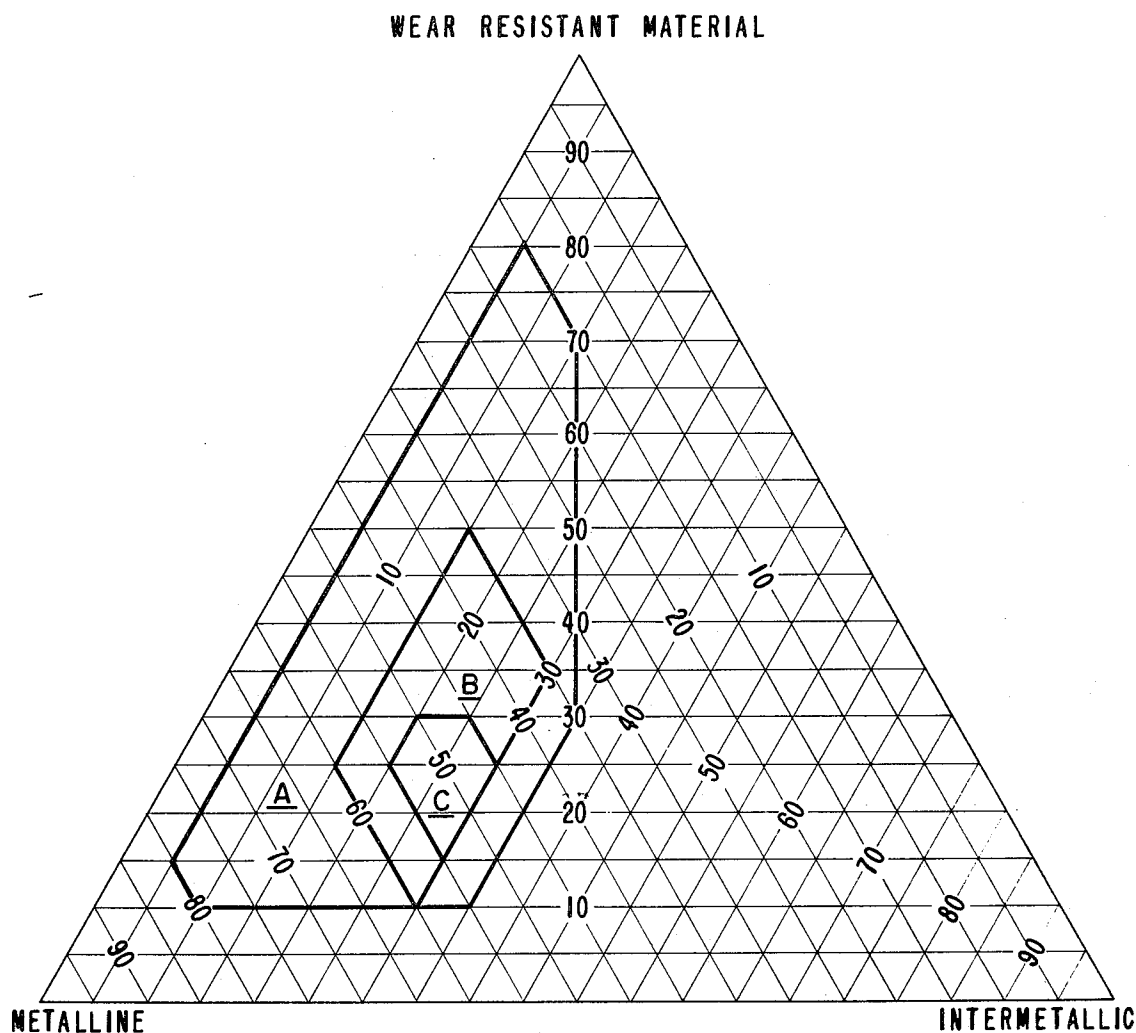


July 11, 1972

P. C. YATES
REFRACTORIES BONDED WITH ALUMINIDES, NICKELIDES, OR
TITANIDES
Filed March 3, 1969

3,676,161



INVENTOR
PAUL C. YATES

BY *Fred E. McKelvey*

ATTORNEY

1

3,676,161

REFRATORIES BONDED WITH ALUMINIDES, NICKELIDES, OR TITANIDES

Paul C. Yates, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.

Filed Mar. 3, 1969, Ser. No. 803,817

Int. Cl. C04b 35/70

U.S. Cl. 106—55

14 Claims

ABSTRACT OF THE DISCLOSURE

Dense compositions having a grain size smaller than 10 microns and containing from 10 to 80 volume percent of a wear-resistant material selected from the group consisting of (a) aluminum nitride, (b) tantalum nitride, (c) mixtures of (a) and (b), and (d) a refractory oxide of an element selected from the group consisting of magnesium, zirconium, hafnium, titanium, chromium, beryllium, zinc, calcium, thorium, barium, strontium, silicon, the rare earth metals, and mixtures thereof; 15 to 80 volume percent of a metalline selected from the group consisting of titanium carbide, titanium nitride, zirconium carbide, zirconium nitride, tantalum carbide, niobium carbide, niobium nitride, and mixtures thereof; and 5 to 35 volume percent of an intermetallic selected from the group consisting of molybdenum nickelide, tantalum nickelide, zirconium nickelide, niobium nickelide, cobalt aluminide, cobalt titanide, iron aluminide, iron titanide, nickel aluminide, nickel titanide, tungsten aluminide, molybdenum aluminide, niobium aluminide, tantalum aluminide, titanium aluminide, zirconium aluminide, and mixtures thereof are (1) effective for cutting tools for high speed machining and (2) resistant to oxidation.

