ABSTRACT OF THE DISCLOSURE

Dense compositions having a grain size smaller than 10 microns and containing from 20 to 80 volume percent alumina: 10 to 78 volume percent of a metalline selected from the group consisting of titanium carbide, titanium nitride, zirconium carbide, zirconium nitride, niobium carbide, niobium nitride, tantalum carbide, tantalum nitride, and mixtures thereof; and 2 to 30 volume percent of an intermetallic selected from the group consisting of iron aluminate, iron nitride, niobium nitride, tantalum carbide, tantalum nitride, and mixtures thereof; and an intermetallic selected from the group consisting of iron aluminate, iron nitride, niobium nitride, tantalum carbide, tantalum nitride, and mixtures thereof; are (1) effective tools for cutting steel and cast iron and (2) useful as oxidation resistant materials of construction.

BACKGROUND OF THE INVENTION

Aluminum oxide cutting tips are well known. Such tips possess advantages of extreme hardness and wear-resistance as well as superior hot-bending strength. They are resistant to erosion and show little welding or diffusion between the chips and the tip. They are also oxidation resistant. However, these advantages are largely offset by the brittleness and lack of toughness of ceramic tips and a marked tendency toward stress, cracks, and eruptions.

Many attempts have been made to combine alumina with materials which would mitigate these disadvantages while not appreciably decreasing the advantages of pure alumina. Often alumina is bonded with up to 30-50 percent of a metal to increase the strength and toughness. Such compositions, generically called "cermets," demonstrate better thermal conductivity than pure alumina ceramics as well as increased strength. However the presence of the metal results in a decrease in overall wear-resistance of the cutting tip.

The addition of carbides to metal-alumina compositions was a further development aimed at improving the wear-resistance and hardness which accompany the presence of the metal. Such compositions are disclosed generally in British patent specification No. 841,576 and with more particularity in German Pat. No. 1,072,182 and British patent specification No. 821,596. However, even those compositions of alumina, carbides, and metal suffer from (1) poor wear-resistance because of the metal and (2) brittleness and poor thermal shock resistance because of the variety of thermal coefficients of expansion found in such mixed refractories.

It has been discovered that particular compositions of alumina 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 oxidation-resistant and chemical-resistant materials of construction.

SUMMARY OF THE INVENTION

This invention is directed to dense compositions having an average grain size smaller than 10 microns and composed of two interpenetrating three-dimensional networks, one network consisting essentially of alumina and the other network consisting essentially of a metalline selected from titanium carbide, titanium nitride, zirconium carbide, zirconium nitride, niobium carbide, niobium nitride, tantalum carbide, tantalum nitride, and mixtures thereof; and an intermetallic selected from the group consisting of:

- iron aluminate,
- iron nitride,
- niobium nitride,
- tantalum carbide,
- tantalum nitride,
- and mixtures thereof;

the alumina being present in an amount ranging from 20 to 80 volume percent; the metalline being present in an amount ranging from 10 to 78 volume percent; and the intermetallic being present in an amount ranging from 2 to 30 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 compositions 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 alumina; a metalline; and an intermetallic.

(a) Alumina: The alumina is present in the compositions of this invention in amounts ranging from 20 to 80 volume percent. The need for at least 20 percent alumina is based on the desire to have the alumina present as a continuous phase. Amounts of alumina below 20 percent are less satisfactory because at these low levels the alumina phase tends to be discontinuous. The presence of at least 20 volume percent alumina insures continuity of the alumina phase under most ordinary conditions.

Conversely the amount of alumina is restricted to 80 volume percent because more alumina tends to prevent...
continuity of the electrically conductive phase of metal-
line and intermetallic.

It is preferred to have the alumina present in the com-
positions of this invention in amounts ranging from
30 to 70 volume percent and most preferably in amounts
ranging from 40 to 60 volume percent, because such
amounts virtually guarantee uninterrupted phases of al-
umina and the electrically conductive phase.

Alumina suitable for use in the compositions of this
invention can be in many forms so long as it is finely
divided. Thus, it can be in the form of gamma, eta, or
alpha alumina or mixtures of these. Alpha alumina is a
preferred starting material because it does not have as
high a specific surface area as gamma or eta alumina
and is likely to contain less adsorbed water which can be
deleterious.

