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3,525,610

## PREPARATION OF COBALT-BONDED TUNGSTEN CARBIDE BODIES

Geoffrey W. Meadows, Kennett Square, Pa., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 660,986, Aug. 16, 1967, which is a continuation-in-part of applications Ser. No. 582,924, Sept. 29, 1966, and Ser. No. 516,825, Nov. 24, 1965. Application Ser. No. 582,924 is a continuation-in-part of application Ser. No. 516,825, both being continuations-in-part of application Ser. No. 418,808, Dec. 16, 1964. This application June 4, 1969, Ser. No. 830,545

Int. Cl. C22c 29/00

U.S. Cl. 75—204

10 Claims

### ABSTRACT OF THE DISCLOSURE

Hard metal compositions of tungsten carbide bonded with from 1 to 30 percent by weight of cobalt-tungsten alloy are prepared by heating an intimate mixture of cobalt and tungsten carbide powder to a temperature above 1000° C. for a short time; then compressing the composition to a density in excess of 95% of its theoretical density; and then cooling rapidly the dense composition.

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my copending application Ser. No. 660,986 filed Aug. 16, 1967, now Pat. No. 3,451,791 which in turn was a continuation-in-part of my then copending application Ser. No. 582,924 filed Sept. 29, 1966 now abandoned and my then copending application Ser. No. 516,825 filed Nov. 24, 1965 now abandoned. My copending application Ser. No. 582,924 was a continuation-in-part of my copending application Ser. No. 516,825 and both of these were continuations-in-part of my application Ser. No. 418,808 filed Dec. 16, 1964 now abandoned.

### BACKGROUND OF THE INVENTION

This invention relates to a process for preparing hard metal compositions of tungsten carbide and cobalt comprising heating an intimate mixture of cobalt and tungsten carbide powders to a temperature above 1000° C. for a short time, compressing the hot mixture to a density in excess of 95% of theoretical and rapidly cooling the dense composition.

The products of the process 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.

It has been generally accepted, by those skilled in the cobalt-bonded tungsten carbide art, that it is not possible to achieve maximum hardness and maximum strength and toughness simultaneously in a single composition. It was commonly recognized that for greatest hardness the composition should contain a minimum of cobalt binder and have the finest tungsten carbide grain size. Conversely for greatest strength and toughness the composition should contain large amounts of cobalt. See Cemented Carbides by Schwartzkopf and Kiefer, Macmillan Co., 1960, page 137. Tungsten carbide grain size and cobalt content were the only two variables known to effect marked property changes in the compositions. See American Machinist, vol. 105 (12), p. 95.

More recently a further variable, the composition of the metal phase has come under study. H. Kubota, R.

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Ishida and A. Hara in Indian Institute of Metals, Transactions, vol. 9, pp. 132-138 (1964) pointed out that when tungsten carbide grain size is not very fine and when the carbon to tungsten atomic ratio is below theoretical, as much as 10% tungsten can be present in solid solution in the cobalt phase. Increased tungsten in the cobalt was correlated with increased transverse rupture strength, hardness, and fatigue strength of high cobalt compositions.

However, it was further substantiated by H. Kubota along with H. Suzuki that if the tungsten carbide grain size was smaller than 2 microns the presence of tungsten in the cobalt corresponds to a decrease in the strength of the compositions. See Planseherichte für Pulver metallurgie, vol. 14, No. 2, pp. 96-109, August (1966). That a tungsten carbide grain size of 2 microns is optimum is reported by others such as J. Gurland and P. Bardzil, Journal of Metals, February, 1955, pp. 311-315.

I have discovered however that cobalt-bonded tungsten carbide compositions can be prepared which have an outstanding combination of hardness, strength and toughness. Surprisingly, the bonded compositions prepared by the process of this invention must have a very fine tungsten carbide grain size with the mean grain size smaller than one micron and at least 60% of the grains smaller than one micron in diameter. It is also essential that the bonded compositions contain at least 8 percent by weight of tungsten in the cobalt phase and demonstrate a high resistance to removal of the metal binder with concentrated hydrochloric acid. The bonded products made by the process of this invention are generally characterized by having an un-annealed or quench-strengthened structure as shown by at least a 10% loss of transverse rupture strength at 30° C. when they are heated in a vacuum to 1400° C. at 100° C. per minute and immediately cooled to 700° C. at 5° per minute.

### SUMMARY

In summary, this invention relates to a process for forming cobalt-bonded tungsten carbide bodies and is more particularly directed to the preparation of cobalt-bonded tungsten carbide compositions in which the mean grain size of tungsten carbide is less than one micron and at least 60% of the grains are smaller than one micron in diameter; the cobalt binder is acid resistant and contains from 8 to 33% by weight of tungsten; the composition containing 1 to 30 percent by weight of cobalt and usually being further characterized by a loss of at least 10% in transverse rupture strength at 30° C. when heated in a vacuum to 1400° C. at 100° C. per minute followed by immediate cooling at 5° C. per minute to 700° C. The process is directed to preparing both anisodimensional and isodimensional tungsten carbide particles bonded with cobalt.

The process of this invention comprises intimately mixing from 1 to 30% by weight of cobalt powder with a tungsten carbide powder having an average particle size of less than one micron, a specific surface area of at least 3 square meters per gram and an atomic ratio of carbon:tungsten of more than 0.81 and less than 1.0; heating the mixture in an inert atmosphere at a temperature  $T_s$  between 1000° C. and  $T_h$  ° C. for from  $t_s$  to 20  $t_s$  minutes where

$$\log_{10} t_s = \frac{13250}{T_s + 273} - 8.2$$

and

$$T_h = \frac{6.5 - \log_{10} (P - 0.3)}{0.0039}$$

wherein P is the percent by weight of cobalt; compressing the mixed composition to a density in excess of 95%

of its theoretical density in a heated zone at a temperature of  $T_m$  for a time of from  $t_m$  to  $20 t_m$  minutes where

$$\log_{10} t_m = \frac{13250}{T_m + 273} - 8.2$$

and

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

wherein P is the percent by weight of cobalt; and then cooling the dense composition at a rapid rate.

The bonded compositions made by the process of this invention combine surprisingly high transverse rupture strength and toughness with extreme hardness and acid resistance to provide refractory materials of exceptional utility for cutting, drilling, shaping, punching or otherwise working very tough hard materials.

This invention is directed to a process for preparing dense cobalt-bonded tungsten carbide bodies. The process comprises intimately mixing finely divided cobalt with a uniformly fine tungsten carbide powder. The tungsten carbide powder should have a particle size of less than 1000 millimicrons and a specific surface area of 3 to 15 square meters per gram and should contain between 0.81 and 1.0 atomic weights of tungsten. After the cobalt and tungsten carbide powder is homogeneously intermixed it is heated to a temperature above  $1000^\circ \text{ C.}$  and is then consolidated to a density in excess of 95% of the theoretical density. When preferred starting powders are used, this process results in the preparation of anisodimensional tungsten carbide and under selected conditions the anisodimensional crystals are oriented in the dense product.

The cobalt/tungsten carbide compositions made by the process of this invention are referred to from time to time as interdispersions. This term is meant to describe a relationship of cobalt and tungsten carbide which includes traditional dispersions, in which there is a dispersed particulate phase and a dispersant continuous phase; traditional mixtures in which both phases are particulate or interrupted and homogeneously intermixed; and mixtures in which both phases are continuous and are interpenetrating into each other.

### STARTING MATERIALS

The starting materials suitable for use in this process are tungsten carbide and cobalt which have a requisite degree of purity and a sufficiently fine particle size as pointed out below.

#### Tungsten carbide

The tungsten carbide suitable for use in this process is a finely divided composition containing tungsten and carbon in a ratio corresponding to from 0.81 to about 1.0 atomic weights of carbon per atomic weight of tungsten and which can contain tungsten monocarbide and ditungsten carbide along with metallic tungsten or suitable materials serving as a subsequent source of metallic tungsten, such as a cobalt-tungsten alloy powder. Such powders can be reduced in particle size by grinding to disaggregated, discrete particles substantially all of which have a particle size smaller than one micron.

Commercially available tungsten carbide is generally prepared at high temperature and then ground to obtain a powder. In some instances the particles are as small as a micron in diameter. The finest tungsten carbide powders of commerce have a specific surface area of from 0.1 to 1.0 square meters per gram. Microscopic examination of such powders shows most of the material in the form of particles ranging from one to 50 microns in diameter, with a minor weight fraction of finer material which contributes disproportionately to the specific surface area.

By prolonged ballmilling of tungsten carbide powders, in which most of the particles are initially smaller than a few microns, in a fluid medium such as acetone or

alcohol it is possible to convert a portion of the tungsten carbide to particles less than 100 millimicrons in size. Such prolonged milling results in a wide distribution of sizes of particles which range from less than 10 to 1000 or more millimicrons in diameter. From this material, a fraction of colloidal size consisting of particles ranging in size from more than 10 to less than 100 millimicrons in size can be separated by controlled sedimentation. Such finely divided tungsten carbide is characterized by its freedom from coherent aggregates and by a range of particle sizes.

A suitable commercial tungsten carbide with a stoichiometric ratio of carbon to tungsten and a relatively uniform ultimate particle size of about 1 micron is Type 1 tungsten carbide sold by the Wah Chang Corporation. When ball-milled in acetone for from three days to a week by methods described hereinafter, this product results in a finely divided tungsten carbide having an average grain size of 0.1 to 0.2 micron with a specific surface area of 2 to 5 square meters per gram. This product can then be further milled in acetone with cobalt powder for several days and dried out of contact with air to give an interspersed cobalt/tungsten carbide powder which has a carbon to tungsten atomic ratio of between 0.99 and 1.0, some carbon having been lost in the milling and drying process.

Another suitable starting material is finely divided tungsten carbide consisting of colloidal particles admixed with a minor proportion of supercolloidal particles up to five microns in diameter. Such material produces tungsten carbide grains in the dense bodies made by the process of this invention which are isodimensional, i.e., the particles have approximately equal diameters in all three dimensions.

Such heterogeneous mixtures of colloidal and supercolloidal particles of tungsten carbide are prepared, for example, by prolonged ballmilling of a commercial tungsten carbide powder of initial particle size ranging from 0.5 to 5 microns and a specific surface area of about 0.5 square meters per gram, in an organic liquid medium such as acetone. Preferred grinding materials are hard balls or cylinders from 0.1 to 0.3 inch in diameter, made of dense cobalt-bonded tungsten carbide containing, for example, from 90 to 95% tungsten carbide and 10 to 5% by weight of cobalt. Milling of the heterogeneous mixture is continued until, without separating the colloidal fraction, the milled material has a specific surface area of at least 3 square meters per gram, although the mixture can still contain a proportion of tungsten carbide particles up to five microns in diameter. It is essential that the proportion of crystals larger than one micron remaining after milling is not too large, since during sintering and hot pressing these serve as nuclei which grow at the expense of the colloidal fraction to produce an undesirably coarse-structured, weak body. Generally speaking, to prepare colloidal tungsten carbide from commercial tungsten carbide powder for use in the present invention, it is necessary to mill the powder in a liquid medium until the specific surface area of the mixture is at least 3 square meters per gram and preferably until no more than 5 percent by weight of the milled material is larger than five microns. Most preferably, milling is continued until most of the particles are smaller than one micron.

A preferred tungsten carbide starting material for this process is that disclosed in copending application Ser. No. 772,810, filed Nov. 1, 1968. This tungsten carbide is in the form of crystallites of colloidal size, well under half a micron in diameter and typically 30 or 40 millimicrons in diameter, the crystallites being linked together in porous aggregates. It is prepared by forming and precipitating tungsten carbide from a reaction medium of molten salt. Such powder, after purification, consists of crystallites of uniform size, greater than 90% of them being between 10 and 60 millimicrons in diameter. The packing density of this powder is about 6 grams per cc. The crystallites are linked together into aggregates consisting of three dimen-

sional porous networks which are friable and permit the tungsten carbide crystallites to be readily broken apart by milling or grinding. Such grinding will produce fine fragments of the aggregates as well as discrete crystallites, of colloidal dimensions, with a packing density of about 9 grams/cubic centimeter. This disaggregated tungsten carbide is characterized by a specific surface area of from 3 to 15 square meters per gram and consists predominantly of ultimate crystals ranging from 10 to 60 millimicrons. Some of the crystallites are still linked as aggregates at this point but all such aggregates are less than half a micron in average diameter, and usually contain only a few crystallites of tungsten carbide. Such starting material produces anisodimensional tungsten carbide grains in the dense bodies made by the process of this invention under conditions set out hereinafter. The term anisodimensional means "not having equal diameters in all three dimensions."

As disclosed in my copending application Ser. No. 660,986 filed Aug. 16, 1967 anisodimensional tungsten carbide platelets are formed when very finely divided, very uniformly divided tungsten monocarbide powder, free from larger particles which may serve as nuclei for crystal growth, is heated to bring about recrystallization. The temperature required depends on the initial size of the tungsten carbide crystals and the amount of cobalt or other metal that is present. When essentially all the crystals of tungsten carbide in the starting powder are less than about 0.5 micron in diameter, and preferably when 90% of the crystals are between 10 and 60 millimicrons, recrystallization at high temperature results in the formation of platelets or other anisodimensional shapes of crystals. But if an appreciable amount of the starting tungsten carbide powder, such as 1 to 5% consists of crystals or fragments of crystals appreciably larger than the average size, such as those ordinarily obtained by grinding commercial tungsten carbide powder, then at high temperature, recrystallization occurs in such a way that the larger crystals grow as the smaller ones disappear, and since such larger crystals are not initially anisodimensional they grow more or less uniformly in all directions without becoming anisodimensional.

To obtain anisodimensional tungsten carbide platelets, it is thus preferred that the starting powder of tungsten carbide have a unimodal size distribution and contain less than 5 percent by number of crystals larger than 1 micron and most preferably less than 1 percent by number of crystals 0.5 micron or larger in size.

The composition of tungsten carbide powder can be established by the ordinary analytical procedures for tungsten, carbon and oxygen. It is desirable for the purposes of this process that the oxygen content of the dried powder be as low as possible, preferably lower than 0.5%, and that the combined carbon content should correspond to from about 80 to just slightly less than 100 percent of the theoretical value for tungsten carbide WC, of 6.12% carbon by weight. Powders having a carbon content of as low as 81% of theoretical for WC, can be used with an amount of 30% by weight of cobalt binder, but if less cobalt is employed, powders less deficient in carbon are much preferred. It is also important that essentially all the carbon be combined in the tungsten carbide lattice; no more than 0.3 percent and preferably less than 0.1% uncombined carbon should be present in the powder. Under some circumstances it is possible to include larger amounts of free carbon in the starting powder, but this increases the probability of leaving unreacted free carbon in the product, which is undesirable. The total carbon content ordinarily should not be so high as to cause the carbon content in the final composition with cobalt to exceed that theoretically required for the WC content.

The uncombined carbon content or free carbon content of tungsten carbide can be determined by dissolving the tungsten carbide in a 1:3 mixture of nitric and hydrofluoric acids which oxidizes and dissolves the tungsten carbide

but does not attack the free carbon. The solution can then be diluted and filtered through a Gooch crucible which is then washed, dried, and weighed. After weighing the crucible it is fired to remove the carbon and is then weighed again. The loss in weight on firing, after correction for any standard blank loss, is the weight of free carbon in the tungsten carbide sample. Alternatively the carbon is burned and the carbon dioxide is determined.