SUMMARY OF THE INVENTION

It has been discovered that particular compositions of aluminum nitride, tantalum nitride or refractory oxides (other than aluminum oxide) and certain carbides and nitrides bonded with an intermetallic are useful for making cutting tips having unusual properties. These compositions can be used to produce a cutting tip with an unusual combination of hardness and strength and one which is very resistant to wear and thermal shock. In addition the dense compositions of this invention are useful as wear resistant, oxidation-resistant and chemical-resistant materials of construction.

This invention is directed to such dense compositions which have an average grain size smaller than 10 microns and are composed to two interpenetrating three-dimensional networks; one network consisting essentially of a wear-resistant material selected from the group consisting of:

- (a) aluminum nitride;
- (b) tantalum nitride;
- (c) mixtures of aluminum nitride and tantalum nitride; and
- (d) a refractory oxide an element selected from the group consisting of magnesium, zirconium, hafnium, titanium, chromium, beryllium, zinc, calcium, thorium, barium, strontium, silicon, the rare earth metals, and mixtures thereof;

2

the other network consisting essentially of a metalline selected from the group consisting of:

- titanium carbide,
- titanium nitride,
- 5 zirconium carbide,
- zirconium nitride,
- tantalum carbide,
- niobium carbide,
- niobium nitride, and
- 10 mixtures thereof;

and an intermetallic selected from the group consisting of:

- molybdenum nickelide,
- 15 tantalum nickelide,
- zirconium nickelide,
- niobium nickelide,
- cobalt aluminide,
- cobalt titanide,
- 20 iron aluminide,
- iron titanide,
- nickel aluminide,
- nickel titanide,
- 25 tungsten aluminide,
- molybdenum aluminide,
- niobium aluminide,
- tantalum aluminide,
- titanium aluminide,
- zirconium aluminide,
- 30 and mixtures thereof;

the wear-resistant material being present in an amount ranging from 10 to 80 volume percent; the metalline being present in an amount ranging from 15 to 80 volume percent; and the intermetallic being present in an amount ranging from 5 to 35 volume percent, with the limitation that the volume percent of the metalline must not be less than the volume percent of the intermetallic.

- Surprisingly these composition demonstrate exceptional advantages over similar compositions consisting of closely related compounds and over compositions of these same compounds in different amounts. As a result of their exceptional properties the compositions of this invention are useful in cutting and milling ferrous alloys even at very high cutting speeds.

DESCRIPTION OF DRAWING

- The figure is a graphical representation of the amounts of the components embraced within the compositional limits of this invention. Area A is that area in which the compositional ratios are within the limits of this invention, Area B is that area in which the compositional ratios are within the preferred limits of this invention, and Area C is that area in which the compositional ratios are most preferred. Percentages shown on the graph are volume percents.

DESCRIPTION OF THE INVENTION

Components

- The refractory compositions of this invention consist essentially of a wear-resistant material, a metalline, and an intermetallic.

- (a) Wear-resistant material.—The wear resistant materials are commercially available as fine powders. Although minus 80 mesh powders (U.S. Standard Sieve Series) may

be used to prepare compositions of the invention, minus 200 mesh powders are preferred and minus 325 mesh powders most preferred. Aluminum nitride powders are available from Consolidated Astronautics, Inc. or Materials for Industry; tantalum nitride powders from Cerac, Inc.; and the refractory oxide powders may be obtained from sources such as Zirconium Corporation, Beryllium Corporation, Foote Minerals, and Materials for Industry.

The wear resistant material is selected from the group consisting of:

- (a) aluminum nitride;
- (b) tantalum nitride;
- (c) mixtures of aluminum nitride and tantalum nitride; and
- (d) a refractory oxide of an element selected from the group consisting of magnesium, zirconium, hafnium, titanium, chromium, beryllium, zinc, calcium, thorium, barium, strontium, silicon, the rare earth metals, and mixtures thereof,

and is present in the composition in amounts ranging from 10 to 80 volume percent. Compositions containing less than 10 volume percent do not possess adequate wear resistance, and above 80 volume percent the compositions are excessively brittle.

The wear-resistant material is preferably present in amounts ranging from 10 to 50 volume percent and more preferably from 15 to 30 volume percent, since these amounts give rise to compositions having an excellent balance of wear resistance, strength and toughness.

(b) Carbides or nitrides (metalline).—The metalline compounds are used in the compositions of this invention in amounts ranging from 15 to 80 volume percent and are selected from the group consisting of titanium carbide, titanium nitride, zirconium carbide, zirconium nitride, tantalum carbide, niobium carbide, niobium nitride, and mixtures thereof.