The alumina to be used should be sufficiently finely
divided to produce the compositions of this invention
with an average grain size of 10 microns. A suitable
starting alumina is alpha alumina with a specific
surface area of more than 2 m²/g. and preferably 5
25 m²/g. Alumina with an ultimate crystallite size of
less than 0.5 micron, as measured by X-ray line broaden-
ing techniques, is particularly preferred. Such alumina
can be obtained most simply by heating amorphous alu-
minum sulfate to 1200° C. for 3 or more hours.

Representative of suitable commercially available alu-
mina is Alcoa Superground Alumina XA-16 which is
characterized by X-ray examination as alpha alumina,
and has a specific surface area of about 13 square meters
per gram which is equivalent to a spherical particle size
of about 115 millimeters.

(b) Carbides or nitrides (metalline): The metalline is
used in the compositions of this invention in amounts
ranging from 10 to 78 volume percent and is selected
from the group consisting of titanium carbide, titanium
nitride, zirconium carbide, zirconium nitride, niobium

carbide, niobium nitride, tantalum carbide, tantalum ni-
tride, 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 15 to 45
volume percent and most preferred amounts range from
20 to 40 volume percent. These amounts contribute most
effectively to properties such as hardness and wear re-
sistance of the compositions of this invention.

The metallines 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 mi-
crons 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 carbide and the other starting
components.

Titanium nitride, titanium carbide, zirconium nitride,
and zirconium carbide are preferred for use in the com-
positions 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.

(c) Intermetallic: The intermetallics suitable for use
in this invention are selected from the group consisting of
iron aluminate, iron titanide, cobalt aluminate, cobalt
titanide, nickel aluminate, nickel titanide, tungsten alu-
minide, molybdenum aluminate, niobium aluminate, tanta-
lum aluminate, titanium aluminate, zirconium aluminate,
and mixtures thereof. The intermetallic should be present
in amounts ranging from 2 to 30 volume percent. At
least two 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 30 volume
percent little further improvement in strength is obtained
but the wear resistance is decreased considerably.

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

Preferred amounts of the intermetallic are from 3 to
25 volume percent and are more preferably from 4 to 20
volume percent since it is over these ranges that the best
balance between strength, toughness and wear resistance
has been obtained.

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

Aluminides of nickel, molybdenum, and niobium avail-
able from Corcar, Inc.; iron titanide from Shielddaloy
Corp.; iron titanide from Shielddaloy Corp. or Fotte Min-
eral 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 to-
gether the stoichiometric ratio of the components in an
inert refractory crucible in a vacuum furnace. After al-
lowing 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 pre-
ferred.

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 composi-
tions 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 com-
positions 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 some-
times picked up in grinding, can be present. Even oxygen
can be tolerated in small amounts, 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.

Structural characteristics

Structural characteristics are important in determining
the performance of the components of this invention.

In addition to characterizing the compositions 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 con-
taining two interpenetrating three-dimensional networks:
one of alumina and one of intermetallic bonded carbide
or nitride.

While the effects of the presence of these two networks
is not completely understood it is believed that they con-

3,565,643
contribute substantially to the unusual properties of the compositions of this invention, resulting in compositions much stronger and more impact-resistant than conventional aluminum-ceramic cutting tools.

The presence of these co-continuous networks can be determined from analysis of the dense composition. The continuity of the network of alumina can be ascertained by removing the metalline and intermetallic by anodic etching in 10% ammonium bifluoride solution. Such etching while not apparently affecting the appearance of the composition, removes the electrically conducting material from the outer portion of the compositions nearest the surface and results in a non-conducting surface having an electrical resistivity of greater than 100,000 micro-ohm-centimeter. Proof of continuity of the alumina phase is the solid coherent surface that exists despite the obvious removal of the conducting materials.

