgically bonded of interface 717. Hard tip 702 is in contacting communication with elongated body 705 by an attachment means 703. The attachment means 703 may include  
30 braising, shrink fitting, interference fitting and combination thereof. Conical tool 701 may further comprise a retaining means depicted in Fig. 7 as a retainer sleeve or clip 708.

35                   The cutting system was used with a Joy 12HN9 Continuous Miner (Joy Manufacturing Co., Ltd.,

Johannesburg, South Africa) to mine coal.

Particularly, coal having a compressive strength or hardness of about 12 megapascal (MPa) (3.5 kilo pounds per square inch (ksi)) was mined about 3 meters (9.8 feet) high for a given distance using prior art tools made from a coarse grained tungsten carbide-cobalt alloy (see sample 10 in Table V) and the tools incorporating the articles made according to the present Example. After 4 meters (13.1 feet), 8 meters (26.2 feet) and 12 meters (39.4 feet) of mining, the length change of the tools incorporating the prior art and the tools incorporating articles made according to the present Example were determined. The included angle of the tip of some tools was also measured.

The results determined after 4 meters (13.1 feet), 8 meters (26.2 feet) and 12 meters (39.4 feet) for various positions are summarized in Tables II, III and IV, respectively. Specifically, Tables II, III and IV show the position of the tool, the change in length for the tool incorporating the prior art and the tool incorporating articles of the present Example, the ratio of the change in length, the magnitude of the included tip angle for the prior art tool, the magnitude of the included angle for the present invention and the ratio of the change in tip included angle for the prior art tool to the change in tip included angle for the present invention. It should be noted that the included tip angle for all of the tools started at about 75°.

To graphically demonstrate various aspects of the present invention, Figures 8 and 9 present a comparison of profile measurements of the tips of the present invention (—), tips of the prior art ( - - - - ) and the starting tip profile (·····) as a function of position in the cutting system for positions 1, 3 and 5 after 4 meters (13.1 feet) of

**TABLE II**

TOOL CHARACTERIZATION AFTER MINING FOR FOUR METERS						
Position†	Length Change (Inches)			Included Angle (Degrees)		
	Prior Art	Present Invention	Ratio	Prior Art	Present Invention	Ratio*
1	0.075	0.033	2.3:1	89	80	2.8:1
2	0.028	0.032	0.9:1	80	80	1.0:1
3	0.039	0.039	1.0:1	81	80	1.2:1
4	0.076	0.050	1.5:1	91	83	2.0:1
5	0.107	0.035	3.1:1	96	80	4.2:1
6	0.061	0.044	1.4:1	88	80	2.6:1
Average	0.064	0.039	1.6:1	88	81	2.2:1

**TABLE III**

TOOL CHARACTERIZATION AFTER MINING FOR EIGHT METERS						
Position†	Length Change (Inches)			Included Angle (Degrees)		
	Prior Art	Present Invention	Ratio	Prior Art	Present Invention	Ratio*
1	0.090	0.022	4.0:1	92	80	3.4:1
2	0.069	0.087	0.8:1	90	87	1.3:1
5	0.084	0.053	1.6:1	94	83	2.4:1
6	0.093	0.059	1.6:1	96	85	2.1:1
Average	0.084	0.055	1.5:1	93	84	2.0:1

**TABLE IV**

TOOL CHARACTERIZATION AFTER MINING FOR TWELVE METERS						
Position†	Length Change (Inches)			Included Angle (Degrees)		
	Prior Art	Present Invention	Ratio	Prior Art	Present Invention	Ratio*
2	0.121	0.043	2.8:1	97	81	3.7:1
3	0.038	0.066	0.6:1	83	78	2.7:1
4	0.076	0.098	0.8:1	86	82	1.6:1
6	0.093	0.118	0.8:1	91	93	0.9:1
Average	0.082	0.081	1.0:1	89	84	1.6:1

\* Change in tip included angle of the present invention:  
change in tip included angle of the prior art

† Data for positions 3 & 4 in Table III and 1 & 5 in Table IV could not be reported because either the tools of the present invention or the prior art failed by, for example, brazing failure or other tool breakage.

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mining and positions 1, 5 and 6 after 8 meters (26.2 feet) of mining. The data for Tables II, III and IV and the comparisons shown in Figures 8 and 9 demonstrate, among other things, that articles made according to the present invention exhibit superior wear properties while substantially maintaining their original profiles. Thus, the present Example demonstrates, among other things, the method for making articles exhibiting superior properties for applications involving the removal of materials.

#### EXAMPLE II

The present Example demonstrates, among other things, that a range of amounts of a first powder blend may be combined with an at least one additional powder blend to form articles of the present invention. In particular, the methods of Example 1 were substantially repeated to form sintered articles having about 17.5 mm (0.689 inch) diameter, except that a total mass of the green body measured about 47 grams rather than 27 grams and the green body diameter measured about 21 mm (0.827 inch). In addition, the consolidation load used to form the green bodies of this Example was about 37,365 N (8400 lbs) rather than 31,138 N (7000 lbs).

As in Example 1, control samples comprised only of the first powder blend or only of the second powder blend were made for comparison. The resultant articles of the present Examples were characterized in a manner similar to those of Example 1. Table V summarizes the weight percent of the first powder blend and the second powder blend which were combined to form the green bodies and eventually the densified articles, the dimension of the first powder blend zone, the results of wet chemical analysis, the results of hardness measurements, the results of magnetic properties measurements. Thus, the present Examples,

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among other things, teaches a method for tailoring the binder content of a first region and a second region for an article made by the methods of the present invention.

TABLE V

Sample No.	FPB* Zone Dimensions		Charging Portions		Results of Wet Chemical Analysis (Wt%): <sup>1</sup>							Average Calculated Grain Size	Hardness	Coercive Force, H <sub>c</sub>	Magnetic Saturation
	Length mm (inch)	Diameter mm (inch)	Wt% FPB*	Wt% SPB**	Location Within Sample	Co	Ta	Ti	Nb	Fe	Cr				
88	15.5 (0.61)	8.1 (0.32)	21.3	78.7	Second Region	9.89	0.27	0.18	0.05	0.14	0.01	2.91	88.6	115	91
					First Region	5.79	0.23	0.15	0.04	0.13	0.02				
74	17.3 (0.68)	8.6 (0.34)	26.8	73.2	Second Region	10.14	0.28	0.17	0.05	0.15	0.01	2.92	88.4	112	91
					First Region	10.09	0.28	0.17	0.04	0.16	0.01				
91	19.6 (0.77)	8.6 (0.34)	31.1	68.9	Second Region	10.52	0.29	0.19	0.06	0.15	<0.01	7.07	87.7	76	92
					First Region	10.49	0.30	0.18	0.05	0.15	0.02				
92	19.6 (0.77)	8.6 (0.34)	31.1	68.9	Second Region	10.41	0.28	0.17	0.04	0.15	<0.01	2.90	88.4	111	91
					First Region	10.41	0.27	0.17	0.04	0.13	0.01				
82	19.3 (0.76)	9.4 (0.37)	36.0	64.0	Second Region	10.74	0.29	0.18	0.05	0.17	0.01	2.90	88.3	109	91
					First Region	6.33	0.23	0.15	0.04	0.12	0.02				
10	N/A	N/A	100	0	N/A	9.55	0.25	0.16	0.04	0.17	<0.01	6.93	87.6	74	94
					N/A	9.56	0.24	0.16	0.05	0.17	<0.01				
22	N/A	N/A	0	100	N/A	9.05	0.27	0.17	0.04	0.13	<0.01	2.82	89.1	125	89
					N/A	9.06	0.28	0.17	0.04	0.13	<0.01				

\* FPB = First Powder Blend

\*\* SPB = Second Powder Blend

† Each sample contained less than about 0.01 wt% of each of Ni, Hf, and V. The balance of each sample comprised W + C + other minor impurities.