When zirconium carbide or zirconium nitride is used, it may contain a small amount of hafnium carbide or nitride (i.e., 1% to 5% by weight, usually about 2%), which is normally present as an impurity in technical grades of zirconium compounds.

Preferred amounts of metalline range from 30 to 60 volume percent and most preferred amounts range from 45 to 55 volume percent. These amounts contribute most effectively to properties such as hardness and wear resistance in the compositions of this invention.

The metalline can be obtained commercially or can be synthesized by methods well known to the art. The metallines should preferably have a particle size of less than 5 microns and more preferably less than 2 microns. If the starting material is appreciably larger than 5 microns in particle size it can be pre-ground to reduce its size to that which is acceptable. Of course the milling of the components of this invention, which is carried out to obtain a high degree of homogeneity, will result in some comminution of the metalline and the other starting components.

Titanium nitride, titanium carbide, zirconium nitride, and zirconium carbide are preferred for use in the compositions of this invention as they are readily available, result in compositions which have an excellent balance of physical properties, and demonstrate great effectiveness when used to cut or mill ferrous alloys. The most preferred metalline is titanium nitride.

(c) Intermetallic.—The intermetallics suitable for use in this invention are selected from the group consisting of molybdenum nickelide, tantalum nickelide, zirconium nickelide, niobium nickelide, iron aluminide, iron titanide, cobalt aluminide, tungsten aluminide, molybdenum aluminide, niobium aluminide, titanium aluminide, zirconium aluminide, and mixtures thereof. The intermetallic is present in amounts ranging from 5 to 35 percent. At least five volume percent is necessary in order to provide any significant bonding in the body and amounts greater than this give rise to additional strength and toughness although

decreased wear resistance. Above 35 volume percent little further improvement in strength is obtained, but the wear resistance is decreased considerably.

The intermetallic is preferably present in amounts ranging from 15 to 30 volume percent, and more preferably from 20 to 30 volume percent, since these amounts result in strong compositions without adversely affecting wear resistance.

When zirconium aluminide or zirconium titanide is used, it may contain the usual amounts of hafnium, i.e., from 1% to 5% by weight.

The most preferred intermetallics are molybdenum nickelide, iron aluminide, cobalt aluminide, and nickel aluminide, because they are the most ductile of the refractory intermetallic binders used in the compositions of the invention.

Aluminides of nickel, molybdenum, and niobium available from Cerac, Inc.; iron aluminide from Shieldalloy Corp.; iron titanide from Shieldalloy Corp. or Foote Mineral Co.; and nickel titanide from Metal Hydrides, Inc. may be used. Also the intermetallic compounds can be synthesized in situ by mixing together the correct ratio of elements in the powder from which the dense bodies of the invention are made.

The intermetallics can be synthesized by melting together the stoichiometric ratio of the components in an inert refractory crucible in a vacuum furnace. After allowing to cool, the solid billet of the intermetallic can frequently be broken up in a hammer mill and ground to a fine mesh size in a ball mill. Alternatively, a fine powder can be obtained by atomizing the molten intermetallic by the procedures known to the art for the production of atomized metal powders. Although minus 50 mesh powders (U.S. Standard Sieve Series) may be used to prepare compositions of the invention, minus 200 mesh powders are preferred, and minus 325 mesh most preferred.

The fine intermetallic powders prepared as described above can then be incorporated in compositions to be used in fabricating dense bodies of the invention.

(d) Impurities.—The components used in the compositions of this invention should be essentially pure. It is desirable to exclude impurities such as oxygen which would tend to have deleterious effects on the dense compositions of this invention.

However, minor amounts of many impurities can be tolerated with no appreciable loss of properties.

Thus, the intermetallic can contain small amounts of metals such as titanium, zirconium, tantalum or niobium as minor impurities, although low melting metals like lead should be excluded. Small amounts of carbides other than titanium, zirconium, niobium or tantalum carbide, such as several percent of tungsten carbide, which is sometimes picked up in grinding, can be present. Even oxygen can be tolerated in small amounts such as occurs when titanium carbide has been exposed to air resulting in a few percent of titanium oxy-carbide. However, after the powder components have been milled together and are in a highly reactive state, oxidation, particularly of the intermetallic, occurs easily and should be avoided.

When aluminum nitride is used as the wear-resistant material, it may contain the amount of Al_2O_3 usually present in commercial grade aluminum nitride, i.e., from 1% to 5% by weight.

Structural characteristics

In addition to characterizing the composition of this invention on the basis of the components discussed above, the compositions can also be characterized on the basis of their structural characteristics.

(a) Interpenetrating three-dimensional networks.—The compositions of this invention are characterized as containing two interpenetrating three-dimensional networks: one of wear-resistant material and one of intermetallic bonded carbide or nitride. The two networks may be observed in optical micrographs taken on etched polished

surfaces of compositions of the invention. Using conventional metallographic techniques and various etches known to those in the art, the contrast between the various phases can be brought out and it can be seen that there are interpenetrating networks. This can be demonstrated even further using the scanning electron microscope on heavily etched surfaces.