A convenient method for removing all of the metalline and intermetallic from the compositions of this invention and thus demonstrating the presence of a three-dimensional skeleton of alumina is to immerse small bars of the composition in a mixture of 25 cc. of 12 percent hydrofluoric acid and 5 cc. of concentrated nitric acid. A bar 0.070 inch by 0.070 inch by 1.00 inch in dimensions can be left in the acid mixture for 24 hours during which the mixture is heated on a steam bath. The portion of the bar which remains after 24 hours is alumina and can be examined for continuity and strength by the usual means.

The compositions of this invention containing 40 or more volume percent of alumina yield very strong alumina skeletons by the above method of analysis. Thus, an alumina skeleton obtained from a composition of this invention which contains about 60 volume percent alumina retains a transverse rupture strength of 15,000 p.s.i. The presence of alumina in amounts of about 20 volume percent tends to produce a fairly strong skeleton with transverse rupture strengths of about 1,400 p.s.i. At about 20 volume percent alumina there is usually a weak, but self-supporting structure, and below 20 volume percent there is often little or no continuous skeleton of alumina. Removal of electrically conducting phases from the compositions containing less than 20 volume percent alumina usually results in the recovery of alumina powder.

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 alumina phase as well as the metalline and intermetallic phases will range between $4 \times 10^{-5}$ and $5 \times 10^{-6}$ inches/°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 by 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 average grain size, smaller than 10 microns and preferably smaller than 5 microns in number average grain diameter. The number average grain size and the size distribution are obtained from enhanced 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 co-continuous phases (i.e., alumina skeleton and the metalline-intermetallic matrix) is also uniform and homogeneous, and generally speaking any area 100 microns square which is examined microscopically at 1000× 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 (i.e., alumina skeleton and the metalline-intermetallic matrix) 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 abrasive 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 cutting 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 hot press 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 150–200° 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. Maxi-
mum 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 content. 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 6 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.) hydraulically.

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 fiber glass-plastic laminates and ceramic compositions.

The compositions of this invention are best suited for cutting at very high speeds such 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, metallurgical 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.

Their resistance to oxidation and their excellent hot hardness make them particularly attractive as materials of construction for high temperature extrusion dies.

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

EXAMPLE 1

This is an example of a composition containing 50 volume percent of aluminum oxide, 45 volume percent of titanium carbide and 5 volume percent of nickel aluminate.

The alumina in the form of very finely divided alpha alumina is prepared from colloidial boehmite, as described in U.S. 2,915,475 by heating for 20 hours in air at 350° C., then increasing the heat to 500° C. and holding at this temperature for 15 hours, and finally increasing the heat to 800° C. per hour to a goal temperature of 1240° C., where it is held for 3 days. A sample of the cooled product is then treated with hydrofluoric acid and is 88.5% insoluble in 24% aqueous hydrofluoric acid over a period of 16 hours, indicating an alpha alumina content of about 88.5%. The specific surface area of the hydrofluoric acid insoluble alumina is 63 m²/g, as measured by nitrogen adsorption using the Brunauer, Emmett, Teller method.

This surface area corresponds to a crystallite size of alpha alumina of about 240 micromicrons average particle diameter. Under an electron microscope the alpha alumina appears as aggregates of alumina crystals in the range from 100 to 300 micromicrons in diameter.

The density of the free-flowing finely divided alpha alumina is 0.5 g/cc, as obtained by measuring the volume of a weighed sample after tapping in a 100 cc glass cylinder.

The titanium carbide to be used has a nominal particle size of 2 microns and a specific surface area of 3 m²/g, as determined by nitrogen adsorption. An electron micrograph shows that the titanium carbide grains are approximately 2 microns in diameter and are clustered in the form of loose aggregates. The carbon content is 19.0%, and the oxygen analysis indicates a titanium dioxide content of about 2.5%.

The nickel aluminate to be used has a particle size such that it all passes through a 325 mesh screen. The specific surface area of the powder is 0.3 m²/g, as determined by nitrogen adsorption. This specific area corresponds to particles of nickel aluminate of about 3.4 microns average particle diameter. The oxygen content is 0.5%.