‡ 100 percent = about 160 emu per gram or 1.7 tesla or 17,000 gauss

§ 1 oersted = 79.58 ampere-turns per meter (A/m) = 0.08 kiloampere-turns per meter (kA/m)



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**WHAT IS CLAIMED IS:**

1. A method of making a composite body comprising the steps of:

5 (a) providing at least two powder blends comprising a first powder blend comprising a first ceramic component having a preselected particle size and a first binder at a preselected amount; and at least one additional powder blend comprising a second ceramic component having a particle size less than the  
10 preselected particle size of the first powder blend and a second binder at an amount substantially the same as the preselected amount of the first powder blend;

15 (b) juxtaposing the first powder blend and the at least one additional powder blend thereby forming at least one at least partial interface between the at least two powder blends;

20 (c) heating the juxtaposed at least two powder blends to a temperature sufficient to at least partially densify and autogeneously bond the at least two powder blends thereby forming a composite body comprising at least two at least partially autogeneously bonded regions having at least one property that differs.

25 2. The method of claim 1, wherein said ceramic component comprises at least one of boride(s), carbide(s), nitride(s), oxide(s), silicide(s), their mixtures, their solutions, and combinations thereof.

3. The method of claim 2, wherein a metal of said at least one of boride(s), carbide(s), nitride(s), oxide(s), silicide(s), their mixtures, their solutions and combinations thereof comprises one or more metals of IUPAC groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14.

4. The method of claim 1, wherein said ceramic component comprises at least one carbide of one or more metals of IUPAC groups 3, 4, 5, and 6.

5. The method of claim 4, wherein said at least one carbide comprises at least one carbide of one or more of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W.

6. The method of claim 5, wherein said at least one carbide comprises tungsten carbide.

7. The method of claim 1, wherein said preselected particle size ranges from about submicrometer to about 420 micrometers.

8. The method of claim 7, wherein said preselected particle size ranges from about submicrometer to about 30 micrometers with possibly a scattering of particles in the order of about 40 micrometers.

9. The method of claim 8, wherein said preselected particle size ranges from about 1 micrometer to about 30 micrometers with possibly a scattering of particles in the order of about 40 micrometers.

10. The method of claim 1, wherein said binder of said first powder blend and said at least one additional powder blend comprises one or more metals of IUPAC groups 8, 9 and 10, their mixtures, their alloys, and combinations thereof.

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11. The method of claim 10, wherein said binder comprises one or more of iron, nickel, cobalt, their mixtures and their alloys.

5           12. The method of claim 11, wherein said binder consists essentially of cobalt or its alloys.

13. The method of claim 1, wherein said juxtaposing includes forming a green body by at least one of compaction, slip casting, slurry casting, tape  
10 casting, injection molding, extrusion, and combinations thereof.

14. The method of claim 13, wherein the green body is formed by compaction.

15           15. The method of claim 1, wherein during at least a portion of said at least partial densification at said temperature, said at least two powder blends are at least partially subjected to a pressure.

20           16. The method of claim 1, wherein the preselected amount of first binder comprises, by weight, from about 2 percent to about 25 percent.

25           17. The method of claim 16, wherein the preselected amount of binder comprises, by weight, from about 5 to about 15 percent.

30           18. The method of claim 17, wherein the preselected amount of binder comprises, by weight, from about 8 to about 10 percent.

35           19. The method of claim 1, wherein the ratio of the ceramic component average particle size of the first powder blend to the ceramic component average particle size of the at least one additional powder blend comprises from about 1.5 to about 12.

20. The method of claim 19, wherein the ratio of the ceramic component average particle size of the first powder blend to the ceramic component average particle size of the at least one addition power blend comprises from about 2 to about 3.

21. The method of claim 1, wherein the at least one partial interface between the at least two powder blends intersect at least one surface of the green body.

22. The method of claim 1, wherein during juxtaposing, the at least a portion of the least two powder blends are formed into a preselected geometry.

23. An article comprising:

(a) a first region comprising a first ceramic component having an average coarse grain size and a first binder;

(b) at least one additional region comprising a second ceramic component and a second binder, wherein the average grain size of the second ceramic component is less than the average grain size of the ceramic component of the first region, the second binder amount of the at least one additional region is greater than the first binder amount of the first region and the first region and at least one additional region at least partially share at least one autogeneously formed interface.

24 The article of claim 23, further comprising at least one surface at least partially comprised of said first region and said at least one additional region and at least partially intersected by said at least partially shared autogeneously formed interface.

25 The article of claim 23, wherein the  
first and second ceramic component comprise at least  
one of boride(s), carbide(s), nitride(s), oxide(s),  
5 silicide(s), their mixtures, their solutions, and  
combinations thereof.

26. The article of claim 25, wherein a metal  
of said at least one boride(s), carbide(s), nitride(s),  
10 oxide(s), silicide(s), their mixtures, their solutions,  
and combinations thereof comprises one or more metals  
of IUPAC groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,  
and 14.

15 27. The article of claim 25, wherein the  
first and second ceramic component comprise at least  
one carbide of one or more metals of IUPAC groups 3, 4,  
5, and 6.

20 28. The article of claim 27, wherein said at  
least one carbide comprises at least one carbide of one  
or more of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W.

25 29. The article of claim 28, wherein said at  
least one carbide comprises tungsten carbide.

30 30. The article of claim 23, wherein the  
first ceramic component grain size of said first  
portion ranges from about submicrometer to about 420  
micrometers.

31. The article of claim 30, wherein the  
first ceramic component grain size of said first  
portion ranges from about submicrometer to about 30  
35 micrometers with possibly a scattering of grain sizes  
in the order of about 40 micrometers.

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32. The article of claim 31, wherein the first ceramic component grain size of said first portion ranges from about 1 micrometer to about 30 micrometers with possibly a scattering of grain sizes in the order of about 40 micrometers.

33. The article of claim 23, wherein said binder comprises one or more metals from IUPAC groups 8, 9, and 10, their mixtures and their alloys.

34. The article of claim 33, wherein said binder comprises one or more of iron, nickel, cobalt, their mixtures, and their alloys.

35. The article of claim 34, wherein said binder consisting essentially of cobalt or its alloys.

36. The article of claim 35, wherein the first binder of the first region comprises a mean free path of from about 0.5 micrometers to about 2.5 micrometers.

37. The article of claim 36, wherein the binder of the at least one additional region comprises mean free path size from about 0.5 to about 1.5 micrometers.

38. The article of claim 37, wherein the binder of the at least one additional region comprises mean free path of about 0.8 micrometer.

39. The article of claim 23, wherein the binder content comprises, by weight, from about 2 percent to about 25 percent.

40. The article of claim 39, wherein the binder content comprises, by weight, from about 5 percent to about 15 percent.

5                   41. The article of claim 40, wherein the binder content comprises, by weight, from about 8 percent to about 10 percent.