While the effects of the presence of these two networks is not completely understood it is believed that they contribute substantially to the unusual properties of the compositions of this invention, resulting in compositions much stronger and more impact-resistant than conventional alumina ceramic cutting tools.

The presence of a continuous phase of the electrically conducting metalline and intermetallic is apparent from the electrical conductivity of the hot-pressed compositions of this invention. The compositions of this invention preferably have a specific electrical resistivity of less than about 1 ohm-centimeter, more preferably less than about 25,000 micro-ohm-centimeter and most preferably less than 5,000 micro-ohm-centimeter. The preferred compositions of this invention, in which metalline plus intermetallic amount to 35 volume percent or more, often have a specific electrical resistivity of less than 1000 micro-ohm-centimeter.

(b) Thermal coefficients of expansion.—The compositions of this invention are also characterized as having two continuous interpenetrating networks with very similar thermal coefficients of expansion. Generally the coefficient of expansion of the wear-resistant phase as well as the metalline and intermetallic phase will range between 4×10^{-6} and 5×10^{-6} inches/inch/ $^{\circ}$ F. at temperatures from room temperature up to 1000° F.

As a result of the similarity of these thermal coefficients, cutting tips of the compositions of this invention are able to undergo extreme temperature change with little or no thermal strain being generated within the composition. The compositions are very resistant to thermal shock both as regards shattering and as regards surface heat cracking.

(c) Homogeneity and fine-grained structure.—The compositions of this invention are also characterized as having a fine number average grain size, smaller than 10 microns and preferably smaller than 5 microns in average grain diameter. The number average grain size and the size distribution are obtained from enlarged electron micrographs on polished etched surfaces using an extension of the methods of John E. Hilliard described in "Metal Progress," May 1964, pages 99 to 102, and of R. L. Fullman, described in the Journal of Metals, March 1953, page 447, et seq. The grain size is uniform and homogeneous throughout the composition and there is essentially no porosity in the dense compositions of this invention. Distribution of the two co-continuous phases is also uniform and homogeneous, and generally speaking any area 100 microns square which is examined microscopically at $1000\times$ magnification will appear the same as any other area 100 microns square, within conventional statistical distribution limits.

The fine grain size of the compositions of this invention is of course at least partly responsible for the continuity of the interpenetrating phases. However it also contributes along with the homogeneity and low porosity to the abrasion resistance of the compositions of this invention. Metal inclusions such as the carbide inclusions in cast iron abrade even the hardest of the metal-bonded, carbide cutting tools. Nevertheless the compositions of this invention are outstandingly abrasion resistant.

Preparation

The preparation of the compositions of this invention is important because many of the characteristics of the compositions are achieved as a result of the manner in which they are prepared. Thus, the use of fine-grained starting materials and thorough milling of the mixed

components are directly related to the fine grain size and uniform homogeneity of the compositions. Other precautions observed in preparing the compositions of this invention which have important effects on the products are:

- (1) the prevention of excessive contamination from grinding media and moisture or oxygen in the air;
- (2) hot-pressing or sintering under conditions which permit the escape of volatile materials prior to densification;
- (3) avoiding undue absorption of carbon from pressing molds by limiting their contact under absorption-promoting conditions;
- (4) avoiding excessive component recrystallization and resultant segregation by avoiding prolonged subjection to very high temperatures.

(a) Milling and powder recovery.—Milling of the components, to homogeneously intermix them and obtain very fine grain sizes, is carried out according to the practices common in the art. Optimum milling conditions will ordinarily involve a mill half-filled with a grinding medium such as cobalt bonded tungsten carbide balls or rods, a liquid medium such as a hydrocarbon oil, an inert atmosphere, grinding periods of from a few days to several weeks, and powder recovery also in an inert atmosphere. The recovered powder is ordinarily dried at temperatures of around $150\text{--}200^{\circ}$ C. under vacuum, followed by screening and storage when desirable in an inert atmosphere.

(b) Consolidation.—The compositions of this invention are ordinarily consolidated to dense pore-free bodies by sintering under pressure. Consolidation is ordinarily carried out by hot-pressing the mixed powders in a graphite mold under vacuum.

When the powders are hot-pressed they are placed in the mold and inserted into the heated zone of the hot press without application of pressure thus allowing volatile impurities to escape before the composition is densified. Full pressure is usually applied at or near the maximum temperature.

Maximum temperatures range between 1400 and 1900° C. depending upon the amount of intermetallic present and will ordinarily be between 1600 and 1800° C. Maximum pressures range between 500 and 4000 p.s.i. with lower pressures being used usually in combination with lower temperatures for compositions with a high intermetallic content. Conversely, higher pressures and temperatures are employed for compositions low in intermetallic.

As will be apparent, at higher temperatures and pressures some of the lower melting intermetallic components will tend to squeeze out of the compositions during densification. This tendency can be used to advantage by starting with a little more intermetallic than is desired, and operating at a high temperature and pressure. By this procedure some of the intermetallic will be squeezed out to give the desired intermetallic content and the molten intermetallic that is eliminated will act as a lubricant and sintering aid during pressing. By this means voids can be eliminated in spite of the highly refractory nature of the final composition.