The packing density of tungsten carbide powder is determined as follows: About 15 grams of tungsten carbide powder is passed through a screen of 45 meshes per inch and loaded into a 0.5 inch diameter cylindrical cavity of a steel die fitted with two close-fitting, flat-ended steel pistons, one of which is inserted after the powder is loaded. The internal surface of the die and the surface of the pistons are previously lubricated by applying to them a 3% solution of stearic acid in carbon tetrachloride and permitting the solvent to evaporate. The powder is compacted in the die with sufficient pressure to apply a load of 9 tons per square inch on the powder. The pressure is maintained for one minute, then gently released over a period of 15 seconds. The compacted pellet is pushed from the die, weighed to the nearest hundredth of a gram and the height and diameter measured to the nearest thousandth of an inch. The packed density is calculated directly from the weight and dimensions of the pellet and expressed in grams per cubic centimeter.

The particle size can be determined by any of the methods familiar to the art. Thus in characterizing the tungsten carbide powders to be used in the process of this invention, the number average particle size can be determined by direct observation of electron micrographs. It can also be calculated from the specific surface area as determined by nitrogen adsorption data as described in "A New Method for Measuring the Surface Area of Finely Divided Materials and for Determining the Size of the Particles," by P. H. Emmett in "Symposium on New Methods for Particle Size Determination and the Subsieve Range," Philadelphia; American Society for Testing Materials, 1941, p. 95.

The various tungsten carbide particles involved in this process are microcrystalline and are readily characterized by X-ray diffraction analysis of the powders. Methods of characterizing such particles are fully explained in copending application Ser. No. 660,986 referred to above.

An estimation of particle shape can also be made by the X-ray diffraction method as described by J. Jirgensons and M. E. Straumanis in "A Short Textbook of Colloid Chemistry," second revised edition, published by the MacMillan Company, New York, 1962, page 256.

An estimate of crystallite size can be calculated from the line broadening of the X-ray diffraction lines as described by B. D. Cullity in "Elements of X-ray Diffraction," Addison-Wesley Publishing Co., Inc., Reading, Mass. 1959, pages 261 to 263.

The average crystallite size as determined by X-ray line broadening of the diffraction lines is less than the average diameter calculated from nitrogen surface area measurements and the magnitude of the difference is directly related to the degree of aggregation of the ultimate crystals. The more extensive the aggregation, that is the larger the number of intercrystalline bonds, the less surface available for nitrogen adsorption.

The nature and size of the colloidal tungsten carbide aggregates and anisodimensional grains is also ascertained directly by observation of electron micrographs for purposes of characterization, and can also be determined by sedimentation techniques.

#### Cobalt

Cobalt suitable for use in this process includes any source of cobalt metal which can be used to prepare an interdispersion of cobalt with tungsten carbide powder. Thus a form of cobalt readily suited for use in this process is cobalt metal in the form of a finely divided powder

which can, if desired, be further reduced in size by ball-milling with the tungsten carbide. Commercially available metal powders such as "Cobalt F" sold by the Welded Carbide Tool Co. are suitable. The metal to be used should be of high purity, preferably more than 99.5% pure cobalt, and should be free from any of the impurities known to be harmful to the properties of cemented tungsten carbide.

The amount of cobalt metal present in the powder mixtures used in the process of this invention, as previously stated, ranges from about 1% to about 30% by weight, a preferred amount of cobalt being from 3 to 30% by weight. Such cobalt levels produce very desirable compositions for cutting or forming metals such as steel.

A particularly preferred amount of cobalt powder mixtures used in the process of this invention is from about 3 to about 15% by weight based on the total weight of the composition. Such cobalt contents result in bodies which have a very desirable combination of strength, hardness and toughness and display great strength for a given hardness as compared to commercial cemented carbides.

### POWDER INTERDISPERSIONS OF COBALT TUNGSTEN CARBIDE

#### Methods of mixing the raw materials

The first step in the process of this invention can be the intimate mixing of cobalt and tungsten carbide powders to form a homogeneous cobalt/tungsten carbide powder interdispersion. This homogeneous interdispersion is then fabricated into dense cobalt-bonded tungsten carbide bodies.

In order to distribute cobalt homogeneously throughout tungsten carbide, extensive ballmilling is ordinarily employed.

For interdispersions containing only one or two percent cobalt, colloidal, milled tungsten carbide can also be interdispersed with cobalt by dispersing the tungsten carbide in a suitable fluid such as normal propyl alcohol, and mixing the dispersion with a dilute solution of a salt of the cobalt to be incorporated such as an alcoholic solution of cobalt acetate. Adsorption of the cobalt ions causes aggregation of the dispersed tungsten carbide, which can then be readily recovered and dried. Throughout the milling, purification, incorporation of the cobalt, recovery and drying, air should be excluded by maintaining an inert atmosphere of nitrogen or argon in the equipment. Following the above steps the mixture is reduced in hydrogen.

Another suitable method of interdispersion is that disclosed in my copending application Ser. No. 629,428 filed Apr. 10, 1967.

Preparation of powders containing more than 1% cobalt is best accomplished by milling fine tungsten carbide powder, preferably consisting of ultimate particles having an average diameter of less than 100 millimicrons, with a suitable cobalt powder in a liquid medium. It is preferred to use a mill and grinding material from which a negligible amount of metal is removed. It is generally preferred to use ballmills or similar rotating or vibrating mills. Suitable materials of construction for such mills are steel, stainless steel, nickel, or nickel-steel alloys. Mills plated on the inside with nickel or lined with cobalt-bonded tungsten carbide, are also satisfactory. 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 preferred. This can be in such 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 .01% loss in weight per day. Mill loadings and rotational speeds should be optimized as will be apparent to those skilled in the art. However, the proportion of charge to milling medium is preferably low, as illustrated in the examples which follow.

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 with the tungsten carbide powder charged to the mill. It is preferred to use non-aqueous liquids which are inert toward the highly reactive surface of the colloidal particles. A liquid medium which is 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. However, when more than two or three percent cobalt is present in the mixture it tends to minimize the attrition of the tungsten carbide. Thus, when higher cobalt levels are desired and 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. Accordingly, to produce a milled mixture of tungsten carbide and cobalt in which essentially all of the tungsten carbide particles are smaller than about one micron and the tungsten carbide has a specific surface area of greater than three square meters per gram, it is preferred to start with tungsten carbide particles no larger than about  $\frac{1}{2}$  to 5 microns and whose specific surface area is at least 0.1 square meter per gram, and preferably at least 0.5 square meter per gram. It is most advantageous to start with the preferred colloidal tungsten carbide disclosed in copending application Ser. No. 772,810, since it is not necessary to mill that tungsten carbide before it is milled with cobalt.

The carbon content can be adjusted to within the desired range by the addition of suitable amounts of finely divided tungsten, ditungsten carbide or carbon to the mill, as will be evident to one skilled in the art. For example, in certain instances where the tungsten carbide is not sufficiently deficient in carbon or contains a small amount of free carbon, it is necessary to produce a carbon deficiency in the composition by adding a small amount of suitable materials that will combine with carbon yet not leave an undesirable carbide in the product. Thus finely divided tungsten powder, preferably a micron or finer in particle size, can be added to the composition before milling. If only a small carbon deficiency such as an atomic ratio of carbon to tungsten of 0.99 or 0.97 is to be created, small amounts of other metals such as tantalum, niobium, zirconium or titanium can be used instead, but in determining the carbon to tungsten ratio in the final composition, the presence of small amounts of such added metals or their carbides must be taken into account in the analysis. The addition of such other metals to create an overall carbon deficiency is an alternative to the addition of tungsten. Of such other metals, tantalum is preferred because its carbide acts as a grain growth inhibitor and enhances hardness at high temperatures. For compositions in which the carbon content is outside the desired range, batches may be blended, preferably in the mill, to achieve the desired composition.

Milling of cobalt/tungsten carbide mixtures is continued until the cobalt is homogeneously interspersed with the finely divided tungsten carbide; most of the tungsten carbide is present as particles smaller than one micron; and the tungsten carbide has a specific surface area of at least 3 square meters per gram. The tungsten carbide can be analyzed and characterized by dissolving the metal with hydrochloric acid, and washing, and drying the tungsten carbide powder. 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 a vacuum, nitrogen or argon. It should be understood that the term inert atmosphere includes a vacuum or space filled with inert gas at low absolute pressure.

As the powder is being dried it goes through a sticky condition at which point it can be extruded or pelleted if desired. Formation of fine spherical pellets occurs if the slightly moist powder is passed through a 60 mesh screen and is gently shaken or rolled. A preferred form of powder made in this way consists of fairly uniform, spherical aggregates from 20 to 200 microns in diameter, depending on the forming conditions. These remain coherent even without addition of a binder or lubricant.

It should be noted that the very fine powder used in the process of this invention contains components in a substantially colloidal state of subdivision and is much more reactive toward oxygen than coarser tungsten carbide powders which are milled with cobalt under the same conditions. Thus milled compositions of the prior art are generally handled in the air without becoming hot or burning and are not seriously contaminated by exposure to the atmosphere. While the powders dried from the milled mixtures of the present invention do not always ignite spontaneously when exposed to air, they nevertheless rapidly absorb oxygen and form oxides.

When such powders are heated, the oxides react with tungsten carbide to form carbon monoxide which is evolved, leaving the composition with a lower atomic ratio of carbon to tungsten. Excessive oxidation can thus lead to excessive loss of carbon and produce bodies in which most of the cobalt is no longer present as metallic binder, but as the brittle eta phase,  $\text{Co}_3\text{W}_2\text{C}$ .

In one of the preferred aspects of the process of this invention, the dry powder recovered from the milling process is kept out of contact with the atmosphere and is subjected to the further process steps without a reduction or carburization treatment. This can be done only when the milled powder is sufficiently low in oxygen, (ordinarily less than one percent by weight); has the desired content of combined carbon; and contains no appreciable amount of free carbon, so that the resulting densified composition contains less than 1.03 atomic weight of carbon per atomic weight of tungsten. To produce products with most homogeneous structures, there should be no more than 0.3 percent by weight of free carbon in the powder, and less than 0.1 percent is preferred.

If the dried milled powder is to be precompact before being heated to above  $1000^\circ\text{C}$ ., it is preferred to degas the powder, removing volatile materials by heating the loose powder in an inert atmosphere, preferably a vacuum, at from  $400$  to  $700^\circ\text{C}$ . At these temperatures there is essentially no sintering and the subsequently cooled powder remains soft and easily compacted under pressure. This is a desirable step when the powder is to be isostatically compacted under a pressure of 5000 to 60,000 pounds or more per square inch, so as to avoid disruption of the compact by gases when it is subsequently heated.

For making compositions which have an atomic ratio of carbon to tungsten in the range from about 0.97 to slightly less than 1.0, it is especially important that the interspersed powder contain minimum oxygen and free carbon. For such products, 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. The powder can be in a molded or precompact state prior to this purification step.

Traces of oxygen as well as 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  $750^\circ$  to  $1000^\circ\text{C}$ ., depending on the metal content of the powder, in from three to five hours, taking half an hour to raise the temperature the last hundred degrees. For a cobalt content of about 1%,  $1000^\circ\text{C}$ . is used, and for powders containing 12% cobalt, the temperature is  $800^\circ$ – $900^\circ\text{C}$ .

The reducing gas should consist of a stream of hydrogen containing methane and about 10 percent of inert carrier gas such as argon. The proportions of methane to hydrogen are adjusted to provide a very slightly carburizing atmosphere at the temperature used, such that tungsten would be converted to tungsten carbide yet free carbon will be removed as methane. Thus, at  $1000^\circ\text{C}$ . the stream should contain 1 mole percent methane in hydrogen; at  $900^\circ\text{C}$ ., 2 mole percent methane; and at  $800^\circ\text{C}$ ., 4 mole percent 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.

Samples for analysis should be taken without contact with oxygen or air and sealed in suitable vials. In view of their reactive surfaces, and the necessity to avoid contamination with oxygen, the powders are subsequently handled without contacting the atmosphere. The capacity of the powder to absorb oxygen is considerably reduced by the reduction-carburization step, especially when conducted at  $900^\circ\text{C}$ . or higher, and such powders which do not absorb more than 0.5% by weight of oxygen when exposed to air may, in most cases thereafter be handled in the atmosphere.

Care must be employed to assure that in the reduction-carburization step an excess of methane is avoided so that no free carbon is introduced into the powder. It is to be noted that although the reaction conditions are such that tungsten metal would ordinarily be converted to tungsten carbide, nevertheless very finely divided tungsten carbide used in the process of this invention remains slightly deficient in carbon and is not carburized completely to a stoichiometric ratio for WC. It can be calculated from the density of tungsten carbide and the molecular weight, that a tungsten carbide powder having a specific surface area of 5 square meters per gram will have about 2 percent of the tungsten atoms on the surface. It is thus possible that a relationship exists between the small particle size of the tungsten carbide and its deficiency in carbon. It may be that each tungsten atom on the surface of these fine tungsten carbide particles combines on the average with less than one atom of carbon under the prescribed reaction conditions of the process of this invention. Hence the powder would contain slightly less than one atomic weight of carbon per atomic weight of tungsten.

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

Generally speaking, in making compositions of higher cobalt content, lower atomic ratios of carbon to tungsten may be employed.

Since the effect of the carbon deficiency is to allow tungsten to dissolve in cobalt which strengthens the metal binder phase and renders it acid resistant, the more cobalt binder in the composition, the more tungsten needed and

the lower the atomic ratio of carbon to tungsten desired in the composition. Generally, the carbon deficiency is preferred to be such as to provide at least about 12% by weight of tungsten in solution in the cobalt phase after hot pressing by the recommended procedures.

However, the minimum atomic ratio of carbon to 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 1.0. Thus, for making a composition containing 10% by weight of cobalt, for example, the minimum ratio is about 0.94 and excellent products are obtained with ratios ranging from 0.95 to more than 0.99. For making a body containing 30% cobalt, ratios of around 0.85 to 0.95 are preferred.

A preferred maximum ratio  $R_{\max}$  for most purposes is  $R_{\max} = 1.0 - 0.00166(P - 15)$  where P is percent by weight of cobalt.

Interdispersion of finely divided cobalt and very finely divided carbon deficient powders of tungsten carbide can also be prepared by suitable mechanical blending, followed by heat treatment, as described below.

It will, of course, be recognized by those skilled in the art, that, to the extent that mixed powders described above are commercially available, they can be obtained and used with the process of this invention comprising only the steps necessary to bring such commercially available powder to the condition required for use in this process.

#### Heat deactivation

One of the preferred embodiments of the process of this invention is the use of a cobalt/tungsten carbide powder in which the cobalt is alloyed with 8 to 25 percent by weight of tungsten, the tungsten carbide has a specific surface area of greater than 0.5 square meters per gram, and which is not highly reactive with the oxygen in the atmosphere.

Although powders which have been reduced at temperatures up to 1000° C. are considerably less reactive chemically, even they must be further heated to a somewhat higher temperature to deactivate them before sufficient pressure is applied to cause the composition to conform to a carbon mold. Some pressure can be applied as long as the composition is not pressed tightly against the walls of the graphite mold as it is being heated.

In the case of unreduced powders which have not previously been heated, it is possible to apply pressure while the composition is being heated in a non-carbonizing mold, such as one made from or lined with alumina, without the product becoming carburized. However, in such instances the evolution of gas within the body as it is being heated under pressure and the fragility of mold materials other than graphite, make it difficult to produce a pore-free strong body.

I have discovered that homogeneously interdispersed, carbon deficient, cobalt/tungsten carbide mixtures can be heat treated in an inert atmosphere or in hydrogen to inactivate them. The tungsten carbide in the powder interdispersion to be treated has a specific surface area of at least three square meters per gram; consists of crystallites or dense particles in the range from 10 to 1000 millimicrons in size; and contains from 0.8 to less than 1.0 atomic weights of combined carbon per atomic weight of tungsten. There should be present less free carbon than that required to raise the atomic ratio of carbon to tungsten to reach unity. Ordinarily free carbon content is maintained at less than 0.3%.

When this interdispersed powder composition is heated as prescribed, irreversible changes occur which result in the formation of a material which can be consolidated to dense bodies of exceptional strength and unusual resistance to removal of the metal by acid. The greater

strength and acid resistance is due to a change in the cobalt binder which occurs when the compositions are heated to a critical temperature, namely the formation of a solid solution of tungsten in the cobalt phase. Such properties are not developed, however, unless the starting powder has the required characteristics recited above.

During the heating process, the composition can be in the form of a loose mass of powder or a molded compact formed by a preconsolidation step. The term "preconsolidation" is used herein to mean that the powder is consolidated before this heating step, to distinguish such compacting operation from the later consolidation step which is carried out at higher temperature to form dense compositions. During the heating step, the composition undergoes some sintering and the mass of powder, or molded compact of powder, undergoes some shrinkage. Also in the range from 400° to 900° C. gases are evolved from the powder.

It is especially important that when the 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. At this stage of the process excessive compression appears to cause irreparable harm. This may be caused either by 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 arm also may be due to trapping of gasses 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.

It is most surprising that if the composition is previously heated to the prescribed temperature it can thereafter be consolidated to density and molded by hot pressing in a carbon mold without absorbing undesirable amounts of carbon. I have found that after the tungsten has dissolved in the solid cobalt phase during the heat treatment it is much less readily carburized.

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

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

and

$$T_h = \frac{6.5 - \log_{10} (P - 0.3)}{0.0039}$$

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 1200° C., the time should not exceed about 20  $t_s$ . For example, at 1000° C., it is necessary to heat for at least 2½ 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 two hours; at 1400° C. the hold time is less than 10 minutes, and at 1500° C. it is less than 4 minutes.



It is of course preferred to heat to a temperature  $T_s$  intermediate between  $1000^\circ\text{C.}$  and  $T_h$  and for a time that is convenient. Thus heating at around  $1200^\circ\text{C.}$  is preferred. However, the temperature  $T_s$  that is selected and the rate of heating depends on the physical nature of the composition being heated. When the composition is a powder of finely pelleted material which is to be heated with minimum cohesion so that it can be used for subsequent molding, a slow heating rate such as  $100^\circ\text{C.}$  per hour to  $900^\circ\text{C.}$  and then  $50^\circ$  per hour to  $1150^\circ\text{C.}$  and a minimum heating temperature is preferred. In such instances an extended heating period is acceptable as the transfer of tungsten into the cobalt phase must be effected at as low a temperature as possible to avoid sintering the powder and to avoid formation of eta phase. On the other hand, if a preconsolidated composition is employed, it can be heated more rapidly and to higher temperature, requiring a shorter hold time.

When a powder which has not been heat-treated is pressed in a graphite mold by applying pressure above  $1000\text{ p.s.i.}$  at  $1000^\circ\text{C.}$  and continuing the application of pressure while the temperature is raised to  $1400^\circ\text{C.}$ , and then cooled rapidly, the dense body produced is no stronger or more resistant to acid than conventional tungsten carbide bodies of similar metal content. It has become carburized. However, if the powder is first heat-treated as described above, and then molded in the above way, a very strong acid-resistant product is obtained. Such a product has not become carburized during the pressing operation.

Heat-treatment of conventional powders of tungsten carbide and cobalt which fall outside of the limits prescribed by this invention such as particle size or carbon content, does not impart to such powders any advantage over the same materials lacking heat treatment and when heat-treated conventional powders are densified, only conventional properties are obtained.

It should be noted that the temperatures and times required to bring about the irreversible change in the compositions made by the process of this invention 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  $1200^\circ\text{C.}$ , 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.

#### PREPARATION OF CONSOLIDATED BODIES

Consolidated bodies are prepared from the inter-dispersed cobalt/tungsten carbide powders described above. A preferred method of fabrication is by hot pressing the foregoing powders in the manner described below.

Various types of hot pressing equipment are known in the art and have been described in various publications. Especially suitable is the equipment described in U.S. application Ser. No. 750,360 filed Aug. 5, 1968.

Depending on press design and desired operating characteristics, heating can be by resistance heating, dielectric heating, heating by hot vapors or gases, induction heating, or plasma torch heating. Extremely short heating times of a few seconds duration are attainable, by "resistance sintering under pressure," as described by F. B. Lanel, Trans. Amer. Inst. of Mining & Met. Eng., 158, 203 (1955), but such a technique is most applicable only to relatively small pieces.

Temperature can be measured very near the sample itself by means of a radiation pyrometer and 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. Thermocouples, properly selected for the desired temperature range, can also be used, but pyrometers, even though somewhat less accurate, are more dependable and have vastly superior life.

The mold can be of a variety of shapes but is usually cylindrical, with a wall thickness of up to an inch or more. A round cross-section gives greater strength than square or other shapes. 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 diameter finished pressed round disc, the shell is cylindrical, 1 inch inside diameter,  $1\frac{1}{2}$  inches outside diameter, 4 inches in length. Thin graphite discs  $\frac{1}{4}$  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 small depression 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 then loaded in both ends of the cylinder in contact with the  $\frac{1}{4}$  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 an inert 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 a mold removed from the furnace at  $1850^\circ\text{C.}$  cools to dull red heat, about  $800^\circ\text{C.}$ , in about 3 minutes. The cooling rate in an inert gas atmosphere is somewhat greater than in a vacuum, due to convection losses, but most of the heat loss is by radiation at the temperatures involved. The importance of rapid cooling in obtaining products of maximum strength will be further explained.

To avoid excessive oxidation leading to undesirable carbon deficiency, especially with powders not preheated or reduced, the powder should be loaded to the mold in a non-oxidizing atmosphere, preferably 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 and more uniformity.

In a preferred aspect of this process, a cobalt-colloidal tungsten carbide powder is pressed at about 200 p.s.i. when it is loaded into the mold, is brought to the maximum temperature with no pressure on the pistons, and is 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 has attained 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 five minutes or less.

The precise conditions should be established for a particular composition and the type of structure desired before the cycle is begun. Unduly long presintering times 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 because it brings the body into prolonged contact with the graphite mold causing carburization. Also in the case of bodies containing anisodimensional crystals of tungsten carbide, early application of pressure tends to prevent orientation. Holding the sample for too long a time at maximum temperature should also be avoided, not only because of carburization but also since secondary crystallite growth tends to cause a coarsening of the structure and eventually the development of porosity. Cooling too slowly can also be detrimental, since the sample remains at high temperature long enough for undesirable crystallite growth and structural changes to occur. This includes 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 a third of the cobalt converted to eta phase.

While it is preferred that the process of this invention consist of heating and sintering lightly compacted finely divided tungsten carbide-cobalt 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 molds can then be removed from the furnace and permitted to cool, still under an inert atmosphere. Subsequently these sintered bodies can be hot pressed. Preferably, the mold and its partially sintered contents, while still hot, can be passed directly into a hot pressing operation, since this avoids heating the bodies twice.

Still another fabrication variation is employed to obtain "irregularly" oriented structures which contain a network of cobalt-rich veins. For this variation the starting powder after reduction is pressed under 200-500 p.s.i. and then sintered to a point at which there is slight fusion of the aggregates, but short of complete fusion. At this point the body is relatively strong and coherent, the aggregates having been sintered until they are essentially non-porous, there still being pores in the body between the aggregates. This structure is then hot pressed at maximum allowable temperature under controlled pressure, squeezing cobalt into voids to form, as the pressure is increased, a network of cobalt-rich veins running around and between areas of orientation. Pressing should not be continued, since this squeezes the meal out of the veins.

It should be emphasized that the degree of sintering, where the sintering step is carried out as a separate operation, is very important, and over sintering will produce a powder or a partially sintered body in which the tungsten carbide crystals have grown together into a continuous tungsten carbide network which can be further

molded or shaped only with difficulty. It is for this reason that one of the preferred aspects of the process of this invention involves simultaneous sintering, recrystallization to platelets and orientation of the platelets in a preferred direction while the mass is being molded to its final dense, non-porous form.

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 to be pressed are conveniently subjected to a temperature of  $T_m$  for a period of  $t_m$  to  $20t_m$  minutes, where

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

and

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

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

Thus, for compositions containing 6% cobalt it is about 1450° C., and for compositions containing 12% cobalt, it 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 preheated 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 where the atomic ratio of carbon to tungsten is 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 samples 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 30 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 1 to 3 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 three to fifteen percent cobalt the required pressure can also vary according to the physical nature of the composition. Thus if a sintered powder composition of the invention, which has been heat-treated at a temperature  $T_s$  close to the maximum allowable temperature  $T_m$  is used, a high pressure



such as 4000 p.s.i. is preferably applied over a prolonged period, such as 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% of the 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 free from macropores, and 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  $T_m$ .

The final products require application of pressure at the defined maximum temperature,  $T_m$ , to eliminate voids. In such instances the consolidation is carried out preferably until the pressed body reaches a density of 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 pressed bodies 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, the final bodies are preferably pressed until a porosity rating of A-1 is obtained especially where the material to be subjected to heavy impact or compression. This corresponds to a density of essentially 100% of theoretical or a volume porosity of 0.1%. However, porosities as great as A-5 are suitable for some uses, since such bodies nevertheless have very high transverse bending strength. This latter rating corresponds to a density of about 98% and a porosity of around 2%.

Pressures of from 500 to 6000 p.s.i. can be used in graphite equipment, but generally speaking not over 4000 p.s.i. 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.

Another procedure which permits very efficient utilization of a hot press involves use of the sintered or heat-treated powder composition as described above in which tungsten is dissolved in the cobalt phase. Such powder is ordinarily heat-treated in a separate furnace and then stored ready for use. It is loaded into a graphite mold, pressure is applied at a convenient temperature such as 800° to 1000° C. and application of pressure is continued as the temperature is raised as rapidly as practicable to the prescribed maximum. The prescribed maximum temperature and the pressure are maintained for the minimum time required to eliminate porosity in the body, but for not over 20  $t_m$  minutes, and the consolidated body is then removed from the hot zone. This procedure requires a minimum of time in the hot press and has the further advantage that the pressure is applied over a longer period of time, resulting in lower porosity.

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 can be further shaped by bending, swaging or forging at about temperature  $T_m$  in an inert atmosphere. Similarly, pieces can be welded together by bringing two clean surfaces together under pressure.

When the bodies have been hot pressed, they are removed from the hot zone of the furnace and allowed to cool. The surroundings are at ordinary temperature and the body cools from white heat very rapidly to dull red heat in a minute or so, and is below 700° C. in less than

five minutes. As stated previously, the cooling rate may be as rapid as around 300 degrees per minute.

I have found that if the body is left in the furnace and cooled at 5 degrees per minute from 1400° to 700° C., the transverse rupture strength of the cooled product is appreciably less than that of an otherwise identical product which was cooled more rapidly. Preferably it is cooled at a rate faster than 10 degrees per minute. The difference in strength is at least 10 percent. Part of the outstanding strength of the product produced by the process of this invention is therefore due to the fact that it is always cooled rapidly. Such a product is said to be "unannealed" or "quench strengthened." If a product is cooled slowly or "annealed," its strength can be brought back up to normal by reheating and cooling rapidly as described above.

Such rapid cooling, particularly in the range above about 1300° C. is most essential for compositions which are especially susceptible to grain growth, namely those having an atomic ratio of carbon to tungsten greater than 0.99.

Additional methods of fabrication are of course suitable to achieve a high degree of orientation for anisodimensional tungsten carbide platelets. These include orienting the platelets after fabrication such as by hot swaging, and orienting the platelets during fabrication such as by hot extrusion.

Thus when the crystallization of the colloidal tungsten carbide powder admixed with metal has reached the point where platelets are present, the latter may be oriented in a preferred direction by subjecting the plastic mass to shearing forces. For example, the hot plastic mass in the form of a cylindrical billet can be flattened by pressing the billet between two flat surfaces. When the heat softened mass of metal and anisodimensional tungsten carbide is thus flattened, the anisodimensional platelets, particularly those half-way toward the periphery of the flattened mass, are substantially oriented with their faces perpendicular to the pressing direction.

Alternatively, extrusion of the heat-softened mass through an orifice by exerting pressure on the mass with a piston, causes the anisodimensional tungsten carbide platelets to align themselves parallel to the direction of extrusion and parallel to the axis of the extruded mass. Thus a cross-section of the extruded mass, taken perpendicular to the axis of the extruded mass will show the edges of the platelets with their faces parallel to the line of the central axis of the extruded mass. Similarly, if a hot billet of metal-bonded anisodimensional tungsten carbide is flattened by rolling, there will be an orientation of the platelets parallel to the direction of elongation.

The particular method selected for bringing about the orientation depends upon such factors as the metal content of the composition. Compositions containing about 10% or more of metal can be oriented by extension, and those containing more than about 25% of metal can be oriented by hot rolling, providing not too great a reduction in thickness is attempted per pass. The degree of orientation in extruded rods may be further improved by swaging, particularly in compositions containing more than about 20% metal. Other methods of obtaining orientation are by hot forging or hot coining.

It is important that orientation be accomplished before tungsten carbide recrystallization has proceeded to a stage in which the platelets have grown together into a rigid, three-dimensional network of tungsten. Subsequent deformation of such a mass during molding tends to cause fracturing of the carbide network reduces the strength of the final body. In some instances, the platelets in the network can be broken apart sufficiently to be oriented, but if recrystallization has been essentially completed, the oriented platelets do not grow together into a new network. In compositions where recrystallization to platelets has been completed, the mass may be broken

up and reduced to a powder that will pass a screen of 100 meshes per inch, and then mixed with more of the original powder that has not yet been heated; the mix can then be heated and molded before the added powder has completely recrystallized.

The products which are produced by the process of this invention can be characterized in a number of ways as disclosed in my copending application Ser. No. 660,986 filed Aug. 16, 1967. The products have an unusually desirable combination of hardness and strength. Hardness of the products can be determined by any of the procedures well known to the art. For the determination of strength I prefer a modification of a measurement transverse rupture strength.

For the latter measurement I use a modified twenty kilogram Ohaus triple beam balance for measuring transverse rupture strength at room temperature of  $0.055 \pm 0.005$  inch square bars about 0.75 inch long. The sample bars are supported on 0.25 inch diameter, round, cobalt-bonded tungsten carbide rods embedded in a steel block. These are spaced with a span of 0.5 inch, and are supported on the pan of the balance. The cross head consists of a round, cobalt-bonded tungsten carbide breaker rod,  $\frac{3}{32}$  inch in diameter. The breaker rod is rigidly held in contact with the mid-point of the test bar by a saddle above the sample. The load is applied by running lead shot into a bucket suspended on the balance arm until the sample breaks, the maximum load being reached in approximately 20 seconds. The load is calculated from the weight required to break the sample and the mechanical advantage of the balance beam.

The transverse rupture modulus, in pounds per square inch, is calculated from the following formula:

$$R = \frac{3We}{2bd^2}$$

where:

R=modulus of rupture in pounds per square inch  
W=total load in pounds at which the specimen fails  
e=distance between the supports in inches  
b=width of the specimen in inches  
d=depth of specimen in inches

#### UTILITY

Some of the metal-bonded tungsten carbide bodies produced by the process of this invention are extremely hard and strong.

For example, anisodimensional platelets of tungsten carbide 0.05 to 2 microns in thickness and from about 0.2 to 10 microns in breadth substantially oriented in 10 percent by weight of cobalt, based on the weight of the total composition, said orientation obtained by hot-pressing in accordance with the methods previously disclosed, exhibits a hardness of 91.5 Rockwell A and a transverse bending strength in a direction parallel to the direction of the tungsten carbide platelets of about 550,000 p.s.i.

Some of the bodies produced by the process of this invention are extremely dense, impact resistant, wear resistant, extremely hard, resistant to attack by acids, and are very strong. They are therefore suitable for use in the numerous ways in which such refractory materials are conventionally used.

For example, anisodimensional tungsten carbide bonded with cobalt and having a random or non-oriented structure is particularly suitable for such uses as anvils in high temperature and high pressure synthesis such as diamond synthesis.

Some of the other uses to which the bodies produced by the process of this invention could be put include acid resistant valves, parts for pumps handling corrosive liquids, cutting tools, drilling bits, as binders or matrices for other hard abrasives, and many other specific uses apparent to those skilled in the art.

For example oriented structures of anisodimensional tungsten carbide platelets from .05 to 1 micron thick and from .2 to 4 microns long bonded with 8 to 15% cobalt are particularly effective for use in metal removal such as form cutting, cut-off, milling, broaching and grooving.

Bodies produced by the process 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 fails by flaking, chipping, or cracking. 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 produced by the process 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 compositions containing more than about 15% cobalt are not stronger than compositions containing from 8 to 15% 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. For highest impact strength, compositions containing from 15 to 30% cobalt are employed, as in dies and punches.

In order to more fully illustrate the invention the following examples are given wherein parts and percentages are by weight unless otherwise noted.

#### EXAMPLE 1

Twenty-two thousand seven hundred parts of calcium chloride are melted and brought to 985° C. in a carbon crucible, maintaining an atmosphere of argon in the system. To the melt, continuously agitated with a carbon stirrer, are added, simultaneously through separate hoppers attached to the head of the reactor, charges of (a) 243 parts of a blended mixture consisting of 230 parts of tungstic oxide and 13 parts of carbon having specific surface areas of 5 and 340 square meters per gram, respectively pre-fired for 4 hours at 750° C. under argon to remove water, and (b) 120 parts of pure granulated calcium metal. The charging hoppers are fitted with a double valve system, to exclude the atmosphere when introducing the reactants. Twenty additions of each of the materials (a) and (b) are charged at 3 to 4 minute intervals over a period of 1.5 hours, the temperature being maintained in the range between 990–1000° C. After the addition of all the reactants, the melt is maintained at temperature, with stirring, for a further twenty minutes, and is then drained from the carbon crucible into an Inconel bucket, maintaining an atmosphere of argon throughout, and allowed to solidify and cool. The solid cake, which has contracted away from the walls of the bucket, is removed and divided into two portions. The dark layer at the bottom of the solid cake is rich in tungsten carbide, whereas the upper, lighter gray portion is low in tungsten carbide, and contains considerable amounts of free carbon and oxide. The lower portion of the solid cake is broken into coarse pieces which are charged to a polyethylene tank and 23,000 parts of water are then added. The pieces of salt cake are leached by continuously agitating the water in the tank and adding ice as necessary to keep the temperature below 85° C. When the initial temperature rise due to hydration is complete, concentrated hydrochloric acid is added in 1200 part increments. As the cake disintegrates, dissolves, and reacts, the pH decreases from strongly basic to acidic values. Because of the high salt concentration in the slurry, actual pH values are higher than those which are measured. Sufficient acid is

added to lower the pH to slightly less than one. When a pH of one is achieved and maintained, with continuous agitation, for 15 minutes, the stirring is discontinued and the salts are allowed to settle. The supernatant liquid is siphoned off and the sludge washed through a 100 mesh screen into a second polyethylene tank. Material retained on the screen is discarded and the sludge is diluted to about 38,000 parts with distilled water having a pH between 6 and 7 and a specific resistivity greater than 100,000 ohms per centimeter, and the resultant slurry is agitated for 15 minutes. More hydrochloric acid is then added until the pH is finally stabilized at 3, in the well-stirred slurry. The stirring is discontinued, the solids are allowed to settle and the supernatant liquid is siphoned off, as before. The washing operation is repeated until the specific resistivity of the stirred slurry is between 2500 and 5000 ohms per centimeter, which requires five washings. After removing the final supernatant liquid, the aqueous sludge is diluted with an equal volume of acetone, the solids are allowed to settle, and the supernatant liquid is decanted. The washing of the sludge with acetone is repeated three times. The acetone-rinsed sludge is transferred to shallow metal trays and the acetone is evaporated in a vacuum oven using a purge of pure nitrogen. After the bulk of the acetone is evaporated, the trays are heated to 80° C. to completely dry the powder. The oven is cooled to 40° C., filled with nitrogen, and the dried product is removed and screened through a 100 mesh sieve. Three thousand two hundred fifty parts of tungsten carbide powder are recovered, corresponding to an overall yield of 84% of theoretical.

By analysis this powder contains 93.5% tungsten, 6.05% total carbon, less than 0.1% free carbon and 0.3% oxygen.

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 31 millimicrons. The specific surface area is 7.1 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 bonding phase is accomplished by milling the bonding metal in powder form with tungsten carbide powder. To an 8 inch diameter, 1 gallon steel mill the following are charged: (a) 14,000 parts of "Carboly" grade 883 cobalt bonded tungsten carbide rods, ¼ inch in diameter, and ¼ inch long, the rods being previously conditioned by tumbling for two weeks; (b) fifteen hundred parts of the aggregated colloidal tungsten carbide powder prepared above; (c) 205 parts of Cobalt F, a fine cobalt powder having a specific surface area of 0.7 square meters per gram and a grain size of about 1 micron; and (d) 1185 parts of acetone. This charge occupies about ½ 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 under a nitrogen atmosphere. 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 a 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.

As an alternative, the mill lid can be replaced by a

cover attached to a vacuum system with condensing trap and the acetone is removed under vacuum at a temperature of about 95 to 100° C. maintained on the mill walls by live steam. After the acetone has been removed, as indicated by a vacuum of 0.1 millimeter of mercury maintained in the mill, the mill is filled with nitrogen, the milled powder is recovered from the milling medium and removed under a nitrogen atmosphere. The powder is then screened under nitrogen as before.

The analysis of this unreduced powder mixture indicates that there is present 12.0% cobalt, 0.2% free carbon, and 5.45% total carbon of which some is due to adsorbed organic matter; the specific surface area is 5.5 square meters per gram; and the oxygen content is 0.45% by weight.

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 forty milliliters per minute. The methane is present to minimize excessive decarburization of the tungsten carbide by the hydrogen. The powder is held in this gas stream at 900° C. for two 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 cobalt-containing tungsten carbide powder is characterized by analysis as follows: tungsten 82.3%; total carbon 5.33%; free carbon less than 0.1%; cobalt 12.1%; oxygen 0.26%. The carbon content found by analysis corresponds to an atomic weight of carbon of 0.99 per atomic weight of tungsten. X-ray diffraction line broadening corresponds to a tungsten carbide having a crystallite size of 42 millimicrons average diameter. The specific surface area is 2.6 square meters per gram.

Forty-five grams of the powder described above is charged in an oxygen-free environment to a cylindrical carbon mold and close-fitting carbon piston are inserted in each end. The mold containing the powder pressed at 200 p.s.i. is then transferred to a vacuum hot press. After evacuation the sample, under no pressure, is brought to 1420° C. by induction heating in seven minutes and held at this temperature with no application of pressure for five minutes. During the heating the sample sinters and shrinks away from contact with the carbon surface, thus avoiding carburization.

At this point the tungsten carbide is in the form of platelets which are of a size when measured by optical microscope of up to a micron in thickness and up to several microns across, and are distributed randomly throughout a billet sintered to about 85 percent of theoretical density. Hydraulic pressure is then applied to both pistons and the pressure on the sample in the mold is brought to 4000 p.s.i. in a period of half a minute. The sample is subjected to a pressure of 4000 p.s.i. at 1420° C. for one 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 two 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 1 inch in diameter 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 for measurement of strength and hardness. The modulus of rupture of the hot pressed composition is 530,000 p.s.i., the unnotched impact strength on a Tinius-Olsen impact tester is 92 ft. lb./square inch, and 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% cobalt; the reduction in

cobalt content as compared with the powder is due to the extrusion of some metal during fabrication.

Chemical analysis of the dense tungsten carbide body gives the following percentages: Tungsten 84.7%; total carbon 5.48%; cobalt 9.8%; oxygen and free carbon less than 0.1%. The carbon and tungsten content found by analysis corresponds to an atomic weight of carbon of 0.99 per atomic weight of tungsten.

A fragment of one of the bars used in measuring physical properties of the tungsten carbide body is optically polished on two faces, one face parallel to the direction of the pressing axis and the other face perpendicular to the direction of the pressing axis. The polished faces are then etched, using alkaline potassium ferricyanide solution, and examined in an optical microscope at a magnification of one thousand fold. Cross-sections of grains of tungsten carbide are visible as platelets with diameters of up to six microns and thicknesses of up to one micron. Most of the platelets visible through the optical microscope are oriented with their long axis perpendicular to the direction of the pressing axis. The porosity of the composition is estimated from the optical micrograph to be A-2 on the standard ASTM scale. More detailed examination of a cross-section of the structure parallel to the direction of the pressing axis with an electron microscope shows the long dimension of individual platelets ranging from 0.2 microns to 6 microns with more than 94 percent of the particles having a longest dimension less than one micron and more than 50% less than half a micron. The platelets have a longest dimension; thickness ratio ranging from 3:1 to 6:1 and the overall average dimension of the platelet cross-sections visible in the electron micrograph is about 0.4 microns. This corresponds to an average tungsten carbide grain diameter of about 0.6 microns. Several sections of the same sample are examined and the mean grain size from one region to another ranges from 0.47 to 0.76 microns, the latter being characteristic of a region which appeared to contain more than a typical amount of cobalt. Non-representative regions such as those within a sixteenth of an inch of the outside of the billet or those surrounding occasional inclusions of impurities are not used in measuring the average grain size.

A sample of the metal binder phase is separated by etching away the tungsten carbide. The lattice spacing of the cobalt by X-ray diffraction is found to be 3.567 angstroms corresponding to about 18 percent by weight of tungsten in solid solution in the cobalt. The metal binder phase is heated in 35% hydrochloric acid for 1 hour; the weight percentage of tungsten based on total weight of cobalt and tungsten dissolved, is 15 percent. About 2% by weight of the binder is insoluble and found by X-ray diffraction to consist of tungsten-rich eta phase,  $\text{Co}_3\text{W}_3\text{C}$ .

Another bar fragment is used to measure the resistance of this composition to attack by concentrated hydrochloric acid at 25° C. More than 100 hours exposure to the acid is required to remove 0.25 milligrams of cobalt per square centimeter of surface area of the bar per percent of cobalt originally present.

The second portion of the hot pressed disc is cut with a diamond wheel and ground to a piece one-half inch square and one-quarter of an inch thick, for use as a cutting tip in a milling head. The corners are ground to a radius of one thirty-second of an inch. Using a single tooth cutter, the tip is used to face mill a 2 inch wide bar of "Udimet" 500, at six and a half mils feed per tooth and sixty mils depth of cut. The tip mills the face of the bar a distance of 25 inches at a speed of 50 surface feet per minute before failure, and at 75 surface feet per minute, a distance of 27 inches is achieved.

The unannealed or quench-strengthened character of the product is shown by its characteristic of losing strength when cooled slowly from 1300° or 1400° C. Samples are heated in vacuum in alumina crucibles to 1400° C. in about 20 minutes and cooled at 5° C. per minute

to 700° C. and then removed from the furnace and cooled to room temperature out of contact with air. The transverse rupture strength is found to have been reduced from 530,000 p.s.i. to 440,000 p.s.i. and the hardness from 91.8 Rockwell A to 91.2. When another sample is heated similarly to 1300° C. and cooled and strength is 437,000 p.s.i. and the hardness is 91.3.

#### EXAMPLE 2

To a steel mill are charged 14,000 parts of "Carboly" grade 883 cobalt-bonded tungsten carbide rods, previously conditioned as described in Example 1, 1800 parts of a fine commercial tungsten carbide powder and 1450 parts of acetone.

The tungsten carbide powder has a nitrogen surface area of 0.66 m.<sup>2</sup>/gram which corresponds to an average particle size of 580 millimicrons. 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 range of from 2 to 10 microns, the aggregates being comprised of rough-surfaced particles in the size range of from 0.5 to 2 microns. Chemical analysis of this powder gives the following percentages: tungsten 93.2%; total carbon 6.32%; oxygen and free carbon, less than 0.1%.

Milling under acetone is continued for 7 days, as described in Example 1. One hundred eighty parts of fine cobalt powder are then added to the mill, maintaining an atmosphere of nitrogen in the mill while this is being done, and milling is continued for a further 7 days, the mill being then discharged and the dry powder product recovered and screened through a 70 mesh sieve without exposure to the atmosphere, as described in Example 1.

Prior to adding the cobalt, a small sample of the tungsten carbide-acetone slurry is removed and the dry powder is recovered without exposure to the atmosphere. The nitrogen surface area of this powder is 5.0 m.<sup>2</sup>/gram, corresponding to an average particle size of 75 millimicrons. By X-ray line broadening the average crystallite size is 50 millimicrons. By electron microscope the powder is seen to be a mixture of very fine particles, in the size range of 25 to 50 millimicrons, together with coarser fragments, in the size range of about 250 to 3000 millimicrons. 95% of the particles are less than one micron in size.

Removal of the cobalt from the milled dried cobalt-tungsten carbide composition, by dissolution in hydrochloric acid, and recovery of the tungsten carbide component, taking precautions to avoid contact with the atmosphere, gives a powder having a nitrogen surface area of 5.7 m.<sup>2</sup>/gram and an X-ray line broadening crystallite size of 32 millimicrons. This shows that only a small reduction in particle size results from milling the premilled tungsten carbide powder in the presence of cobalt.

The dried screened cobalt-tungsten carbide powder is heated at 900° C. for two hours in an atmosphere of hydrogen containing a small amount of methane as described in Example 1 and the resulting powder is discharged under argon as before.

The cobalt-containing tungsten carbide powder is characterized by analysis as follows: tungsten 85.7%; total carbon 5.53%; cobalt 8.5%; oxygen and free carbon less than 0.3%. The carbon content found by analysis corresponds to an atomic weight of carbon of 0.99 per atomic weight of tungsten. The nitrogen surface area is 3.6 m.<sup>2</sup>/gram.

Fifty parts of the above powder 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 pressed at 200 p.s.i. is then transferred to a vacuum hot press and inserted in the furnace at 1000° C. With no pressure applied to the pistons the sample is heated in the mold, by induction heating, to a temperature of 1400° C. over a period of seven minutes, and held at this temperature for five minutes,

during which time the sample sinters to about 85% density.

At this point the tungsten carbide is in the form of isodimensional crystallites in the size range 50 millimicrons to about 2 microns, with 95% of the tungsten carbide crystallites being less than one micron. This is apparent from electron microscopic examination of the polished surface etched with alkaline potassium ferricyanide solution.

Hydraulic pressure is then applied to both pistons and the pressure on the sample in the mold is brought to 4000 p.s.i. in a period of half a minute. The sample is subjected to a pressure of 4000 p.s.i. at 1400° C. for one minute and the mold containing the sample is then ejected from the hot zone and allowed to cool to 800° C. in two 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 is recovered.

The modulus of rupture and hardness of the hot pressed composition are measured and found to be, respectively, 482,000 p.s.i. and 92.2 Rockwell A. The density is measured as 14.75 grams per cubic centimeter, which corresponds to a dense composition containing 8.1% cobalt.

A fragment of one of the bars used in measuring physical properties is used to measure the resistance of this composition to attack by concentrated hydrochloric acid at 25° C. More than 100 hours exposure to the acid is required to remove 0.25 milligrams of metal per square centimeter of surface area of the bar per percent of metal originally present. The cobalt metal binder phase contains more than 19 percent by weight of tungsten in solid solution.

Detailed structural examination of both the hydrochloric acid and alkaline ferricyanide etched polished surfaces using both optical and electron microscopes shows that the hot pressed composition is a dense body with a few smallpores, less than one micron in size and the porosity is designated A-2 on the ASTM porosity scale. The tungsten carbide is present as isodimensional crystals in the size range of 100 millimicrons to 5 microns, with 85% of the tungsten carbide crystallites being less than one micron and more than 50% less than 0.5 micron. The mean grain size of tungsten carbide is 0.6 microns, and the grain size distribution is unimodal.

Upon reheating a portion of the body to 1400° C. in argon in a period of 20 minutes and cooling at the rate of 5° per minute, a loss of more than 10 percent in transverse rupture strength is found in the resulting annealed material.

A metal cutting tip,  $\frac{1}{2} \times \frac{1}{2}'' \times \frac{3}{16}''$  thick is prepared from the dense hot pressed body as described in Example 1. The corners of this tip are ground to a nose radius of 31 mils.

The tip is used to cut gray cast iron by turning at a feed of 10 mils per revolution, a depth of cut of 63 mils, and a speed of 370 surface feet per minute. It cut for 60 minutes without failure.

The metal phase contains about 15 percent by weight of tungsten in solid solution in the cobalt as determined from the lattice spacings. A sample is annealed by cooling from 1400° C. at a rate of 5° C. per minute and loses 11 percent of its transverse rupture strength. The acid resistance is more than 100 hours and the specific resistivity is 24 ohm centimeters.

### EXAMPLE 3

Eighteen hundred parts of aggregated colloidal tungsten carbide, prepared as in Example 1, 56 parts of fine cobalt powder, and 1450 parts of acetone are charged to a steel mill containing 14,000 parts of the cobalt-bonded tungsten carbide rods described in Example 1. The charge is milled for 7 days and the product is recovered, dried, screened through a 70 mesh screen, and

reduced in a hydrogen-methane stream as described in Example 1.

A dense body is made from this powder using the fabrication procedure described in Example 1, with the modification that, the composition is brought to 1530° C. and held at this temperature for about 3 minutes without the application of pressure, followed by the application of 4000 p.s.i. for one minute while the sample is at 1530° C. The body has an 0.98 carbon to tungsten atomic ratio.

The modulus of rupture of the hot pressed composition is 420,000 p.s.i., the Rockwell A hardness is 92.8, and the density is 99% of theoretical. The cobalt phase contains 24% by weight of tungsten in solid solution. In the standard annealing test the transverse rupture strength decreases by 7%. The mean grain diameter is less one micron and 60% of the grains are smaller than one micron. The acid resistance is greater than 200 hours.

### EXAMPLE 4

Fifteen hundred and fifty parts of aggregated colloidal tungsten carbide prepared as in Example 1, 100 parts of fine cobalt powder and 1185 parts of acetone are charged to a steel mill containing 15,000 parts of cobalt bonded tungsten carbide rods described in Example 1. The charge is milled for 7 days and the cobalt-tungsten carbide powder of the invention is recovered, dried, screened and reduced as described in Example 1, except that the reduction temperature is 955° C. The powder contains tungsten—87.8%; total carbon—5.74%; free carbon less than 0.1%; cobalt—6.2% oxygen—0.16%. X-ray diffraction line broadening of this reduced powder corresponds to tungsten carbide having an average crystallite size of 51 millimicrons. The specific surface area is 1.9 m.<sup>2</sup>/gram.

Fifty parts of this powder is charged in an oxygen-free environment to a cylindrical mold with close fitting carbide pistons. The mold, containing the powder pressed at 200 p.s.i., is transferred to a vacuum hot press. After evacuation the sample is brought in six minutes to 1450° C. by induction heating with no pressure on the pistons, and held at this temperature with no pressure for 5 minutes. At this point, the tungsten carbide as observed by optical microscope at 500× is in the form of platelets up to one micron in thickness and several microns across, randomly distributed throughout the billet sintered to about 85% of theoretical density. Hydraulic pressure is then applied to both pistons and the pressure on the sample in the mold is brought to 4000 p.s.i. in a period of half a minute and held at this pressure at 1450° C. for one minute. The sintered billet is thus subject to hot working and densification and the mold containing the sample is then ejected from the hot zone and allowed to cool in the evacuated chamber of the hot press. The sample cools to 800° C. in two minutes and then to room temperature. The cool mold is removed from the press chamber and a dense sample in the form of a disc is recovered.

The disc is cut into two segments, one of which is cut into bars for measurement of strength and hardness. The modulus of rupture is 460,000 p.s.i., the unnotched impact strength is 97 ft. lbs./in.<sup>2</sup>, and the Rockwell A hardness is 92.3. The density of the hot pressed body is measured as 14.92 grams per cc.

The hot pressed body contains tungsten—88.1%; total carbon—5.65%; cobalt—6.2%; free carbon and oxygen less than 0.1%. This analysis corresponds to 0.98 atomic weight of carbon per atomic weight of tungsten. Metallographic examination of the dense body by optical microscopy, as described in Example 1, shows the presence of platelets of tungsten carbide having a length or breadth to thickness ratio of about 5 to 1. Examination by electron microscope shows that the longest dimension of the platelets seen in cross-section ranges from 0.4 to 10 microns with about 85 percent of the platelets having a longest dimension less than 1 micron. The platelets are

highly oriented with their long axis perpendicular to the direction in which the pressure is applied in the hot press. In a cross-section parallel to the direction of pressing, the mean grain size of tungsten carbide is 0.7 microns. The metal binder phase contains 24 percent by weight of tungsten in solid solution in the cobalt. After heating a sample to 1300° C. and cooling to 700° C. per minute the transverse rupture strength at room temperature is reduced by ten percent, but the hardness is reduced only by 0.2 to 92.1 Rockwell A. When a similar sample is heated to 1400° C. and similarly cooled, the hardness decreases by 0.5 and some grain growth occurs; there is more than 10% loss in strength.

The other portion of the hot pressed disc is finished by cutting and grinding to the dimensions 0.525 by 0.50 by 0.093 inches, one side of the piece being tapered to an included angle of 118°. This tip is brazed into a ½ inch diameter rotary twist drill shank and used to drill holes in granite. The drill is run at a speed of 20 r.p.m. while a constant load of 500 pounds is applied. Fifteen holes, each one inch deep, are drilled in a total drilling time of one hour.

When used to mill a high temperature alloy, at a feed rate of 6.7 mils per tooth and a depth of 60 mils, a distance of 12 inches is cut at a speed of 75 surface feet per minute, and 17 inches at 96 surface feet per minute, before the wear is sufficient for the tip to require replacement. The bar is milled across its full width of 2 inches.

#### EXAMPLE 5

Four hundred parts of aggregated colloidal tungsten carbide, prepared as in Example 1, 100 parts of fine cobalt powder and 373 parts of acetone are charged to a one quart steel mill containing 3500 parts of one quarter inch cemented tungsten carbide rods, previously conditioned as described in Example 1. The charge is milled for seven days and the cobalt-tungsten carbide composition is recovered, dried and reduced as described in Example 1, the reduction temperature being 900° C. The cobalt-containing tungsten carbide powder is characterized by analysis as follows: tungsten—74.9%; total carbon—4.95%; free carbon less than 0.1%; cobalt—19.8%; oxygen—0.12%. X-ray diffraction line broadening of the reduced powder corresponds to tungsten carbide having an average crystallite size of 42 millimicrons. The specific surface area is 2.1 m.<sup>2</sup>/g.

Fifty parts of the powder described above is charged in an oxygen-free environment, to a cylindrical die with close-fitting carbon pistons inserted in each end. The mold containing the powder pressed at 200 p.s.i. is then transferred to a vacuum hot press and the pressure removed from the pistons. The powder is brought to 1350° C. by induction heating under vacuum, as described in Example 1, and held at this temperature with no application of pressure for 5 minutes. At this point examination by optical microscope at 500× shows that the tungsten carbide is in the form of platelets, up to 2 microns in thickness and several microns across, randomly distributed throughout the billet which is sintered to about 85% of theoretical density. Hydraulic pressure is then applied to both pistons, and the pressure on the sample in the mold is brought to 4000 p.s.i. at 1350° C. for one minute. The sintered billet is thus subjected to hot working and densification. The mold containing the sample is at once ejected from the hot zone and allowed to cool to 800° C. in two minutes in the evacuated chamber.

After cooling, the resultant disc is cut into bars for measurement of strength and hardness. The modulus of rupture is 476,000 p.s.i., the unnotched impact strength is 163 ft. lbs./in.<sup>2</sup> and the Rockwell A hardness is 88.8. The density of the hot pressed body is measured as 14.52 g./cc.

The hot pressed body contains: tungsten—75.6%; total carbon—4.76%; cobalt—19.4%; free carbon and oxygen less than 0.1%. This analysis corresponds to 0.97 atomic

weights of carbon per atomic weight of tungsten. Metallographic examination of polished, etched surfaces of the body reveals the presence of crystalline platelets of tungsten carbide having a maximum diameter of 12 microns and a maximum thickness of 2.5 microns as measured by optical micrography at 1000×. The platelets are preferentially oriented with their faces perpendicular to the direction in which the pressure is applied in the hot press. Examination by electron microscope shows that the longest dimension of the platelets ranges from 0.3 to 12 microns with about 92 percent of the platelets having a maximum dimension less than 1 micron. The average grain diameter is about 0.6 microns.

Examination of the metal phase indicates that about 11% by weight of tungsten is in solid solution in cobalt. The acid resistance is greater than 50 hours. The binder phase contains about two percent of eta phase. The body is unannealed.

#### EXAMPLE 6

Four hundred parts of aggregated colloidal tungsten carbide prepared as described in Example 1, 170 parts of fine cobalt powder and 373 parts of acetone are charged to a one quart steel mill containing 3500 parts of the cemented carbide grinding cylinders used in Example 1. The charge is milled for seven days and the cobalt-tungsten carbide composition is recovered, dried, and reduced as described in Example 1, the reduction temperature being 900° C. The powder contains: tungsten—66.5%; total carbon—4.26%; free carbon less than 0.1%; cobalt—29.3%; oxygen—0.08%. X-ray diffraction line broadening of the reduced powder corresponds to tungsten carbide having an average crystallite size of 45 millimicrons. The specific surface area is 1.6 m.<sup>2</sup>/g.

Fifty parts of the powder described above is hot pressed using the procedure described in Example 5, with the difference that the pressing temperature is 1330° C.

The pressed disc is cut into bars for measurement of strength and hardness. The modulus of rupture is 493,000 p.s.i., the unnotched impact strength is 192 ft. lbs./in.<sup>2</sup>, and the Rockwell A hardness is 85.4. The density of the hot pressed body is 12.64 grams per cc. The hot pressed body contains: tungsten—68.1%; total carbon—4.40%; cobalt—27.2%; free carbon and oxygen less than 0.1%. This analysis corresponds to 0.99 atomic weights of carbon per atomic weight of tungsten. Metallographic examination with an optical microscope at 1000× of the polished, etched surfaces of the body shows that it consists mostly of crystalline platelets of tungsten carbide having a maximum breadth of 15 microns and a maximum thickness of 3 microns. The platelets are preferentially oriented with their long axis perpendicular to the direction in which the pressure is applied in the hot press. Examination by electron microscope shows that the longest dimension of the platelets ranges from 0.4 to 15 microns with about 88 percent of the platelets having a longest dimension less than 1 micron. The mean grain size is about 0.5 micron. The cobalt binder contains 8% tungsten in solid solution. After the standard annealing test the transverse rupture strength decreases to less than 440,000 p.s.i.

#### EXAMPLE 7

The 12% cobalt-tungsten carbide powder utilized as a starting material is prepared as described in Example 1, and has a carbon to tungsten atomic ratio of about 0.98. The mill loading being changed to 1800 parts tungsten carbide, 250 parts cobalt, and 1450 parts acetone.

Fifty parts of the powder described above are charged in an oxygen-free environment to a cylindrical carbon mold. Close-fitting graphite discs are inserted in each end. Two close-fitting graphite pistons are then inserted into each end and the powder is pressed at 500 p.s.i. to a density of about 25% of the theoretical density. The pistons are removed and the graphite cylinder with powder is placed into a sintering furnace under a hydrogen atmosphere for 30 minutes at 1200° C. The sintered billet



having reached 67% of theoretical density, is centered inside the graphite cylinder, close-fitting carbon pistons are inserted, and the entire sample is transferred to a vacuum hot press. After evacuation, the sample, under no pressure, is brought to 1400° C. by induction heating in six minutes and held at this temperature for two minutes. Hydraulic pressure is applied to both pistons, and the pressure on the sample in the mold is subjected to 4000 p.s.i. for one minute. The mold containing the sample is then ejected from the hot zone and allowed to cool to 800° C. in two minutes. After cooling to less than 100° C., the mold is removed and a dense sample is obtained in the form of a cylindrical disc.

Analysis reveals that the modulus of rupture of the hot pressed composition is 500,000 p.s.i., the Rockwell A hardness is 92.1, and the density is over 99% of theoretical.

The acid resistance is more than 100 hours on exposure to concentrated hydrochloric acid at 25° C. The mean grain size of the tungsten carbide is less than 0.75 micron.

#### EXAMPLE 8

Fifty parts of the cobalt tungsten carbide powder prepared as described in Example 1 are charged in an oxygen-free environment to a cylindrical rubber mold. The powder is tamped into the bottom of the mold which is then sealed air tight with a rubber stopper and black electrical tape. The encased sample is placed in a wire basket and lowered into the pressure vessel of an isostatic press. This consists of a steel cylinder having thick walls and containing as the hydraulic fluid a 5% dispersion of oil in water. The pressure is increased to 100,000 p.s.i. by means of a hydraulic pump and maintained at this level for 5 minutes. The pressure is then lowered to one atmosphere, and the sample removed. The density of the sample is 55% of theoretical.

The cold pressed sample is removed from the rubber mold and inserted into the sintering furnace in a graphite boat. Care is exercised to protect the sample from oxidation by keeping the sample in an inert atmosphere during transfer, and it is sintered in argon at 1250° C. for 30 minutes. Its sintered density is 90% of theoretical. The hot pressing step is similar to that performed on the sintered piece of Example 7. The modulus of rupture of the hot pressed composition is 530,000 p.s.i., the Rockwell A hardness is 92.0, and the ASTM porosity is A-2.

More than 100 hours exposure to concentrated hydrochloric acid at 25° C. is required to remove 0.25 milligrams of metal per square centimeter of surface area of the body per percent of metal originally present. The body has a carbon to tungsten atomic ratio of 0.98 and the cobalt contains 18% tungsten in solid solution.

#### EXAMPLE 9

A tungsten carbide composition containing about 12% of cobalt is prepared by preconsolidating a fairly dense compact prior to the heat treating step. The materials and methods are the same as described in Example 8 except that the powder is preconsolidated at 10,000 p.s.i. and the pressure during hot pressing is 2000 p.s.i. The properties of the molded body are substantially the same as those of the product of Example 8.

#### EXAMPLE 10

Fifty parts of a 12% cobalt-tungsten carbide powder, prepared as in Example 1, is charged to a cylindrical carbon mold and close-fitting carbon pistons are inserted in each end. The mold containing the powder is pressed at 200 p.s.i. and then transferred to a vacuum hot press. After evacuation, a sample, under no pressure, is brought to 1000° C. by induction heating, and a pressure of 4000 p.s.i. is then applied to the sample for a period of one minute during which the temperature is increased to 110° C. The temperature is maintained at 1100° C. with the pressure of 4000 p.s.i. still on, for a period of

5 minutes. The pressure is then removed and the sample is heated to 1400° C. and held at this temperature without the application of pressure for two minutes. A pressure of 4000 p.s.i. is again applied and the sample is subjected to this pressure while maintaining the temperature at 1400° C. for a period of 1 minute. The mold containing the sample is then ejected from the hot zone and allowed to cool in the evacuated chamber of the press to 800° C. in two minutes.

The modulus of rupture of the body prepared as described above is 495,000 p.s.i. and the Rockwell A hardness is 91.0. The other properties are substantially the same as those of the product of Example 8.

#### EXAMPLE 11

Colloidal tungsten carbide powder prepared in a molten salt medium and milled with 12% of cobalt in the form of a fine powder, as described in Example 1, is dried, and screened through a 70 mesh screen in an inert atmosphere as described in Example 1. At this stage 40 parts of the unreduced powder is loaded into a graphite container in a nitrogen atmosphere. The container is tapped gently to pack the powder. The tapped density of the powder is about 20 percent of theoretical. To pack the powder in the container about 50 p.s.i. is applied with a plunger by hand.

The container is then placed in the chamber but outside the hot zone of an inductively heated vacuum furnace which is then evacuated. When about 0.5 mm. Hg vacuum is reached, the furnace is heated at the rate of about 30° C./min. to 800° C., at which temperature the container is moved into the hot zone of the furnace. The temperature of the initially cool container is permitted to equilibrate with the furnace temperature by holding it for 3 minutes while maintaining 800° C. At the end of the 3 minute soaking, the furnace is heated to 1400° C. at the uniform rate of about 30° C./minute. Upon reaching 1400° C., as measured by an optical pyrometer, the sample is allowed to sinter for 5 minutes at the temperature, and the container is then ejected immediately from the hot zone of the furnace and is allowed to cool to 800° C. in less than one hour.

Examination of the microstructure shows that the sintered billet has a porosity of A-4 on the ASTM scale. The tungsten carbide crystallites are platelike with a shape and size similar to those in Example 1 after hot pressing. The cobalt content is found to be 12% and the carbon was 5.3%.

This presintered billet is later preheated in a vacuum furnace to 1425° C. in less than 3 minutes and forged in a vacuum forging press with graphite dies activated with continuous hydraulic pressure, the dies being maintained at about 1450° C. and being designed so as to not deform any dimension of the billet by more than 10% in each forging step. The total time during which the material is above 1350° C. is less than 10 minutes and the forged body is cooled to less than 1250° C. in less than 5 minutes and to 600° C. in less than 15 minutes.

After two forging steps the shaped body has a transverse rupture strength of 470,000 p.s.i. and a hardness of over 91 Rockwell A. The mean grain size of tungsten carbide is less than one micron.

More than 100 hours exposure to concentrated hydrochloric acid at 25° C. is required to remove 0.25 milligram of metal per square centimeter of surface area of the body per percent of metal originally present, and more than 12 percent by weight of tungsten is in solid solution in the cobalt binder phase. After the standard annealing test the strength of the body was 420,000 p.s.i.

#### EXAMPLE 12

A tungsten carbide cobalt powder containing about 12% cobalt is prepared by the procedure of Example 1 up to and including drying the powder after recovery from the ball milling operation, and screening under nitrogen.

Sixty parts of this unreduced powder is loaded into a cylindrical carbon mold, and close fitting carbon pistons are inserted in each end. The mold containing the powder is pressed at 200 p.s.i. and is then transferred to a vacuum hot press. After evacuation, the sample is heated to 400° C. and held for 15 minutes to allow gases to come off and the temperature is then raised to 1100° C., and the sample is held at this temperature with no application of pressure for 30 minutes.

At this point a rapidly cooled sample is found to contain 15 percent by weight of tungsten in solid solution in the cobalt.

Three thousand seven hundred and fifty p.s.i. pressure is then applied to the sample and simultaneously the temperature is increased to 1400° C. over a period of about 6 minutes. The sample is then held for 3 minutes at a temperature of 1400° C., maintaining a pressure of 3750 p.s.i., at which point the mold containing the sample is ejected from the hot zone and cooled to less than 800° C. in about 5 minutes.

The modulus of rupture of the body prepared in this manner is found to be 580,000 p.s.i. and the Rockwell A hardness is 92.0. The atomic ratio of carbon to tungsten is 0.98.

Examination of the microstructure reveals that the material is practically free from pores and is designated A-1 on the ASTM porosity scale. It also contains about 5 volume percent eta carbide. About 80% of the tungsten carbide grains are less than one micron in size and the mean size is 0.75 micron. The metal binder phase is uniformly distributed throughout the main body.

More than 100 hours exposure to concentrated hydrochloric acid at 25° C. is required to remove 0.25 milligram of metal per square centimeter of surface area of the body per percent of metal originally present. The cobalt phase still contains 15 percent by weight of tungsten in solid solution. Upon being subjected to the standard annealing test the body loses 12 percent of its strength.

#### EXAMPLE 13

Fifteen parts of unreduced 12% cobalt-tungsten carbide composition prepared as described in Example 12 and 85 parts of 6% cobalt-tungsten carbide powder prepared as in Example 4 are intimately mixed by thoroughly tumbling in a container, keeping the powder under an inert atmosphere.

Sixty parts of this mixture are charged in an oxygen free environment to a cylindrical carbon mold, care being taken not to vibrate the powder unduly while charging to the mold, and close fitting carbon pistons are inserted in each end. The powder is pressed at 200 p.s.i. and transferred to a vacuum hot press. After evacuation, the sample is brought to 1400° C. by induction heating in about 7 minutes without the application of pressure, and held at this temperature for 5 minutes. Hydraulic pressure is then applied to both pistons and the pressure on the sample in the mold is brought to 4000 p.s.i. and the sample subjected to this pressure at 1400° C. for 1 minute. The mold containing the sample is then ejected from the hot zone and is cooled to 600° C. in 20 minutes.

The dense body thus obtained is found to have a modulus of rupture of 550,000 p.s.i. and Rockwell A hardness of 92.9.

More than 100 hours exposure to concentrated hydrochloric acid at 25° C. is required to remove 0.25 milligram of metal per square centimeter of surface area of the body per percent of metal originally present. The atomic ratio of carbon to tungsten in the body is slightly less than one. The cobalt phase contains more than 12% by weight of tungsten in solid solution. The body loses 10 percent of its strength when subjected to the standard annealing test. The tungsten carbide grains have a mean diameter of 0.6 micron and 90% of the grains are smaller than one micron.

#### EXAMPLE 14

One hundred fifty parts of the cobalt-containing tungsten carbide powder of Example 1, containing 12.1% cobalt, are charged in an oxygen free environment to a cylindrical graphite mold, close-fitting graphite pistons are inserted in each end of the mold, and the powder is pressed at 250 p.s.i. at room temperature and the pressure removed. The mold containing the powder is then heated in a vacuum induction furnace at 1500° C. for 5 minutes with no pressure applied and cooled in the furnace to 1000° C. and then removed and cooled to room temperature under vacuum. A porous, sintered cylindrical billet  $1\frac{3}{16}$  inch in diameter and 1 and  $\frac{3}{8}$  inches long is recovered from the graphite mold. The density of this piece is 12.3 grams per cc. which is 86% of the theoretical density of powder composition charged to the mold. At this point examination by optical microscope at 500× shows the tungsten carbide is in the form of platelets, up to about one micron in thickness and several microns across, distributed in random orientation throughout the billet.

The billet is then loaded into a cylindrical mold one inch in diameter and 4 inches long, and close-fitting carbon pistons are inserted in each end. The upper piston, which is 2 inches long, has a  $\frac{3}{8}$  inch diameter hole drilled along its axis for a length of 1 and  $\frac{7}{8}$  inches. The die and piston assembly containing the sintered billet is loaded to a vacuum hot press and after evacuation, the sample is heated to 1500° C. by induction heating in 6 minutes and held at this temperature with no application of pressure for 5 minutes. Hydraulic pressure is then applied to both pistons and the pressure on the billet in the mold is brought to 4000 p.s.i. in a period of half a minute. The temperature is maintained at 1500° C. and the pressure at 4000 p.s.i. for two minutes, at which time no further movement of the pistons is observed. The mold containing the sample is then at once ejected from the hot zone and allowed to cool in the evacuated chamber of the press.

The cobalt-bonded tungsten carbide body is recovered by breaking away the adhering carbon cylinder and the pistons. The pressed body consists of a one inch diameter cylinder,  $\frac{5}{8}$  inch high to which is attached a  $\frac{3}{8}$  inch diameter rod, one inch long, the latter having been extruded into the hole in the upper piston. The  $\frac{3}{8}$  inch diameter rod is characterized with respect to structure. In bars cut parallel with the axis of the rod, the modulus of rupture is found to be 454,000 p.s.i. and the Rockwell A hardness is 89.0. The density is 14.3 g./cc.

A  $\frac{1}{4}$  inch long piece of  $\frac{5}{8}$  inch diameter rod is ground on one side to a  $\frac{1}{4}$  inch wide flat. This flat and one end of the rod are smoothly polished and the polished faces are etched and examined with an optical microscope at a magnification of 1000×, as described in Example 1.

Individual grains of tungsten carbide are visible in cross section by optical microscope at 1000× as crystalline platelets with a maximum diameter of 12 microns and a maximum thickness of 2 microns. The platelets are preferentially oriented with their long axes parallel to the axis of the extruded rod. Examination by electron microscope shows that the longest dimension of the platelets in cross-section ranges from 0.6 to 12 microns, with about 80% of the platelets having a longest dimension less than 1 micron.

#### EXAMPLE 15

Tungsten carbide powder containing cobalt is prepared as described in Example 1, and characterized as containing: tungsten—82.8%; total carbon—5.23%; free carbon less than 0.1%; cobalt—11.8%; oxygen—0.26%. X-ray line broadening of the reduced powder corresponds to tungsten carbide having an average crystallite size of 34 millimicrons. The specific surface area is 2.4 m.<sup>2</sup>/g.

Four discs, one inch in diameter and  $\frac{3}{4}$  inch thick, are fabricated using 135 parts of the above described

powder for each disc and the hot pressing procedure similar to that described in Example 1, with some modification being that the full pressure of 4000 p.s.i. is applied to the sample at 1420° C. for 2½ minutes and the sample cooled to 600° C. in less than ten minutes.

Percussion rock drilling bit inserts are made from the discs by diamond sawing and grinding to dimensions ⅝ by ⅜ by ⅞ inches, with an included angle at the tip of 108°. The inserts are cut and brazed into a 1¾ inch diameter percussion bit so that the direction of the axis of the bit is parallel with the direction of the pressing axis of the inserts during fabrication. The bit, attached to a pneumatic rotary percussion drill, is used to drill holes in a block of Barre Vermont granite. Forty-nine holes, each 32 inches deep, are drilled in an average time of six minutes per hole, the drilling time for the last hole being seven minutes, only two minutes longer than the drilling time for the first hole and the cutting edges of the inserts are still not dull enough to necessitate resharpening.

One of the inserts is removed from the bit which drilled forty-nine holes and cut into several pieces for examination. Analysis shows the insert to contain: tungsten—83.2%; total carbon—5.33%; cobalt—11.4%; oxygen—0.07%. The Rockwell A hardness is 91.2 and the density 14.37 grams per cc., corresponding to a composition consisting of 11.6% cobalt and 88.4% tungsten carbide. The acid resistance is more than 50 hours and the atomic ratio of carbon to tungsten is 0.98 and there is 18% by weight of tungsten in the cobalt phase.

Metallographic examination, with an optical microscope, as described in Example 1, reveals a structure comprising a three-dimensional matrix of a cobalt-rich phase interspersed with regions 10 to 100 microns in diameter, consisting primarily of tungsten carbide. More detailed examination of the structure, using the electron microscope, shows the tungsten carbide-rich regions to be made up of closely packed platelets of tungsten carbide bonded together with a highly dispersed cobalt binder phase. The tungsten carbide platelets have a ratio of longest diameter to thickness in the range of from 3:1 to 7:1. The longest diameter of individual platelets ranges from 0.2 microns to 7 microns, with 95% of the particles having longest diameters less than 1 micron. The platelets are oriented with their long axes perpendicular to the pressing direction. The mean grain size is less than 0.75 microns.

#### EXAMPLE 16

An interdispersed powder of tungsten carbide and cobalt similar to that of Example 1, which has not been subjected to a reduction step, is loaded directly into the graphite mold out of contact with air. The powder contains 0.42% oxygen, has a specific surface area of 5.8 m.<sup>2</sup>/g., the crystallite size of tungsten carbide determined by X-ray diffraction is 35 millimicrons, and the atomic ratio of carbon to tungsten is 0.97. The powder is compressed in the mold at 200 p.s.i., then the pressure is removed while the mold and contents are heated to 1400° C., at which temperature it is held for 5 minutes, and then 4000 p.s.i. pressure is applied through the pistons to the material for one minute. At once the pressure is removed and the sample ejected from the furnace and cooled to 800° C. in 2 minutes. The resulting body contains an atomic ratio of carbon to tungsten of 0.97 and contains 9.62% cobalt, some of the cobalt having been squeezed out of the mold. The density is 14.43 g./cc. The transverse rupture strength is 539,000 p.s.i. and the hardness is 91.6 Rockwell A. The cobalt metal binder phase contains 20% by weight of tungsten. The body has an acid resistance of greater than 100 hours; the specific resistivity is 33 micro-ohm-cm. From electron micrographs the mean grain size is 0.6 microns, and 90% of the tungsten carbide grains are less than one micron in size. The ASTM porosity is A-2. When subjected to the standard annealing test, the strength is reduced to 460,000 p.s.i.

Inserts made of this body are brazed into cutoff tools, ⅝ of an inch wide, and employed on an automatic screw machine. In cutting off AISI 52100 steel, this tool cuts off three times as many pieces as a High Speed Steel cutoff tool before failure, while operating under cutting conditions under which inserts made with commercial cobalt-bonded tungsten carbide are unreliable, failing by chipping.

#### EXAMPLE 17

The tungsten carbide powder used in this example contains 12% cobalt and is the same as the reduced powder employed in Example 1, the hot pressing procedure is also identical with that of Example 1, except that the powder in the mold is subjected continuously to a pressure corresponding to 100 pounds per square inch while the temperature is being raised from 1000 to 1400° C. In a separate but otherwise identical experiment, the body is removed from the mold after having been heated under 100 p.s.i. pressure to 1400° C., and is found to have shrunk away from the graphite walls of the mold in spite of the applied pressure. When the body which had been heated under 100 p.s.i. pressure to 1400° C. is then immediately pressed at 4000 p.s.i. for a period of one minute, and the body and mold removed from the furnace and cooled to 800° C. within two minutes, the resulting product is found to have a transverse rupture strength of 505,000 p.s.i. and a hardness of 92.1. The molded body comes away cleanly from the graphite without sticking and is well formed. This procedure permits a local carburization of the ends of the body through contact with the pistons, but the sides of the billet do not touch the walls during the heating period and the central part of the body is not carburized and contains an atomic ratio of carbon to tungsten of less than one. There is more than 8% by weight of the tungsten in solid solution in the cobalt phase, and the body exhibits the characteristics of an unannealed body. The grain size of the tungsten carbide in the final body is about 0.6 microns.

#### EXAMPLE 18

An interdispersed powder of tungsten, tungsten carbide and cobalt is prepared by ballmilling as in Example 1, using 1380 parts of the aggregated colloidal tungsten carbide of Example 1, 205 parts of fine cobalt powder, 125 parts of finely divided tungsten metal powder having a grain size of one micron, and 1185 parts of acetone. After 7 days milling the interdispersed powder is recovered and screened through a screen of 70 meshes per inch, out of contact with the atmosphere and moisture. Because of the added tungsten, the atomic ratio of carbon to tungsten is 0.92. The powder is reduced in an atmosphere of hydrogen without addition of methane by heating it at a uniform rate in about 3 hours from 30° to 900° C., while passing over it a mixture containing 85% hydrogen and 15% argon. The powder is held at 900° C. for 2 hours, and then heated at a uniform rate from 900° C. to 1150° C., over a period of 5 hours. It is held at this temperature for 6 hours, and then cooled from 1150° C. to 700° C. in about 90 minutes, and then at a somewhat slower rate to ordinary temperature.

In this powder it is found that the cobalt phase contains 23% by weight of tungsten, while the remainder of the tungsten is in uncombined form.

Fifty grams of this powder is loaded in the atmosphere into a graphite mold with a cylindrical cavity one inch in diameter and hot pressing is carried out by heating the mold and powder in a vacuum to 1000° C. and applying 4000 p.s.i. to the powder as it is heated from 1000° C. to 1400° C. in a period of 5 minutes, and held under continuing pressure at 1400° C. for 2 minutes. The pressure is then removed and the compacted body is removed from the furnace and cooled to 600° C. in a period of 7 minutes.

The resulting billet is 1 inch in diameter, about ¼ inch thick. Transverse rupture strength of the body is 475,000

p.s.i., the hardness is 92.0, the body contains 10.5% cobalt by weight, and 27% by weight of tungsten is in solid solution in the cobalt phase. The body is extremely resistant to dissolution by hydrochloric acid, the acid resistance being over 300 hours in the standard test. The hardness of the body is 92.0 Rockwell A, the mean grain size is less than 0.7 microns and 80% of the grains are less than 1 micron in diameter.

Upon subjecting the body to the standard annealing test, there is a marked increase in the amount of eta phase present, and the transverse rupture strength decreases to 450,000 p.s.i. The metal phase remains acid-resistant and the cobalt contains 18% by weight of tungsten in solid solution.

#### EXAMPLE 19

A commercially available milled mixture containing 91% tungsten carbide and 9% by weight of cobalt is used in this example. Chemical analysis of the powder indicates 5.7% total carbon, 9.2% cobalt, 0.13% oxygen, and 0.12% free carbon. The atomic ratio of carbon to tungsten in this powder is 1.0, and the specific surface area is 1.2 m.<sup>2</sup>/g., as determined by nitrogen adsorption.

This powder is ballmilled for 7 days, dried, reduced, and hot pressed, as in Example 2. The surface area of the reduced powder is 1.3 m.<sup>2</sup>/g., the free carbon content is less than 0.1% by weight, the oxygen content is 0.09%, and the atomic ratio of carbon to tungsten is 0.99, some carbon having been lost in the milling, drying and reduction operation. After hot pressing, the body is cooled from 1400° to 800° C. in 2 minutes. The body contains 8 percent by weight of cobalt. The transverse rupture strength of the body is 508,000 p.s.i., the hardness is 92.0 Rockwell A. The body is dense, essentially non-porous, the porosity rating being A-1. Electron micrographs show that the tungsten carbide grains are isodimensional, that is, on the average are equiaxed, the mean grain size being 0.61 microns and 98% of the grains being less than 1 micron in diameter. The body is acid resistant, having a resistance of over 50 hours. The cobalt metal phase contains 8% by weight of tungsten in solid solution. The specific resistivity of the body is 23 micro-ohm-cm. After the standard annealing test the transverse rupture strength is 455,000 p.s.i.

#### EXAMPLE 20

A powder consisting of 12 parts by weight of cobalt and 88 parts by weight of tungsten carbide is prepared as described in Example 1 up to the point where the dried product is recovered after milling. The vacuum dried material is screened under nitrogen, using a 70 mesh screen vibrated mechanically, and it is further hand screened through a 40 mesh screen to break up clumps which tend to form in the collecting pan on the vibrated screen. The powder is aggregated in the form of soft spheres a few hundred microns in diameter.

The screened powder is poured loosely into shallow trays which are then loaded to a 5 inch diameter Inconel tube furnace, the powder being handled throughout under a protective nitrogen atmosphere. The furnace is at 400° C. when the powder is loaded and the gas passing through the furnace consists of hydrogen, at a flow rate of 4 liters per minute, with methane introduced at a flow rate of 40 milliliters per minute, together with argon at a flow rate of about 700 milliliters per minute. The furnace is slowly brought to a temperature of 1150° C., using the heating cycle as follows: 400 to 900° C. in 2 hours, 900 to 1000° C. in 1½ hours, 1000 to 1150° C. in 3½ hours. The powder is then held at 1150° C. for 9 hours, but during the last seven hours only argon passes through the furnace. The furnace is then cooled from 1150° C. to 800° C. in one hour, the powder being in an atmosphere of argon during the cooling cycle. The trays containing the powder are then moved into a water-cooled zone outside the furnace and cooled rapidly from

800° to 300° C. in 15 minutes. The powder is discharged into a nitrogen filled box and it is transferred from the trays and screened through a 40 mesh screen. The powder consists of hard, sintered, free-flowing spheres a few hundred microns in diameter. It is characterized by analysis as follows: total carbon—5.31%; free carbon—less than 0.1%; oxygen—0.02%; cobalt—12.65%. The specific surface area is 0.2 m.<sup>2</sup>/g. The carbon content found by analysis corresponds to an atomic weight of carbon of 0.99 per atomic weight of tungsten. The cobalt phase separated from the tungsten carbide by anodic oxidation of a thin layer of powder in alkaline potassium ferricyanide is found by analysis to contain 12% tungsten in solid solution. The powder has been sintered to a relatively hard, impervious condition, as indicated by the low specific surface area and low oxygen content.

This powder is hot pressed by loading 50 grams of this powder in air into a 1 inch diameter mold of graphite fitted with graphite pistons and heated to 1000° C., at which point 4000 p.s.i. pressure is applied and the mold and contents is brought to 1400° C. in 4½ minutes and held under pressure at this temperature for 6 minutes; immediately the pressure is released and the sample removed from the furnace and cooled to 600° C. in four minutes.

The heat-inactivated powder is pressed with maximum application of pressure and at 1400° C. as an optimum temperature. When only 2000 p.s.i. pressure is applied, only half the strength is developed. It also differs from the other powders of this invention which have not been heat treated, in that if the pressure is not applied while the powder is being heated from 1000° C. to 1400° C. the physical properties of the product are poor.

Analysis of the metal phase indicates that there is 19.5% by weight of tungsten in solid solution in the cobalt, and that the body contains 7.6% by weight of cobalt. The body has an acid resistance of more than 50 hours. During the hot pressing, carburization of the outer surfaces of the billet occurs, while the interior of the billet remains uncarburized.

The transverse rupture strength of this body is 521,000 p.s.i., and the hardness is 91.0 Rockwell A. The mean grain size of the tungsten carbide is 0.7 microns, and 80% of the grains are smaller than one micron. The ASTM porosity rating is A-2.

After the standard annealing test, the body loses 50% of its strength.

#### EXAMPLE 21

A composition is prepared from a reduced powder containing 15% cobalt by weight, and is hot pressed at 1340° C., by a procedure similar to that of Example 1, except that the mill is charged with 1800 grams of aggregated colloidal tungsten carbide and 318 grams of "Cobalt F" powder and 1800 milliliters of acetone. The milled, dried and reduced powder has an atomic ratio of carbon to tungsten of 0.99. The hot pressing cycle is the same as in Example 1, except that a maximum pressing temperature of 1340° C. is employed. The rapidly cooled sample has a transverse rupture strength of 524,000 p.s.i. and a hardness of 91.0 Rockwell A. The density is 99% of theoretical. The cobalt content is 14% by weight, there is 9% by weight of tungsten in solid solution in the cobalt phase, and after the standard annealing test, the transverse rupture strength is found to be 460,000 p.s.i.

#### EXAMPLE 22

A ball mill containing 14,000 parts of milling inserts similar to that of Example 1 is loaded with a mixture blended for four hours in a cone blender and consisting of 1260 parts of aggregated colloidal tungsten carbide powder of Example 1, 210 parts of tungsten powder having a crystallite size of about 0.2 microns, by X-ray diffraction line broadening and a nitrogen surface area of 2 m.<sup>2</sup>/g., 630 parts of fine cobalt powder and 1800 parts

of acetone. Seven days of milling and drying the powder are carried out without exposing the powder to atmosphere or moisture.

Hot pressing is carried out by loading about 50 grams of powder into a 1 inch diameter mold and compacting with 200 p.s.i. pressure. The pressure then is removed and the sample is heated in the mold to 1000° C. and then from 1000 to 1350° C. in about 7 minutes. At this point, the sample is held at 1350° C. to sinter without pressure for 5 minutes, and then 2000 p.s.i. is applied for a period of one minute. Pressure is immediately removed and the sample is ejected from the furnace and cooled to below 600° C. in 5 minutes. The transverse rupture strength of the product is 601,000 p.s.i. and the hardness is 84.7 Rockwell A. The density is greater than 98% of theoretical. The body is extremely resistant to acid, the acid resistance being over 200 hours. The mean grain size of the tungsten carbide is 0.5 microns, and 90% of all the grains are less than 1 micron in size. When the sample is subjected to the standard annealing test by heating to 1400° C. and cooling at the prescribed rate, it is subsequently found to have lost 10% of its transverse rupture strength. Examination of the microstructure shows that during the annealing step substantial amounts of the cobalt binder are converted by reaction with the tungsten carbide to a cobalt-rich type of eta phase.

The body is employed as a drawing die for copper wire. The composition is tough and resistant to impact.

#### EXAMPLE 23

A commercial tungsten carbide powder is milled to reduce its particle size and increase its specific surface area to greater than 2 m.<sup>2</sup>/g. Two percent by weight of tungsten is added to provide tungsten to be dissolved in the cobalt binder phase, along with finely divided cobalt powder.

The fine commercial tungsten carbide powder was that employed in Example 2, having a particle size of about a micron and a specific surface area of 0.66 m.<sup>2</sup>/g. To a steel mill and carbide grinding medium as described in Example 1 are charged 1470 parts by weight of the commercial tungsten carbide powder and 1185 parts by weight of acetone. The carbide is milled for 48 hours. Then 30 parts of one micron tungsten powder and 205 parts of fine cobalt powder are added to the mill and milling continued for 72 hours. The inter-dispersed powder is then removed from the mill and dried and screened in an inert atmosphere, loaded in the molds and hot pressed in accordance with the procedure described in Example 2. The powder contains an atomic ratio of carbon to tungsten of 1.0, but due to the very finely divided nature of the material it combines with enough oxygen, either from the acetone or, in spite of precautions, from the inert atmosphere employed to reduce the atomic ratio of carbon to tungsten in the final hot pressed body to slightly less than one.

Analysis of the body shows a carbon to tungsten atomic ratio of 0.98 and a cobalt content of 10 percent by weight. The body has a porosity of A-1, 90% of the grains of tungsten carbide are smaller than one micron and the mean grain size is 0.6 microns. The acid resistance is greater than 150 hours. The cobalt phase contains 20% by weight of tungsten in solid solution. The body contains about 1% of tungsten-rich eta phase based on the weight of the composition. When subjected to the standard annealing test the tungsten dissolved in the cobalt phase is reduced to 9% by weight and the transverse rupture strength of the body decreases from 539,000 to 475,000 p.s.i. and the hardness is reduced from 91.5 to 91.0 Rockwell A.

#### EXAMPLE 24

The composition of this example is prepared from an aggregated colloidal tungsten carbide powder prepared as in Example 1, except with a smaller amount of carbon, so as to produce an aggregated colloidal tungsten

carbide powder having an atomic ratio of carbon to tungsten of 0.99.

Fourteen hundred parts of this powder are milled for 7 days in acetone along with 250 parts of cobalt to give an interdispersion, and the mixture is then recovered, dried and screened out of contact with the atmosphere. The powder is then heated at 900° C. for two hours in an atmosphere consisting of 85% hydrogen and 15% oxygen, cooled to room temperature and screened in a nitrogen atmosphere. Ninety grams of the powder is loaded into a graphite mold of 1 inch by 1 inch cross-section, and pressed between graphite pistons at room temperature and 200 p.s.i. The pressure is then removed and the powder and mold heated in 6 minutes to 1350° C. without pressure, held at this temperature for 5 minutes to heat-treat the powder, permitting the mass to sinter, and then 2000 p.s.i. pressure is applied while the temperature remains at 1350° C. for a period of one minute. The pressure is then removed and the sample is ejected from the furnace and permitted to cool to 800° C. in 2 minutes.

The transverse rupture strength is 441,000 p.s.i., the hardness is 91.0 Rockwell A. The density is greater than 98% of theoretical. The cobalt metal phase contains 18% tungsten in solid solution and about 30% by weight of eta phase. When subjected to the standard annealing test, the transverse rupture strength as subsequently measured size of a micron, are placed in a V-blender revolving at size is less than 0.75 microns. Because of the very low atomic ratio of carbon to tungsten, there is a considerable amount of eta phase in the pressed body and thus less cobalt metal phase is present, so that annealing caused only a slight decrease in strength.

#### EXAMPLE 25

A reduced tungsten carbide powder containing 12% by weight of cobalt of the type employed for hot pressing billets in Example 1, is loaded as a loose powder in a rectangular graphite mold, 1 inch by 1 and  $\frac{5}{16}$  inches cross-section, employing 85 grams of powder. This is placed in the vacuum hot press and the loaded mold fitted with pistons is moved into the hot zone of the furnace at a temperature of about 1000° C., without applying more than 200 p.s.i. to the powder held in place by the pistons as it is being moved into the furnace. All pressure is then removed, and the mold and contents are heated in a period of 4.5 minutes from 1000° to 1350° C., and at once sufficient pressure is exerted on the pistons to subject the sample to a mechanical pressure of 500 p.s.i., while heating is continued for a period of 3.5 minutes while the temperature is slowly and continuously raised from 1350° to 1400° C. Of the 3.5 minutes, about one minute is required for the temperature to increase from 1350° to 1400° C. and the remaining 2.5 minutes the temperature of the sample is held at 1400° C. under pressure. Immediately thereafter, the pressure is removed and the sample and mold are removed from the hot zone of the furnace into a cooling zone and the temperature of the mold and sample drops to around 800° C. in a period of about two minutes. It is thereafter permitted to cool to room temperature over the next 30 minutes before being removed from the furnace, thereby avoiding oxidation of the mold. The body so obtained is tested and found to have a transverse rupture strength of 591,000 p.s.i. and a hardness of 92.0 Rockwell A. The AISI porosity rating is A-2. The pressed body contains about 10% by weight of cobalt; there is more than 15% tungsten in solid solution in the cobalt phase, and material shows a behavior upon being reheated and cooled slowly, of an unannealed body of the invention. The mean grain size of the tungsten carbide is 0.56 microns.

#### EXAMPLE 26

Blending of colloiddally subdivided tungsten carbide and cobalt is carried out as follows: 1408 grams of tungsten

carbide of Example 1, having a specific surface area of 7.1 square meters per gram, and an individual crystallite size of around 31 millimicrons as determined by X-ray line broadening, and 192 grams of "Cobalt F" powder, also of the type used in Example 1, and having a particle size of a micron, are placed in a V-blender revolving at about one revolution per second, for a period of about one hour, and are then removed and screened through a 60 mesh screen and again blended for another hour.

The blended powder is then reduced in hydrogen-methane by the same procedure as described in Example 1. The resultant powder is hot pressed as in Example 1, except that the temperature is 1400° C. instead of 1420° C. The resulting body has a transverse rupture strength of 505,000 p.s.i. and a hardness of 92.1 Rockwell A. The density is over 98% of theoretical. Although this method avoids the step of ball-milling, it has the disadvantage that the powder is considerably more voluminous than the milled and reduced powder of Example 1, and less material can be loaded into a mold of given volume. However, for pressing smaller pieces, the powder is satisfactory and omission of the prolonged milling operation is of considerable advantage. The body contains 10% by weight of cobalt, has more than 12% by weight of tungsten dissolved in the cobalt phase, and behaves characteristically as an unannealed body, and has a mean grain size less than one micron.

#### EXAMPLE 27

The commercial tungsten carbide employed in this example contains 6.33% by weight of carbon, 93.6% by weight of tungsten, 0.05% by weight of oxygen; the specific surface area of the powder as determined by nitrogen adsorption is 0.62 m.<sup>2</sup>/g.; and it contains less than 0.05% of iron, nickel and cobalt.

Four hundred grams of this tungsten carbide powder and 5.2 g. of the finely divided type of cobalt metal powder employed in Example 1 are placed in a one quart steel ballmill containing 3 kilograms of ¼ inch diameter by ¼ inch long cylinders of commercial tungsten carbide bonded with 6% cobalt, of the type used in Example 1. The mill is half filled with a saturated aliphatic hydrocarbon having a flash point of 130° F., the amount added to the mill being sufficient to just cover the carbide grinding media. The mill is run for 8 days, at 60 r.p.m., being tightly sealed during the period to prevent loss of solvent or intake of air. At the end of the milling period, the contents are washed out with normal hexane, while keeping the product out of contact with the atmosphere. The hexane suspension is permitted to stand until the black tungsten carbide-cobalt mixture has settled, the excess solvent then is removed by decantation and the residual black slurry is dried by distilling off the hydrocarbon under vacuum. The dried powder is then passed through a screen of 60 meshes per inch, and stored in a closed container. All the foregoing operations are carried out with the exclusion of air, and under an atmosphere of nitrogen containing less than 50 p.p.m. of oxygen.

The tungsten carbide grinding cylinders, after being washed and dried, are found to have lost less than 20 grams in weight. The milled powder contains an average of 1.2% oxygen, in spite of the precautions, has a specific surface area of 4.3 m.<sup>2</sup>/g., and by X-ray analysis consists of tungsten carbide crystallites 19 millimicrons in average diameter. It contains 6.7% by weight of carbon. The powder is then reduced by being heated at 950° C. for 2 hours in an atmosphere containing 15% argon, 83% hydrogen and about 2% methane, and is then allowed to cool in a stream of argon.

The resulting powder is handled and stored under nitrogen. The powder contains: carbon—6.00%; oxygen—0.22%; and the specific surface area is 1.6 m.<sup>2</sup>/g. It consists of tungsten carbide crystallites of 30 millimicrons average size, according to X-ray line broadening. No free carbon is present and the atomic ratio of carbon to tung-

sten is about 0.99. The powder is passed under nitrogen, through a screen of 40 meshes per inch, and the fines removed through a screen of 100 meshes per inch. The resulting 40 to 100 mesh powder is vacuum hot pressed as follows: Fifty grams is loaded into a one inch diameter graphite mold and compressed between graphite pistons under a pressure of 200 p.s.i. and moved into the hot zone of the furnace at 1200° C. and the pressure immediately removed. The temperature is then raised at a uniform rate over a period of 6 minutes to 1800° C. where it is held for 5 minutes, after which a pressure of 4000 p.s.i. is applied for a period of one minute. During this time the material is fully consolidated. The molded material in its container is removed immediately from the hot zone and permitted to cool to about 1000° C. within a period of 2 minutes and to room temperature over a period of the next hour.

The product, hereinafter called product "A," has a transverse rupture strength of 230,000 p.s.i., an impact strength of 11 ft. lbs./in.<sup>2</sup>, a Rockwell A hardness of 92.3, and a density of 15.4 grams per cc.

Another sample of the reduced powder which has been passed through a 40 mesh screen but from which the finer material has not been removed, is pressed in exactly the same manner and the resulting molded body has a transverse rupture strength of 235,000 p.s.i. an impact strength of 6 ft. lbs./in.<sup>2</sup>, a Rockwell A hardness of 92.3, and a density of 15.40 grams per cc. Examination of the test body by X-ray diffraction indicates that it contains about 1% of eta phase, Co<sub>3</sub>W<sub>3</sub>C. There is 31 percent by weight of tungsten in the cobalt phase.

For examination of the microstructure, a specimen is cut from the molded bodies in a plane parallel to the pressing direction. Examination of the polished and etched sections by metallographic microscope reveals that the structures consist largely of platelets of tungsten carbide from 2 to 5 microns in diameter and from 2 to less than 1 micron in thickness. The platelets are visible in cross-section, appearing as longitudinal areas predominantly aligned at right angles to the pressing direction. It will be noted that since in an array of platelets lying for the most part parallel to each other and at right angles to the plane of the cross-section, only a small portion of the platelets will by chance have been cut through the center to reveal the maximum platelet diameter or breadth. In most cases, less than the whole breadth of a platelet is revealed. Thus, judging by the cross-sections of the platelets, one can at least judge the maximum breadth, which in this case is about 5 microns. The thickness of different plates appears to be similar and about one micron. Electron micrographs show a mean grain size slightly less than one micron.

A glass cutting knife is made by cementing a triangular section of material "A," ¼ inch to a side and ⅛ inch in thickness in a suitable holder. The two corners of the triangular point are sharpened by diamond grinding, and prove to be very durable for scoring glass.

#### EXAMPLE 28

A colloiddally subdivided tungsten carbide is made by reaction in fused calcium chloride as described in Example 1, but with a deficiency of carbon in the reaction mixture, so that the aggregated colloidal tungsten carbide contains small amounts of tungsten and ditungsten carbide in addition to tungsten monocarbide, and the overall atomic ratio of carbon to tungsten is 0.94. This product is milled with cobalt as in Example 1, giving an interdispersed powder containing 12% cobalt by weight. It is not reduced, but handled out of contact with air and loaded directly into the graphite mold. A body is fabricated and rapidly cooled as described in Example 1.

The transverse rupture strength is 511,000 p.s.i., the hardness is 92.0. Examination by X-rays and the electron microscope shows that more than 90% of the tungsten carbide grains are smaller than one micron. Estimating from electron micrographs, roughly 10% by volume of



tungsten-rich eta phase,  $\text{Co}_3\text{W}_3\text{C}$  is present, which accounts for roughly half of the total cobalt.

The body thus contains 10.1% by weight of cobalt, of which an appreciable portion remains as metal binder phase; this phase contains 24% by weight of tungsten in solid solution.

When the body is subjected to the standard annealing test, a further proportion of cobalt in the metal binder phase is converted along with the tungsten-rich eta phase to a cobalt-rich eta phase, which is characteristics of an annealed body. The presence of finely divided eta phase minimizes the crystallization of tungsten carbide during the annealing test, and high hardness is maintained; the body loses 10 percent in strength.

The advantage of such bodies over those available from processes of the prior art is that a finer grain structure and higher hardness is thus possible for a given cobalt content, and the resulting body is not subject to recrystallization to a coarser carbide structure when heated to temperatures above  $1250^\circ\text{C}$ . for re-shaping as in twisting inserts for boring tools.

#### EXAMPLE 29

As an example of molding a large billet, the reduced powder of Example 1 is cold pressed to a billet 3 inches in diameter and 1 inch thick, by isostatic pressing in a rubber mold at 50,000 p.s.i. The billet is then heated very slowly in a vacuum furnace in an alumina crucible and degassed by heating over a period of eight hours at a uniform rate of temperature rise to  $1000^\circ\text{C}$ . The billet is then cooled to room temperature and hot pressed while embedded in alumina in a graphite cylindrical mold, 3 inches in inside diameter, fitted with graphite pistons. A quarter inch layer of 325 mesh tabular alpha alumina powder is placed on the lower piston; while the mold is held with its axis in an upright position, the billet is placed on the powder and additional alumina is poured around it and over it to a depth of  $\frac{1}{4}$  inch. The upper graphite piston is then inserted. The mold assembly is heated in a vacuum hot press without pressure from room temperature to  $1000^\circ\text{C}$ . in 20 minutes and then 4000 p.s.i. is applied and the temperature raised from 1000 to  $1425^\circ\text{C}$ . in eight minutes. A pressure of 4000 p.s.i. is maintained on the pistons to the alumina-encapsulating billet for a period of a total of 5 minutes while the temperature is maintained at  $1425^\circ\text{C}$ . Then the pressure is released and the mold removed from the furnace and cooled to  $700^\circ\text{C}$ . by radiation in 15 minutes.

After the alumina ceramic is broken away from the billet, it is tested as follows: The resulting body has a transverse rupture strength of 470,000 p.s.i.; a hardness of 90.5 Rockwell A; contains 11.7% cobalt and the cobalt binder phase contains 17% by weight of tungsten in solid solution. The acid resistance of the body is greater than 50 hours. The mean grain size of the tungsten carbide is 0.8 microns and 81% of the grains are smaller than one micron. The billet is shaped by electrodischarge machining into an extrusion die.

I claim:

1. A process for preparing a body of tungsten carbide interdispersed with from 1 to 30 percent of cobalt based on the total weight of the body, comprising the steps of:

(a) heating a composition consisting of cobalt homogeneously interdispersed with tungsten carbide, in an inert atmosphere at a temperature  $T_s$  between  $1000^\circ\text{C}$ . and  $T_h^\circ\text{C}$ . for from  $t_s$  to 20  $t_s$  minutes where

$$\log_{10} t_s = \frac{13250}{T_s + 273} - 8.2$$

and

$$T_h = \frac{6.5 - \log_{10} (P - 0.3)}{0.0039}$$

where P is the percent by weight of cobalt, said tungsten carbide having an average particle size of less than 1 micron, a specific surface area of at least

3 square meters per gram, and containing more than 0.81 and less than 1.0 atomic weights of combined carbon per atomic weight of tungsten.

(b) thereafter pressing the composition to a density in excess of 95% of theoretical in a heated zone at a temperature of  $T_m$  for a time of from  $t_m$  to 20  $t_m$  minutes, where

$$\log_{10} t_m = \frac{13250}{T_m + 273} - 8.2$$

and where

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

and cooling the pressed composition at a rapid rate.

2. The process of claim 1 wherein the cooling rate is in excess of  $10^\circ\text{C}$ . per minute.

3. A process for preparing a body of tungsten carbide interdispersed with from 1 to 30 percent of cobalt based on the total weight of the body, comprising the steps of

(a) milling a cobalt powder with tungsten carbide powder in an inert liquid until the average particle size of the tungsten carbide is smaller than one micron, and the tungsten carbide has a specific surface area of at least 3 square meters per gram,

(b) recovering the interdispersed powder mixture from the liquid medium in an inert atmosphere and drying it in an inert atmosphere, the milled mixture being further characterized in that the tungsten carbide contains more than 0.81 and less than 1.0 atomic weights of carbon per atomic weight of tungsten,

(c) heating the powder without mechanical restraint in an inert atmosphere at a temperature  $T_s$  between  $1000^\circ\text{C}$ . and  $T_h^\circ\text{C}$ . for from  $t_s$  to 20  $t_s$  minutes, where

$$\log_{10} t_s = \frac{13250}{T_s + 273} - 8.2$$

and

$$T_h = \frac{6.5 - \log_{10} (P - 0.3)}{0.0039}$$

where P is the percent by weight of cobalt.

(d) thereafter pressing the mixture to a density in excess of 95% of theoretical at a temperature of up to  $T_m$  for a time of from  $t_m$  to 20  $t_m$  minutes where

$$\log_{10} t_m = \frac{13250}{T_m + 273} - 8.2$$

and where

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

and cooling the composition at a rapid rate.

4. The process of claim 3 wherein the cooling rate is in excess of  $10^\circ\text{C}$ . per minute.

5. The process of claim 3 wherein the dried powder mixture recovered in step (b) is subjected to a stream of a slightly carburizing mixture of hydrogen and methane at a temperature of  $750$  to  $1000^\circ\text{C}$ ., and thereafter following steps (c) and (d).

6. The process of claim 3 in which the dry powder mixture of step (b) is preconsolidated at a temperature of up to  $T_s$  for up to  $t_s$  minutes with the limitation that preconsolidation temperature is not above  $1250^\circ\text{C}$ ., and thereafter following steps (c) and (d).

7. The process of claim 3 in which the dry powder mixture from step (b) is subjected to a stream of a slightly carburizing mixture of hydrogen and methane at a temperature of  $750$  to  $1000^\circ\text{C}$ . and is preconsolidated at temperatures up to  $T_s$  for up to  $t_s$  minutes with the limitation that the preconsolidation temperature is not above  $1250^\circ\text{C}$ ., and thereafter following steps (c) and (d).

8. The process of claim 3 in which the dry powder mixture from step (b) is degassed at a temperature of  $400$  to  $700^\circ\text{C}$ . in an inert atmosphere and is then con-

solidated at a temperature below 400° C. under mechanical pressure of at least 5000 pounds per square inch, and thereafter following steps (c) and (d).

9. A process for preparing a body of tungsten carbide interdispersed with from 3 to 15 percent cobalt based on the total weight of the body, comprising the steps of

(a) milling cobalt powder with tungsten carbide powder in an inert liquid until the particle size of the tungsten carbide is in the range of 10 to 1000 millimicrons, the average particle size is less than 750 millimicrons, and the metal and tungsten carbide are homogeneously interdispersed,

(b) recovering the powder mixture from the liquid medium in an inert atmosphere and drying it in an inert atmosphere, the milled mixture being further characterized as containing less than 1.0% by weight of oxygen and tungsten carbide which contains more than 0.81 and less than 1.0 atomic weights of carbon per atomic weight of tungsten, and has a specific surface area of from 3 to 15 square meters per gram,

(c) heating the powder without mechanical restraint in an inert atmosphere at a temperature  $T_s$  between 1000° C. and  $T_h$ ° C., for from  $t_s$  to 20  $t_s$  minutes, where

$$\log_{10} t_s = \frac{13250}{T_s + 273} - 8.2$$

and

$$T_h = \frac{6.5 - \log_{10} (P - 0.3)}{0.0039}$$

where P is the percent by weight of cobalt.

(d) thereafter, pressing the mixture to a density in excess of 95% of theoretical at a temperature of up to  $T_m$  for a time of from  $t_m$  to 20  $t_m$  minutes where

$$\log_{10} t_m = \frac{13250}{T_m + 273} - 8.2$$

and where

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

and cooling the pressed composition at a rate in excess of 10° C. per minute.

10. A process for preparing a powder of tungsten carbide interdispersed with from 1 to 30 percent cobalt based

on the total weight of the powder, comprising heating a powder composition in an inert atmosphere at a temperature from  $T_s$  between 1000° C. and  $T_h$ ° C. for from  $t_s$  to 20  $t_s$  minutes where

$$\log_{10} t_s = \frac{13250}{T_s + 273} - 8.2$$

and

$$T_h = \frac{6.5 - \log_{10} (P - 0.3)}{0.0039}$$

where P is the percent by weight of metal, the starting composition consisting of cobalt in powder form homogeneously interdispersed with tungsten carbide, said tungsten carbide having a particle size of from 10 to 1000 millimicrons and a specific surface area of 3 to 15 square meters per gram, and containing more than 0.81 and less than 1.0 atomic weights of combined carbon per atomic weight of tungsten.

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A. J. STEINER, Assistant Examiner

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75—211, 214, 226, 227