10                   42. The article of claim 23, wherein the ratio of the first ceramic component average grain size of the first region to the second ceramic component average grain size of the at least one additional region comprise from about 1.5 to about 12.

15                   43. The article of claim 42, wherein the ratio of the first ceramic component average grain size of the first powder blend to the second ceramic component average grain size of the at least one additional region comprise from about 2.0 to about 3.0.

20                   44. A method of using an article comprising the steps of:

- (a) engaging at least a portion of a first region of the article with a material;
- 25                   (b) engaging at least a portion of an at least one additional region of the article with the material;
- (c) gouging at least a portion of the material;
- 30                   (d) wearing at least a portion of the first region of the article;
- (e) wearing at least a portion of the at least one additional region of the article to the substantially the same extent of the at least a portion
- 35                   of the first region; and

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(f) continuing steps (a) through (e) and thereby extending the useful life of the article relative to a prior-art article consisting one region, wherein at least a portion of said article comprises at least two regions exhibiting at least one property that differs and wherein said first region comprises a first ceramic component and a first binder and said at least one additional region comprises a second ceramic component having a grain size smaller than the grain size of the first ceramic component of the first region and a second binder.

45. The method of claim 44, wherein said material comprises an ore or mineral and said article comprises a conical bit.

46. The method of claim 44, wherein said material comprise concrete or other man made materials and said article comprises a conical bit.

47. The method of claim 44, wherein said article comprise at least one of an agricultural tool with cermet inserts, disc blades, stump cutter or grinder, a furrowing tool, an earth working tool, a mining digging or cutting tool, an earth auger, a mineral or rock drill, a construction equipment blade, a roll cutter, a comminution machine and a cutting insert with or without either coating or chip control designs.

48. The method of claim 44, wherein said material comprises at least one of natural materials, synthetic materials and combinations thereof.

49. The method of claim 47, wherein said article comprises a conical bit.



50. A tip for use in excavation comprising:  
a forward portion having a surface  
extending radially outwardly while extending rearwardly  
5 along a longitudinal axis x-x;  
a rearward portion for attachment to a  
tool body;  
said rearward portion joined to and  
located behind said forward portion along said  
10 longitudinal axis x-x;  
a first cermet composition;  
a second cermet composition;  
wherein said first cermet composition  
has a first ceramic component grain size and a first  
15 binder content;  
wherein said second cermet composition  
has a second ceramic component grain size and a second  
binder content;  
wherein said first binder content is  
20 less than said second binder content, and said first  
grain size is greater than said second grain size;  
wherein said first cermet composition is  
located radially inside of and is autogeneously  
metallurgically bonded to said second cermet  
25 composition; and  
wherein during use in said excavation  
the first cermet composition is more wear resistant  
than said second cermet composition.

30 51. The tip according to Claim 50 wherein  
said first cermet composition has a first forwardmost  
portion and said second cermet composition has a second  
forwardmost portion and wherein said first forwardmost  
portion extends forwardly beyond the second forwardmost  
35 portion.

52. The tip according to Claim 50 wherein  
said first cermet composition has a first hardness and  
said second cermet composition has a second hardness  
wherein said second hardness is greater than said first  
hardness.

53. The tip according to Claim 51 wherein  
said first cermet composition has a first hardness and  
said second cermet composition has a second hardness  
wherein said second hardness is greater than said first  
hardness.

54. The tip according to Claim 50 wherein  
said first cermet composition consists essentially of  
tungsten carbide and said first binder is selected from  
the group consisting of cobalt and cobalt alloys, and  
wherein said second cemented carbide composition  
consists essentially of tungsten carbide and said  
second binder is selected from the group consisting of  
cobalt and cobalt alloys.

55. The tip according to Claim 50 wherein  
both said first and said second cermet compositions  
contain zero volume percent eta phase.

56. The tip according to Claim 54 wherein  
said first cermet composition has from about 3 to about  
15 weight percent and said second cermet composition  
has from about 5 to about 25 weight percent cobalt.

57. The cermet tip according to Claim 54  
wherein said first cermet composition has from about 5  
to about 10 weight percent cobalt and said second  
cermet composition has from about 8 to about 15 weight  
percent cobalt.

58. The tip according to Claim 50 wherein  
said first ceramic component grain size comprises from  
about submicrometer to about 30 micrometers with  
possibly a scattering of particles in the order of  
5 about 40 micrometers.

59. The tip according to Claim 58 wherein  
said first ceramic component grain size comprises from  
about 5 micrometers to about 10 micrometers.

60. A method of manufacturing a cemented  
carbide member comprising the steps of:  
producing a green body having a first  
powder blend and a second powder blend segregated from  
15 said first powder blend by compressing a juxtaposition  
of said first powder blend and said second powder  
blend;

said first powder blend comprising  
carbide particles of a first particle size and a first  
20 binder;

said second powder blend comprising  
carbide particles of a second particle size and a  
second binder;

densifying said green body by liquid  
25 phase sintering and causing migration of at least a  
portion of said first binder into said second binder  
and increasing the concentration of binder in said  
second powder blend to produce a higher binder  
concentration;

30 wherein said first particle size is  
greater than said second particle size.

61. A tool for manipulating a material  
formation whereby such manipulation creates abrasive  
35 cuttings, the tool comprising:

an elongated tool body having opposite  
forward and rearward ends; and

a hard tip being affixed on the forward end of said tool body, said hard tip comprising:

(a) a first region comprising a first ceramic component having an average coarse grain size and a first binder; and

(b) at least one additional region comprising a second ceramic component and a second binder, wherein the average grain size of the second ceramic component is less than the average grain size of the ceramic component of the first region, the second binder amount of the at least one additional region is greater than the first binder amount of the first region and the first region and at least one additional region at least partially share at least one autogeneously formed interface.

62. The tool according to claim 62, further comprising at least one surface at least partially comprised of said first region and said at least one additional region and at least partially intersected by said at least partially shared autogeneously formed interface.

63. The tool according to claim 62 wherein said hard tip is further self sharpening.

64. The tool according to claim 62 wherein said first ceramic component consists essentially of tungsten carbide and said first binder is selected from the group consisting of cobalt and cobalt alloys, and wherein said second ceramic component consists essentially of tungsten carbide and said second binder is selected from the group consisting of cobalt and cobalt alloys.

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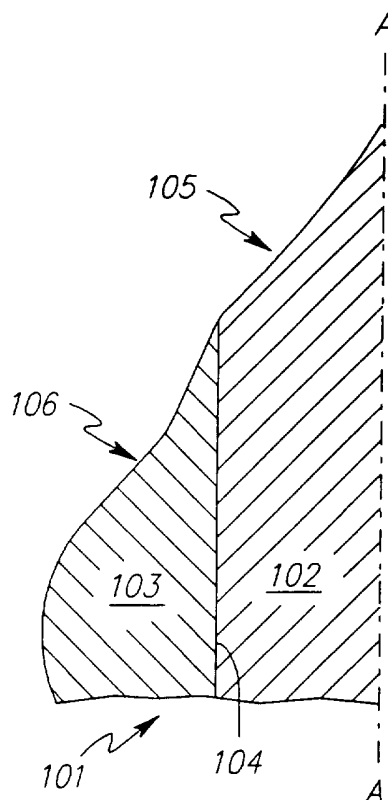


Fig. 1

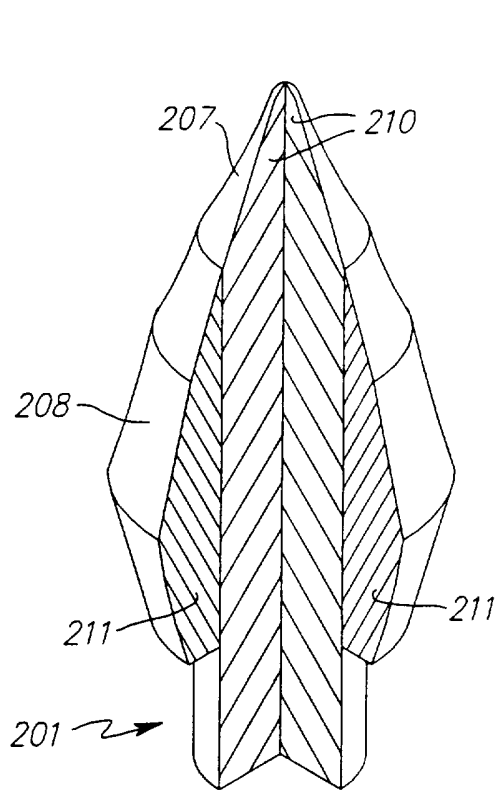


Fig. 2A

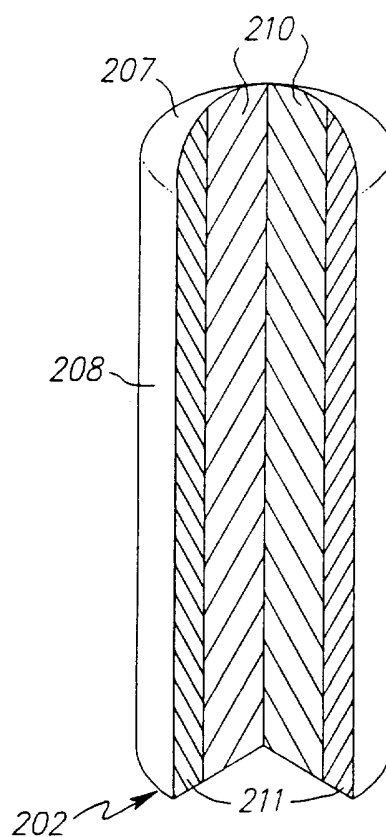
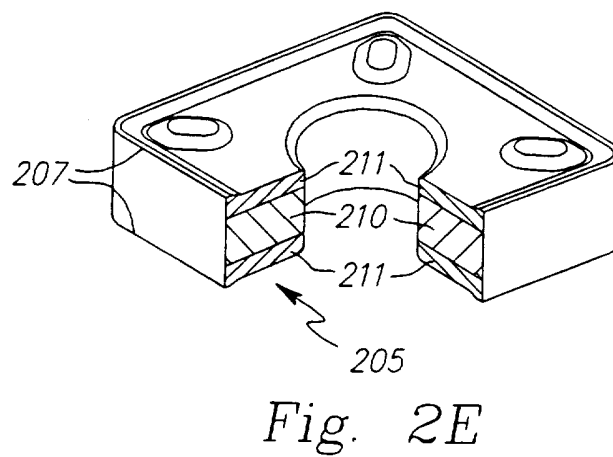
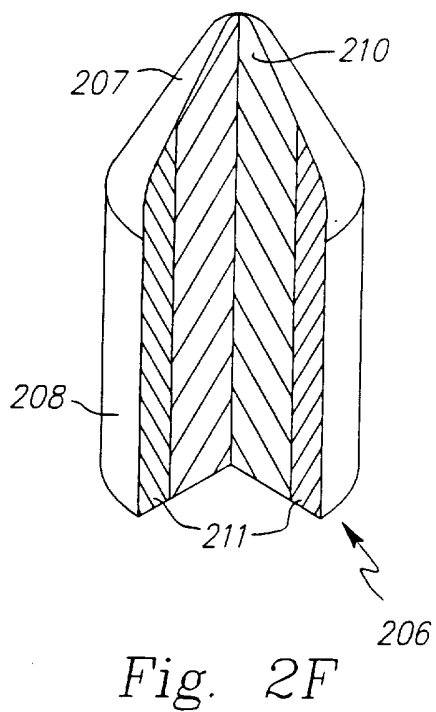
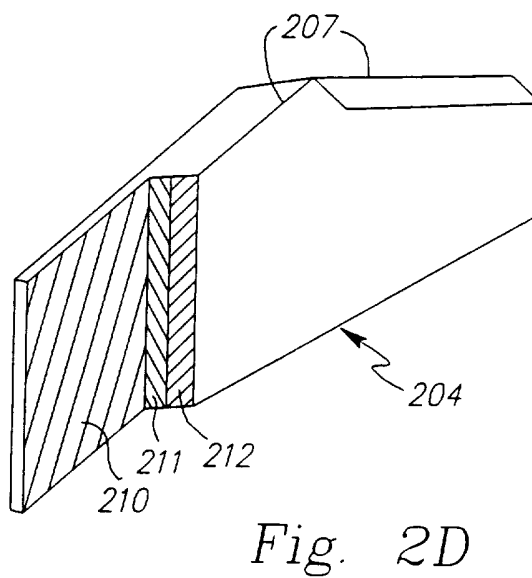
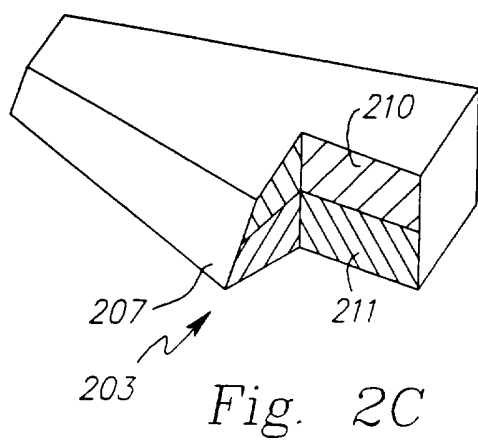


Fig. 2B

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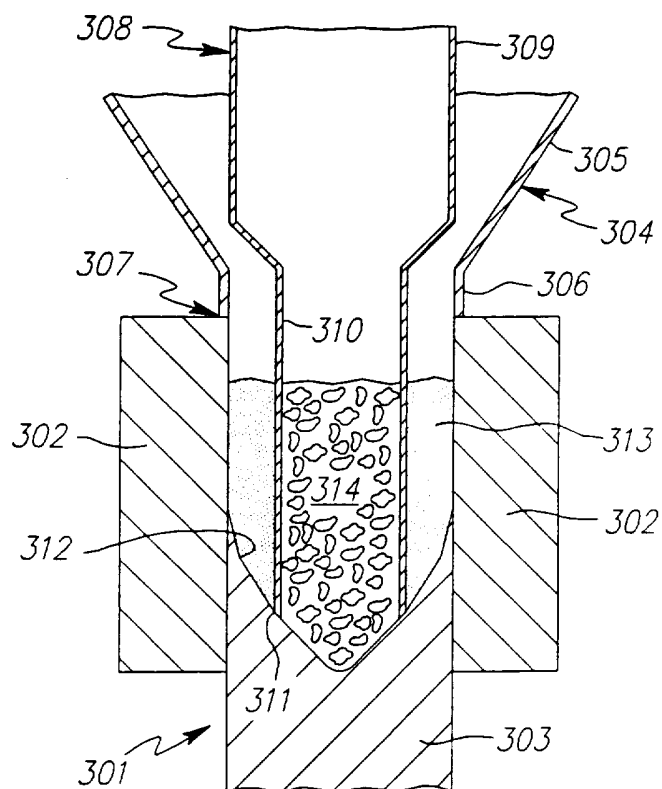