It is important that the composition not be heated to a temperature, or for a period of time, which is in excess of that required to eliminate porosity and achieve density. Such higher temperatures or longer times result in undesirable grain growth and a resultant coarsening of the structure, and can even result in development of secondary porosity due to recrystallization, or in the formation of undesirable phases.

As will be demonstrated hereinafter, pressing temperatures in the range of 1700 to 1900° C. are usually employed for the preferred products of this invention and maximum temperature is applied for less than 30 minutes, usually no more than 10 minutes and preferably

no more than 5 minutes after which the product is removed from the hot zone. By these procedures the compositions of this invention are compacted such that porosity is eliminated and maximum density attained without undue recrystallization. Such products are characterized by their fine grain size and outstanding transverse rupture strength.

The compositions of this invention, particularly those with high intermetallic content and small particle sizes, can also be densified by cold-pressing and sintering under high vacuum provided that the above limitation on minimum sintering time at maximum temperature is followed. It is preferred to isostatically press the powder in a sealed rubber mold suspended in water in an isostatic press capable of applying high pressures (60,000 p.s.i.) hydrostatically.

Utility

The compositions of this invention can be employed in a variety of types of cutting tools designed for numerous use applications. They can be molded or cut into standardized disposable inserts, suitable for turning, boring or milling. Or, they can be laminated with or otherwise bonded to metal-bonded carbides or tool steels for regrindable types of tooling. They are suitable generally for metal removal of ferrous metals including machining or cutting hardened steels, alloy steels, maraging steels, cast iron, cast steel, nickel, nickel-chromium alloys, nickel based and cobalt superalloys, as well as for cutting non-metallic materials such as fiberglass-plastic laminates and ceramic compositions.

The compositions of this invention are best suited for cutting at very high speeds such metals as alloy steels (800 surface feet per minute) and cast iron (1200 surface feet per minute). This is so because of the great resistance to cratering and edge wear and retention of good hardness of the compositions of this invention at elevated temperatures. Because of their good thermal shock resistance they are particularly well suited for making repeated short cuts or other interrupted cuts in which the temperature of the cutting edge fluctuates rapidly.

The compositions of this invention can also be used in general refractory uses such as thread guides, bearings, wear-resistant mechanical parts, and as grit in resin-bonded grinding wheels and cutoff blades. In addition the compositions of this invention are useful in any application where their combination of refractory properties, electrical conductivity, metallophilic nature, and thermal shock resistance offer an advantage such as in making an electrically conducting ceramic-like grit for grinding wheels to be employed in electrolytic grinding.

The bodies of the invention are extremely resistant to oxidation at high temperatures and this, together with their electrical conductivity, enables them to be used as furnace heating elements which can maintain high temperatures for long periods in oxidizing atmospheres.

This invention will be better understood by reference to the following illustrative examples.

EXAMPLE 1

This is an example of a composition containing 50 volume percent of titanium nitride, 25 volume percent of aluminum nitride and 25 volume percent of nickel aluminide.

The titanium nitride to be used in the form of a very finely divided powder with a specific surface area of 3.6 m.²/g. as measured by nitrogen adsorption using the Brunauer, Emmett, Teller method. Chemical analysis shows the powder to contain 21.40% nitrogen, 77.4% titanium, 0.07% chloride, and 0.007% iron.

The aluminum nitride to be used is in the form of a finely divided powder with a specific surface area of 5.4 m.²/g. as measured by nitrogen adsorption. Chemical analysis shows the powder to contain 31.43% nitrogen, 64.94% aluminum, 0.075% carbon, and 0.15% iron. Examination by X-ray shows it to consist of 99% AlN of

an average crystallite size of 197 mμ as measured by X-ray line broadening, and 1% Al₂O₃.

The nickel aluminide to be used has such a particle size that it all passes through a 325 mesh screen. The specific surface area of the powder is 0.3 m.²/g. as determined by nitrogen adsorption. This specific surface area corresponds to particles of nickel aluminide of about 3.4 microns average particle diameter. The oxygen content is 0.5%.

The powders are milled by loading 4290 grams of pre-conditioned cylindrical cobalt-bonded tungsten carbide inserts, ¼ inch long and ¼ inch in diameter, into a 1.3 liter steel rolling mill about 6 inches in diameter, also charged with 350 ml. of "Soltrol" 130 (saturated paraffinic hydrocarbon, approximate boiling point 175° C.). The mill is then charged with 81.4 grams of the titanium nitride powder, 24.45 grams of the aluminum nitride powder, and 44.2 grams of the nickel aluminide powder, all as above described.

The mill is sealed and rotated at 90 r.p.m. for 5 days. The mill is then opened and the contents emptied while keeping the milling inserts inside. The mill is rinsed out with "Soltrol" 130 several times until all of the milled solids are removed.

The milled powder is transferred to a vacuum evaporator, and the excess hydrocarbon is decanted off after the suspended material has settled. The wet residual cake is then dried under vacuum with the application of heat until the temperature within the evaporator is between 200 and 300° C., and the pressure is less than about 0.1 millimeter of mercury. Thereafter the powder is handled entirely in the absence of air.