The powders are milled by loading 4000 grams of pre-conditioned cylindrical cobalt-bonded tungsten carbide inserts, % inch long and % inch in diameter, into a 1.3 liter steel rolling mill about 6 inches in diameter, also charged with 375 ml. of "Sellotol" 100 (saturated paraffinic hydrocarbon), approximate boiling point 175° C.). The mill is then charged with 59.75 grams of the alpha alumina, 67.50 grams of the titanium carbide powder, and 8.78 grams of the nickel aluminate powder, all as above described.

The mill is then sealed and rotated at 90 r.p.m. for 5 days. The mill is then opened and the contents emptied through a No. 7 sieve size screen while keeping the mill-
ing inserts inside. The mill is then 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 required 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 1.0 millimeter of mercury. Thereafter the powder is handled entirely in the absence of air.

The dry powder is passed through a 40 mesh screen in a nitrogen atmosphere, and then 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 square cavity 1 1/4 inches x 1 3/8 inches and fitted with opposing close-fitting pistons. One piston is held in place in one end of the mold cavity while 25 grams of the powder is charged 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 1500 °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 1500 to 1800 °C in 10 minutes, and the temperature of the mold is then held at 1800 °C for another 2 minutes to ensure uniform heating of the sample. A pressure of 4000 p.s.i. is then applied through the pistons for four 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 billet, which is a 1 1/4 inch square about 0.30 inch in thickness, is cut so that a piece slightly larger than one half inch square is removed from the center. Strips 0.070 inch in thickness are cut from the material remaining on each side of this center piece and are further cut in 0.70 inch x 0.70 inch square bars for testing transverse rupture strength. Other portions of the billet are used for indentation hardness tests and for other product characterization. The transverse rupture strength as measured by bending the 0.070 inch x 0.070 inch test bars on a ½ inch span is 165,000 p.s.i. The hardness is 95.2 on the Rockwell A scale.

The square center piece is finished as a cutting tip to exact dimensions, ½ inch x ½ inch x ½ inch and the corners are finished with a ½ inch radius, a style known in the industry as SNG-452. This tip is employed as a single tooth in a 4 inch diameter milling cutter to face mill dry and on center 4340 steel (Rc 36) bars 2 inches wide at a surface speed of 535 feet per minute and a feed rate of 0.005 inch per tooth with a depth of cut of 0.100 inch.

Milling is continued under these conditions for 36 inches of bar length and upon examination the cutting tip shows only 0.005 inch of uniform flank wear, and 0.008 inch of local flank wear, with no cratering on the face of the tool and no breaking or chipping of the edge. Under these same cutting conditions, commercially available ceramic cutting inserts chip and break after cutting 2 to 11 inches.

The tip is employed as a cutting tool on Class 30 (170 BHN) gray cast iron in a high speed turning test at 1250 surface feet per minute, using a feed of 0.005 inch per revolution and a depth of cut of 0.050 inch. After 10 minutes of operation, the tip has a uniform flank wear of only 0.004 inch.

Under the same conditions a commercial ceramic tool is found to have 0.006" uniform flank wear in 10 minutes, and a commercial TiC-Mo-Ni tool is found to have 0.011" wear. A WC-Co commercial tool is found to fail almost immediately at this high speed.

The tool is also used to dry turn extremely hard 4340 steel (54 Rb) at 400 surface feet per minute, 0.005 inch per tooth and 0.050" depth and is found to have a tool life of 15 minutes. Under the same conditions, a commercial ceramic tool is found to have a tool life of 5 minutes and a commercial TiC-Mo-Ni tool fails immediately.

EXAMPLE 2

The procedure of Example 1 is repeated except that the components are used in amounts as follows: 66.3 grams of alumina powder, 34.2 grams of titanium carbide powder, and 8.18 grams of nickel aluminide. These amounts correspond to a composition containing 70 volume percent alumina, 25 volume percent titanium carbide and 5 volume percent nickel aluminide.

A cutting tip, prepared as in Example 1 from this hot pressed composition, performs exceptionally well as a tip for metal cutting by turning and milling.