Fig. 3A

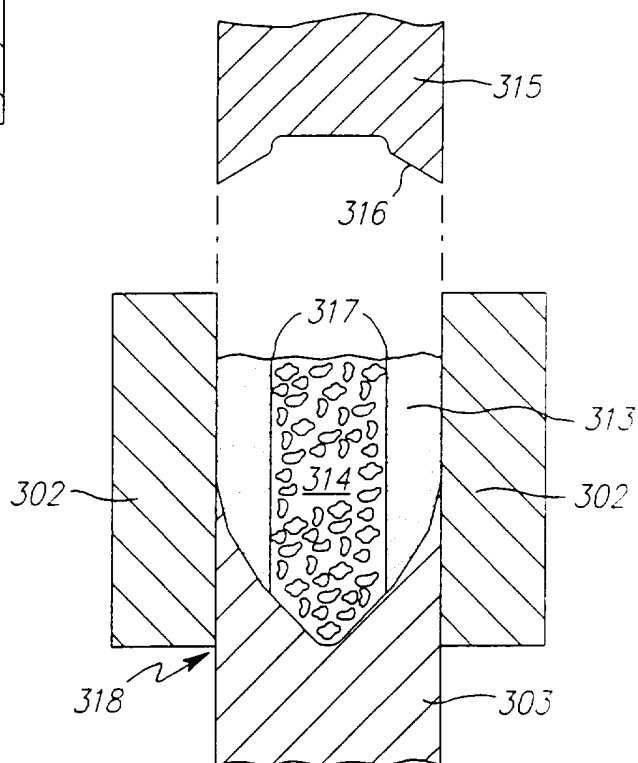


Fig. 3B

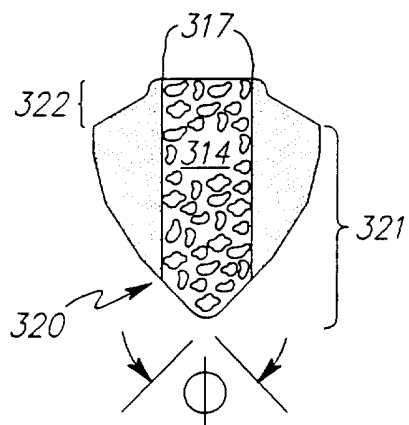
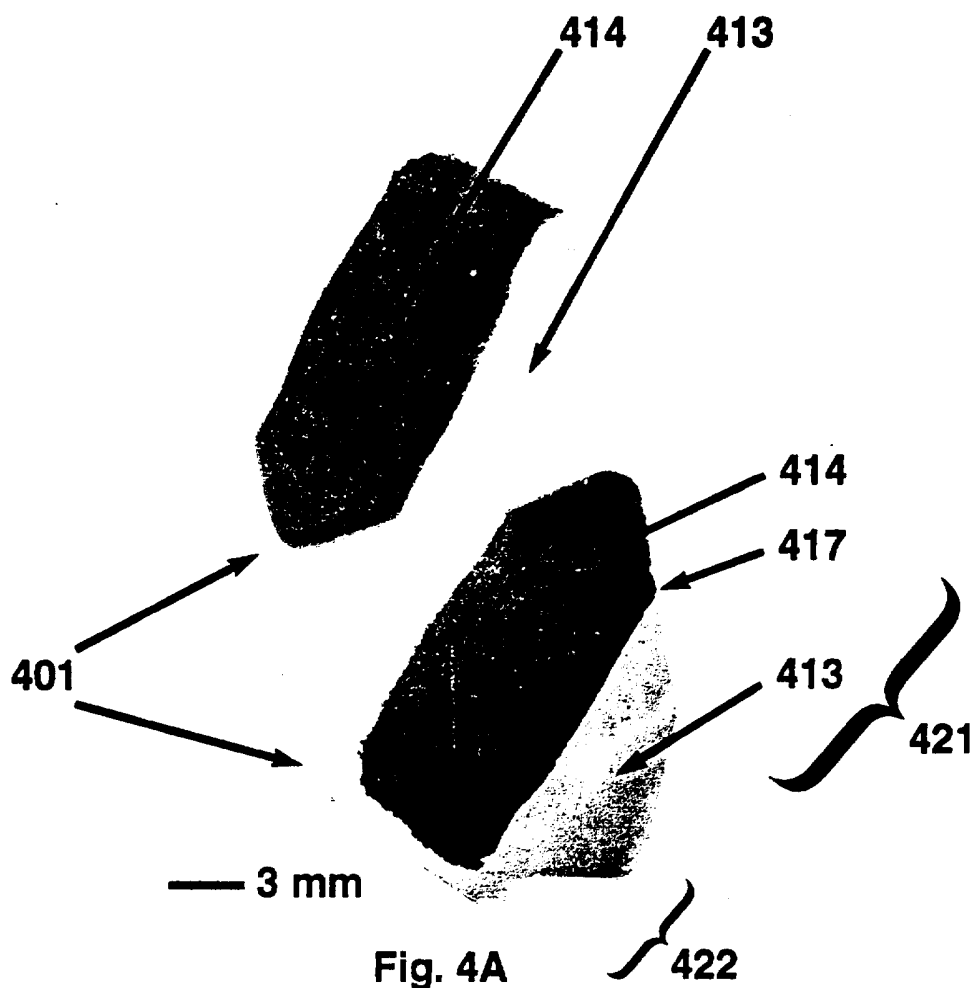


Fig. 3C

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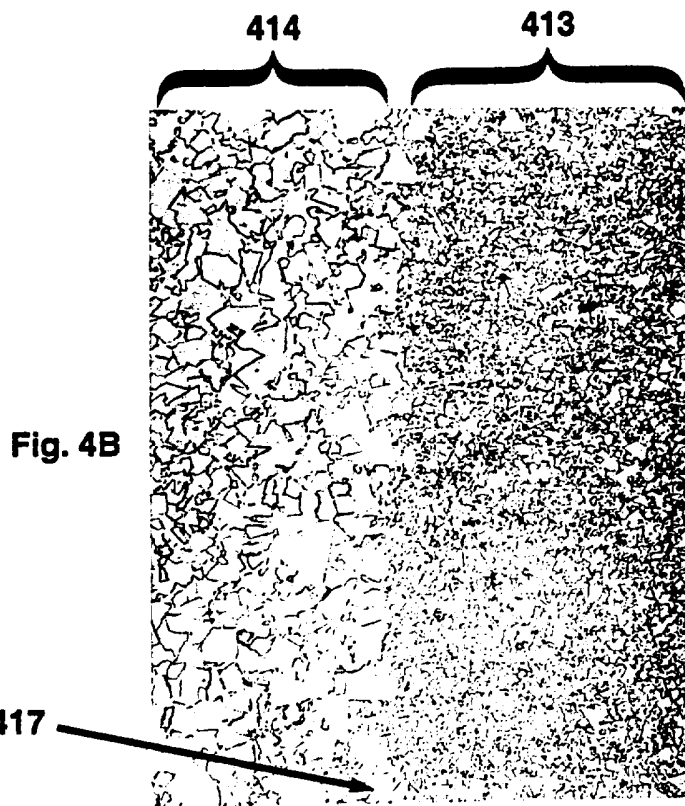