The dry powder is passed through a 70 mesh screen in a nitrogen atmosphere and stored under nitrogen in sealed plastic containers.

A consolidated billet is prepared from this powder by hot pressing the powder in a cylindrical graphite mold having a squared cavity with ⅝ inch cross-section and fitted with opposing close-fitting pistons. One piston is held in place in one end of the mold cavity while 7.5 grams of the powder is dropped into the cavity under nitrogen and evenly distributed by rotating the mold and tapping it lightly on the side. The upper piston is then put in place under hand pressure. The assembled mold and contents are then placed in a vacuum chamber of a vacuum hot press, the mold is held in a vertical position, and the pistons extending above and below are engaged between opposing graphite rams of the press under pressure of about 100 to 200 p.s.i. Within a period of a minute the mold is raised into the hot zone of the furnace at 1000° C. and at once the furnace temperature is increased while the positions of the rams are locked so as to prevent further movement during the heatup period. The temperature is raised from 1000 to 1700° C. in 10 minutes. The temperature of the mold is held at 1700° C. for another 2 minutes to insure uniform heating of the sample. A pressure of 4000 p.s.i. is then applied through the pistons for six minutes. Immediately after pressing, the mold and contents, still being held between the opposing rams, is moved out of the furnace into a cool zone where the mold and contents are cooled to dull red heat in about 5 minutes.

The mold and contents are then removed from the vacuum furnace and the billet is removed from the mold and sand blasted to remove any adhering carbon.

The hot pressed composition is nonporous, having no visible porosity under 1000× magnification.

The billet, which is a square with ⅝ inch cross-section and about 0.30 inch in thickness, is cut and finished as a cutting tip to exact dimensions, ½ inch x ½ inch x ⅝ inch and the corners are finished with a ⅜ inch radius, a style known in the industry as SNG-432. This tip is used for indentation hardness test. The hardness is 91.8 on the Rockwell A scale. The tip is also employed as a single tooth in a 6 inch diameter milling cutter to face mill dry

and on center bars 2 inches wide of AiSi 4340 steel (R_c 36) at a surface speed of 1000 feet per minute and a feed rate of 0.0060 inch per tooth with a depth of cut of 0.050 inch.

Milling is continued under these conditions for 178 inches of bar length without wearing out.

Under these same conditions commercially available alumina cutting tools will not cut at all and commercially available carbide tools will cut less than 40–45 inches of bar length per tooth before complete failure.

The same tip is employed as a cutting tool in a high speed turning test on AISI 1045 steel (170 BHN). The speed is 900 surface feet per minute, the feed is 0.005 inch per revolution, the depth of cut is 0.050 inch. Uniform flank wear as measured after 5 minutes of dry turning is only 0.008 inch.

Under the same conditions a Co-bonded WC-TaC-TiC commercial tool showed 0.015 inch uniform flank wear after five minutes.

EXAMPLE 2

The procedure of Example 1 is repeated, except that molybdenum aluminide (Mo_3Al) is used instead of nickel aluminide. The components are used in amounts to give a composition containing 50 volume percent titanium nitride, 25 volume percent aluminum nitride, and 25 volume percent molybdenum aluminide.

The molybdenum aluminide to be used has such a particle size that it all passes through a 325 mesh screen. The specific surface area of this powder is 0.2 m^2/g . as determined by nitrogen adsorption. This specific surface area corresponds to particles of molybdenum aluminide of about 2 to 3 microns average particle diameter. The oxygen content is 0.11%.

A cutting tip prepared as in Example 1 from this hot pressed composition performs very well as a cutting tip for metal cutting by milling and turning in tests similar to those of Example 1.

EXAMPLE 3

The procedure of Example 1 is repeated except that titanium aluminide ($TiAl$) is used instead of nickel aluminide. The components are used in amounts to give a composition containing 50 volume percent titanium nitride, 25 volume percent aluminum nitride, and 25 volume percent titanium aluminide.

The titanium aluminide to be used has such a particle size that it all passes through a 325 mesh screen. The crystallite size as measured by the X-ray diffraction line broadening method is 64 millimicrons. X-rays also show the presence of some Fe_2Ti and free Ti metal as impurities. Analysis by emission spectroscopy shows that titanium is the major component of the powder. Other elements detected by emission spectroscopy are aluminum 3–15%; iron 1–5%; magnesium 0.2–1%; chromium 0.1–0.5%; silicon 0.1–0.5%; calcium 500–2500 parts per million (p.p.m.); antimony 200–1000 p.p.m.; lead 20–1000; manganese 10–50 p.p.m.; copper 10–50 p.p.m.; sodium 10–50 p.p.m.

A cutting tip prepared as in Example 1 from the hot pressed composition of this example performs very well as a cutting tip for metal cutting by milling and turning in tests similar to those of Example 1.

EXAMPLES 4–10

The following examples were carried out using the raw materials and procedures described in Example 1 except as otherwise noted. The raw materials used in the following examples, other than titanium nitride, aluminum nitride and nickel aluminide are characterized as follows:

(A) Zirconium carbide—Materials for Industry, Inc., fine zirconium carbide powder with a specific surface area of 0.5 square meters per gram and an oxygen content of 0.18%.

