

[54] **HETEROGENEOUS COBALT-BONDED
TUNGSTEN CARBIDE**

[72] Inventors: **Ralph K. Iler; Eugene G. Rigby**, both of
Wilmington, Del.

[73] Assignee: **E. I. du Pont de Nemours and Company**,
Wilmington, Del.

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[51] Int. Cl. **C22c 29/00**

[58] Field of Search **29/182.8; 75/204**

[56] **References Cited**

UNITED STATES PATENTS

3,165,822	1/1965	Beeghly	29/182.7
3,451,791	6/1969	Meadows	29/182.8

Primary Examiner—Carl D. Quarforth

Assistant Examiner—R. L. Tate

Attorney—John R. Powell

[57] **ABSTRACT**

Strong, hard, impact-resistant bodies comprising tungsten carbide bonded with from 3 to 25% by weight of heterogeneous cobalt-tungsten solid-solution alloy, useful as cutting tools, are prepared by heating an intimately mixed cobalt/tungsten carbide powder to a temperature above 1000° C and consolidating the powder to a density of at least 98% of its theoretical density, having either.

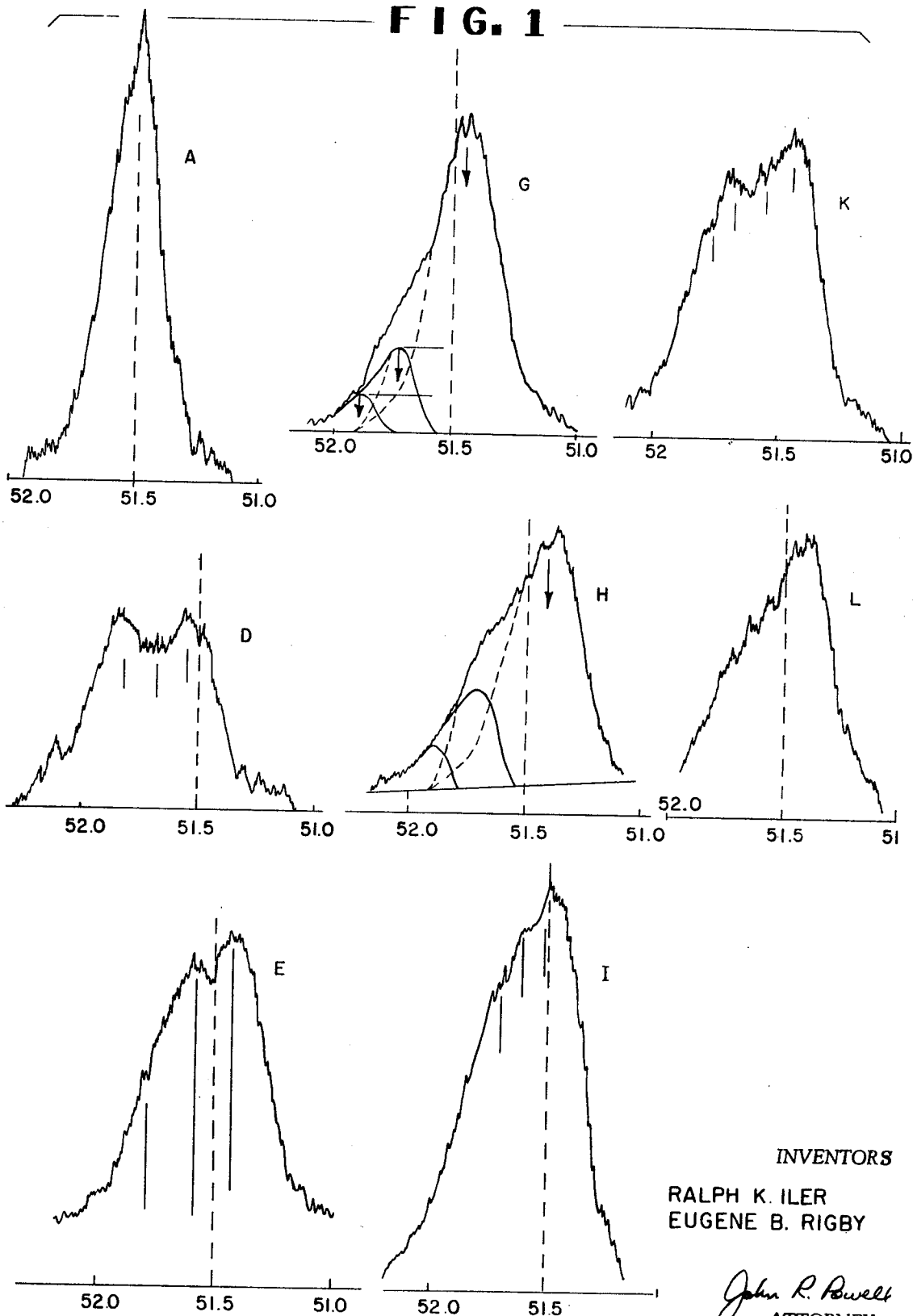
1. mixed a carbon-rich and a carbon-deficient powder together prior to consolidation to produce a non-homogeneous binder;

2. added free carbon to a carbon-deficient powder to produce local areas where tungsten is removed from the binder alloy as tungsten carbide; or

3. allowed a portion of the carbon in the tungsten carbide to oxidize during consolidation to produce areas in the binder phase which are then carbon deficient and high in tungsten.

8 Claims, 4 Drawing Figures

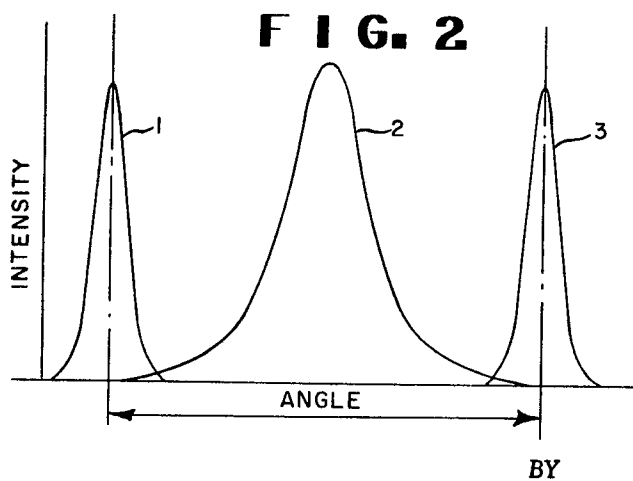
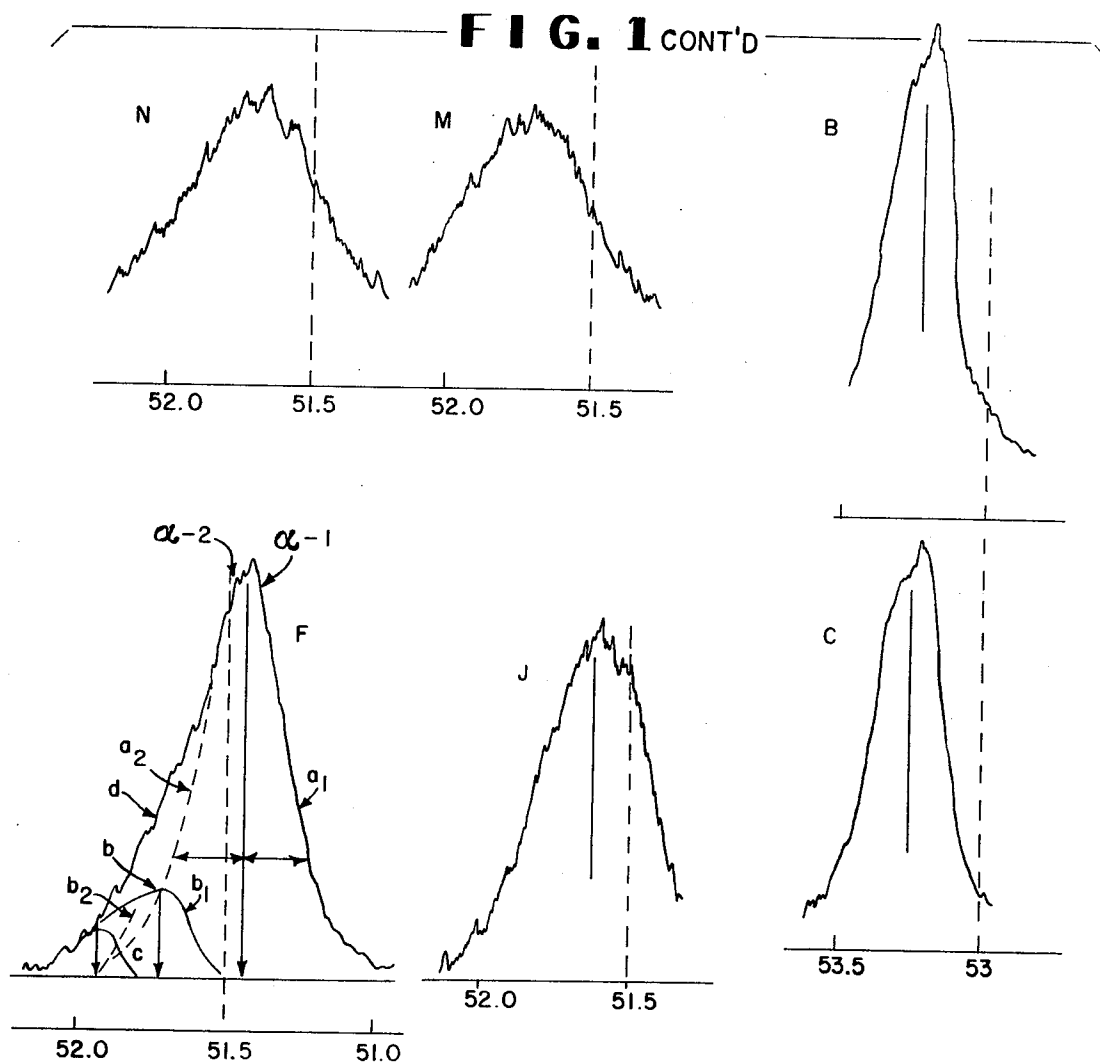
FIG. 1



INVENTORS

RALPH K. ILER
EUGENE B. RIGBY

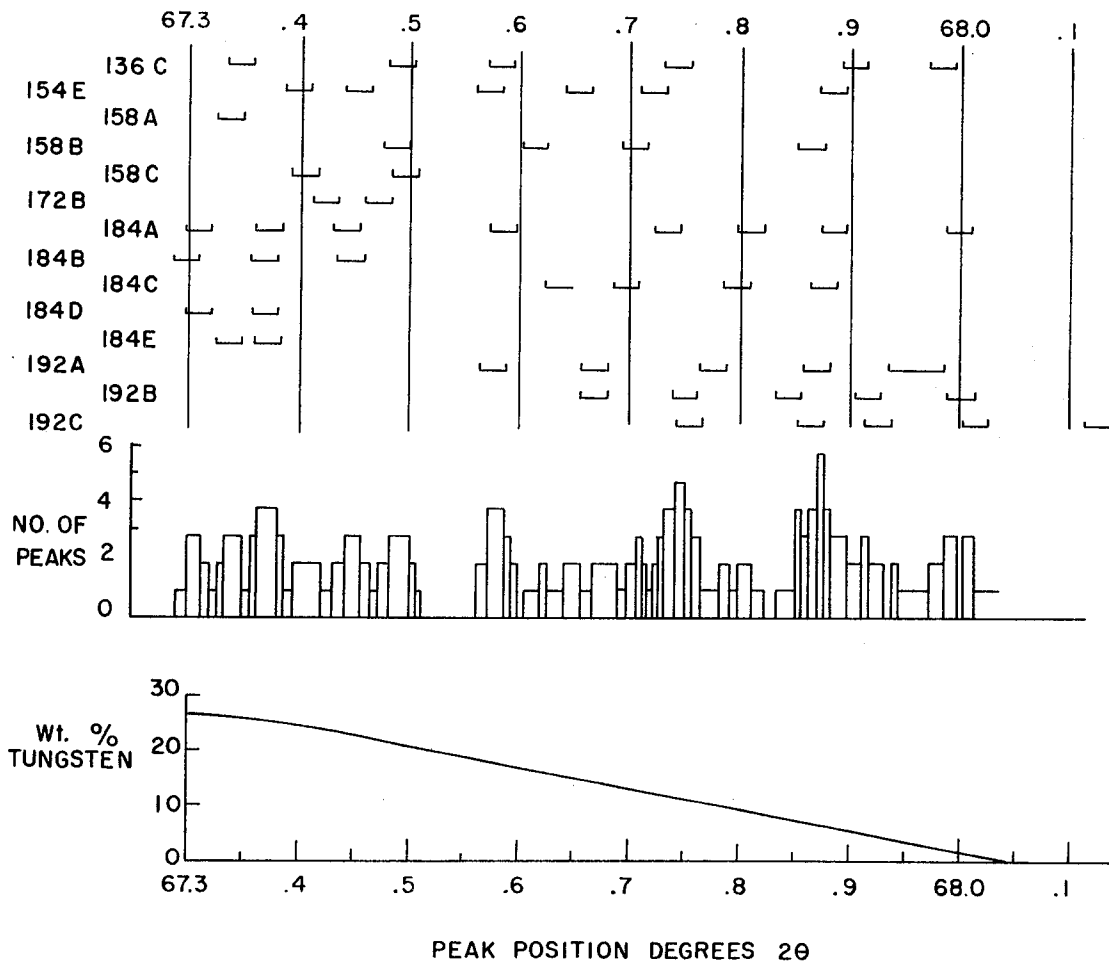
John R. Powell
ATTORNEY



INVENTORS
RALPH K. ILER
EUGENE B. RIGBY

John R. Powell
ATTORNEY

FIG. 3



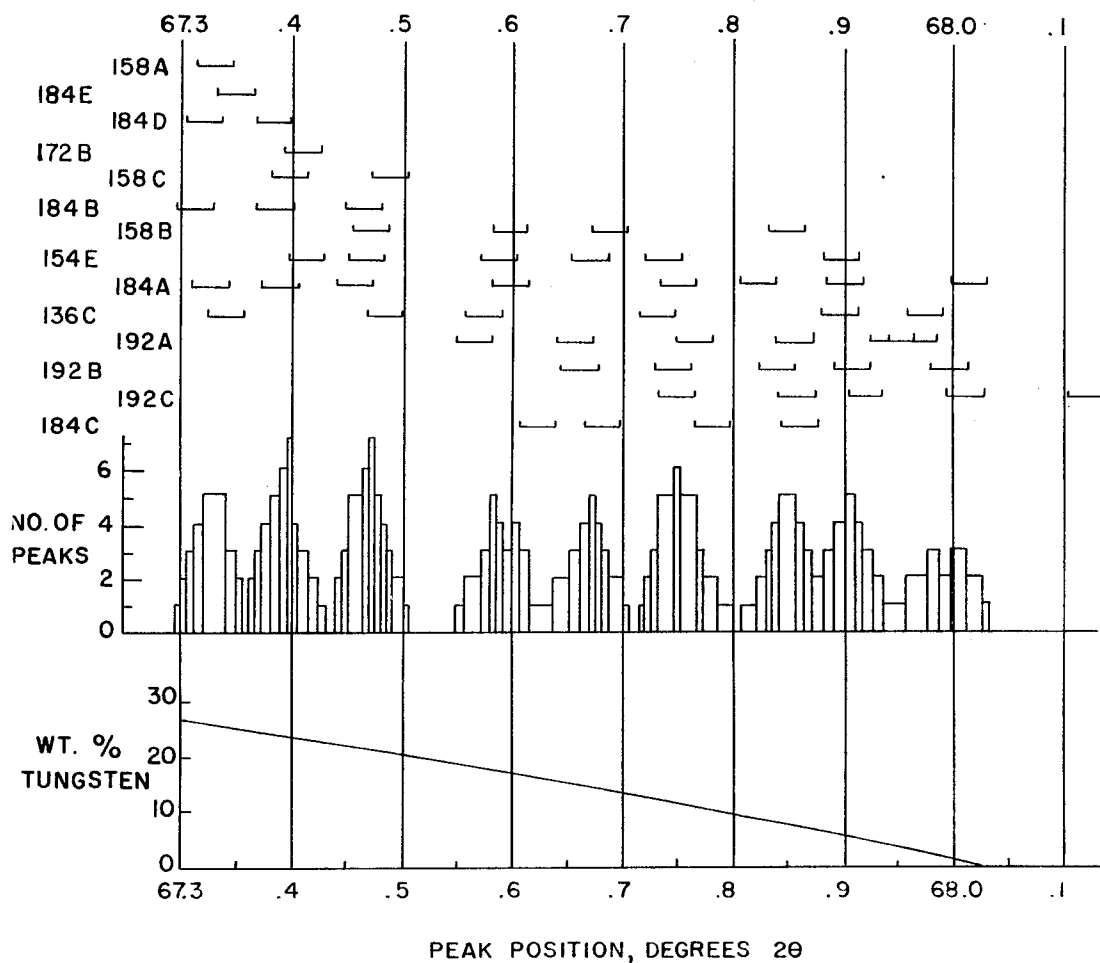
INVENTORS

RALPH K. ILER
EUGENE B. RIGBY

BY

John R. Powell
ATTORNEY

FIG. 4



INVENTORS

RALPH K. ILER
EUGENE B. RIGBY

BY

John R. Powell
ATTORNEY

HETEROGENEOUS COBALT-BONDED TUNGSTEN CARBIDE

BACKGROUND OF THE INVENTION

This invention relates to hard metal compositions of tungsten carbide bonded with a heterogeneous cobalt-tungsten alloy, to methods for preparing them, and to the use of the final products in cutting or shaping very hard materials.