Fig. 4B



Fig. 4C



Fig. 4D

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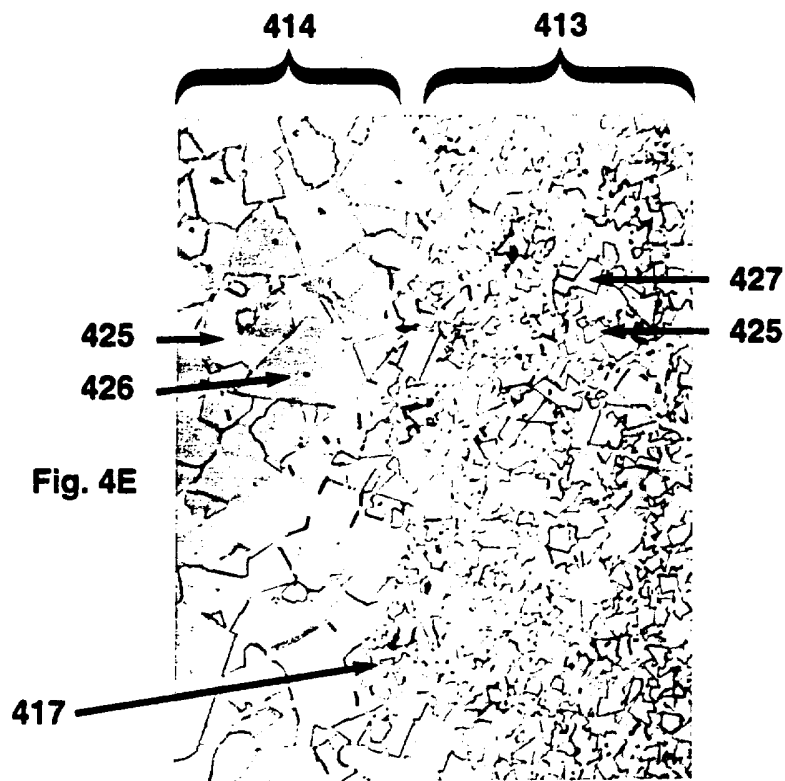


Fig. 4E



425

Fig. 4F

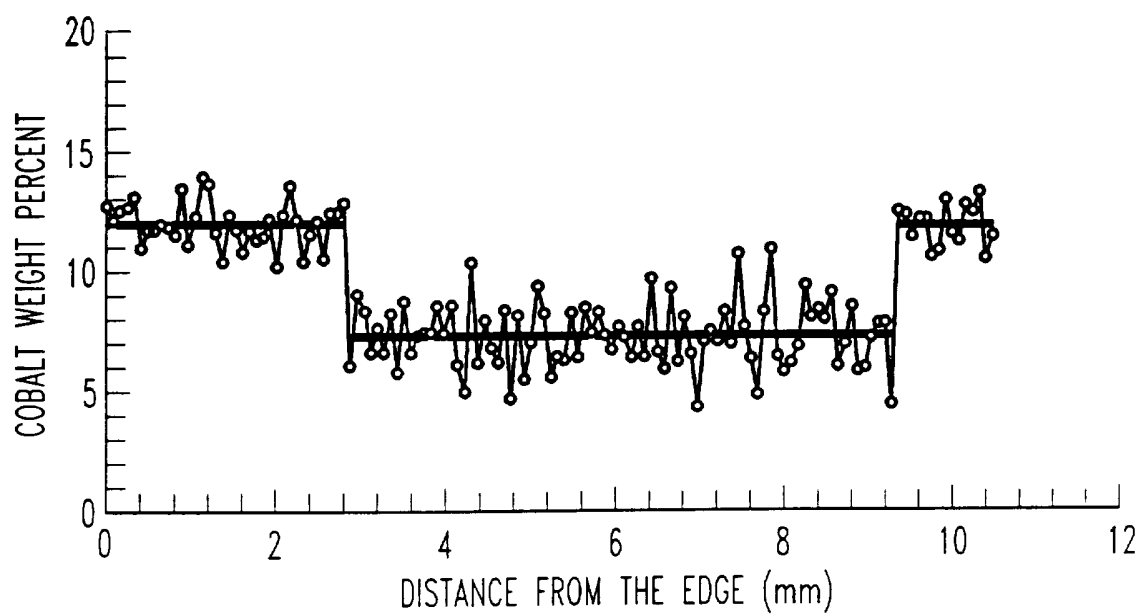
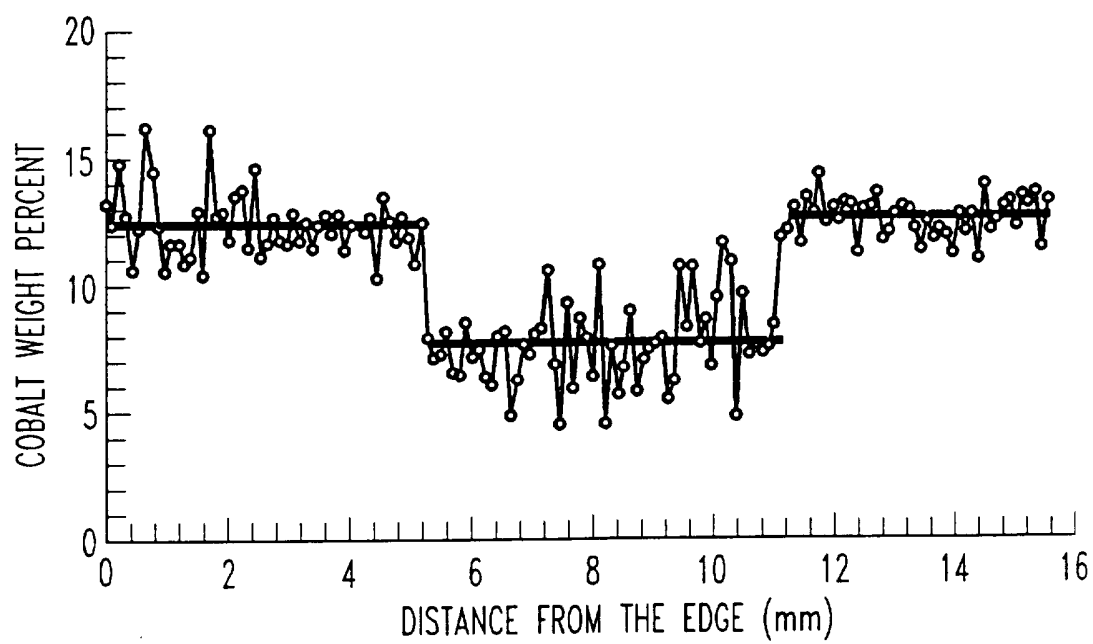
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Fig. 4G

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*Fig. 5A**Fig. 5B*

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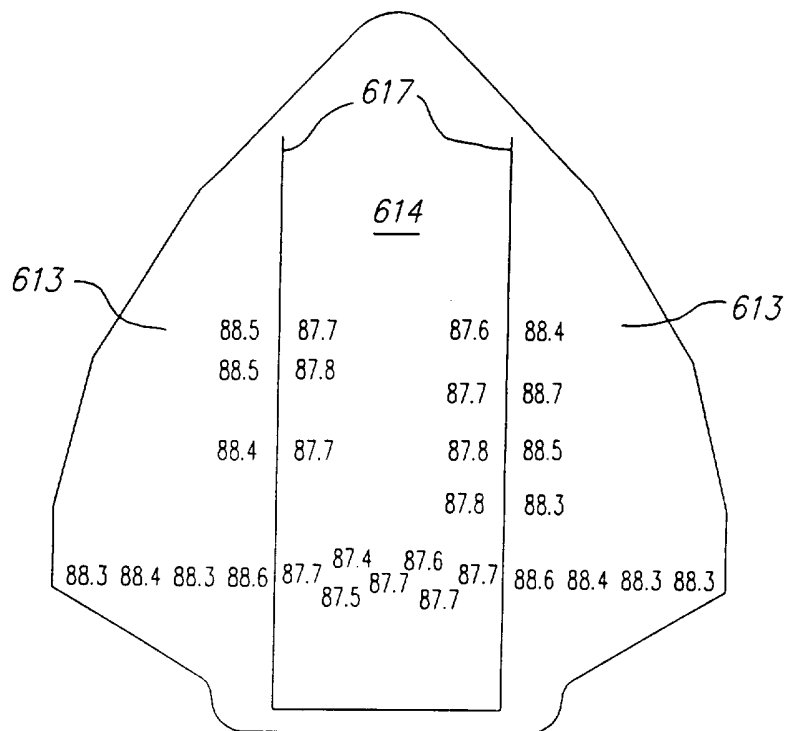


Fig. 6

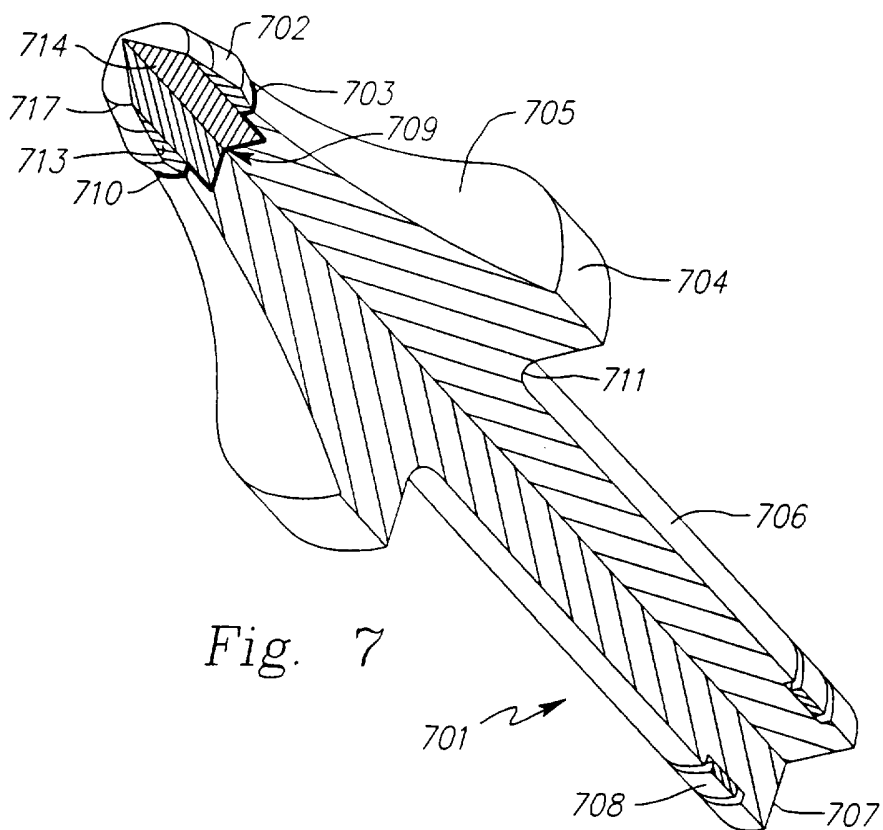


Fig. 7

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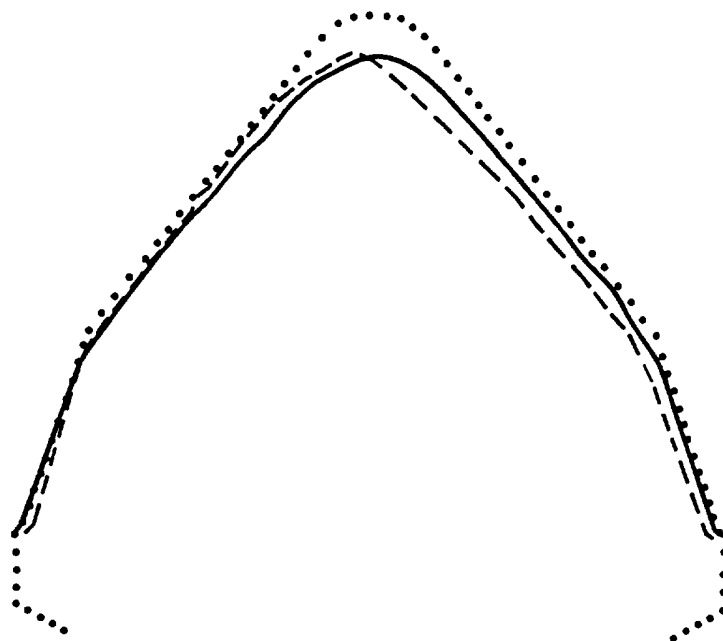


Fig. 8B

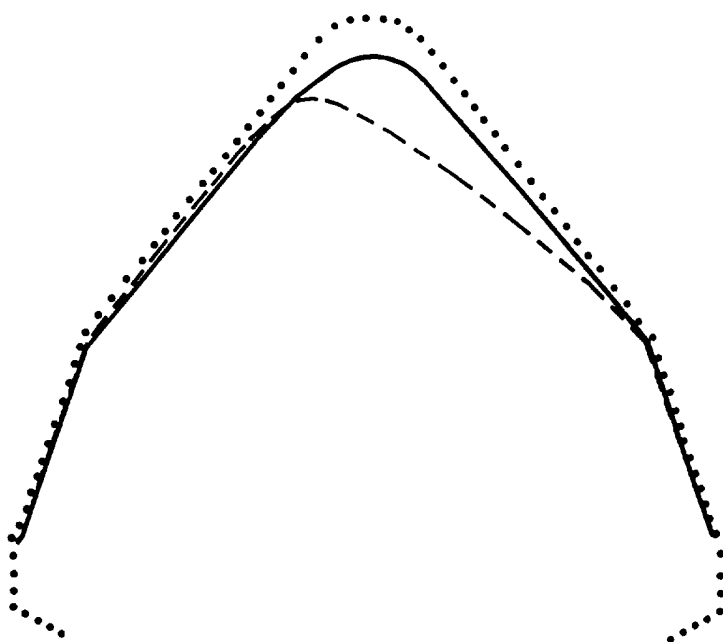


Fig. 8A

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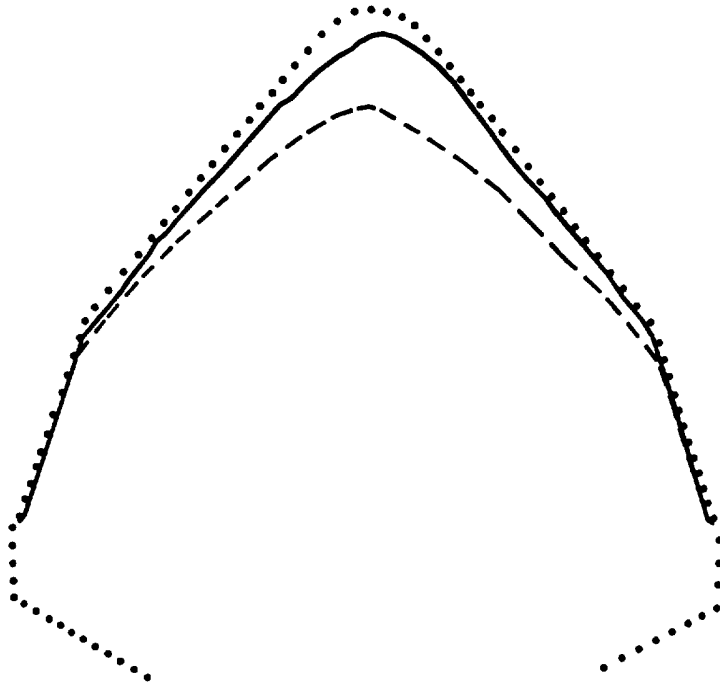


Fig. 9A

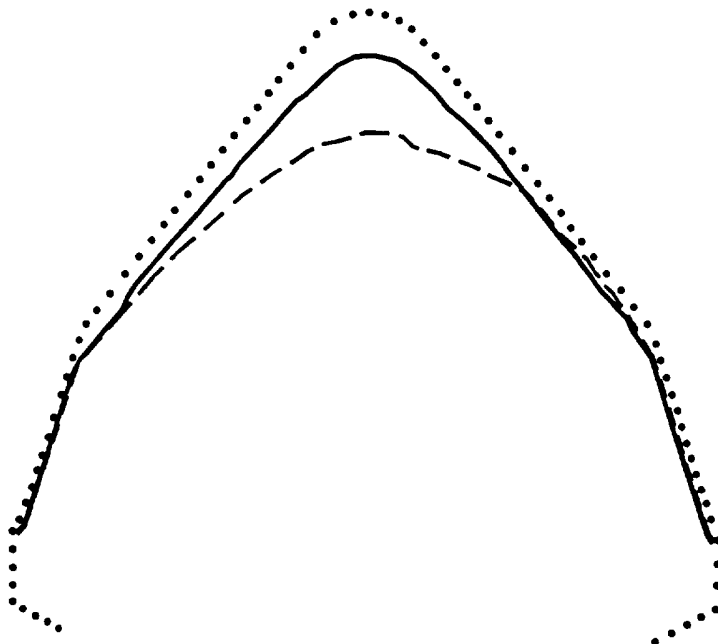


Fig. 8C

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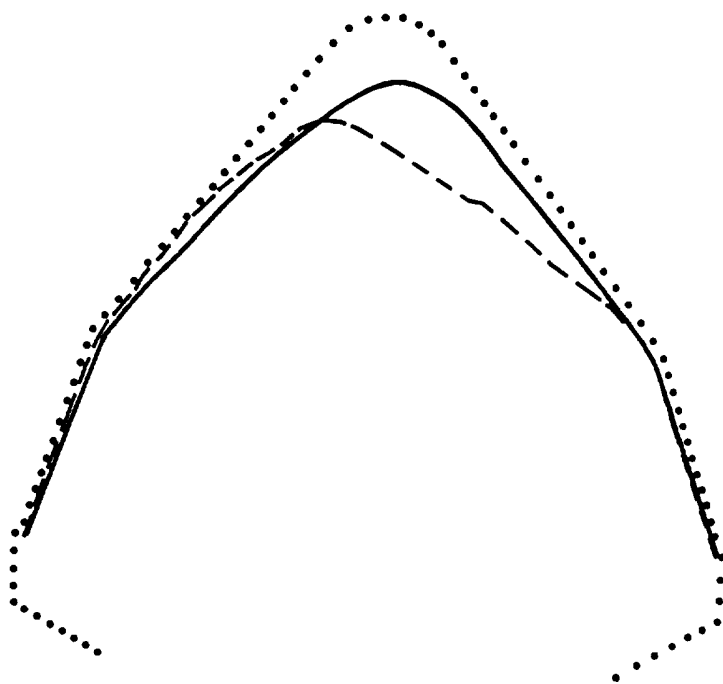


Fig. 9C

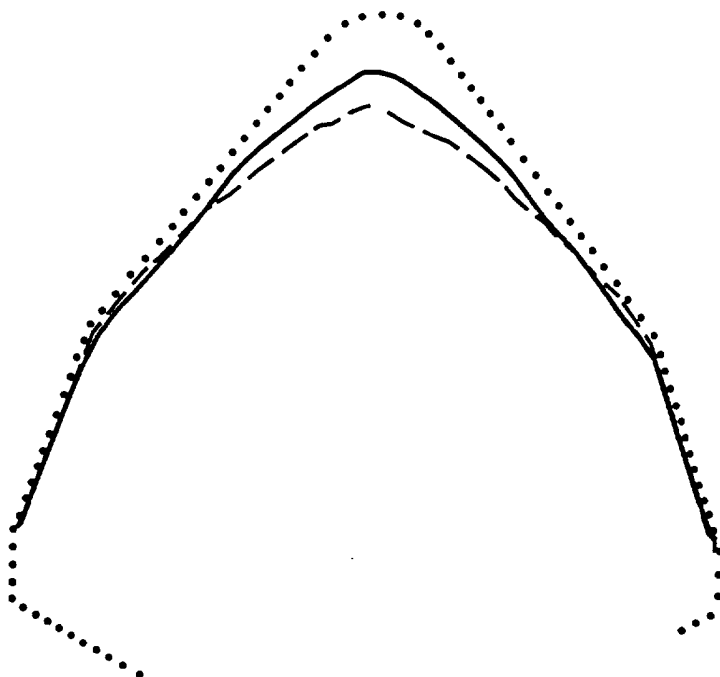


Fig. 9B

# INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/US 95/14042

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B22F7/06 E21B10/56 E21C35/183

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)

IPC 6 B22F E21B E21C

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 practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	INTERNATIONAL JOURNAL OF POWDER METALLURGY, OCT. 1987, USA, vol. 23, no. 4, ISSN 0361-3488, pages 229-235, VISWANADHAM R K 'Stability of microstructural discontinuities in cemented carbides'	1-49,60
Y	see whole document	50-59, 61-64
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document 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
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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 95/14042

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	3RD INTERNATIONAL SYMPOSIUM ON STRUCTURAL AND FUNCTIONAL GRADIENT MATERIALS, PROCEEDINGS OF FGM '94. THIRD INTERNATIONAL SYMPOSIUM ON STRUCTURAL AND FUNCTIONAL GRADIENT MATERIALS, LAUSANNE, SWITZERLAND, 10-12 OCT. 1994, 1995, LAUSANNE, SWITZERLAND, PRESSES POLYTECH. UNIV. ROMANDES, SWITZERLAND, RICHTER V 'Fabrication and properties of gradient hard metals' see whole document	1-49,60
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