(B) Tantalum nitride—Vahlco Chemical Co., fine

powder minus 325 mesh with a specific surface area of 0.43 m^2/g . and an oxygen content of 0.43%.

(C) Niobium nitride—Cerac, Inc., fine powder minus 325 mesh with a specific surface area of 0.18 m^2/g . Oxygen content of this powder is 0.3%, carbon content 0.86%, and nitrogen content 11.56%. When observed under the electron microscope the powder shows dense particles between 1 and 5 microns in size, with most of the particles around 4 microns in size.

(D) Titanium carbide—TAM Division of the National Lead Co., fine titanium carbide powder with a specific surface area of 2.5 m^2/g . Analysis of this powder shows that total carbon content is 19.4%; free carbon is 0.12%; oxygen content is 0.42%.

(E) Zirconium nitride—Cerac, Inc. minus 325 mesh zirconium nitride powder characterized by X-ray as pure ZrN . Compositions containing this powder should be handled with special care, since very fine ZrN is highly pyrophoric and may react explosively.

(F) Titanium oxide—Materials for Industry fine titanium oxide powder characterized by X-ray examination as pure TiO_2 and has a specific surface area of 8.8 m^2/g . Examination of a dry mount specimen in the electron microscope shows particles of around 250 millimicrons forming larger aggregates.

(G) Zirconium oxide—Zircoa AHC 1.3 micron average particle size zirconium oxide powder characterized by X-ray examination as pure ZrO_2 and has a specific surface area of 1.0 m^2/g . Chemical analysis shows that the powder contains 0.1% CaO .

(H) Tantalum aluminide—Fine powder, minus 325 mesh, characterized by X-ray examination as pure $TaAl_3$.

(I) Nickel titanide—Fine powder, minus 325 mesh, characterized by X-ray examination as pure Ni_3Ti .

(J) Molybdenum nickelide—Fine powder characterized by X-ray examination as pure $MoNi_4$.

The milling conditions designated A, B, and C in Table I correspond to the general conditions of Example 1 with the following provisions:

(A) 4000 grams of cobalt-bonded tungsten carbide inserts are used in a 1.3 liter steel mill with 375 ml. of "Soltrol" oil.

(B) 14,000 grams of cobalt-bonded tungsten carbide inserts are used in a one gallon steel mill with 814 ml. of "Soltrol" oil.

(C) 600 grams of cobalt-bonded tungsten carbide inserts are used in a 1.3 liter steel mill with 375 ml. of "Soltrol" oil.

The pressing cycle designated I, II and III in Table I corresponds to the general conditions of Example 1 with the following provisions:

(I) The sample and mold are inserted into the hot zone at a temperature of 1500° C.

(II) The sample and mold are inserted into the hot zone at a temperature of 1175° C.

(III) The sample and mold are inserted into the hot zone at a temperature of 1000° C.

The metal cutting tests designated 1 and 2 in Table I correspond to the general conditions of the cutting tests in Example 1 with the following provisions:

(1) High Speed Turning Test on AISI 1045 steel (Brinell Hardness Number of 183). The speed is 900 surface feet per minute (s.f.m.); the feed is 0.005 inch per revolution (i.p.r.); the depth of cut is 0.050 inch; and there is a negative rake. Uniform and local flank wear is measured after 10 minutes of dry turning.

(2) Single Tooth Face Milling Test on AISI 4340 steel (Rockwell C Hardness of 36). A 6 inch milling head is used; the work is on center; dry; speed is 1000 s.f.m.; the feed is 0.60 i.p.r.; the depth of cut is 0.050, the width of cut 2 inches; and there is negative rake. Tool life is measured in length of cut in inches.

TABLE I

	Powder composition			Preparation and fabrication			Metal cutting test	
	Metalline phase	Wear resistant phase	Intermetallic	Milling	Hot press cycle and maximum temperature, ° C.		Type of test	Performance
Example 4:								
Volume percent.....	60 TiN	10 AlN	30 NiAl	} B	II	1,700 {	1	Good.
Grams.....	329.22	35.32	195.30				2	Excellent.
Weight percent.....	59.0	6.00	35.0					
Example 5:								
Volume percent.....	25 ZrC	60 AlN	15 Mo ₃ Al	} C	I	1,800 {	1	Excellent.
Grams.....	50.36	58.67	45.03				2	Good.
Weight percent.....	32.7	38.1	29.2					
Example 6:								
Volume percent.....	55 TaN	20 ZrN	25 NiAl	} A	II	1,700 {	1	Very good.
Grams.....	232.96	42.62	44.32				2	Do.
Weight percent.....	72.8	13.3	13.85					
Example 7:								
Volume percent.....	55 TiN	20 AlN-5TiO ₂	20 TiAl	} A	III	1,500 {	1	Very good.
Grams.....	95.51	20.85	6.80				2	Good.
Weight percent.....	77.65	16.95	5.53					
Example 8:								
Volume percent.....	55 NbN	20 ZrO ₂	25 TaAl ₃	} A	I	1,800 {	1	Good.
Grams.....	147.21	35.7	111.51				2	Very good.
Weight percent.....	49.9	12.1	37.8					
Example 9:								
Volume percent.....	55 TiC	40 AlN	5 Ni ₃ Ti	} A	III	1,500 {	1	Excellent.
Grams.....	86.62	41.48	12.75				2	Good.
Weight percent.....	61.43	29.48	9.04					
Example 10:								
Volume percent.....	60 TiN	35 AlN	5 MoNi ₃	} A	II	1,800 {	1	Good.
Grams.....	103.46	36.22	14.23				2	Do.
Weight percent.....	67.18	23.52	9.27					