For instance, the tip is employed as a cutting tool on Class 30 (170 BHN) gray cast iron in a high speed turning test at 1250 surface feet per minute, using a feed of 0.005 inch per revolution and a depth of cut of 0.050 inch. After 10 minutes of operation the tip has a uniform flank wear of 0.008 inch and a local flank wear of 0.012 inch.

This tip is also employed as a single tooth in a 4 inch diameter milling cutter to face mill dry and on center 30 (170 BHN) gray cast iron bars 2 inches wide at a surface speed of 1575 feet per minute and a feed rate of 0.010 inch per tooth with a depth of cut of 0.250 inch.

Milling is continued under these conditions for 220 inches of bar length without wearing out. Upon examination the cutting tip shows only 0.012 inch of uniform flank wear, and 0.036 inch of local flank wear, with no cratering on the face of the tool and no breaking or chipping of the edge. Under these same cutting conditions, commercially available ceramic cutting inserts break immediately.

EXAMPLE 3

The procedure of Example 1 is repeated except that the following components are used: 71.6 grams of alumina powder, 37.0 grams of titanium carbide powder, and 14.8 grams of molybdenum aluminide (Mo2Al) powder. These amounts correspond to a composition containing 70 volume percent alumina, 25 volume percent titanium carbide and 5 volume percent molybdenum aluminide.

A cutting tip, prepared as in Example 1 from this hot pressed composition, performs exceptionally well as a cutting tool for metal cutting by turning and milling.

For instance, the tip is employed as a cutting tool on Class 30 (70 BHN) gray cast iron in a high speed turning test at 1250 surface feet per minute, using a feed of 0.005 inch per revolution and a depth of cut of 0.050 inch. After 10 minutes of operation the tip has a uniform flank wear of only 0.002 inch.

The same tip is also employed as a single tooth in a 4 inch diameter milling cutter to face mill dry and on center 4340 steel (Rc 36) bars 2 inches wide at a surface speed of 535 feet per minute and a feed rate of 0.005 inch per tooth with a depth of cut of 0.100 inch.

Milling is continued under these conditions for 36 inches of bar length and upon examination the cutting tip shows only 0.005 inch of uniform flank wear, and 0.008 inch of local flank wear, with no cratering on the face of the tool and no breaking or chipping of the edge. Under these same cutting condi-
The following examples are 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 carbide and nickel aluminide are characterized as follows:

1. Alumina—Alcoa Supergrass Alumina XA-16, characterized by X-ray examination as alpha alumina and has a specific surface area of 13 square meters per gram.

2. Zirconium carbide—Materials for Industry, fine powder characterized by X-ray examination as pure zirconium carbide and has a particle size of 3 microns as measured with a Fisher Sub-Sieve Sizer. Specific surface area of the powder is 0.5 m²/g, and oxygen content only 0.18%.

3. Tantalum carbide—Adamas Carbide Co, fine tantalum carbide powder characterized by X-ray examination as pure tantalum carbide and has a particle size of 3 microns as measured with a Fisher Sub-Sieve Sizer. Specific surface area of the powder is 0.5 m²/g, and oxygen content only 0.07%. Electron micrographs of a dry mount specimen of this powder shows particles between 0.4 microns and 4 to 6 microns, but most around 2 to 3 microns diameter.

4. Titanium nitride—Materials for Industry, minus 325 mesh titanium nitride powder, characterized by X-ray as pure titanium nitride. The specific surface area of the powder is 1.1 m²/g, oxygen content is 0.87%, and total carbon content 0.33%. Chemical analysis shows that the titanium content of the powder is 76.19%.

5. Tantalum aluminide—Fine powder, minus 325 mesh, characterized by X-ray examination as pure TaAl₃.

6. Iron aluminide—Fine powder, minus 325 mesh, characterized by X-ray examination as pure FeAl.

7. Nickel titania—Fine powder, minus 325 mesh characterized by X-ray examination as pure NiTi.

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) 6000 grams of cobalt-bonded tungsten carbide inserts are used in a 1.3 liter steel mill with 375 ml of "Soltrol" oil.

The metal cutting tests in Table I correspond to the general conditions of the cutting tests in Example 1 with the following additional: High Speed Turning Test on AISI 1045 carbon 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.f.); the depth of cut is 0.030 inch; and there is negative rake. Uniform and local flank wear is measured after 10 minutes of dry turning.

I claim:

1. A dense refractory composition consisting essentially of:

   (1) 20 to 80 volume percent of alumina; and

   (2) 10 to 70 volume percent of a metalline selected from the group consisting of titanium carbide, titanium nitride, zirconium carbide, zirconium nitride, niobium carbide, niobium nitride, tantalum carbide, tantalum nitride, and mixtures thereof;

   (3) 2 to 30 volume percent of an intermetallic selected from the group consisting of iron aluminide, iron titania, cobalt aluminide, cobalt titania, nickel aluminide, nickel titania, 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 less than 10 microns;

   (B) the composition is composed of two interpenetrating three-dimensional networks, one network consisting essentially of alumina 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 alumina ranges from 30 to 70.

3. The refractory composition of claim 2 wherein the volume percent of alumina ranges from 40 to 60.

4. The refractory composition of claim 1 wherein the volume percent of metalline ranges from 15 to 45.

5. The refractory composition of claim 4 wherein the volume percent of metalline ranges from 20 to 40.

6. The refractory composition of claim 1 wherein the metalline is selected from the group consisting of titanium nitride, titanium carbide, zirconium nitride, and zirconium carbide.

### Table I

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Powder composition</th>
<th>Milling conditions</th>
<th>Hold time at max. temp., min.</th>
<th>T.R. (Kp, d)</th>
<th>Type of test</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>V/o 1</td>
<td>30 45 TIC</td>
<td>B</td>
<td>1,500 1,000</td>
<td>4</td>
<td>140 High speed turning gray cast iron... Very good.</td>
</tr>
<tr>
<td></td>
<td>Grams...</td>
<td>131 254</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>W/o 5</td>
<td>4.4 44.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>V/o 2</td>
<td>70 41 ZrO</td>
<td>A</td>
<td>1,000 1,400</td>
<td>3</td>
<td>130 Turning hardened carbon steel (60+R) ... Do.</td>
</tr>
<tr>
<td></td>
<td>Grams...</td>
<td>80.7 80.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>W/o 5</td>
<td>40.4 40.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>V/o 3</td>
<td>80 14 TaC</td>
<td>A</td>
<td>1,500 1,800</td>
<td>6</td>
<td>140 High speed turning carbon steel... Do.</td>
</tr>
<tr>
<td></td>
<td>Grams...</td>
<td>95 45.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>W/o 5</td>
<td>42.8 42.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>V/o 4</td>
<td>25 65 Y1N</td>
<td>C</td>
<td>1,175 1,700</td>
<td>4</td>
<td>150 High speed turning gray cast iron... Good.</td>
</tr>
<tr>
<td></td>
<td>Grams...</td>
<td>28 8 106</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>W/o 5</td>
<td>19.5 58.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Volume percent.
2. Weight percent.
7. The refractory composition of claim 1 wherein the volume percent of intermetallic ranges from 3 to 25.
8. The refractory composition of claim 7 wherein the volume percent of intermetallic ranges from 4 to 20.
9. The refractory composition of claim 1 wherein the intermetallic is selected from the group consisting of iron aluminide, cobalt aluminide, and nickel aluminide.
10. The refractory composition of claim 1 wherein the average grain size is less than 5 microns.
11. The dense refractory composition consisting essentially of:
   (1) 40 to 60 volume percent of alumina;
   (2) 20 to 40 volume percent of a metalline selected from the group consisting of titanium nitride, titanium carbide, zirconium nitride, and zirconium carbide; and
   (3) 4 to 20 volume percent of an intermetallic selected from the group consisting of iron aluminide, cobalt aluminide, and nickel aluminide;
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, one network consisting essentially of alumina and the other network consisting essentially of the metalline and the intermetallic.

References Cited
UNITED STATES PATENTS
2,781,261 2/1957 Kamlet 75—175.5X

TOBIAS E. LEVOW, Primary Examiner
W. R. SATTERFIELD, Assistant Examiner
U.S. Cl. X.R.
106—55, 57, 62, 65