The products of this invention will ordinarily be referred to herein as cobalt-bonded tungsten carbide, a term commonly employed to describe a well-known class of compositions, but it will be understood that the cobalt binder phase contains appreciable amounts of tungsten and is thus in reality a cobalt-tungsten alloy.

As shown in copending application Ser. No. 660,986, filed Aug. 16, 1967, now U.S. Pat. 3,451,791 substantially non-porous compositions of tungsten carbide bonded with a cobalt alloy having a novel combination of strength and hardness are obtained when the cobalt phase contains over about 8 percent by weight of tungsten in solid solution, the grain size of the tungsten carbide is less than a micron and the composition is homogeneous in composition and structure.

We have discovered a further class of useful carbide structures in which the composition of the cobalt alloy binder is not homogeneous but varies from region to region on a microscopic scale throughout the composition. In this new class of carbide structures, regions bonded with cobalt solid-solution alloys rich in tungsten, with high strength and hardness but greater brittleness, are interspersed on a microscopic scale with regions bonded with a weaker but more ductile and tougher cobalt phase containing less tungsten than in the aforesaid regions. In this way regions of high strength, modulus and hardness are interdispersed with regions of high ductility and toughness.

The effect of tungsten in solid solution in the cobalt binder, on the acid resistance of the cobalt phase is well known in the art, which teaches that for at least some tungsten to be free to dissolve in the cobalt phase, the atomic ratio of carbon-to-tungsten in the system must be less than 1.0. However, a carbon-deficiency is generally considered to be undesirable because during sintering it promotes at least a partial reaction of the tungsten-containing cobalt binder phase with tungsten carbide to form the brittle eta phase, $\text{Co}_3\text{W}_3\text{C}$, with attendant loss of desirable strength properties, especially resistance to impact.

Thus, it has been demonstrated by Kubota, Ishida and Hara in the Indian Institute of Metals Transactions Vol. 9, 132-138, September, 1964, that in carbon-deficient, cobalt-bonded, tungsten carbide compositions, the higher the concentration of tungsten in solid solution in the cobalt the greater the resistance of the metal phase to attack by concentrated hydrochloric acid.

The relationship between acid resistance and the amount of tungsten in the cobalt metal phase calculated from the data of the above authors for compositions containing 5% and 25% of cobalt is shown in their FIG. 1. Such behavior is characteristic of a body in which the metal binder phase is homogeneous, the amount of tungsten in the cobalt phase being relatively uniform throughout the body.

As shown by these authors, the yield strength of cobalt-tungsten alloys increases with tungsten content. However, Adkins, Williams and Jaffee show these alloys also become more brittle in "Cobalt" (1960) page 8, and 16-29.

Kubota and associates show that in metal-bonded tungsten carbide compositions, when the tungsten carbide average particle size is less than 3 microns, those bodies which are carbon deficient are inferior in strength. The carbon deficiency, of course, produces a tungsten-rich cobalt binder phase. Such fine-grained bodies are reported to be weaker than bodies of similar fine-grain size which are not carbon-deficient and thus have less tungsten in the cobalt phase.

Regardless of grain size of the tungsten carbide, bodies with more tungsten dissolved in the cobalt are known to have more acid resistance.

We have now found it possible to prepare cobalt-bonded tungsten carbide bodies in which the cobalt binder contains on the average more than 8% by weight of tungsten dissolved in the cobalt, yet in which the cobalt phase is low in acid resistance. The variations in the concentration of tungsten in solid solution in the cobalt binder result in lower average resistance of the binder phase to removal by hydro-chloric acid, than when the same amount of tungsten is uniformly distributed in the cobalt phase. The products of this invention are thus characterized by having a relatively low resistance to attack by acid in spite of having a substantial amount of tungsten dissolved in the cobalt phase.

It is also well-known in the art, that in cobalt-bonded tungsten carbide compositions, carbon deficiency leads to formation of eta phase, $\text{Co}_3\text{W}_3\text{C}$, during consolidation at high temperature. Formation of eta phase leaves less ductile cobalt binder phase and thus causes brittleness in the resulting bodies. The localized carbon deficiency in the compositions of this invention surprisingly does not result in formation of brittle cobalt-bonded compositions. On the contrary, the compositions of this invention are surprisingly tough, frequently possessing transverse rupture strengths in excess of commercially available cobalt-bonded tungsten carbide compositions which are free of eta phase.

The dense, cobalt-bonded compositions of this invention are prepared by hot-pressing heterogeneous powder mixtures of cobalt/tungsten carbides. Variations necessary for heterogeneity are induced in the powders by any one of the following techniques:

Blending dissimilar powders. Variations can be achieved by selecting and blending dissimilar tungsten carbide powders, each respectively having atomic ratios of carbon to tungsten of greater and less than one. Even after ballmilling the tungsten carbide with cobalt and consolidating to dense bodies, local variations in the amount of tungsten dissolves in cobalt occur on a microscopic scale, as a result of admixing the different powders.

Blending carbon with powder. Variations can also be achieved by admixing and dispersing small amounts of finely divided carbon in a cobalt/tungsten carbide mixture which has a carbon:tungsten atomic ratio less than one. When the composition is heated during consolidation, the carbon particles dissolve and carburize the region around each particle, raising the local carbon:tungsten ratio to one or higher.

Oxidizing the powder. Variations can also be obtained by slightly oxidizing cobalt/tungsten carbide powders having a carbon:tungsten ratio of 1.0 or slightly higher. Thus, finely milled powder, when dried, will absorb from 0.1 to 1.0 percent by weight of oxygen when exposed to air. Oxidation of powder is generally non-uniform, the outer surfaces of granules being oxidized first (in a mass, generally the upper surface of the powder is oxidized more than the interior).

SUMMARY OF THE INVENTION

In summary, this invention is directed to dense bodies consisting essentially of tungsten carbide bonded with from 3 to 25% by weight of a heterogeneous cobalt-tungsten alloy, said alloy consisting essentially of cobalt and an average of from 5 to 25% by weight of tungsten, said alloy comprising regions containing less than 8% by weight of tungsten interspersed with regions containing more than 8% by weight of tungsten. This invention is further directed to the use of the dense bodies as cutting tools, and to a method for preparing these compositions comprising milling finely divided carbon with cobalt and tungsten carbide in sufficient amounts to produce a mixture containing from 0.01 to 0.5% free carbon and having a carbon:tungsten ratio about 1; heating the milled mixture in an inert atmosphere at an elevated temperature; densifying the composition to at least 98% of its theoretical density by hot-pressing; and then rapidly cooling the dense composition.

The dense bodies of this invention demonstrate an unusual combination of extremely good strength and hardness while sacrificing little in such properties as ductility and toughness.

As a result, the bodies are useful in a variety of applications as cutting tools and bits with particular advantage in uses usually confined to high speed steel cutting tools.

The overall or average atomic ratio of carbon:tungsten can range from 0.85 to 1.02, depending on the cobalt content. However, the dense bodies of this invention have a surprising combination of strength and toughness in view of prior art teachings, and are exceptionally effective for use as tips or bits in metal cutting and metal-removal operations.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts X-ray diffractometer tracings of twelve various cobalt-bonded tungsten carbide compositions, indicating the degree of heterogeneity of tungsten in the cobalt binder, along with two reference curves for sodium chloride.

FIG. 2 depicts two X-ray diffraction curves for sodium chloride superimposed at the extreme ends of a diffraction curve for cobalt.

FIG. 3 is a plot of the profiles of 14 cobalt-bonded tungsten carbide compositions analyzed according to procedure B described hereinafter.

FIG. 4 is a plot of the profiles of FIG. 3 after adjusting the relative positions of the sample patterns by the estimated error in determining the sodium chloride peak position.

DESCRIPTION OF THE INVENTION

As stated above, this invention is directed to dense bodies of tungsten carbide bonded with a cobalt-tungsten alloy. The bodies have a density of at least 98% of their theoretical density and comprise a polycrystalline, three-dimensional network structure of tungsten carbide, the pores of which are interpenetrating and filled with from 3 to 25% by weight of a three-dimensional, continuous, cobalt-tungsten alloy binder phase containing an average of from about 5 to 25% and preferably 8 to 12% by weight of tungsten in solid solution in the cobalt. The cobalt-tungsten binder phase is characterized by being heterogeneous and substantially less resistant to dissolution in concentrated hydrochloric acid at room temperature than the cobalt phase in bodies of similar constitution in which the tungsten is homogeneously and uniformly distributed throughout the cobalt phase. The dense bodies of this invention are prepared by several means including by suitably admixing separately prepared tungsten carbide-cobalt powders and consolidating the powders to density to produce bodies consisting of interspersed regions smaller than about 100 microns in cross-section, having substantially different concentrations of tungsten in cobalt, there being present cobalt regions containing more than 8% by weight of tungsten as well as cobalt regions containing less than 8% by weight of tungsten as indicated by the cobalt lattice constants as determined by X-ray diffraction, the difference between the varying regions ordinarily exceeding 1 to 2% and preferably being at least 2 to 3% or more.

1. DENSE COMPOSITIONS OF THIS INVENTION

a. Structure

The bodies of this invention consist of two interpenetrating continuous phases, the major one is tungsten carbide and the minor one is cobalt-tungsten alloy. The latter is also referred to as a binder phase because it has generally been thought that it surrounded and bound together the grains of tungsten carbide. Since it greatly contributes to the strength of the composition, it must, in fact, bind the structure together. We have found additional proof of this by accurately measuring the length of a thin bar of a tungsten carbide body of this invention, containing 10 percent by weight of cobalt-tungsten alloy, and then removing the tungsten carbide phase without disturbing the metal phase, which is porous but coherent, and measuring the length, of this metallic skeleton. We found that it is about two percent shorter than the original length, showing that in the original composition, the metal phase was subjected to a two percent elongation. This shows that the cobalt

in bodies of this invention is under considerable tension and strain, and that it thus keeps the tungsten carbide phase under compression and truly acts as a "binder."

The amount of cobalt metal present as binder in the bonded compositions of this invention, ranges from about 3 to 25% by weight, preferably from 5 to 12% by weight. Bodies containing an amount of cobalt within the 3 to 25% range have a very desirable combination of strength, hardness and toughness, and those bodies containing from 5 to 12% by weight are particularly suitable, because of their toughness, for replacing high speed steel tools.

The tungsten carbide phase, also referred to as the tungsten carbide skeleton, contributes markedly to the outstanding properties of the dense bodies of this invention. The tungsten carbide skeleton is polycrystalline; that is, it consists of many small crystals separated by grain boundaries. Some of these boundaries are scarcely visible when a polished section is etched with acid, which removes cobalt, but can be revealed by etching with a suitable reagent for dissolving tungsten carbide by methods known to those skilled in the art. By these means the individual grains making up the carbide skeleton can be distinguished through an optical microscope and surface replicas can be made and examined by the electron microscope.

A significant characteristic of the tungsten carbide in the preferred bodies of this invention is the presence of a substantial proportion of the structure as a fine grain structure. The carbide grains, as measured in metallographic polysections described hereinafter, consist of a substantial proportion having an average grain diameter of less than a micron, but the remainder may be larger than 1 micron.

The tungsten carbide skeleton contributes substantially to the overall strength and hardness of the dense compositions of this invention.

Another structural characteristic of the compositions of this invention is the heterogeneous nature of the cobalt-tungsten alloy binder. Thus, where compositions of the prior art are generally characterized as containing a binder phase which is essentially homogeneous throughout the composition the products of this invention are characterized by a variety of cobalt-tungsten ratios throughout the binder phase.

b. Tungsten in the cobalt

In prior art compositions the cobalt phase contains an amount of tungsten that is related to the atomic ratio of carbon:tungsten in the body. The tungsten which is not combined with carbon as tungsten monocarbide, WC, could be present in one of the possible states which have been described in the prior art in carbon-tungsten-cobalt ternary systems, namely: ditungsten carbide W_2C ; various cobalt tungsten carbide phases such as kappa or eta (Co_3W_2C), this latter also being known in some countries as "delta"; metallic tungsten; the intermetallic compound Co_3W or in solid solution in the face-centered cubic form of cobalt which is the main constituent of the binder phase.

Regardless of the heterogeneous distribution of tungsten in the cobalt phase, in bodies of this invention, it is preferred to have most of the tungsten which is present in the bodies and which is not present as tungsten monocarbide, in solid solution in cobalt. By suitably relating the atomic ratio of carbon: tungsten to the cobalt content, maintaining the tungsten carbide with a very fine grain size, permitting at least some of the tungsten to dissolve in the cobalt phase before hot pressing and then pressing and cooling rapidly, we have found that it is possible to maintain a large portion of the tungsten in solution in the cobalt and to minimize formation of eta and other solid phases. By controlling the conditions during preparation of these compositions, we have found it possible to vary the amount of tungsten in the cobalt from region to region throughout the composition. These regions can be ascertained and characterized by a variety of techniques. The regions in which the tungsten concentration in the cobalt is less than 8% by weight and the binder phase is readily attacked by acid, may be as large as 100 microns, or they may be very small,

such as less than a micron in cross-sectional diameter. Where they are large, as when powders in granular form, high and low in carbon are mechanically mixed and hot pressed, the regions can be detected easily by metallographic procedures. The low carbon regions often contain some eta phase which is easily distinguished. In such cases, the attack of the binder by acid occurs irregularly and can be observed in microscopic cross-section. On the other hand, when the low-tungsten-in-cobalt regions are only a micron or so in size they can be detected by X-ray diffraction, as will be further described.

c. Carbon:tungsten ratio

We have found that if the tungsten content of the cobalt binder phase exceeds about a third of the metal binder phase by weight, it becomes very difficult to prevent the conversion of substantial amounts of the cobalt binder to the more brittle eta phase. For this reason, the atomic ratio of carbon: tungsten ordinarily ranges from 0.85 up to 1.02 and should be greater than about $[1.0 - 0.0062(P-1)]$ and less than about $[1.0 - 0.00166(P-15)]$ where P is percent by weight of cobalt in the composition. A preferred lower limit is about $[1.0 - 0.004(P-1)AH]$ (OR A MINIMUM C:W ratio of about 0.90).

On the other hand, the carbon deficiency must be sufficient to provide a measurable amount of tungsten in the cobalt phase, and the deficiency must be greater as the amount of cobalt in the composition is increased. Thus for example, when the cobalt concentration is less than 12% by weight, only a minute carbon deficiency, scarcely, scarcely measurable by analytical means, such as a carbon:tungsten atomic ratio of 0.99, will provide sufficient tungsten to reach a concentration of an average of 8% by weight in the cobalt phase. On the other hand, a carbon:tungsten ratio of 0.94 will provide up to an average of 24% tungsten in the cobalt. It is desirable that the free carbon content be as low as possible, preferably less than 0.15 percent.

d. Eta phase

With a deficiency of carbon, a part of the tungsten carbide-cobalt bond may consist of eta phase, Co_3W_3C , although this is generally undesirable. Up to 10 or 20 percent by weight of eta phase may be present in the binder phase isolated after removal of tungsten carbide, but less than 5% is preferred, since as much of the tungsten as possible should remain in solid solution in the cobalt and as little as possible consumed to form eta phase. The presence of tungsten dissolved in the cobalt binder phase is at least partly responsible for the unusual combination of properties of the products of this invention.

e. Anisodimensional tungsten carbide

One of the preferred products of this invention is a dense body comprising anisodimensional tungsten carbide platelets bonded with from 3 to 25% by weight of heterogeneous cobalt-tungsten alloy.

The term isodimensional means having the same dimensions, while anisodimensional means not having the same dimensions. A particle that is isodimensional is therefore one having approximately equal length, breadth and width. The term isodiametric is employed in the same sense, an isodiametric particle being one having equal diameters when measured in different directions. A sphere is perfectly isodiametric; a grain of sand or of sugar is approximately isodiametric and can also be described as being isodimensional. The size and shape of ultimate particles and their arrangement in aggregates is more fully described by Dr. A. Von Buzagh, in "Colloid Systems," published by the Technical Press, Ltd. (London, 1937).

Finely divided tungsten carbide of the prior art has ordinarily been obtained by pulverizing coarser crystals. The finely divided particles so obtained are, broadly speaking, isodimensional. When milled tungsten carbide is bonded with metal by the processes of the prior art to form hard, cemented carbide bodies, there occurs a recrystallization and grain growth of the tungsten carbide. By metallographic methods, the size and shape of the resulting carbide grains can be observed. A review of published micrographs of the grain structure of com-

mercial cemented carbides, as well as examination of a range of cobalt-bonded tungsten carbide products of commerce, indicates that the tungsten carbide grains are isodimensional. While in some instances the polished cross sections of individual grains indicate a length or maximum dimension two or even three times that of the minimum dimension, this is the exception rather than the rule. In micrographs, grains give the impression of being anisodimensional when a substantial proportion of the grains show a maximum dimension at least three times that of the minimum dimension.

For purposes of this invention, anisodimensional particles are therefore those having a maximum dimension at least three times that of their minimum dimension. Some of the products of the present invention consist largely of anisodimensional tungsten carbide crystals of which the maximum dimension is at least three and preferably at least four times that of the minimum dimension. In such products the tungsten monocarbide grains, which appear to be crystals, are typically present as triangular platelets, the thickness of which is no more than one-fourth and usually no more than one-sixth the length of the side of the platelet. Preferred anisodimensional tungsten carbide particles are from 0.05 to 1 micron in thickness and from 0.2 to 4 microns in length or breadth. The commonest particles are triangular platelets, although polygonal platelets are also observed.

To obtain a body containing tungsten carbide platelets, the physical state of the starting powder is important. The tungsten carbide in the powder admixed with cobalt before being heated must have a crystal size of less than 0.1 microns, and preferably has a crystal size of less than 0.05 microns as calculated from X-ray line broadening or specific surface area.

f. Impurities

Foreign materials such as organic dirt, mineral dust or fragments of enamel or glass such as from equipment should be scrupulously avoided in preparing the bodies of this invention. Organic matter can result in holes or inclusions of carbon in the final body and mineral materials such as silicates leave inclusions of glass which is very harmful because the inclusions cause localized internal stresses upon cooling, thereby contributing to brittleness. Other mineral dust as well as glass or enamel fragments are similarly deleterious. Localized carburization of powder during manufacture results in regions high in carbon in the final structure. If a portion of powder, such as the outer layer of powder inclosed in a graphite mold, is carburized before it is pressed, there may be found homogeneous regions near the surface of pressed pieces that contain an excess of carbon and show excessive grain growth. Such homogeneously carbon-rich regions due to gross contamination with carbon are to be avoided and they do not correspond to the type of heterogeneity of regions found throughout the structures of the present invention.

g. Properties of the compositions

1. Acid resistance

As shown by Kubota, Isheda and Hara in the reference mentioned above, in cobalt-bonded tungsten carbide bodies of the prior art in which the distribution of tungsten in cobalt is apparently homogeneous, a small decrease in the atomic ratio of carbon:tungsten to a ratio less than 1.0 remarkably increases resistance of the metal phase to dissolution in hydrochloric acid. This is believed due to the increased amount of tungsten in solid solution in the cobalt phase.

In the products of the present invention, while some regions of cobalt are rich in tungsten, others are low in tungsten and are therefore not acid resistant. The acid penetrates the structures via these non-acid resistant regions, with the result that the overall acid resistance is low, in spite of a relatively high average tungsten content in the cobalt.

The amount of tungsten in solid solution in the cobalt can be determined as described by Kubota, et al. A preferred method for measuring the amount of tungsten in the cobalt is described hereinafter in the methods of characterization. The dense bodies of the prior art disclosed in copending application Ser. No. 660,986, which contain an average of more than

8% tungsten in the cobalt, are characterized as having a resistance to etching, R, of greater than 50 hours, where resistance is expressed in terms of number of hours required at room temperature for concentrated hydrochloric acid to remove 0.25 milligrams of metal per square centimeter of surface area per percent of metal present in the original sample.

The dense bodies of the present invention, which contain an average of from 5 to 25% tungsten in the cobalt phase are low in acid resistance, characteristically having an acid resistance of less than 50 and generally less than 30 hours. Bodies in which the acid resistance is over 50 hours are termed "acid resistant." Bodies of the present invention are not "acid-resistant."

2. Strength

The unusual strength of the dense bodies of this invention is described in greater detail in the subsequent sections. Much of the strength of the dense bodies of this invention is of course attributable to the skeletal strength of the tungsten carbide, however, the cobalt phase also quite evidently contributes substantially to the overall strength.

Characteristically, a body of this invention containing about 12 percent cobalt has a transverse rupture strength of about 500,000 psi and possesses a carbide skeleton with a strength of over 60,000 psi. Most commercial tungsten carbide bodies of the same cobalt content characteristically will have a transverse rupture strength of only 380,000 psi and a skeleton with a strength of about 46,000 psi.

Removal of the tungsten carbide from the dense bodies of this invention by anodic etching leaves a coherent but porous and weak metal structure. Conversely, removal of the metal from the dense bodies of this invention leaves a porous body of tungsten carbide which has a much lower transverse rupture strength than before removal of the metal. It is the combination of the interpenetrating metal and carbide phase which provide the high strength.

3. Hardness

The hardness of the dense bodies of this invention, measured at ordinary and high temperatures is higher than that of many of the prior art tungsten carbide bodies of equivalent cobalt content. This is one of the most important characteristics of the bodies of this invention. High hardness at high temperatures is of special value in cutting tools. A representative dense body of this invention containing 10 to 12 percent cobalt will measure 87 on the Rockwell A scale at 800°C., while most commercially available tungsten carbide bodies prepared by methods of the prior art containing 12% cobalt have a hardness of only about 75 Rockwell A, and many commercially available carbides containing as little as 6% cobalt have a hardness of only 83 Rockwell A.

The unusual hardness of bodies of this invention is largely dependent upon the structure of the tungsten carbide skeleton which bears most of the load in the composite body. The hardness increases with finer grain size of tungsten carbide in the carbide skeleton. In the compositions of this invention the hardness is not appreciably reduced by the fact that the tungsten content in the cobalt phase is not uniform, so long as over half of the metal binder contains more than 8% tungsten. This is true because hardness is mainly determined by the grain size and coherent nature of the tungsten carbide phase.

4. Density

The relation between the apparent density of bodies of this invention and their theoretical density as calculated from the volumes and individual densities of the components, permits an estimate of the internal porosity. The bodies of this invention have an apparent density of over 98% of the theoretical density, and preferably at least 99% of the theoretical density. Expressed in another way, the volume of a given weight of a preferred body of this invention is generally equal to the sum of the volumes of the components calculated from the weight of each component divided by its density.

2. PREPARATION OF COMPOSITIONS OF THIS INVENTION

a. Preparation of the Powder Mixtures

1. Starting materials

Starting materials for use in this invention are tungsten carbide and cobalt which are substantially pure, that is, containing no more extraneous matter than is found in the tungsten carbide and cobalt powders conventionally employed in making cobalt-bonded tungsten carbide cutting tools. Small amounts of iron, up to 0.5%, may be present from erosion of process equipment; but other than iron, the total impurities amount to less than 0.5% by weight, and preferably are present only in spectroscopically detectable amounts.

Suitable colloiddally subdivided tungsten carbide powder is described in copending application Ser. No. 772,810 filed Nov. 1, 1968, now abandoned. This tungsten carbide is in the form of crystallites of colloidal size well under half a micron in diameter, typically 30 or 40 millimicrons in diameter, the crystallites being linked together in porous aggregates, prepared by forming and precipitating tungsten carbide from a reaction medium of molten salt.

Cobalt suitable for use in this invention includes any source of cobalt metal which can be used to prepare an interdispersion of cobalt with tungsten carbide powder; for example, finely divided powder such as "Cobalt F," sold by the Welded Carbide Tool Co. The metal is preferably more than 99.5% pure cobalt, and should be free from impurities that would be harmful to the properties of cemented tungsten carbide.

2. Blending Components

The cobalt and tungsten carbide powders suitable to be used in this invention must be intimately mixed. Extensive milling of the tungsten carbide with the metal is ordinarily employed to achieve an intimate mixture.

It is preferred to use a mill and grinding material from which a negligible amount of metal is removed, and it is usually preferred to use ballmills or similar rotating or vibrating mills. Suitable materials of construction for such mills are steel, stainless steel, or mills lined with cobalt-bonded tungsten carbide. The grinding medium, which is more susceptible to wear than the mill itself, should be of a hard, wear-resistant material such as a metal-bonded tungsten carbide. Cobalt-bonded tungsten carbide containing about 6% cobalt is a preferred grinding medium. The grinding medium can be in various forms as balls or short cylindrical rods about one-eighth to one-quarter inch in diameter, which have been previously conditioned by running in a mill in a liquid medium for several weeks until the rate of wear is less than 0.01% loss in weight per day. Mill loadings and rotational speeds should be optimized as will be apparent to those skilled in the art.

In order to avoid caking of the solids on the side of the mill, a sufficient amount of an inert liquid medium is ordinarily used to give a thin slurry of the tungsten carbide powder charged to the mill. One of the liquid media which are suitable for this purpose is acetone.

Ballmilling tungsten carbide in the presence of cobalt reduces the particle size of the tungsten carbide and distributes the cobalt uniformly among the fine particles of carbide. It is often advantageous to have at least 25% of the carbide smaller than a micron, and most preferably the average particle size is less than a micron. When it is necessary to reduce the particle size of the tungsten carbide it is preferred to mill the tungsten carbide separately prior to interspersing the carbide with cobalt. It is advantageous to start with the preferred colloiddal tungsten carbide disclosed in copending application Ser. No. 772,810 referred to above, since it is not necessary to mill the tungsten carbide before it is milled with cobalt.

Milling of cobalt/tungsten carbide mixtures is continued until the cobalt is homogeneously interspersed with the finely divided tungsten carbide. Homogeneous interspersion is evidenced by the fact that it is essentially impossible to

separate the cobalt from the tungsten carbide by physical means such as sedimentation or a magnetic field.

The mill is ordinarily fitted with suitable attachments to enable it to be discharged by pressurizing it with an inert gas. The grinding material can be retained in the mill by means of a suitable screen over the exit port. The liquid medium is separated from the milled powder such as by distillation and the powder is then dried under vacuum. Alternatively the solvent can be distilled off directly from the mill. The dry powder is then crushed and screened, while maintaining an oxygen-free atmosphere such as with nitrogen or argon, or by maintaining a vacuum.

3. Adjusting the Carbon:Tungsten Ratio

Various means are known in the art for adjusting the ratio of carbon:tungsten in cobalt/tungsten carbide compositions. Thus, the ratio can be adjusted by simply adding suitable amounts of finely divided tungsten, ditungsten carbide, or carbon to the mill. For the purposes of this invention, it is necessary to produce a carbon deficiency in the powder compositions which will result in carbon deficient regions in the dense bodies. The term "carbon deficient" will be understood to mean "containing less than one atom of carbon per atom of tungsten after consolidation at 1,300° to 1,500°C." Similarly when referring to the "atomic ratio of carbon:tungsten" of a powder, it will be understood that this means the atomic ratio after consolidation at high temperature. In other words, although the powder has some carbon:tungsten ratio, it is not this ratio that is significant as it changes during heating. Thus, it is the ratio after heating which is significant.

Carbon deficiency can be produced in tungsten carbide or mixtures of tungsten carbide and cobalt binders by

- synthesizing tungsten carbide of colloidal particle size such that the surface of the particles consists mainly of tungsten atoms which are not accompanied by corresponding carbon atoms.
- making a composition of tungsten monocarbide intermingled with ditungsten carbide or finely divided tungsten metal or phases such as $\text{Co}_3\text{W}_3\text{C}$ or eta phase, in which there is less than one carbon atom per tungsten atom.
- oxidizing part of the tungsten or intermingled cobalt to an oxidized form from which during subsequent heating with the remaining tungsten monocarbide reacts to form carbon oxides which escape leaving carbon deficient regions in the final product corresponding to the oxidized regions.

If only a small carbon deficiency, such as an atomic ratio of carbon:tungsten of 0.97 or 0.99 is to be created, small amounts of other metals such as tantalum or titanium can be used in place of tungsten. However, in determining the carbon:tungsten ratio in final compositions, the presence of such added metals or their carbides must be taken into account. Of titanium and tantalum, it is preferred to use tantalum because its carbide acts as a grain growth inhibitor, and enhances hardness at high temperature.

4. Heterogeneity in the powder

Means for deliberately producing heterogeneity or local variations in the carbon:tungsten ratio have not been described in the prior art. Such variations can be produced by any of the following methods:

Blending dissimilar powders

A powder mixture of tungsten carbide and cobalt which is carbon deficient can be blended with a tungsten carbide or cobalt/tungsten carbide powder mixture which contains a theoretical amount or a slight excess of carbon over that required to form tungsten monocarbide, and then the blend is consolidated at high temperature. For example, the carbon deficient powder can be a mixture of tungsten carbide and cobalt which has been milled to develop a specific surface area in excess of three square meters/gram which is permitted to absorb oxygen; this can be blended with a powder which is not carbon deficient, such as a milled powder of the tungsten carbide and cobalt of the prior art commonly used for producing cemented tungsten carbide bodies with an atomic ratio of carbon to tungsten of from 1.0 to 1.03, as commonly em-

ployed in carbide cutting tools. The carbon deficient powders can also be prepared by ballmilling a composition of cobalt and tungsten carbide along with finely divided tungsten powder to provide the carbon deficiency; this powder can be blended as described with a powder which is not carbon deficient. Powders having atomic C:W ratios as low as 0.80 and as high as 1.1 can be used for blending.

Blending carbon with powder

Another method for preparing a heterogeneous powder comprises milling finely divided carbon with tungsten carbide and cobalt, preferably in sufficient amounts to produce a carbon:tungsten atomic ratio of about 1.0. Generally more than 0.01 and less than 0.5 percent by weight of carbon is added based on the weight of tungsten carbide. In the consolidated body the region around each carbon particle is carburized as the carbon dissolves, producing local regions which are not carbon-deficient, the remainder of the body being carbon-deficient and having a higher tungsten concentration in the cobalt. The tungsten carbide should have a C:W ratio of at least 0.8 prior to addition of the carbon, and should have a ratio between 0.85 and 1.02 after addition of the carbon.

Many commercially available carbon blacks have a particle size in the millimicron range and any of these is a suitable source of carbon. Ordinarily it is preferred that the carbon be in a form which, after the milling step, will have a particle size of less than 5 microns and most preferably less than 1 micron.

Oxidizing the powder

Still another method for producing heterogeneity in the consolidated bodies comprises partially oxidizing a pelletized powder prepared by ballmilling cobalt and tungsten carbide containing a slight excess of carbon, subsequently pelletized by tumbling, for example, so that the outer surface of the pellets becomes more highly oxidized than the interior. Thus a mixture of tungsten carbide and cobalt powders each from 1 to 10 microns in ultimate particle diameter can be ballmilled in an acetone medium for several days and then the mixture can be removed from the mill and the powder dried without exposure to the air. A small amount of non-volatile organic matter from the acetone remains on the powder. The powder can then be screened through a mechanically shaken screen of 60 meshes per inch under nitrogen, producing spherical pellets 10 to 100 microns in diameter. The pelletized powder will ordinarily be stored under nitrogen containing a low concentration of oxygen which is absorbed to an amount of from about 0.1 up to about 1% by weight. The powders can alternatively be brought slowly into the air providing the exposure is gradual enough to avoid local heating and excessive oxidation. Such an oxidized powder gives a consolidated body containing an average atomic ratio of carbon to tungsten of greater than 1.0, yet the body contains cobalt having more than 8% by weight of tungsten in solid solution. If oxidation is excessive, as much as 20% by weight of tungsten on the average is found in the cobalt phase, and the acid resistance may approach 50 hours. It is believed that the surface regions of the spherical pellets becomes more highly oxidized than the interior, and that when the powder is compressed and the composition is heated there results a three-dimensional continuum of carbon deficient composition derived from the surface regions of the pellets in which the cobalt binder phase is rich in dissolved tungsten, while those portions of the body derived from the interior regions of the pellets remain as regions less deficient in carbon, containing little or no tungsten and having low acid resistance. It is believed that these interior-derived regions of the composition reduce brittleness because of the ductility of the pure cobalt binder.

Identification of the heterogeneous regions is sometimes difficult. However, by metallographic procedures, X-ray diffraction analysis, electrical resistivity measurements and Curie temperature measurements, regions high in carbon and cobalt regions low in tungsten can be identified in the presence of regions low in carbon, and cobalt regions high in tungsten.

Heterogeneity preferably occurs only on a microscopic scale, but may occur in regions as large as a tenth of a millime-

ter. Thus, 50 micron-sized granules of cobalt/tungsten carbide powder which have been heated in hydrogen at 900° C. and have a carbon:tungsten ratio of 0.95 can be blended with granules of a similar powder which have been heated in hydrogen containing enough methane to deposit a small amount of free carbon and have a carbon:tungsten ratio of 1.03. Polished cross-sections of consolidated bodies made from such mixed powders show localized regions high and low in carbon, about 50 microns in size, corresponding to the size of granules of the respective powders.

Preferred powders are those which produce bodies in which the heterogeneous regions are so fine and intermixed that they cannot be identified under the microscope but are still known to be present from either X-ray diffraction patterns of the cobalt phase or from the fact that the acid resistance is lower than that of a similar body having the same degree of porosity in which there is the same overall concentration of tungsten in cobalt, but the tungsten is homogeneously distributed. Homogeneous distribution of tungsten in cobalt is attained when steps are taken to eliminate the causes of heterogeneity as described above.

5. Reducing the powder

When the dried milled mixture of tungsten carbide and cobalt contains over about 0.1 percent by weight of free carbon or more than about 0.5 percent by weight of oxygen, it is preferred to remove these impurities by treatment at a minimum elevated temperature in a very slightly carburizing atmosphere. Under these conditions extreme local variations in carbon to tungsten ratio are corrected, but the desirable variations within the limits of the present invention are not affected.

Oxygen as well as excessive free carbon can be removed during this purification, and at the same time the combined carbon content can be adjusted, all by heating the powder in a stream of hydrogen containing a carefully regulated concentration of methane. The powder can be charged to shallow trays made from a high temperature alloy, such as Inconel, and the trays loaded directly from the inert atmosphere environment to a tube furnace also made from Inconel or some similar high temperature alloy.

The powder in a stream of the reducing gas is brought to a temperature ranging from 750° to 1,000°C., depending on the metal content of the powder, in from 3 to 5 hours, taking half an hour to raise the temperature the last hundred degrees. For a cobalt content of about 1%, 1,000°C. is used, and for powders containing 12% cobalt, the temperature is 800°-900°C.

The reducing gas should consist of a stream of hydrogen containing methane and about 10 percent of inert carrier gas such as argon. Thus, at 1000°C. the stream should contain 1 mole percent of methane in hydrogen; at 900° C., 2 mole percent of methane; and at 800°C., 4 mole percent of methane in the hydrogen. The reduction/carburization at the maximum temperature is carried on for a period of 0.5 to 3 hours, and after cooling to room temperature under argon the powder is discharged to an inert atmosphere environment where it is screened through a seventy mesh screen. If desired this powder can be stored for extended periods in sealed containers or it can be used directly in the next step of this process.

Care must be employed to assure that in the reduction/carburization step an excess of methane is avoided so that an undesirable amount of free carbon is not introduced into the powder. It is to be noted that although the reaction conditions are such that free tungsten metal would ordinarily be converted to tungsten carbide, nevertheless very finely divided tungsten carbide used in this invention remains slightly deficient in carbon and is not carburized completely to a stoichiometric ratio for tungsten carbide.

For compositions in which the desired atomic ratio of carbon:tungsten is less than about 0.97, and where oxygen is to be removed by the foregoing reduction step, methane or other carburizing environments should be avoided and only hydrogen used. Generally speaking, with compositions of

higher cobalt content, lower atomic ratios of carbon:tungsten can be employed. However, the minimum average atomic ratio of carbon:tungsten, R_{Min} , is found to be

$$R_{Min} = 1.0 - 0.0062(P-1),$$

where P is percent by weight of cobalt.

An optimum ratio will be between this minimum and 1.02. Thus, for a composition containing 10% by weight of cobalt, for example, the minimum ratio is about 0.94. For a body containing 25% cobalt, the minimum ratio is about 0.85. A ratio above 0.90 is preferred. A maximum ratio, R_{max} for most purposes is $R_{max} = 1 - 0.00166(P-15)$. For a composition containing 3% cobalt the maximum ratio is about 1.02.

b. Consolidation of the powder

The consolidated bodies of this invention are prepared from interspersed cobalt/tungsten carbide powders. Generally speaking, consolidation is carried out in the manner described in copending application Ser. No. 660,986, filed Aug. 16, 1967, i.e. by heating and compressing the powders.

It is important that when the powder composition is being heated for the first time it should not be subjected to excessive pressure or mechanical constraint, especially when in a graphite or carbon container. Pressure can be applied providing it is not sufficient to keep the sintering billet in intimate contact with the graphite walls of the mold. With some powders, a pressure of up to 1000 p.s.i. can be applied during the heating step, since even under such pressure the billet shrinks away from the mold and is not seriously carburized. The harm that is caused by excessive compression may be due either to shearing forces which disturb the internal structure of the composition at the beginning of recrystallization and sintering, or it may be due to chemical effects from contact with material such as graphite which is ordinarily used to apply the pressure. Thus it has been observed that application of pressure to the composition while in an alumina mold is less harmful to the resultant bodies, even using pressures higher than 1000 p.s.i. The harm also may be due to trapping of gases in pores that are collapsed by the pressure. In the absence of pressure such pores would not normally become closed at this stage of sintering.

If the powder is first heated without application of pressure to a prescribed temperature it can thereafter be consolidated to density and molded by hot pressing in a carbon mold without absorbing undesirable amounts of carbon. We have found that after the tungsten has dissolved in the cobalt phase during the heat treatment it is much less readily carburized.

Heat treatment is carried out in an inert atmosphere or in a vacuum. An inert atmosphere is one that does not react with the powder, such as argon or hydrogen. Heat treatment is carried out at a temperature T_s which is above 1000°C., but generally below the final consolidating temperature, T_m , and the treatment lasts for about t_s to $20 t_s$ minutes, where:

$$\log_{10} t_s = 13250/(T_s + 273) - 8.2 \text{ minutes}$$

and

$$T_m = \frac{6.5 - \log_{10}(P - 0.3)}{0.0039} \pm 100^\circ \text{C.}$$

where P = percent by weight of metal in the composition.

Thus the composition is heated to temperature T_s and held for a minimum of t_s minutes. The maximum time of heating is not critical at temperatures below which no appreciable grain growth of tungsten carbide occurs, namely below about 1200°C. However, above 1,200°C., the time should not exceed about $20 t_s$. For example, at 1000°C., it is necessary to heat for at least $2\frac{1}{2}$ hours and preferably several times this long; at 1100°C. the composition is heated for at least 13 minutes; at 1200°C. the hold time is a minimum of about 5 minutes and not over 2 hours; at 1400°C. the hold time is less than 10 minutes, and at 1500°C. it is less than 4 minutes.

It should be noted that the temperatures and times required vary to some extent with the size of samples, dimensions of equipment, heating rates attainable and the like. For example, it is possible to carry out the heating step either on loose powder or preconsolidated billet while the sample is being

heated to the temperature at which it is to be finally consolidated. Such heating should be carried out rapidly in the range above 1,200°C., providing the sample is heated relatively uniformly throughout its volume. An integrated combination of temperatures and times equivalent to the fixed times and temperatures described, is in keeping with the spirit of the invention, and will be apparent to those skilled in the art.

A preferred method of fabrication is by hot pressing the powders in the manner described below. Various types of hot pressing equipment are known in the art. Depending on press design and desired operating characteristics, heating can be by resistance heating, induction heating, or plasma torch heating. Short heating times of a few seconds duration are attainable by resistance sintering under pressure.

Temperature can be measured very near the sample itself by means of a radiation pyrometer and can be cross-checked for accuracy with an optical pyrometer. Such instruments should be calibrated against primary standards and against thermocouples positioned in the sample itself so that actual sample temperatures can be determined from their readings. Automatic control of heat-up rate and desired temperature can be achieved by appropriate coupling mechanisms between a radiant pyrometer and the power source.

The mold can be of a variety of shapes but is usually cylindrical, with a wall thickness of up to an inch or more. It is particularly advantageous to use a cylinder with a cross-section which is circular on the outside and square in the inside in pressing bodies to be used as cutting-tip inserts, thereby fabricating them as near as possible to their final desired dimensions.

As an example, for a 1 inch in diameter finished pressed round disc, the shell is cylindrical, 1 inch in inside diameter, 1½ inches in outside diameter, 4 inches in length. Thin graphite discs one-fourth inch in thickness and 1 inch in diameter are loaded in the cylinder on top and bottom of the material to be pressed. The surface of the graphite discs in contact with the sample can have a conical depression one-eighth inch in diameter at the center to form a tip on the sample and keep it positioned in the center of the mold when it shrinks away from the sides due to sintering. Graphite pistons 1 inch in diameter and 2 inches long are loaded in both ends of the cylinder in contact with the one-fourth inch discs and protruding from the cylinder.

Graphite parts used in the press tend to oxidize at the pressing temperatures used, and it is therefore necessary to maintain a non-oxidizing atmosphere or vacuum within the press. In addition to prolonging the life of the graphite parts, the use of a vacuum or an inert atmosphere makes it possible to remove the mold containing the hot pressed body from the heart of the induction heated furnace and cool the sample much more quickly than if it were left to cool in the hot zone of the furnace after shutting off the power. The press can be arranged to permit the mold to be removed from the hot furnace, and when this is done the mold cools very rapidly by radiation. Thus the mold described above, removed from the furnace at 1400°C., cools to dull red heat, about 800°C., in about 3 minutes.

Powders which are pyrophoric or absorb oxygen upon exposure to air, should be loaded into the mold in a non-oxidizing atmosphere, for example in a glove box filled with inert gas. The appropriate discs and pistons can then be inserted and the loaded mold can be handled with the contained powder essentially loosely packed or, for example, with no more pressure than can be applied to the pistons with the fingers. However, it is often convenient to apply about 200 to 400 p.s.i. pressure with a small press, to give a more compacted sample for greatest ease in handling.

In a preferred aspect of this invention, a cobalt/colloidal tungsten carbide powder mixture is pressed at about 200 p.s.i. as it is loaded into the mold, it is then brought to the maximum temperature with no pressure on the pistons, and held for 2 to 5 minutes at maximum temperature before applying any pressure. During the period at maximum temperature with no

pressure applied, the body shrinks due to sintering. At the end of the period, the body attains 80–90% of theoretical density and its diameter is about 60% of the mold diameter. The pressure is then applied, reaching maximum in 15 to 30 seconds, and the presintered body is reformed into conformity with the mold. Maximum pressure and temperature are applied until complete densification is attained, as indicated when movement of the rams ceases. This ordinarily does not require more than 5 minutes, and usually only one minute, after which the sample is immediately removed from the hot zone and permitted to cool rapidly by radiation to below 800°C. in about 5 minutes or less.

The conditions which give rise to the preferred dense cobalt-bonded bodies are quite important and should be precisely established for the particular composition and the type of structure desired.

Unduly long presintering times before application of pressure can be harmful due to excessive crystallite growth and the development of too extensive and rigid a cross-linked carbide structure. Too early an application of pressure can also be harmful as pointed out above. Holding the sample for too long a time at maximum temperature should also be avoided, not only because of a tendency towards carburization but also because secondary crystallite growth tends to cause a coarsening of the structure and eventually the development of porosity. Cooling too slowly can also be detrimental if the sample remains at high temperature long enough for undesirable crystallite growth and structural changes to occur. These structural changes can include changes in the composition of the cobalt binder phase. Thus with a low carbon content and the corresponding large amount of tungsten initially in the cobalt phase, precipitation of eta phase occurs at elevated temperatures. This can be minimized by brevity of hot pressing and rapidity of cooling of the pressed product. Generally speaking, it is undesirable to have more than about 20% by weight of eta phase in the binder, and it is preferred to have less than 5% eta phase in the binder.

While it is preferred that the products of this invention be made by heating and sintering lightly compacted finely divided cobalt/tungsten carbide powders, followed immediately by application of pressure, it is sometimes desirable to carry out the sintering step as a separate operation.

Thus, in order to achieve maximum productivity from a hot press, the initial sintering step can be carried out in a separate furnace in an inert atmosphere. This can be accomplished in several ways. For example, the starting powder can be loaded or lightly compacted into molds to be later used for hot pressing, and then heated rapidly in an inert atmosphere to a temperature within from 50° to 200° of the final hot pressing temperature to be employed. The mold and its partially sintered contents, while still hot, can be passed directly into a hot pressing operation.

The maximum temperature at which the bodies should be pressed is largely dependent on the cobalt content, although the proper temperature is to some extent dependent on the size of the molded piece, the heating rate, and the available pressure as well. The compositions of this invention are conveniently subjected to a temperature of T_m for a period of t_m to $20 t_m$ minutes, where

$$T_m = \frac{6.5 - \log_{10}(P - 0.3)}{0.0039} \pm 100^\circ \text{C.}$$

and

$$\log_{10} t_m = 13250 / (T_m + 273) - 8.2 \text{ minutes}$$

where P is the percent by weight of metal in the composition.

Thus, for compositions containing 6% cobalt T_m is about 1450°C., and for compositions containing 12% cobalt, T_m is about 1400°C.

It is preferred to bring the sample to the desired temperature as rapidly as possible. For example, a sample 1 inch in diameter can be heated to 1400°C. in 4 to 5 minutes, or to 1850°C. in 6 to 7 minutes, by introducing the mold into a pre-

heated graphite block, the limiting factor being the rate of heat transfer from the graphite equipment via the mold to the sample. Rapidity of heating is especially important in compositions which have an atomic ratio of carbon:tungsten close to 1.0.

Pressure can be applied to the cobalt/tungsten carbide composition in a hot press through the action of remotely controlled hydraulic pneumatic rams. Applying pressure simultaneously through two rams to the top and bottom gives more uniform pressure distribution within the sample than does applying pressure through only one ram. An indicator can be attached to each ram to show the amount of ram movement, thereby allowing control of sample position within the heat field and indicating the amount of sample compaction. The end section of the rams, which are exposed to the high temperature zone should be made from graphite.

A variation of 100° from the mean specified temperature provides to some extent for the variables mentioned above. Thus, in order to attain temperature equilibrium in the interior without overheating the exterior, larger bodies require a lower temperature, which also permits a longer heating time. Higher temperatures and shorter times can be employed when high molding pressures can be used and smaller molded bodies are being made.

The most important factor in determining consolidation conditions is the physical nature of the heat-treated composition of the invention. When the composition is a heat-treated powder, for example, it can be loaded into graphite molds and heat and pressure simultaneously applied until the material reaches the recommended temperature range, T_m at which the pressure is maintained for the specified time. The required pressure may be as low as 100 to 200 pounds per square inch for compositions such as those containing 15 to 25 percent by weight of cobalt and which are soft at the pressing temperature. Several thousands of pounds per square inch is required for bodies containing one to three percent cobalt, although pressures of not more than 4000 pounds per square inch are usually used where operations are in graphite equipment.

For compositions containing from 5 to 12 percent cobalt the required pressure can also vary according to the physical nature of the composition. Thus if a sintered powder composition is used, which has been heat-treated at a temperature T_s close to the maximum allowable temperature T_m , a high pressure such as 4000 p.s.i. is preferably applied over a prolonged period, often continuously, while the mass is heated from 1000°C. to temperature T_m .

On the other hand, if degassed powder is preconsolidated to relatively high density such as about 50 percent of theoretical density, so that voids or pores larger than about ten microns are eliminated, and this compact is then heat-treated at temperature T_s , it shrinks spontaneously to a coherent body. If T_s is then raised to T_m , sintering continues and a relatively dense body is obtained which can then be molded by brief application of pressure at temperature T_m .

Compositions of the invention require application of pressure at the defined maximum temperature, T_m , to eliminate voids. In such instances the consolidation is carried out until the body of the invention reaches a density of greater than 9 percent and preferably greater than 99 percent of theoretical, corresponding to a porosity of less than one percent by volume. However, for many uses even this degree of porosity may be too high. The porosity of the bodies of this invention is characterized by preparing polished cross-sections of the bodies for examination under a metallurgical microscope. Pores observed in this way are classified according to a standard method recommended by the American Society for Testing Materials (ASTM) and described on pp. 116 to 120 in the book entitled "Cemented Carbides," published by the MacMillan Company of New York (1960). Thus, bodies of this invention are preferably pressed until a porosity rating of A-1 is obtained especially where the material is to be subjected to heavy impact or compression. This corresponds to a density of essentially 100% of theoretical or a volume porosity of about

0.1%. However, porosities as great as A-3 or A-4 are suitable for many uses, since such bodies nevertheless have very high transverse bending strength. Even a porosity rating of A-5 which corresponds to a density of about 98 percent and a porosity around 2 percent, is acceptable for the compositions of this invention.

Pressures of from 500 to 6000 psi can be used in graphite equipment, but generally speaking not over 4000 psi can be applied without danger of breaking the equipment, unless the graphite mold and plungers are reinforced with a refractory metal such as tungsten or molybdenum.

Instead of loading a powder into a mold, preconsolidated compacts in the form of billets can be prepared and heat-treated and then loaded in a mold for hot pressing. Such heat-treated, sintered billets can also be shaped by rolling or forging in an inert atmosphere.

After final consolidation to a dense billet the compositions of this invention can be further shaped by bending, swaging, or forging at about temperature T_m . Similarly, pieces can be welded together by bringing two clean surfaces together under pressure.

3. CHARACTERIZATION OF DENSE COMPOSITIONS

a. Chemical analysis

The chemical composition of the bodies of this invention can be determined by conventional chemical analysis for the elementary constituents. Samples can be pulverized as in a Plattner steel mortar and screened before sampling for analysis. The more convenient methods of analysis for tungsten, cobalt, total carbon, free carbon, oxygen, and density are described in copending application Ser. No. 660,986 referred to above.

b. Examination with optical microscope

To examine homogeneity of the overall structure and detect gross inclusions or localized coarse grain structure polished surfaces can be examined quite satisfactorily at magnification up to 2000X with the light microscope. In order to examine individual tungsten carbide grains and their structural arrangement in consolidated bodies, it is advantageous to fracture a sample and examine the fractured surface or to etch the polished surface with chemical agents which due to the different rates of chemical attack dissolve a thin layer from the exposed grains, enhancing the contrast between the tungsten carbide and metal phases and making grain boundaries more readily visible. Techniques commonly used for preparing fractured and etched surfaces and analysis of those surfaces are fully described in copending application Ser. No. 660,986 referred to above.

c. Examination with electron microscope

Because of the unusually fine-grained structure, especially in preferred bodies of the invention in which over half of the grains of tungsten carbide are less than 0.75 microns in diameter, it is necessary to use the electron microscope to measure the grain size. To measure the grain size of tungsten carbide both the boundaries between tungsten carbide grains and the tungsten carbide-metal phase boundaries must be outlined. Furthermore, the metal phase must be distinguished from tungsten carbide so that the former can be avoided when counting the grain size of tungsten carbide. A multi-step chemical etch accomplishes this objective. The procedure described in copending application Ser. No. 660,986 referred to above is employed in characterizing the products of this invention.

d. Transverse rupture strength

Many suitable procedures have been described in the literature for the measurement of transverse rupture strength. We prefer to use the method described in application Ser. No. 660,986 referred to above.

e. Magnetic characteristics

The Aminco-Brenner "Magne-Gage," basically a torsion balance made by the American Instrument Company, Silver Springs, Maryland, is a device which permits quantitative

determination of the relative force required to pull a magnet away from a specimen containing magnetic material.

Use of the "Magne-Gage" and preparation of samples for analysis are fully described in application Ser. No. 660,986 referred to above.

f. Acid resistance

The method of measuring the acid resistance of metal-bonded tungsten carbide bodies is also described in application Ser. No. 660,986 referred to above.

As pointed out there, the samples to be tested are cut into small bars $0.006 \times 0.006 \times 0.55$ inches. The sample bars are then cleaned and measured to the nearest 0.001 inch, weighed to the nearest tenth of a milligram and suspended individually from a glass rod so that the bars hang about 1 inch below the rod.

The surfaces of the bars are then cleaned again by suspending the bars in boiling trichloroethylene and then washing them with water and acetone. The bars and their support wires are then weighed to the nearest tenth of a milligram and the bars are then immersed in 25°C. hydrochloric acid containing 35% by weight of hydrogen chloride. 50 milliliters of acid are used for each bar, and the acid is agitated throughout the test. The samples are removed periodically and are measured and weighed.

Acid etch resistance R is expressed in terms of the number of hours required for the acid to remove 0.25 milligrams per square centimeter of surface area per percent of metal originally present in the sample.

In measuring acid resistance it is important that the surfaces of the test samples be clean and smooth, free from roughness or scratches. It is also important that the samples be free of cracks and porous defects which lead to low values for R. The pores provide avenues of attack of the cobalt phase by the acid, so that by the above method the acid resistance may appear to be irregularly low. In such instances, the pores can be filled with a resin or wax by impregnating the specimens, for example in hot beeswax, the excess wax is then wiped from the surface with a cloth soaked in acetone and the outer surface of the specimen further cleaned with an aqueous detergent in an ultrasonic cleaning device until the surface is water-wettable, indicating that wax has been removed from the exterior. By this procedure, the fine pores remain blocked and a true value of acid resistance can then be obtained.

g. Tungsten content of the cobalt

A preferred method for measuring the tungsten content of the cobalt is to 1) polish a section of sample; 2) remove tungsten carbide by anodic etching for an hour in a solution containing 10 percent by weight of potassium hydroxide and ten percent of potassium ferricyanide; 3) rinse; 4) remove the residual metal binder layer by dissolving it in a ten percent solution of hydrochloric acid; and 5) then again etch to remove tungsten carbide, thus leaving a film of metal binder a few thousandths of an inch in thickness. The sample is then examined by X-ray diffraction and the lattice constant of the cobalt determined. The percentage of tungsten in the cobalt is calculated, based on the information given in "Handbook of Lattice Spacings and Structure of Metals," Vol. 1, page 528, Pergamon Press, 1958, by W. B. Pearson. When no tungsten is present, the lattice constant of cubic cobalt is 3.545 angstroms, and when the initial binder contains 21% by weight of tungsten and 79% by weight of cobalt in solid solution, the lattice constant is 3.570.

We have found that the metal binder phase can be isolated by electrolytically etching a body of the invention, using it as an anode, in the potassium hydroxide-potassium ferricyanide solution for 24 hours at a current density of 3 amperes per square inch, then rinsing in water and removing the layer of cobalt alloy, which is from 0.005 to 0.010 inches thick, and drying at 60°C. under nitrogen. The tungsten content determined by X-ray diffraction from powder patterns, corresponds within the limit of error to the ratio of weights of tungsten to tungsten plus cobalt, determined by chemical analysis, providing no substantial quantity of Co_3W or carbide phases are

present. In this recovered metal phase, tungsten carbide and cobalt-tungsten carbide phases such as eta, $\text{Co}_3\text{W}_3\text{C}$ are determined by heating the sample in 35% hydrochloric acid at 80°C. for 1 hour, then filtering and weighing the washed and dried insoluble residue which will contain the carbides which are insoluble. If the intermetallic compound Co_3W is present, it will dissolve in the acid, but it is seldom present in the unannealed bodies of this invention.

When eta phase is present in a body of this invention which is rapidly cooled, it is in a form rich in tungsten and corresponds to the conventional formula $\text{Co}_3\text{W}_3\text{C}$ which is reported to have a face-centered cubic lattice constant of 11.08 angstroms. However, when bodies of the present invention are slowly cooled from 1400° or 1300°C. at 5°C. per minute, the eta phase apparently absorbs cobalt or loses tungsten, so that the ratio of cobalt to tungsten changes from 3:3 to 3:2, and the lattice constant changes continuously from 11.09 to 10.75 angstroms. The lattice spacing of the eta phase, when present, serves to indicate whether a body has been rapidly or slowly cooled.

h. Density

The method of measuring apparent density should be selected according to the type of specimen available. Most conveniently the actual density of any given composition is measured on a convenient size sample by weighing the sample first in air and then immersed in water previously boiled to remove dissolved air. The density is then calculated from the equation:

$$d = (W_1 \times S) / (W_1 - W_2)$$

where

d = actual density in grams/cubic centimeter;

W_1 = weight in grams in the air;

W_2 = weight in grams in the water; and

S = specific gravity of water at the temperature of measurement.

The theoretical density of a composition is determined by the equation:

$$t = 1563s/cs + 15.63(100 - c)$$

where

t = theoretical density in grams/cubic centimeter;

c = weight percentage of tungsten carbide; and

s = specific gravity of the tungsten-cobalt alloy binder phase.

Percentage of theoretical density is then calculated by the expression

$$\text{percentage of theoretical density} = d/t \times 100.$$

A method for measuring actual density of irregularly shaped specimens employs mercury displacement, as described by Maczmillian Burke, *Roczniki chem.*, 31, 293-295 (1957), "Pykometer for Determining the Bulk Density of Porous Materials," and further referred to in *J. Am. Chem. Soc.*, 45, (7), p. 352-353 (1962), by the same author.

i. Heterogeneity of tungsten in the cobalt

Variations in the concentration of tungsten in solid solution in the cobalt phase can be observed by careful examination of the X-ray diffraction lines of the cubic cobalt phase of the recovered metal binder. When tungsten is uniformly distributed as in products of the prior art, the lattice spacing of the cobalt is uniform as evidenced by sharp single peaks in the diffraction lines of the cobalt, whereas in products of the present invention different regions of cobalt contain different amounts of tungsten in solid solution so that the diffraction lines, recorded as intensity versus diffraction angle show broadening, or shoulders due to two or more unresolved peaks, or even two or more separate peaks, depending on the degree of resolution obtained and the irregularity of distribution of tungsten in the cobalt phase.

Attainment of resolution in X-ray diffraction is discussed in some detail by Emmett F. Kaelble "Handbook of X-ray," McGraw Hill Book Co., (1967), pages 9-14 to 9-30.

Measurement of exact line position includes the technique of incorporating into the sample of cobalt-tungsten binder a uniform amount of sodium chloride to serve as an internal

standard. (Refer to H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures," John Wiley & Sons, Inc., N.Y. (3rd printing 1962) pages 452-3.) By this means the measured angle two-theta for a cobalt line from cubic cobalt is corrected by the difference between the measured angle for a neighboring sodium chloride line and its known standard value. From the corrected value of two-theta for the cobalt line, the unit cell dimension of the cobalt is calculated as on p. 343 of the foregoing reference.

The tungsten carbide-cobalt composition of this invention is cut or ground to produce a specimen with a smooth surface having an area of several square centimeters. The exposed surface must be representative of the interior of the specimen, outer layers which might be oxidized or carburized by previous treatments being ground away to a depth of at least 0.06 inches.

The method consists in anodically etching the smooth, cleaned surface for 24 hours in alkaline ferricyanide solution to remove the tungsten carbide phase to a depth of up to 1/32 inch, scraping off and recovering the residual, porous cobalt phase, and examining it by X-ray diffraction.

Variations in the "d" spacing for the strongest cobalt line indicate variations in the amount of tungsten in solid solution in the cobalt lattice; and the ratio of the intensity of the strongest eta line to that of the strongest cobalt line, serves as an empirical indication of the relative amount of eta phase present in the cobalt. This is called the "eta ratio."

It appears that the eta phase is precipitated within the cobalt metal phase, since it is not removed by the anodic attack which removes tungsten carbide, in spite of the fact that, by itself, eta phase is quite soluble in this reagent. Similarly, tungsten within the cobalt lattice is not attacked by the anodic etch.

While not ordinarily encountered, destruction of eta phase may occur during anodic attack if most of the cobalt has been converted to eta phase, so that little of the cobalt is left to surround and protect the eta phase. Also, is some unusual specimens of cobalt-bonded tungsten carbide, other than that of Ser. No. 660,986 referred to above, when much eta phase is present the cobalt may be very finely divided, so that the recovered powder is oxidized in air and partially destroyed. These factors have been taken into account in devising the procedure described below.

The surface is cleaned by immersing in boiling dimethylformamide followed by rinsing in acetone and drying. Alternatively, the sample may be held over a gas flame until it is just red hot and permitted to cool slowly, after which it is scrubbed with steel wool in water and dried.

Electrical contact is made with the sample by wrapping a fine platinum wire around the specimen or using platinum clips. The lead-in wire for electrical contact should be covered with rubber insulation. The sample is hung in a 100 cubic centimeter plastic or glass beaker and connected to the positive source of direct current, thus making the specimen an anode.

A cathode of platinum sheet 1 inch $\times$ $\frac{3}{4}$ inch welded to a platinum lead wire is also hung inside the wall of the beaker using the wire as a hook and connected to the negative source of direct current.

Up to four cell-assemblies of this type can be connected in series to a 12 volt DC source. The specimens are connected toward the positive terminal of a 12 volt storage battery, or other source providing a current of up to 1 ampere.

The electrolyte is made by dissolving 100 grams of potassium ferricyanide and 100 grams of potassium hydroxide, adding these to about 30 ml. of distilled water and stirring until the mixture becomes hot, and then diluting to about 1 liter. Sufficient solution should be added to each beaker to cover the sample and most of the cathode. Usually about 75 milliliters of solution is required. The beakers may be covered with a sheet of plastic if desired, to reduce electrolyte spray during electrolysis which is continued for 24 hours with a current to each specimen of 0.7 amperes.

At the end of the electrolysis period, the specimen is removed and rinsed in water to remove alkali without losing any cobalt.

The cobalt within 1/32 inch of the edges of the cut surface, which have been in contact with graphite, is then trimmed away and discarded. Some specimens yield cobalt films which are cracked and only very lightly adherent. In such cases, the cobalt film can be removed from the center of the cut surface leaving the cobalt around the edges.

The cobalt is collected by scraping it off under water in a pan, excess water is decanted and the cobalt is washed with distilled water into a 3 inch diameter porcelain mortar, along with about 10 milliliters of water. Excess water should be decanted from the mortar. The cobalt is then ground by about 10 strokes of the porcelain pestle, to break up the flakes. Excessive grinding must be avoided, since it may affect the cobalt structure. The powder is then washed with distilled water into a thin plastic bag held so that the cobalt will collect in one corner. The cobalt in suspension is drawn toward the corner by holding the latter next to a small magnet. The cobalt is then held in the corner with the magnet while the water is decanted off and replaced with 10 milliliters of n-propyl alcohol. The powder is then suspended and again drawn to the corner and the alcohol discarded.

The corner containing the cobalt is closed off by twisting it several times, tying it loosely, and cutting off the rest of the bag.

Depending on the amount of cobalt in the original composition and the size of the specimen, one or more preparations of this type from the same piece of material may be required to obtain from 50 to 250 milligrams of cobalt powder for examination. In repeating the preparation the etched surface is well scraped, or preferably sand-blasted before being again anodically etched.

Two somewhat different procedures have also been employed in diffraction analysis of the cobalt phase. They are referred to hereinafter as procedure A and procedure B.

In procedure A, described more fully below, a 75 milligram sample is used with a para-focusing device to obtain a diffractometer tracing from which the line position, shape, and intensity is employed to estimate the percent tungsten in the cobalt, and the variation in the amount of tungsten in different portions of the sample, i.e., the heterogeneity of distribution of tungsten.

In procedure B, also described in detail below, a sample of greater weight is used with a flat sample holder, automatic stop scanning every 0.04° and accumulating the same number of counts at each point. The time at each point is recorded on punch tape fed to a computer from which a profile of intensity versus angle is constructed. The punch tape is converted to punch cards fed to a computer programmed to calculate intensity profile at each point, then interpolate to a finer mesh of points spaced apart by one-tenth the separation of alpha-1 and alpha-2 at that point, using a Lagrangian polynomial fit covering a range of eight consecutive points, then applying the Keating correction for the alpha doublet whereby the alpha-2 contribution is subtracted from the total intensity at each point using a series approximation, thus leaving the equivalent alpha-1 profile. From this the amount and distribution of tungsten in the cobalt is more accurately determined than by procedure A. Details of these procedures are as follows:

PROCEDURE A

Apparatus

North American Philips Diffractometer

Power Supply — Type No. 12045

X-ray Target Source — Cobalt with iron filter to give cobalt alpha radiation

Wide Range Goniometer/type No. 42202

Electronic Circuit Panel — Type No. 12049

Advance Metal Research Corp. Autofocusing Attachment, Model No. 3-201

SAMPLE PREPARATION

Thirty-five one hundredths of a gram of sodium chloride is ground in an agate mortar along with a 0.075 gram sample of the powder to be tested, and the mixture is screened through a 325 mesh screen. The salt is present to provide representative peaks of known spacings at 1.99 and 1.628 angstroms. The screened powder is placed on a fiberglass sample holder along with 0.2 milliliters of amyl acetate and 1 drop of 25% collodion solution. These are mixed to disperse the powder and spread it to a film on the holder over an area 3 inches long and 1 inch wide at the center and one-half inch at the ends.

INSTRUMENT CONDITION

The X-ray apparatus is fitted with a cobalt target and iron filter at 25 kilovolts and 20 milliamps. Scanning speeds of 1/2° and 1/4° per minute are used. The chart speed is 30 minutes per hour. The diversion slit is -4°; the receiving slit 0.010 inch wide. Scintillation counter detector, 950 volts, 6 volt base line, gain zero, scale factor 8, multiplier 0.8 and time constant 4.

CALCULATION PROCEDURE

The scans are examined, and the *d* spacings corrected if necessary from the spacings of the known sodium chloride lines, corresponding to 53.3° 2θ corresponding to 1.994 *d* Å.

Cobalt Lattice and Cobalt-Eta Co₃W₃C Ratio

The region 48° 2θ to 52° 2θ is scanned at 1/2° per minute. The counts per second for cobalt in the region corresponding to a *d* value of around 2.06 Å. are recorded.

Cobalt Peak or Multiple Cobalt Peaks

The region 51° 2θ to 54° 2θ is scanned at 1/4° per minute. The location of the cobalt peak or multiple cobalt peaks and the sodium chloride internal standard are read in degrees 2θ. The alpha-1 and alpha-2 peaks are averaged for sodium chloride and cobalt. A correction for the sodium chloride 2θ degree location is appropriately made to the cobalt 2θ degree location. The corrected *d* spacing is then calculated for the lattice constant or constants of cobalt.

The amount of tungsten alloyed with the cobalt phase is calculated from the following linear relationship.

2θ	Cobalt Lattice Constant (Angstroms)	Tungsten in Cobalt (% by wt.)
51.82	3.544	0
51.74	3.550	5
51.68	3.554	8
51.60	3.560	13
51.44	3.570	21
51.28	3.580	29

Products of this invention show the cobalt line with the 2.06 spread out or with pronounced shoulders or even with multiple peaks. This indicates that there are multiple cobalt-tungsten alloys present with different concentrations of tungsten in solid solution. It has been observed that when at least some of the cobalt contains less than 8% tungsten the product has a low resistance to removal of cobalt with hydrochloric acid even though the average concentration of tungsten is well above 8% and even through the amount of alloy which contains less than 8% tungsten is a minor one.

If the tungsten is evenly distributed in the cobalt, all cobalt crystals have the same lattice constant and the upper portion of the line corresponding to a *d*-spacing of 2.06 angstroms is symmetrical about its peak or maximum height, as shown in Curve A of FIG. 1, and its breadth at half height is about the same as that of the nearby sodium chloride line as shown in Curves B and C of FIG. 1 which are symmetrical about a center line.

On the other hand when the 2.06 angstrom line of cobalt clearly consists of several peaks as in curves D and E of FIG. 1 it is evident that there are different regions in the cobalt which

contain two or more different levels of tungsten and thus have different lattice constants. In such instances, heterogeneity is obvious.

The small dimensions and even distribution of these heterogeneous regions is shown by cutting successive thin slices of the composition and showing that in each the cobalt shows the same heterogeneity in regard to tungsten content.

When the cobalt peak shows a shoulder as in portion *d* of the curve F of FIG. 1, as seen by comparison with the right side *a*₁ of curve F, the component peaks can be identified by inspection only after considerable experience, but may be more easily located by a simple graphical procedure: a dotted line *a*₂ is drawn to be symmetrical about the midline between the α-1 and α-2 peaks at 51.47° 2θ corresponding to a lattice constant of 3.568 angstroms. The X-ray radiation is not quite monochromatic and consists of two slightly different wavelengths which causes double peaks known as alpha-1 (α-1) and alpha-2 (α-2) for each *d*-spacing. The symmetrical curve *a*₁*a*₂ would be characteristic of cobalt containing a single homogenous concentration of 19 percent tungsten. However, the curve *d* which is above *a*₂, indicates that some portions of the cobalt also contain lower concentrations of tungsten. The difference in intensity at each angle, between curve *d* and *a*₂ is plotted as a difference, curve *bb*₁. A curve *b*₂ is now drawn symmetrical to the side *b*₁ about the line at angle 51.7°. Then a new curve *c* is drawn plotted as a difference between the lower portion of curve *d* and curve *b*₂. This new curve *c* is centered at 51.9°.

Thus, the curve *da*₁ can be empirically resolved into three component peaks centered at 51.47, 51.7 and 51.9 degrees. These peaks correspond to regions of cobalt containing 19%, 8% and 0% tungsten in the cobalt lattice, and the relative height of the peaks indicates the relative amounts of the different regions present.

This method was employed on three different samples of cobalt recovered from the same specimen of composition of this invention and the following observations were reported indicating the reproducibility of the method:

Sample	% Tungsten Present	Relative Peak Height
1st	19	100
	8	20
	0	9
2nd	19	100
	5.5	27
	0	15
3rd	19	100
	4	24
	0	12

Curve G of FIG. 1 is the X-ray diffraction intensity curve of the strong line of a different cobalt sample obtained from the same composition used for curve F, and graphically analyzed the same way, giving essentially the same results. Curve H of FIG. 1 is a similar graphical analysis of the cobalt peak of another product of this invention.

In curves I and K of FIG. 1, the position of component peaks can be seen by inspection. Where the range of heterogeneity is still greater as in J and L, while it is still possible to observe directly that numerous peaks are present, it becomes more difficult to identify them, and in M and N it is scarcely possible to say what components may be present.

The cobalt in compositions similar to those of this invention except that the distribution of tungsten is homogeneous, is ordinarily not sufficiently fine-grained to cause line broadening. Thus, the shape of the peak is similar to that of the sodium chloride line used for comparison. As the binder phase in the products of this invention is fine-grained the cobalt line in products of this invention is broadened, and the broadening is due to the presence of several component peaks with different *d*-spacings corresponding to different tungsten levels in the cobalt, i.e., heterogeneity.

We have devised means for analyzing these curves into component peaks, simultaneously taking into account the alpha-1 and alpha-2 components.

PROCEDURE B

The cobalt powder isolated by removal of the tungsten carbide as described above is mixed with an equal volume of sodium chloride, and prepared as an X-ray diffraction powder sample. The X-ray data is gathered by an automatic step-scanning diffractometer, using chromium radiation, and the intensity is recorded on a punched paper tape. The tape is then converted to punched cards which are processed using a digital computer. The entire section of the X-ray pattern is first corrected for the $K\alpha$ doublet broadening using the method described by Keating (Rev. Sci. Inst. 30, 752 (1959)). The corrected pattern then gives the instrumental broadening in the form of the (220) sodium chloride peak, as well as the observed (111) cobalt alloy peak. The limits of the sodium chloride peak are chosen as the points where the intensity dropped to the level of the background intensity. The limits of the cobalt alloy peak are chosen so that when the sodium chloride pattern is superimposed at the extreme ends of the cobalt peak, the maximum of the sodium chloride peak falls in the low intensity region of the cobalt peak. This is illustrated in FIG. 2 wherein 1 and 3 represent the superimposed sodium chloride peaks and 2 represents the cobalt peak.

The sample broadening curve is then computed for all data points between those defined by the two positions of the sodium chloride maximum described above.

The computer program first subtracts the background from both peaks. It then computes the sample broadening using a method similar to that described by Patterson (Proc. Phys. Soc. A63, 477 (1950)). The program uses three different schemes to minimize the residuals of the diffraction peak. In phase one, it selects the largest available residual, and reduces it by 10%. If the corresponding subtraction or addition of the instrumental peak reduces the sum of the squares of the residuals, the adjustment is accepted as part of the solution; if not, the step is reversed. In this and all other phases, the condition is imposed that the sample broadening curve may not be negative at any point. The points on either side of the maximum residual are then reduced by 10% if such reduction decreases the sum of squares of residuals. When no further improvement can be made by reducing the largest residual or its two neighbors, the program enters phase two, where each of the residuals is first increased, then decreased, in turn. If an adjustment produces a reduction in the overall sum of squares, it is made a part of the solution. If an improvement of the fit of the solution is achieved during this process, the program returns to phase one and begins again, if not, it goes on to phase three. This involves the simultaneous increase and decrease of adjacent pairs of residuals within the available range. If improvement is made in the solution, the program returns to phase one and restarts; if no further improvement can be made, it prints out the results.

In summary, the (111) cobalt alloy peak and the (220) sodium chloride peak are scanned, using chromium radiation. The diffraction pattern is recorded and processed by Keating's technique to remove the $K\alpha_2$ portion of the diffraction pattern. The sodium chloride peak is then used as an instrument broadening profile, and is employed to determine the nature of the sample broadening present in the cobalt alloy peak, using Patterson's method. The relaxation takes place in three stages: first, the maximum residual and its adjacent neighbors are reduced; when that is no longer effective, each of the residuals is reduced in turn; finally, adjacent pairs of residuals are increased and decreased simultaneously. This process then yields the profile which corresponds to the X-ray broadening of the cobalt-tungsten alloy, free of the effects of instrumental broadening.

To correct for instrumental errors, all calculated profiles are shifted to the angular position which would place the sodium chloride reference peak at its proper diffraction angle. The

resulting peak positions for the cobalt phase recovered from 14 cobalt-bonded tungsten carbide compositions are shown in FIG. 3, together with a plot of percent by weight of tungsten vs. peak position, and a histogram showing the number of peaks whose estimated ranges fall at a given point. The error range shown is $\pm 0.0125^\circ 2\theta$ for each peak and zero for the sodium chloride peak (not shown). These data are then replotted, adjusting the relative positions of the sample patterns within a range of $\pm 0.015^\circ 2\theta$, the estimated error in the determination of the sodium chloride peak position. The relative positions of peaks for a given sample are not changed, but are shifted as a unit. These data are plotted in FIG. 4, with the error estimate increased to $\pm 0.0175^\circ 2\theta$, together with the plot of tungsten concentration and the frequency histogram. As may be seen, a strong correlation in the peak spacing is now evident from the histogram.

These data are itemized in Table I, which lists the peaks for each sample, their indicated compositions, and the closest weight % of tungsten grouping in the histogram. These histogram groupings are summarized in Table II, stated in weight % of tungsten, and converted to atomic % of tungsten, together with possible atomic ratios. The occurrence of integral atomic ratios suggests the possibility of ordered structures at the various compositions. Such order would seem to be required to explain the segregation of composition in these alloys.

Of the 14 different compositions analyzed by the preceding procedure, and identified by the sample numbers 136C to 192C, it will be noted from FIG. 4 that 6 out of the 14 did not contain tungsten-cobalt regions giving peak positions greater than about $67.8^\circ 2\theta$, and which therefore contained no regions containing less than 8% by weight of tungsten in the cobalt. These six compositions are therefore not examples of compositions of this invention. One of these six, numbered 158C, corresponds to the composition represented by Curve A of FIG. 1. The remaining eight compositions are all heterogeneous, containing regions having less than 8% tungsten in the cobalt. Of these eight, number 184A corresponds to the composition represented by Curve D of FIG. 1, which is the composition of Example 4; 136C corresponds to Curve E of FIG. 1 and to Example 192C 184C corresponds to Example 5; 192C corresponds to Example 7; 192B corresponds to Example 8; and 192A corresponds to Example 9.

TABLE I

Sample	No. of Peaks	wt% W	Closest Group
136C	6	25.7 $\pm$.5	26.0
		21.2 $\pm$.5	21.5
		18.0 $\pm$.6	17.2
		12.0 $\pm$.7	11.4
		5.6 $\pm$.8	5.0
154E	6	2.1 $\pm$.9	1.5
		23.4 $\pm$.5	23.9
		21.6 $\pm$.5	21.5
		17.5 $\pm$.6	17.2
		14.5 $\pm$.6	14.3
158A	1	12.0 $\pm$.7	11.4
		5.4 $\pm$.8	5.0
		25.9 $\pm$.5	26.0
		21.5 $\pm$.5	21.5
		17.2 $\pm$.6	17.2
158B	4	13.8 $\pm$.6	14.3
		7.5 $\pm$.7	7.5
		23.9 $\pm$.5	23.9
		21.0 $\pm$.5	21.5
		23.6 $\pm$.5	23.9
158C	2	22.0 $\pm$.5	21.5
		26.2 $\pm$.5	26.0
		24.2 $\pm$.5	23.9
		22.0 $\pm$.5	21.5
		17.2 $\pm$.6	17.2
172B	2	11.3 $\pm$.7	11.4
		8.5 $\pm$.7	7.5
		5.2 $\pm$.8	5.0
		0.5 $\pm$.9	1.5
		26.4 $\pm$.5	26.0
184A	8	24.3 $\pm$.5	23.9
		21.8 $\pm$.5	21.5
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
184B	3	16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
184C	4	16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2
		16.4 $\pm$.6	17.2

		14.0±.6	14.3
		10.1±.7	11.4
		7.0±.7	7.5
184D	2	26.2±.5	26.0
		24.4±.5	23.9
184E	2	25.4±.5	26.0
		24.3±.5	23.9
192A	6	18.2±.6	17.2
		15.0±.6	14.3
		10.8±.7	11.4
		7.3±.7	7.5
		3.8±.8	5.0
		2.8±.8	1.5
192B	5	14.8±.6	14.3
		11.6±.7	11.4
		8.0±.7	7.5
		5.0±.8	5.0
		1.3±.9	1.5
192C	4	11.5±.7	11.4
		7.0±.7	7.5
		4.5±.8	5.0
		1.4±.9	1.5

TABLE II

wt % Group	At % W	Possible Atomic Ratio
26.0±.3	10.12±.15	1/10 (10.0%)
23.9±.3	9.15±.13	1/11 (9.09%)
21.5±.35	8.11±.16	1/12 (8.33%)
17.2±.4	6.24±.17	1/16 (6.25%)
14.3±.4	5.08±.16	1/20 (5.00%)
11.4±.4	3.96±.15	1/25 (4.00%)
7.5±.4	2.53±.14	1/40 (2.50%)
5.0±.4	1.66±.14	1/60 (1.67%)
1.5±.5	0.485±.16	1/180 (0.556%)

4. Utility

Some of the bodies of this invention are extremely dense, impact resistant, wear resistant, extremely hard, and are very strong. They are therefore suitable for use in the numerous ways in which such refractory materials are conventionally used. Some of the other uses to which the bodies of this invention can be put include cutting tools, drilling bits, as binders or matrices for other hard abrasives, and many other specific uses apparent to those skilled in the art.

Bodies of this invention are used in tools in which unusual strength is required in combination with high hardness. They are particularly advantageous in tools in which conventional cobalt-bonded tungsten carbide tools fail by flaking, chipping, or cracking, such as in tools for form cutting, cut-off, milling, broaching and grooving. Thus they find extensive use where, because of the inadequacies of cobalt-bonded tungsten carbide of the prior art, high speed steel tools are still employed.

Because of the unusual fine grain size, compositions of this invention are useful in tools where extremely small cross-sections are encountered, as for example in rotary tools smaller than an eighth of an inch in diameter such as end mills, drills and routers; knives having a cutting edge with an included angle less than about 30°; and steel-cutting tools which cut with high rake angles such as broaches, thread chasers, shaving or planing tools, rotary drills, end mills, and teeth for rotary saws. While the compositions of this invention containing more than about 12% cobalt are not stronger than compositions of this invention containing from 5 to 12% cobalt, nevertheless, the impact strength and toughness is higher. These are generally useful where tool steels are normally employed, and have the advantage of higher hardness than tool steels. For highest impact strength, compositions containing from 12 to 25% cobalt are employed, as in some dies and punches. However where a balance of impact strength and wear resistance is required, compositions containing 5 to 12% cobalt also find uses in dies and punches employed in operations involving high volumes and long production runs.

The products of this invention are further illustrated in the following examples wherein parts and percentages are by weight unless otherwise noted.

EXAMPLE I

This is an example of a composition of this invention in which a heterogeneous distribution of tungsten in the cobalt binder phase is produced by hot pressing a powder of very finely divided tungsten carbide and cobalt containing a very small amount of uniformly distributed, finely divided free carbon. The tungsten carbide employed is made as described in copending application, Ser. No. 772,810 filed Nov. 1, 1968.

By analysis this powder contains 93.4% tungsten, 5.95% total carbon, 0.14% free carbon and 0.46% oxygen. Thus there is 5.81% carbon bound in the tungsten carbide and the atomic ratio of chemically combined carbon to tungsten is 0.95.

The product gives the X-ray diffraction pattern of tungsten carbide and from the broadening of the X-ray lines, the average crystallite size is calculated to be 35 millimicrons. The specific surface area is 6.6 square meters/gram. Electron microscopic examination of the powder shows it to consist of porous aggregates of colloidal crystallites in the size range 20 to 50 millimicrons. The aggregates are mainly in the size range of from 1 to 10 microns, although some aggregates as large as 50 microns can be observed.

This material will hereafter be referred to as aggregated colloidal tungsten carbide powder.

Incorporation of the cobalt bonding phase is accomplished by milling the cobalt in powder form with aggregated colloidal tungsten carbide powder prepared as described above. To an 8 inch diameter one gallon steel mill the following are charged: (a) 14,000 parts of "Carboloy" grade 883 cobalt bonded tungsten carbide cylinders, one-quarter of an inch in diameter, and one quarter inch long, the rods being previously conditioned by tumbling for 2 weeks; (b) 1500 parts of the aggregated colloidal tungsten carbide powder prepared above; (c) 205 parts of a fine cobalt powder, having a specific surface area of 0.7 square meters per gram and a grain size of about 1 micron. This charge occupies about half the volume of the mill. Milling under acetone is continued for 7 days by rotating the mill at 45 revolutions per minute, after which time the mill lid is replaced by a discharge cover and the contents are transferred to a container maintaining an atmosphere of nitrogen throughout the system while this is being done. Three portions of acetone of 395 parts each are used to wash out the mill. The solids in the drying flask are allowed to settle and the bulk of the acetone is siphoned off. The flask is then evacuated and when the bulk of the acetone is evaporated, the temperature of the flask is brought to 125°C., maintaining a vacuum of less than a tenth of millimeter of mercury. After about 4 hours, the flask is cooled, filled with pure argon and transferred to an argon glove box. In this inert environment the solids are removed from the drying flask and screened through a 70 mesh sieve.

The screened powder is charged to shallow trays which are then loaded directly from the argon filled box to a five inch diameter Inconel tube furnace, where the powder is brought to 900°C. at a uniform rate in about 3 hours. The gas passing through the furnace consists of hydrogen, at a flow-rate of four liters per minute, with methane introduced at a flow-rate of 40 milliliters per minute. This treatment removes oxygen impurities, adjusts the carbon content and makes the powder less susceptible to reaction with air. The powder is held in this gas stream at 900°C. for 2 hours, then is cooled and passed through a 40 mesh per inch screen in an argon filled box. Samples are taken under argon for analysis.

The resulting heat-treated tungsten carbide powder is characterized by analysis as follows: tungsten 82.3%, total carbon 5.21%; free carbon 0.01%; cobalt 12.1%; oxygen 0.27%. The carbon content found by analysis corresponds to an atomic weight of combined carbon of 0.965 per atomic weight of tungsten. The free carbon is uniformly distributed throughout the powder as particles generally less than a micron in size.

Forty-five parts of the powder described above is charged in an oxygen-free environment to a cylindrical carbon mold and

close-fitting carbon pistons are inserted in each end. The mold containing the powder is pressed at 200 psi and is then transferred to a vacuum hot press. After evacuation the sample, under no pressure, is brought to 1420°C. by induction heating in 7 minutes and held at this temperature with no application of pressure for 5 minutes. During the heating the sample sinters and shrinks away from contact with the carbon surface, thus avoiding carburization.

Hydraulic pressure is then applied to both pistons and the pressure on the sample in the mold is brought to 4000 psi in a period of half a minute. The sample is subjected to a pressure of 4000 psi at 1420°C. for 1 minute at which time no further movement of the pistons is observed. The mold containing the sample is then ejected from the hot zone and allowed to cool to 800°C. in 2 minutes in the evacuated chamber of the press. After cooling to less than 100°C., the mold is removed from the vacuum chamber and a dense sample in the form of a cylindrical disc or billet, 1 inch in diameter and a quarter of an inch thick, is recovered.

The disc is cut into two segments, using a one hundred and eighty grit diamond saw, and one of the segments is further cut into bars 0.070 × 0.070 inches in cross-section for measurement of strength and hardness. The modulus of rupture of the hot pressed composition as measured by applying a load at the center of a span of 0.5 inches, is 566,000 psi, the Rockwell A hardness is 91.8. The density of the hot pressed body is measured as 14.60 grams per cubic centimeter which corresponds to a composition containing 9.5% of cobalt. The body contains no free carbon, indicating that the carbon particles have dissolved and reacted during hot pressing. The reduction in cobalt content as compared with the powder is due to the extrusion of some metal during fabrication.

The cobalt phase contains tungsten heterogeneously distributed, the tungsten content being about 17% and 7% in different regions as determined by procedure A, described above. Two different specimens of cobalt recovered from different portions of the interior of the billet are scanned by X-ray diffraction repeatedly at one-eighth of a degree per minute in the region of the strongest cobalt line. That cobalt line shows a main peak and a shoulder, and gives lattice constants in angstroms, as follows:

First sample: from peaks: 3.5650, 3.5646; from shoulders 3.5520, 3.5515. Second sample: from peaks 3.5646, 3.5643, 3.5646; from shoulders 3.5527, 3.5527, 3.5558, 3.5552. Average for peaks — 3.565; average for shoulders — 3.553. These values correspond to about 17 and 7% of tungsten in solid solution in the cobalt. The fact that both of these values are obtained on different samples from different parts of the billet tends to prove that the regions high and low in cobalt, respectively, are uniformly interspersed in the same way throughout the billet. Furthermore, the regions low in tungsten are apparently derived from the free carbon particles originally present, which dissolve and combine with the tungsten in the surrounding cobalt, forming tungsten carbide and leaving cobalt regions low in tungsten.

EXAMPLE 2

This is an example of a product of this invention made by blending a tungsten carbide which is deficient in carbon, with graphite powder and cobalt so that in regions surrounding the graphite, which mostly dissolves during hot pressing, the cobalt binder is low in dissolved tungsten while else where the carbon deficient tungsten carbide furnishes tungsten in solid solution in the cobalt binder.

Very finely divided tungsten carbide having a specific surface area of 7.1 square meters per gram is employed. It contains 5.77% total carbon and 0.06 free carbon, and thus the atomic ratio of combined carbon to tungsten is 0.93. It contains 1.41% oxygen. Three thousand six hundred parts of this tungsten carbide are mixed with 15 parts of powdered graphite which has passed a screen of 200 meshes per inch, and 500 parts of fine cobalt powder, and milled as in Example 1

for 5 days. The milled powder is dried, screened and reduced as in Example 1. The resulting powder contains 5.34% of total carbon, 0.02% of free carbon and 0.26% oxygen. Thus the atomic ratio of carbon to tungsten is 0.99, with the free carbon evenly distributed through the powder as particles of graphite of around a micron in size. This powder is hot pressed in a graphite mold as a billet 1.8 inches wide, 3.12 inches long and 0.6 inches in thickness.

The powder is compacted by pushing in the pistons at room temperature with a pressure of 400 pounds/square inch. The compact is then heated in the mold with no pressure applied for a period of 16 minutes, at which time the sample has reached 1390°C. A pressure of 4,000 pounds/square inch is then applied for 1 minute and the mold is then removed from the heated zone.

The resulting dense cobalt-bonded tungsten carbide composition is a very fine-grained, hard, strong material suitable for use as a cutting edge on tools used for high-speed cutting of ferrous alloys, especially in tools such as drills, reamers and form tools where conventional metal-bonded carbides are not strong enough and where tool steels are employed only at low cutting speeds. This use is made possible by the fact that the transverse rupture strength of this product is 540,000 pounds per square inch, which is almost twice that of conventional carbide tooling, and approaches that of tool steels, while the hardness is over 91, Rockwell A scale.

Examination of the microstructure shows that there are carbon particles at the polished surface 10 to 20 microns apart, on the average. These are from about 2 to less than 1 micron in size. These carbon particles are thus within a matrix of cobalt-bonded tungsten carbide in which there is an overall carbon deficiency. However, X-ray diffraction measurements, by procedure B described above, on the recovered cobalt phase show that some of the cobalt contains less than 8% tungsten in solid solution, whereas the remaining cobalt contains more than 8% tungsten. A low-tungsten region surrounds each grain of carbon. This is evidenced by the fact that near the carbon grains the tungsten carbide grains are larger than elsewhere, indicating there is no carbon deficiency in those regions and thus little tungsten in the cobalt in those regions.

EXAMPLE 3

This example describes the preparation of a dense body of tungsten carbide bonded with 12% cobalt possessing unusual high strength and hardness, having an extremely fine grain size and low porosity, and having a heterogeneous distribution of tungsten in the cobalt, made by preparing a very finely divided intimate mixture of cobalt and tungsten carbide powders, cold pressing and sintering under conditions to be described.

To a steel mill having a capacity of about one gallon and a diameter of 8 inches, are charged 14,000 parts of grinding cylinders one-fourth inch long and one-fourth inch in diameter of tungsten carbide bonded with 6% cobalt. The cylinders have been previously conditioned by tumbling in acetone in the mill for 2 weeks in order to wear off all sharp corners. This "pre-conditioning" is continued until the rate of wear under milling conditions is less than about 10 parts in 5 days when used to mill compositions of this invention.

Into the mill is also charged 1800 parts of fine commercial tungsten carbide powder, 2 parts of powdered graphite passed through a screen of 200 meshes per inch and 1450 parts of acetone. The fine tungsten carbide powder has a specific surface area as determined by nitrogen adsorption of 0.66 square meters per gram. By X-ray line broadening the average crystallite size is 370 millimicrons. Examination of the powder with an electron microscope reveals dense aggregates in the size of 2 to 10 microns, the aggregates being comprised of tungsten carbide grains in the size range from 0.5 to 2 microns, with an average of around ½ or 1 micron. Chemical analysis of this powder is 93.2% tungsten, 5.90% total carbon, and 0.31% of oxygen.

The charge occupies about half of the volume of the mill. Milling is carried out by rotating the mill at 45 revolutions per minute, the lid being tightly sealed to prevent loss of contents. Milling is continued for 48 hours. The mill is then permitted to cool and is opened. Two hundred and fifty parts of cobalt powder are added. The cobalt powder has a specific surface area of 0.7 square meters per gram and an average grain size of about 1 micron. The mill is closed and milling continued for 72 hours, at a rate of 45 rpm. The mill is then permitted to cool and the lid is replaced by a discharge cover and fitted with inlet and outlet connections so that the contents are transferred to a container maintained in an atmosphere of nitrogen throughout the operation. Three portions of acetone of 395 parts each are used to wash out the mill. The solids in the receiver flask are allowed to settle and the bulk of the acetone is siphoned off. The flask is then evacuated and warmed from the exterior to distill off the acetone and the temperature of the flask is brought to 125°C. after the distillation is completed. The contents are maintained at that temperature under a vacuum of less than a tenth of a milliliter of mercury for about 4 hours. The flask is then cooled and filled with pure nitrogen and transferred to a nitrogen filled glove box. In this inert environment the solids are removed from the flask and screened through a sieve having 70 meshes per inch to give essentially spherical pellets.

Analysis of the powder, which is maintained continuously under nitrogen is 5.15% total carbon, 0.09% free carbon, 0.46% oxygen, 12.76% cobalt and the remainder being tungsten. The specific surface area by nitrogen adsorption is 2.8 square meters per gram and the crystallite size of the tungsten carbide by X-ray diffraction is 80 millimicrons. The density of this powder when tapped in a container to maximum settling is 35 percent of the theoretical density.

This powder has an atomic ratio of combined carbon to tungsten of 0.97 and the free carbon is uniformly distributed throughout the powder as particles less than a micron in size.

Fifty-five parts of the powder described above is charged in an oxygen-free environment to a 1 inch diameter cylindrical graphite mold and close-fitting graphite pistons are inserted in each end. The mold containing the powder is pressed at 200 psi and is then transferred to a vacuum hot press. After evacuation the sample, under no pressure, is brought to 1400°C. by induction heating in 7 minutes and held at this temperature for 5 minutes. During the heating the sample sinters and shrinks away from contact with the mold surface, thus avoiding carburization.

Hydraulic pressure is then applied to both pistons and the pressure on the sample in the mold is brought to 4000 psi in a period of half a minute. The sample is subjected to a pressure of 4000 psi at 1400°C. for 1 minute, by which time no further movement of the pistons is observed. The mold containing the sample is then ejected from the hot zone and allowed to cool to 800°C. in 2 minutes in the evacuated chamber of the press. After allowing to cool to less than 100°C. the mold is removed from the vacuum chamber and a dense sample in the form of a cylindrical disc or billet, 1 inch in diameter and a quarter of an inch thick is recovered.

The resulting hot pressed billet has a transverse rupture strength of 545,000 psi and a hardness of 91.4 Rockwell A. Examination of the microstructure shows extremely low porosity, with an ASTM rating of A1. The cobalt distribution is extremely uniform, the tungsten carbide grains are substantially all smaller than 1 microns, are generally equiaxed, no eta phase is observed, and the mean grain diameter is 0.5 micron. The carbon content is 5.30 and the atomic ratio of carbon to tungsten is 0.96.

The cobalt recovered after removing the tungsten carbide contains 24 percent of tungsten, as determined by X-ray diffraction according to procedure A. The distribution of tungsten in the cobalt phase ranges from 7% to 29% with most at about 24% as measured by procedure B.

EXAMPLE 4

This is an example of a product of this invention prepared by the methods described in Example 1, except that the reduced powder which is hot pressed contains even more free carbon and the overall level of tungsten in the cobalt is less.

The tungsten carbide is similar to that employed in Example 1 except that it has an atomic ratio of combined carbon to tungsten of 1.0 and contains 0.26% by weight of free carbon. After milling with cobalt and reduction, it contains 0.07% free carbon and the atomic ratio of combined carbon to tungsten is 0.96; the cobalt content is 12.2 percent by weight. After being hot pressed, the dense product has a transverse rupture strength of 547,000 psi, a hardness of Rockwell A = 92.4, and contains 9.03 percent of cobalt and an atomic ratio of carbon to tungsten of 0.958; no free carbon is found. The acid resistance is low — about 15 hours. The distribution of tungsten dissolved in the cobalt phase is heterogeneous, regions being identified by procedure B as containing 26%, 23.9%, 21.5%, 17.2%, 11.4%, 7.5%, 5.0% and 1.5% of tungsten. No eta phase is present in spite of the relatively low average carbon content. By procedure A, regions averaging 22% and 6% tungsten in the cobalt phase are evident, but procedure B shows the value for the regions that gives these averages. Curve D of FIG. 1 reflects the analysis by procedure A, and sample 184A of FIG. 4 and Table 1 reflect the analysis by procedure B.

The billet is cut into cutting tool inserts for turning a high temperature alloy. Less chipping of the cutting edge is encountered than with standard carbide compositions of the prior art.

EXAMPLE 5

This is an example of the invention in which heterogeneous distribution of tungsten in the cobalt phase is effected by blending two lots of reduced tungsten carbide-cobalt powder, one containing more and the other less carbon than required to furnish consolidated bodies of superior strength. The reduced powders are prepared as in Example 1, the first powder is made from tungsten carbide containing 5.23 percent of total carbon, 0.06 percent free carbon and 1.18 percent oxygen, thus having an atomic ratio of bound carbon to tungsten of 0.85; the second powder is made from tungsten carbide containing 6.70% total carbon, 0.79% free carbon and 0.51% oxygen. Each powder contains 12.2% of cobalt. During the screening of the powders through a screen of 70 meshes per inch, the horizontal screen and attached receiving pan are vibrated in a direction parallel to the plane of the screen. The resulting screened powders are obtained in the form of spheres about 50 to 150 microns in size formed by aggregation of the much finer powder components. During the reduction step at 900° C., these spheres are slightly sintered and increase in strength so they can be tumbled in a mixer without breaking apart.

The first powder after reduction contains 4.54% total carbon, no free carbon and has an atomic ratio of carbon to tungsten of 0.85. When this powder is separately hot pressed as in Example 1, the resulting billet contains 10.96% cobalt and has an atomic ratio of carbon to tungsten of 0.83, a Rockwell A hardness of 91.9 and a transverse bending strength of only 404,000 psi.

The second powder after reduction contains 5.53 percent total carbon, 0.14% free carbon, and an atomic ratio of carbon to tungsten of 1.03. When separately hot pressed as in Example 1, it gives a billet containing 8.2 percent cobalt, 5.73 percent total carbon, and an atomic ratio of total carbon to tungsten of 1.02, a small amount of free carbon being present. The hardness is 92.0 on the Rockwell A scale and the transverse rupture strength is 375,000 psi.

To prepare a composition of this invention, 25 parts by weight of the first reduced powder and 75% of the second reduced powder are thoroughly blended by tumbling. This mixture is hot pressed as in Example 1 and gives a billet con-

taining 9.2% cobalt, 5.49% total carbon, an atomic ratio of total carbon to tungsten of 0.99, a hardness of 91.6 on the Rockwell A scale, and a transverse bending strength of 540,000 psi. The microstructure shows regions in which the grain size of tungsten carbide is less than 1 micron, interspersed with regions containing some coarse tungsten carbide two or three microns by 8 microns in cross-section. The latter coarseness is indicative of regions in which the atomic ratio of carbon to tungsten is about 1.0.

The acid resistance for this product is 18 hours. By analysis of the strongest X-ray diffraction line of cobalt, using procedure B, regions of cobalt are found to be present, containing 17.2%, 14.3%, 11.4%, and 7.5% tungsten, respectively. This heterogeneity is reflected in sample 184C of FIG. 4 and Table 1 which correspond to the composition of this example. By procedure A an average value of 14% tungsten in the cobalt is observed. A photomicrograph of a polished cross-section of the composition, etched lightly to reveal the tungsten carbide grains shows the presence of carbon particles in the structure. However, there are regions from 10 to 50 microns in diameter, comprising about a quarter of the area of a typical cross-section, that are free from carbon and in which the tungsten carbide grains are smaller than 2 microns. These are the portions of the structure which are derived from the carbon-deficient powder. At high magnification the carbon particles appear as irregular clusters, 1 or 2 microns in size, and in the regions of the cross-section where they are present, they are 10 to 30 microns apart. There are also pores in the areas containing free carbon, these being distinguished as separate rounded solid black areas, in these regions a substantial portion of the tungsten carbide grains are from 2 to 10 microns in size.

The composition is found to be not only very strong, but also very resistant to chipping under impact, being equal in this respect to many tungsten carbide bodies of the prior art which contain more cobalt, and thus have a hardness of less than $R_A = 90$. The composition is fabricated into an insert for a cut-off tool and used on a screw machine for cutting off stainless steel parts without chipping under conditions where most carbide tools of the prior art chip and break.

EXAMPLE 6

This is an example of the preparation of a product of this invention by starting with two different tungsten carbide powders, one containing more carbon than the other. The tungsten carbide powders are prepared in the same manner as that of Example 1, by incorporating different amounts of carbon in the synthesis. Both powders consist of porous aggregates from 1 to 10 microns in size, of colloidal crystallites of tungsten carbide about 40 millimicrons in average diameter.

The first tungsten carbide powder is low in carbon, the total carbon content being 6.07%. The powder contains 0.09% free carbon and 0.36% oxygen. The second tungsten carbide powder contains 6.19% total carbon, 0.12% free carbon, and 0.43% oxygen.

Equal parts of each of these two powders are ball-milled with sufficient cobalt powder as in Example 1 to provide a mixture containing 12.4% of cobalt. The resulting milled and dried powder is reduced also as in Example 1. The reduced powder contains 5.28% total carbon, less than 0.01% free carbon, 0.23% oxygen and has an atomic ratio of carbon to tungsten of 0.985.

A billet 1 inch in diameter and a quarter of an inch in thickness is pressed by the procedure described in Example 1, resulting in a very strong composition containing 8.61% of cobalt, 5.45% of carbon, and an atomic ratio of carbon to tungsten of 0.97.

The hardness of this composition is 92.0 on the Rockwell A scale, and the transverse rupture strength is 593,000 psi. The distribution of tungsten in the cobalt phase determined by procedure A (see Curve E of FIG. 1) shows the presence of regions containing approximately 20, 10 and 3% of tungsten.

The more sensitive procedure B shows that the major region containing an average of 20% tungsten is an average for regions containing 26.0%, 21.5% and 17.2%; the 10% region was 11.4%, and the 3% region is an average of 5.0% and 1.5% regions. The procedure B analysis is reflected in sample 136C of FIG. 4 and Table I.

The microstructure shows most of the tungsten carbide grains are under one micron in size and the average grain diameter is less than 1 micron. Regions about 10 microns in area and about 20 to 50 microns apart are present and contain coarser tungsten carbide grains up to 5 microns in size. No eta phase is present and no carbon particles evident in micrographs of polished sections.

The composition is converted into twist drills 0.060 inches in diameter and used for drilling electronic circuit boards without breaking.

EXAMPLE 7

This is an example of a composition of this invention in which the overall atomic ratio of carbon to tungsten is 1.0, but some regions contain free carbon while others are carbon-deficient. In the carbon-deficient regions there is 11.4% of tungsten dissolved in the cobalt phase, while in the carbon-rich regions less than 8% tungsten is found in the cobalt. A very finely divided tungsten carbide similar to that employed in Example 1 having a specific surface area of 9.2 square meters/gram, an atomic ratio of combined carbon to tungsten of 0.98 and containing 0.39% free carbon, is milled with sufficient cobalt powder to give a composition containing 12.3% of cobalt. This powder is then reduced as in Example 1 by heating at 900° C. in hydrogen containing methane. The heat-treated powder contains a total of 5.4% of carbon and the overall atomic ratio of total carbon to tungsten is 1.0. However, 0.08% of free carbon is present, so that the atomic ratio of combined carbon to tungsten is 0.99.

This composition is hot pressed as in Example 1 and gives a product containing 8.9 percent by weight of cobalt, having a transverse bending strength of 521,000 pounds per square inch and a hardness of Rockwell A = 91.9. The atomic ratio of total carbon to tungsten is 1.0. The cobalt phase contains an average of 7% of tungsten but, as determined by procedure B, different regions of cobalt contain 11.4%, 7.5%, 5.0%, and 1.5% respectively of tungsten. The analysis by procedure B is reflected in sample 192C of FIG. 4 and Table 1. No eta phase, Co_3W_3C , is present. The acid resistance of the composition is 12 hours. Microscopic examination of a polished etched section shows particles of free carbon less than 2 microns in size, from 30 to 80 microns apart. In the regions near the free carbon particles, there are tungsten carbide grains having cross-sections as large as 3 by 10 microns. In regions between the carbon grains and more distant from them, the tungsten carbide grains are, for the most part, smaller than about 1 micron, and have an average grain size of less than 2 microns. This composition is not as strong as others of this invention in which there are cobalt regions containing more tungsten, but nevertheless, its performance as a form tool on a screw machine cutting mild steel is superior to most compositions of the prior art which have the same overall chemical composition but which do not have the unique distribution of tungsten dissolved in cobalt. The form tool is also very resistant to chipping in interrupted cuts.

EXAMPLE 8

This is an example of a composition similar to that of Example 7, except that the powder mixture contains 11% of cobalt before being hot pressed. It is prepared from finely divided tungsten carbide similar to that employed in Example 1, containing 6.36% of total carbon and 0.33% free carbon, and has a specific surface area of 8.8 square meters per gram. The heat-treated, reduced cobalt-tungsten carbide powder composition also contains 0.09% of free carbon uniformly distributed throughout the mass as particles smaller than five

microns. The atomic ratio of combined carbon to tungsten is 0.985. After being hot pressed as in Example 1, the resulting billet contains 8.9% cobalt and an overall ratio of total carbon to tungsten of 0.99; the transverse rupture strength is 520,000 psi, the hardness 92.0 Rockwell A, and impact tests show that the material is very resistant to chipping. The cobalt phase is isolated and found to contain 8% of dissolved tungsten, which by procedure B is shown to exist in regions containing 14.3%, 11.4%, 7.5%, 5.0%, and 1.5% tungsten. Analysis by procedure B is reflected in sample 192B of FIG. 4 and Table I. The acid resistance is very low, 7 hours. A polished cross-section of a specimen shows the presence of regions high in carbon, about 3 microns across, these regions being on the average about 20 microns apart, the high carbon regions being characterized by the presence of free carbon and grains of tungsten carbide larger than 3 microns in size, while the intermediate regions are characterized by showing no free carbon and having a grain size smaller than 2 microns. This composition is used in fabricating a punch employed in a punch and die assembly for punching razor blades from steel ribbon. It is as chip-resistant as the standard compositions of the prior art containing from 15 to 25% of cobalt, but nevertheless is much harder and more wear resistant, giving two to five times the wear life of such prior art compositions.

EXAMPLE 9

This is a composition similar to that of Example 7, except that in the reducing step only two-thirds as much methane is employed in the gas stream and the reduced powder contains only 0.02% free carbon and an overall ratio of combined carbon to tungsten of 0.99. After being hot pressed, the composition contains 8.9% cobalt, the overall atomic ratio of total carbon to tungsten is 0.988, and there is no apparent free carbon in the composition. The transverse, rupture strength is 572,000 psi and the Rockwell A hardness is 91.9.

The overall concentration of tungsten in the cobalt phase is 9%, and by procedure B the tungsten is shown to be present in different regions containing 17.2%, 14.3%, 11.4%, 7.5%, 5.0%, and 1.5% tungsten respectively. The procedure B analysis corresponds to sample 192A of FIG. 4 and Table I. The acid resistance is about 15 hours. The material is very chip resistant and is employed in a punch similar to that described in Example 8.

EXAMPLE 10

This is an example similar to that of Example 3, except that more cobalt is added so that the composition contains 25% of cobalt. After cold pressing, degassing, sintering at 1300°C. for 5 minutes, and then cooling to below 800°C. in 5 minutes, a dense, pore-free billet is obtained having an overall atomic ratio of total carbon to tungsten of 0.99. The billet contains particles of free carbon about 1 micron in diameter, uniformly distributed over a polished cross-section, on the average about 30 microns apart. The cobalt binder contains an average of 15% of tungsten and by Procedure B it is shown that the tungsten is present in different regions at varied concentrations in the cobalt ranging from 26.0 to 1.5%. The transverse rupture strength is 625,000 psi, the hardness is 88 on the Rockwell A scale. The average grain size of the tungsten carbide is less than one micron. Although grains near the carbon particles range up to 5 microns, in intermediate regions they are smaller than 1 micron. The composition is very resistant to chipping and breakage by impact, and is employed as a knife having an included angle of 20° at the cutting edge, in shears employed for cutting steel sheet. The composition is much harder and more wear resistant than most compositions of the prior art having the same cobalt content and also it is much stronger in bending.

EXAMPLE 11

This is an example of a composition of the invention containing 6% of cobalt made by a procedure like that of Example

3. The body is sintered at 1450°C. for 10 minutes and is then cooled within 20 minutes to less than 800°C.

The milled and dried powder is kept from exposure to the atmosphere, while being cold pressed into $\frac{3}{4}$ inch square blanks, $\frac{1}{4}$ inch thick, on an automatic powder press maintained in a nitrogen atmosphere. The powder contains 0.04% free carbon uniformly distributed as particles from 0.5 to 2 microns in size throughout the mass and the atomic ratio of combined carbon to tungsten is 0.99. The sintered body has a carbon to tungsten atomic ratio of 0.98, a transverse rupture strength of 480,000 psi, and a hardness of 92.5 Rockwell A. A polished cross-section shows a microstructure containing uniformly distributed particles of free carbon about 1 micron in size, their distance apart ranging from 20 to 50 microns. The average grain size of the tungsten carbide is less than 2 microns. The cobalt phase contains an overall average of 18% of tungsten in solid solution which is present in different regions at concentrations which range from 23.9% to 5.0% of tungsten, respectively. The billets are converted to positive rake cutting inserts and are used for turning a nickel-based high temperature alloy.

EXAMPLE 12

The powder of Example 11 is hot-pressed in a manner similar to that described in Example 1 except that the maximum temperature is 1450°C. The cobalt content of the hot-pressed billet is 5.2%, the transverse rupture strength is 510,000 pounds/square inch, and the hardness is 93.0 on the Rockwell A scale.

The atomic ratio of total carbon to tungsten is 0.98 and free carbon is present as finely divided particles as in the product of Example 11. The cobalt contains an average of 15% of tungsten, present in varied regions having concentrations ranging from 5.0% to 21.5%.

This product is useful as a cutting tool insert similar to that of the product of Example 11.

EXAMPLE 13

This is an example of this invention in which two heat-treated and reduced powders, similar to those described in Example 5, are mixed. The powders differ not only in the ratio of carbon to tungsten, but also in cobalt content. Thus, the first powder is prepared from colloidal tungsten carbide similar to that of Example 1, except that it is more deficient in carbon, containing an overall atomic ratio of total carbon to tungsten of 0.93. This is admixed with cobalt to produce a composition containing 6% of cobalt, and is then ballmilled, screened on a vibratory machine to aggregate the powder in the form of spheres about 60 microns in average diameter, and reduced as in Example 1 at 900°C. The resulting powder contains no free carbon and the atomic ratio of total carbon to tungsten is 0.95.

A second powder is prepared identical with the second powder of Example 5, containing 12% of cobalt, an overall atomic ratio of total carbon to tungsten of 1.03, and containing 0.14% of free carbon in the form of particles smaller than 3 microns uniformly distributed through the mass. It is reduced at 900°C., as in Example 1. The reduced powder consists of small spherical aggregates of the same size as those of the first powder.

Equal parts of these two powders are thoroughly blended in a mechanical tumbler. The mixture is loaded into a graphite mold without compaction, and heated to 1400°C. over a period of about 20 minutes in a vacuum. At this point, 2000 pounds per square inch pressure is applied to a graphite piston compressing the powder into the mold for one minute. The mold and contents are then removed from the heated zone of the furnace and permitted to cool under vacuum, the temperature of the mold dropping to less than 800°C. in 15 minutes. The hot-pressed composition has a transverse rupture strength of 510,000 pounds/square inch and a Rockwell A hardness of 92.7, thus combining very high hardness with very high strength. The resistance to chipping is much greater for this

product than that of standard compositions of the prior art containing 9% cobalt, as shown by using milling cutter inserts of this material for face milling rough cast iron engine blocks. The cobalt binder on the average contains 20% of tungsten, which in different regions ranges from 5% to 25%. The atomic ratio of carbon to tungsten is 0.98. The microstructure examined in a polished cross-section indicates that the body consists of interpenetrating networks of regions low in cobalt and high in tungsten carbide, containing no free carbon, and regions high in cobalt and lower in tungsten carbide containing particles of carbon about one micron in size and about 10 to 30 microns apart. The overall cobalt content of the hot pressed body is 8.1%.

We Claim:

1. A dense body consisting essentially of tungsten carbide bonded with from 3 to 25% by weight of a heterogeneous cobalt-tungsten alloy, said alloy consisting essentially of cobalt and an average of from 5 to 25% by weight of tungsten, and said alloy comprising regions containing less than 8% by weight of tungsten interspersed with regions containing more than 8% by weight of tungsten, the difference between the percentages of tungsten in the varying regions being at least 1,

the body having a density in excess of 98% of its theoretical density.

2. A dense body of claim 1 bonded with from 8 to 12% by weight of heterogeneous cobalt-tungsten alloy.

3. A dense body of claim 1 in which the tungsten carbide is present as grains having an average diameter of less than 2 microns.

4. A dense body of claim 1 in which the tungsten carbide is present as grains having an average diameter of less than 1 micron.

5. A dense body of claim 2 in which the tungsten carbide is present as grains having an average diameter of less than 2 microns.

6. A dense body of claim 2 in which the tungsten carbide is present as grains having an average diameter of less than 1 micron, and the body has a density in excess of 99% of its theoretical density.

7. A tool for shaping metal having a cutting edge of a composition of claim 1.

8. A tool for shaping metal having a cutting edge of a composition of claim 6.

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