I claim:

1. A dense refractory composition consisting essentially of:

- (1) 10 to 80 volume percent of a wear-resistant material selected from the group consisting of:
 - (a) aluminum nitride;
 - (b) tantalum nitride;
 - (c) mixtures of aluminum nitride and tantalum nitride; and
 - (d) a refractory oxide of an element selected from the group consisting of magnesium, zirconium, hafnium, titanium, chromium, beryllium, zinc, calcium, thorium, barium, strontium, silicon, the rare earth metals, and mixtures thereof;
- (2) 15 to 80 volume percent of a metalline selected from the group consisting of titanium carbide, tantalum carbide, niobium carbide, niobium nitride, titanium nitride, zirconium carbide, zirconium nitride, and mixtures thereof; and
- (3) 5 to 35 volume percent of an intermetallic selected from the group consisting of molybdenum nickelide, tantalum nickelide, zirconium nickelide, niobium nickelide, cobalt aluminide, cobalt titanide, iron aluminide, iron titanide, nickel aluminide, nickel titanide, tungsten aluminide, molybdenum aluminide, niobium aluminide, tantalum aluminide, titanium aluminide, zirconium aluminide, and mixtures thereof;

the composition having the further limitations that:

- (A) the average grain size is smaller than 10 microns;
- (B) the composition is composed of two interpenetrating three-dimensional networks, one network consisting essentially of the wear-resistant material and the other network consisting essentially of the metalline and the intermetallic; and
- (C) the volume percent of the metalline must not be less than the volume percent of the intermetallic.

2. The refractory composition of claim 1 wherein the volume percent of wear-resistant material ranges from 10 to 50.

3. The refractory composition of claim 2 wherein the volume percent of wear-resistant material ranges from 15 to 30.

4. The refractory composition of claim 1 wherein the wear-resistant material is selected from the group consisting of aluminum nitride, tantalum nitride, or mixtures thereof.

5. The refractory composition of claim 4 wherein the wear-resistant material is aluminum nitride.

6. The refractory composition of claim 1 wherein the volume percent of metalline ranges from 30 to 60.

7. The refractory composition of claim 6 wherein the volume percent of metalline ranges from 45 to 55.

8. The refractory composition of claim 1 wherein the metalline is selected from the group consisting of titanium nitride, zirconium nitride, niobium nitride, and mixtures thereof.

9. The refractory composition of claim 8 wherein the metalline is titanium nitride.

10. The refractory of claim 1 wherein the volume percent of intermetallic ranges from 15 to 30.

11. The refractory composition of claim 10 wherein the volume percent of intermetallic ranges from 20 to 30.

12. The refractory composition of claim 1 wherein the intermetallic is selected from the group consisting of molybdenum nickelide, cobalt aluminide, iron aluminide, nickel aluminide, and mixtures thereof.

13. The refractory composition of claim 1 wherein the average grain size is less than 5 microns.

14. A dense refractory composition consisting essentially of:

- (1) 15 to 30 volume percent of aluminum nitride;
- (2) 45 to 55 volume percent of titanium nitride; and
- (3) 20 to 30 volume percent of an intermetallic selected from the group consisting of molybdenum nickelide, cobalt aluminide, iron aluminide, nickel aluminide, and mixtures thereof;

the composition having the further limitations that:

- (A) the average grain size is less than 5 microns and
- (B) the composition is composed of two interpenetrating three-dimensional networks consisting essentially of the wear-resistant material and the other network consisting essentially of the metalline and the intermetallic.

References Cited

UNITED STATES PATENTS

3,108,887	10/1963	Lenie et al.	106—65
3,236,663	2/1966	Grulke et al.	106—65
3,251,700	5/1966	Mandorf	106—65
3,256,103	6/1966	Roche et al.	106—55
3,261,701	7/1966	Grulke	106—65
3,408,312	10/1968	Richards et al.	106—65

JAMES E. POER, Primary Examiner

U.S. Cl. X.R.

106—43, 57, 58, 65; 252—516, 518, 519, 520, 521

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,676,161 Dated July 11, 1972

Inventor(s) Paul C. Yates

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11 Lines 43/44 read "tantalum carbide, niobium carbide, niobium nitride, tanium nitride, zirconium carbide, zirconium nitride,"
it should read
--tanium nitride, zirconium carbide, zirconium nitride, tantalum carbide, niobium carbide, niobium nitride,--

Signed and sealed this 6th day of February 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents