

Jan. 31, 1967

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3,301,645

TUNGSTEN CARBIDE COMPOSITIONS, METHOD AND CUTTING TOOL

Filed April 3, 1962

3 Sheets-Sheet 1

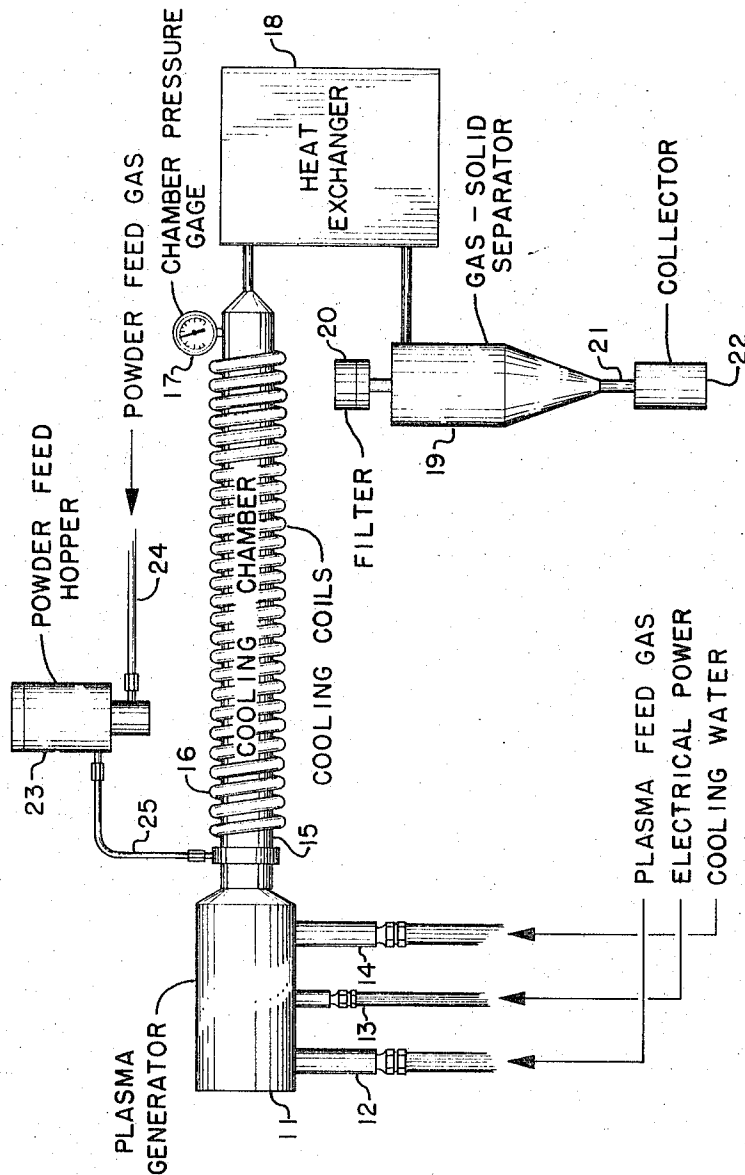


FIG. 1

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3 Sheets-Sheet 2

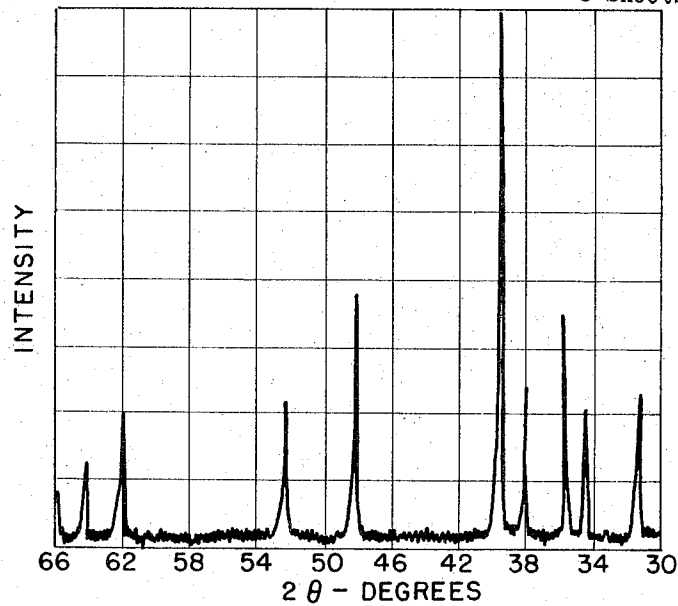


FIG. 2

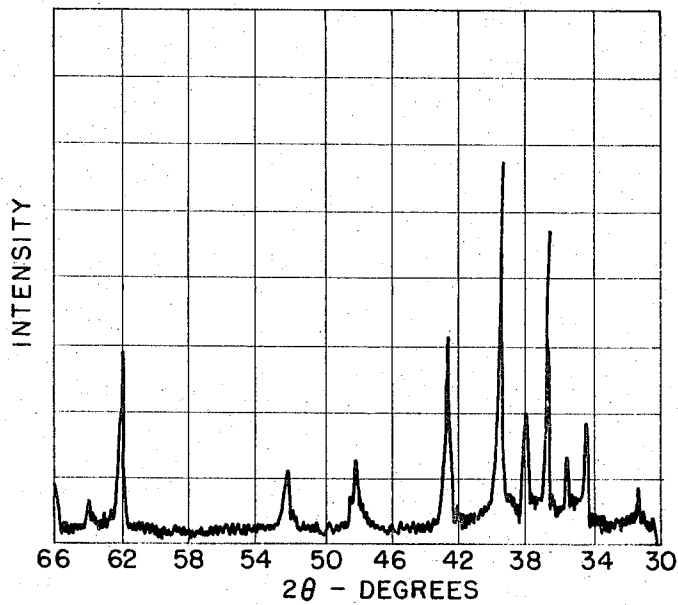


FIG. 3

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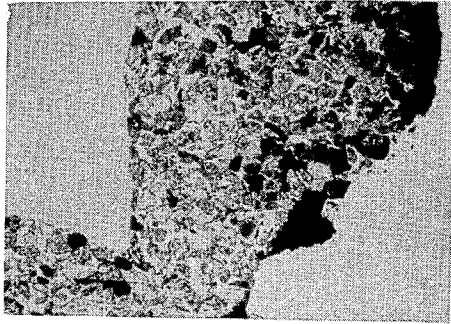


FIG. 4a

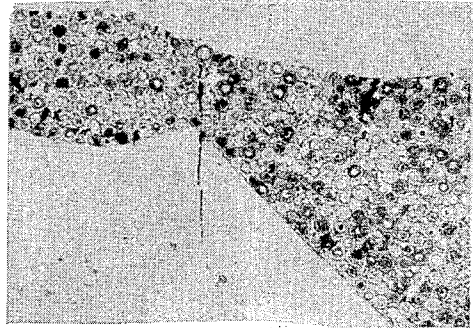


FIG. 5a

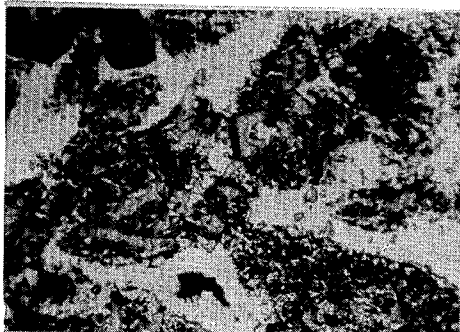


FIG. 4b

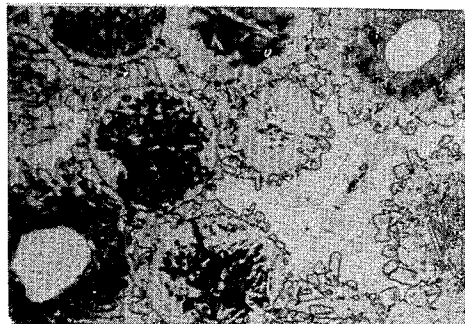


FIG. 5b

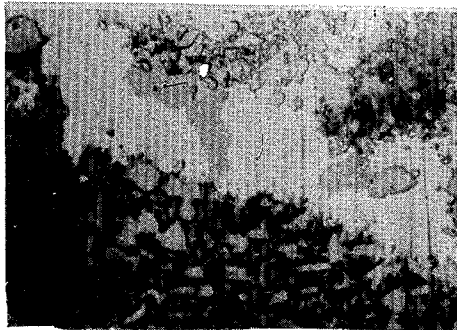


FIG. 4c



FIG. 5c

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3,301,645

**TUNGSTEN CARBIDE COMPOSITIONS, METHOD
AND CUTTING TOOL**

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pany, Houston, Tex., a corporation of Delaware
Filed Apr. 3, 1962, Ser. No. 184,815
20 Claims. (Cl. 51-309)

The present invention relates to refractory metal carbides and is particularly concerned with an improved tungsten carbide useful in the fabrication and hard surfacing of articles normally subjected to severe abrasion or erosion.

Tungsten carbide powder is usually manufactured by the carburization of metallic tungsten in an electric furnace. In a typical carburization process, carbon powder is first added to powdered tungsten metal in an amount slightly in excess of the stoichiometric ratio and the two are then mixed in a ball mill or blender for several hours. The mixed powder is tamped into a carbon boat or crucible and is heated in a tube or induction furnace for a period ranging from about 40 minutes to about 3 hours. The carbon initially reacts with any oxygen present to form carbon monoxide which is vented. Thereafter, the vents are plugged. Hydrogen may be introduced if desired. The tungsten and carbon react to form mon tungsten carbide, WC, and ditungsten carbide, W_2C , during the carburization process. After the charge has cooled following carburization, it is removed from the boats or crucibles and passed through a jaw crusher and ball or hammer mills. The products is a gray angular powder having a high density and extreme hardness. This material may be used for tool fabrication purposes or may be sintered in the presence of cobalt to produce cemented carbides.

Much of the tungsten carbide powder produced in the manner described above is employed in infiltration type operations. In such operations, the powdered tungsten carbide is placed in a carbon mold, a binder metal which will wet the carbide powder in the molten state is added, and the mold and its contents are then heated to an infiltration temperature above the melting point of the binder. As it approaches the infiltration temperature, the binder metal melts and flows into the interstices between the carbide granules. Some of the carbide is normally dissolved in the binder, resulting in metallurgical bonding of the granules in place. The composite product thus consists of a continuous binder phase throughout which tungsten carbide granules are dispersed. In recent years materials of this type have been widely used in the fabrication and hard surfacing of oil field drill bits and similar tools normally subjected to severe abrasion or erosion.

Composite materials produced by infiltrating powdered tungsten carbide with a metallic binder as described in the preceding paragraph are superior to other compositions for certain purposes but have limitations which restrict their usefulness. Due to changes in the volume and distribution of the carbide powder during infiltration, the hardness and compressive strengths of such material may vary widely and are often lower than would be expected. Erosion of the continuous binder phase by high velocity fluids may pose serious problems, particularly in the case of drill bits and similar articles used with circulating fluids containing suspended solids. It has been estimated that the drilling rates and useful life obtained with diamond bits employed in oil field drilling operations could be improved 20 percent or more if better tungsten carbide and more effective infiltration techniques for fabricating and hard surfacing such bits were available.

It is therefore an object of the present invention to provide an improved tungsten carbide useful for the fabrica-

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tion and hard surfacing of oil field drill bits and similar tools normally subjected to severe abrasion or erosion. A further object is to provide an improved process for the production of composite materials from powdered tungsten carbide and metallic binders. Another object is to provide a composite material containing tungsten carbide powder and a metallic binder which has greater compressive strength and overall hardness and is more resistant to erosion than composite materials prepared by infiltration in the past. Still other objects will become apparent as the invention is described in greater detail hereafter.

In accordance with the invention, it has now been found that an improved tungsten carbide composition particularly useful for hard surfacing oil field drill bits and similar tools can be prepared by melting tungsten carbide powder in a high temperature gas stream and then rapidly cooling the spheroidal particles thus formed. Analyses have shown that this procedure results in the formation of a new "quenched-in" phase not found in tungsten carbide powder produced by conventional methods. The existence of this new phase, ordinarily stable only at very high temperatures, increases the solubility of the carbide granules in metallic binders and renders the carbide more effective for hard surfacing and tool fabrication purposes than conventional carbides.

The improved tungsten carbide of the invention is particularly useful in preparing tungsten carbide composite materials by infiltration. Studies and laboratory work have shown that spheroidal particles of the improved carbide bridge together when infiltrated with copper-nickel alloys and similar metallic binders. This bridging effect results in the formation of composite materials in which the carbide particles constitute the continuous phase. Comparative tests have demonstrated that such materials are more uniform in their properties, have significantly higher compressive strengths, and are much more resistant to erosion than the composite materials containing tungsten carbide which have been available in the past.

The nature and objects of the invention can best be understood by referring to the following detailed description of a process for the production of the improved tungsten carbide and to the accompanying drawing, in which:

FIGURE 1 is a schematic representation of apparatus useful for treating powdered tungsten carbide to produce the improved carbide composition;

FIGURE 2 depicts an X-ray diffraction pattern obtained with a typical powdered tungsten carbide obtained from commercial sources;

FIGURE 3 shows an X-ray diffraction pattern obtained with the improved carbide composition of the invention;

FIGURE 4 is a series of photomicrographs of a composite material produced by infiltrating angular tungsten carbide powder with a copper-nickel-tin alloy; and

FIGURE 5 is a series of photomicrographs showing a composite material produced by infiltrating the improved tungsten carbide powder with the same copper-nickel-tin alloy.

The apparatus shown in FIGURE 1 of the drawing includes a plasma generator designated by reference numeral 11. The generator may be of conventional design and will normally include electrodes for producing a high temperature arc in which a gas stream may be partially ionized, may include electrical coils for establishing an electrical field to confine the partially ionized gas stream and produce a further increase in temperature, and will normally contain cooling coils designed to prevent overheating of the apparatus. Suitable plasma generators have been described at length in the technical literature. Feed lines for introducing plasma feed gas, electrical energy and cooling water to the generator are indicated by reference numerals 12, 13 and 14 respectively.

The outlet from plasma generator 11 extends into an elongated cooling chamber 15 which is surrounded by external cooling coils 16 or a suitable cooling jacket. A cooling chamber pressure gage 17 is located near the downstream end of the chamber. Gases discharged from the chamber are passed to a heat exchanger 18 which may contain internal cooling coils or may be provided with injectors for the introduction of water or a similar cooling medium into the gas. A gas-solids separator 19, shown in FIGURE 1 as a cyclone type separator, is connected to the heat exchanger outlet. Filter 20 on the gas discharge line permits the removal of entrained solids not taken out by the separator. The solids removed in separator 19 are discharged through line 21 and recovered in collector 22. Powdered tungsten carbide is introduced into the system from a powder feed hopper 23 by entraining it in a powder feed gas injected through line 24. The gas containing entrained tungsten carbide powder passes from the powder feed hopper through line 25 and is introduced into the plasma stream near the upstream end of cooling chamber 15. Controls for regulating the gas flow, the electrical input and the cooling water circulation rate are not shown in the drawing but will be familiar to those skilled in the art.

In utilizing the apparatus described above to produce the modified tungsten carbide of the invention, powder feed hopper 23 is first charged with finely-divided tungsten carbide powder. The powder employed will preferably consist essentially of mon tungsten carbide and ditungsten carbide produced by the carburization of tungsten metal as described previously but in some cases carbide compositions which consist essentially of mon tungsten carbide and ditungsten carbide but contain minor amounts of cobalt, titanium carbide, tantalum carbide and other constituents may be used. The powder size selected will depend primarily upon the size of the spheroidal carbide granules to be produced. Powder ranging from about 400 mesh on the Tyler screen scale to about 100 mesh will ordinarily be employed where the spheroidal granules are to be later used for infiltration purposes but larger sizes may be employed, provided of course that the gas velocities in the apparatus are sufficient to permit entrainment of the particles. Powder ranging between about 325 and about 270 Tyler mesh has been found particularly effective.

After the powder feed hopper has been charged with tungsten carbide powder, the plasma generator 11 is energized and circulation of the cooling water to the system is commenced. The arc used to ionize the plasma feed gas is struck and the arc intensity is adjusted by regulating the electrode spacing. Plasma feed gas is then introduced into the generator. Any of a variety of inert or reducing gases may be utilized. Excellent results have been obtained with hydrogen, argon and mixtures of hydrogen and argon. Nitrogen, helium and neon are also satisfactory. The gas velocity will depend in part upon the capacity of the generator and the associated apparatus and in part upon the size of the carbide powder employed. In the generator used for the production of the spheroidal particles depicted in the drawing, gas velocities between about 100 and 500 cubic feet per hour were used with a power input between about 15 and about 30 kilowatts. The operating procedure, and the power requirements and the feed rates for other generators may be somewhat different. The feed gas is partially ionized by the arc in the generator and passes through the electrical field created by the generator coils. Here the gas stream is confined so that extremely high temperatures are secured. An adequate supply of cooling water to the generator, cooling chamber and heat exchanger must be maintained at all times to avoid damage to the apparatus.

The plasma jet created in the generator 11 emerges into cooling chamber 15 in the apparatus at a temperature well in excess of 5000° C. The powdered tungsten car-

bide used to produce the spheroidal particles is injected at this point. The carbide powder in the feed hopper 23 is entrained in the gas stream introduced into the system through line 24 and is fed through line 25 to the cooling chamber. The same gas will normally be used to generate the plasma and to introduce the powdered carbide. Again any of a variety of inert or non-reducing gases will normally be satisfactory. Pressures in the cooling chamber are generally low and hence the use of a high pressure injection system is ordinarily not required.

The powdered carbide granules introduced into the cooling chamber melt almost instantaneously and assume a spheroidal shape because of surface tension effects. A new carbide phase which is generally unstable at ordinary temperatures is formed. As the high temperature gas traverses the cooling chamber, the temperature drops in a matter of milliseconds from well in excess of 5000° C. to a level below the melting point of tungsten carbide, about 2800° C. This in effect results in the freezing of the molten carbide droplets before the new carbide phase can be dissipated. The gas and entrained spheroidal particles then pass into the heat exchanger 18 where they are cooled to room temperature. The particles are thereafter removed from the gas stream in separator 21 and recovered in collector 22. The spheroidal particles may then be sized by screening if desired.

The presence of a new third phase in the tungsten carbide composition of the invention is shown by the results of X-ray diffraction studies carried out with an angular tungsten carbide powder obtained from commercial sources and a spheroidal powder produced by melting the commercial powder in a plasma jet and then rapidly cooling it as described above. FIGURE 2 of the drawing is a reproduction of the X-ray diffraction pattern of the commercial product. It will be noted that this pattern contains prominent peaks at 2θ values of about 34.5, 38, 39.5, 52.1 and 61.9 degrees. These peaks indicate the presence of ditungsten carbide, W_2C . Prominent peaks are also evident at about 31.5, 35.6, 48.1, 64 and 65.7 degrees, indicating that mon tungsten carbide was also present in the commercial product. The X-ray diffraction pattern shown in FIGURE 3 was obtained with the spheroidal powder produced from the commercial carbide. The peaks indicating the presence of mon tungsten carbide and ditungsten carbide are evident but there are in addition peaks at 2θ values of about 36.6 and 42.5 degrees. These new peaks show that melting the carbide and rapidly cooling it resulted in the formation of a new component not present in the earlier material. This new component cannot be detected in tungsten carbide which has been fused and slowly cooled and hence its presence is surprising. Tests with various gases in the plasma generator have indicated that the new component is not due to interactions between the gas and carbide particles.

As pointed out earlier, the improved carbide composition of the invention is particularly useful for the manufacture of composite materials by infiltration. A variety of metals and metal alloys which melt at temperatures in the range of about 1750° F. and about 2500° F. and have the ability in the molten state to wet and partially dissolve the carbide granules may be utilized as the binder or infiltrant metal. Typical alloys which are suitable include copper-nickel alloys, copper-nickel-tin alloys, copper-nickel-iron alloys, iron-nickel-carbon alloys, copper-cobalt-tin alloys, copper-nickel-iron-tin alloys, copper-nickel manganese alloys, and the like. Such alloys may contain minor amounts of other metals including zinc, manganese, molybdenum, iron, silicon, beryllium, bismuth, boron, cadmium, cobalt and phosphorus. S-Monel and a number of other commercially available alloys which melt within the above specified temperature range and have the requisite wetting properties may be utilized for purposes of the invention. It will be understood, of course that every alloy has slightly different properties and that certain alloys are therefore considerably more effective.

tive for purposes of the invention than are others. The use of copper-nickel-tin or copper-nickel-manganese alloys is preferred because of the excellent wetting characteristics and high strength of such alloys.

In utilizing the spheroidal carbide powder for infiltration purposes, the powder is first cleaned with dilute nitric acid and alcohol or similar solvents to remove dust, oil and other foreign matter. The powder is then placed in a clean carbon or ceramic mold containing a cavity of the desired shape. The use of a carbon mold is generally preferred, since this insures a reducing atmosphere during infiltration. The mold may be vibrated as the powder is added in order to obtain a densely-packed mass or, if desired, may be pressed at a pressure of about 100 to about 200 pounds per square inch in order to assure close packing of the powder granules. This is seldom necessary, however, because the spheroidal carbide granules readily flow into very small cavities and form a much denser mass than can generally be obtained with angular carbide particles. Up to about 35 weight percent of powdered nickel may be placed in the mold with the spheroidal carbide powder to aid in wetting of the carbide by the infiltrant metal if desired. The use of powdered nickel is not essential. The use of alloys containing substantial quantities of nickel normally permits wetting of the carbide powder without the addition of powdered nickel.

After the mold has been filled with the required amount of the spheroidal tungsten carbide powder, a mold cover containing an opening through which the binder metal may flow is fitted into place. Some molds are provided with an upper recess in the cover to hold pellets of the binder metal. As the pellets melt, the metal flows into the mold and infiltration occurs. In other cases, the binder metal is heated in a separate crucible or other vessel and then poured into the mold at the proper time. This latter procedure generally permits much better control of the infiltration conditions and is therefore preferable.

It is generally preferred to preheat the assembled mold at a temperature between about 300° and about 600° F. for an hour or longer in order to eliminate gases from the mold which might otherwise cause oxidation at the infiltration temperature. Following this preheating step, the mold and a crucible containing the binder metal are placed in an electric furnace and heated to a temperature between about 1750° F. and about 2500° F. The temperature employed should not greatly exceed that required for rapid infiltration of the binder into the interstices between the spheroidal carbide granules. The composition of the binder primarily determines the infiltration temperature. Copper-nickel alloys generally infiltrate readily at temperatures between about 2000° F. and about 2250° F. Slightly higher temperatures are required for the infiltration of iron-nickel-carbon alloys and the like. Still other alloys may be utilized at temperatures below those required for the copper-nickel alloys. As pointed out earlier, the use of powdered nickel in the mold promotes wetting of the carbide granules and therefore generally permits the use of a slightly lower infiltration temperature than might otherwise be necessary. The precise temperature requirement for the infiltration of a particular binder metal into the spheroidal powder can readily be determined by preparing small specimen molds, filling them with the powder, and pouring the molten binder metal into them at various temperatures. Examination of the resulting specimens after they have cooled will clearly show whether infiltration took place at the temperatures used.

After the furnace has returned to temperature following the insertion of the mold and crucible, heating is continued for a period of from about 30 minutes to an hour or more in order to melt the binder metal and bring the contents of the mold up to the infiltration temperature. The time required to reach this temperature will depend

on the type of furnace utilized and upon the size and heat transfer characteristics of the mold. The carbide powder can be held at elevated temperatures for long periods prior to infiltration without adverse effects and hence heating for longer than necessary does not seriously affect the finished composite material. After sufficient time for the mold contents to have reached the infiltration temperature has elapsed, the binder metal is poured from the crucible or other vessel in which it was melted into the mold. The mold is then held at the infiltration temperature for a period which may range from about 1 minute up to about 20 minutes. Periods less than about 6 minutes are normally preferable. The molten binder metal poured into the mold flows into the interstices between the spheroidal carbide granules and, in part because of the high solubility of the improved carbide, dissolves some of the carbide. Thereafter the mold is removed from the furnace and allowed to cool.

It is generally preferred that the mold and its contents be cooled quickly to a temperature below the melting point of the binder metal employed. The method used to cool the mold will depend primarily upon the mold size. In the case of relatively large molds, those a foot or more in diameter for example, a water spray should ordinarily be used to assure cooling at a sufficiently rapid rate. With smaller molds, an air blast will usually suffice. As the mold cools, the tungsten carbide dissolved in the binder metal is precipitated in the form of carbide crystals. These crystals apparently grow within the cooling matrix and result in bridging between the spheroidal granules. This in turn leads to the formation of a continuous carbide phase containing pore spaces filled with the binder metal. Such a structure has considerably more compressive strength and better resistance to erosion than materials in which the carbide constitutes the discontinuous or interrupted phase. After the mold and its contents have cooled to room temperature, the finished composite article may be removed and sand blasted or machined to remove surface irregularities.

Diamonds or particles of hard metal carbide may be bonded within a composite matrix produced as described above by embedding them in the spheroidal carbide powder prior to the infiltration step. A metallurgical bond between the diamond or hard metal carbide and the binder alloy is formed as the molten alloy cools and solidifies in the mold. The carbide particles employed may be angular chips or fragments produced by fracturing larger pieces of tungsten carbide or a similar carbide having a Rockwell A hardness in excess of about 85 or may instead be cubes of other regularly-shaped particles produced by sintering carbide powder in the presence of cobalt or a similar cementing metal. This provides a convenient and highly effective method for mounting diamonds and carbide particles to be used as cutting elements on drill bits and similar tools. The carbide particles employed for this purpose will normally range between about $\frac{1}{32}$ inch and about $\frac{1}{2}$ inch in size. The diamonds employed may be somewhat smaller than the carbide particles because of their higher cost.

The composite materials of the invention can also be bonded to steel or similar ferroalloy surfaces during the infiltration process. By positioning a steel tool or similar ferroalloy article in a suitable mold, placing spheroidal tungsten carbide granules in voids adjacent the surfaces of the tool, and then infiltrating with a molten binder alloy, a bond between the binder metal and steel and between the binder metal and carbide granules can be formed simultaneously. This simplifies the fabrication of bits and other tools which require a hard outer surface resistant to abrasion or erosion. Care should be taken in fabricating such tools to avoid damage to the steel during the cooling step following infiltration. It is generally preferred to cool rapidly to a temperature below the melting point of the binder metal and then cool slowly to room temperature.

The properties of composite materials prepared by the infiltration of spheroidal carbide granules with a binder metal as disclosed in the preceding paragraphs can be seen by considering the results of comparative labora-
loys is preferred because of the excellent wetting char-
specimens prepared with angular powder and spheroidal powder.

In a first series of tests, two sets of specimens were prepared. Commercial grade tungsten carbide powder was screened to obtain powdered granules between about 175 mesh and about 325 mesh in size. This powder was divided into two parts. The first part was placed in small carbon molds, together with chips of tungsten carbide about 1/4 inch in size, and infiltrated at a temperature of 2175° F. with a molten alloy containing about 55% nickel, 35% copper and about 10% tin. The mold was held at the infiltration temperature for a period of 10 minutes and then rapidly cooled. The second set of specimens was prepared by first passing the angular tungsten carbide powder through a plasma generator to produce spheroidal carbide granules as described earlier. The spheroidal powder was then placed in carbon molds with tungsten carbide chips of the same type used in the earlier specimens and infiltrated with the same alloy employed in preparing the earlier specimens. The times and temperatures used for infiltration were the same in both cases. The two sets of specimens thus produced were then polished and etched to permit metallographic examination.

FIGURE 4 in the drawing is a series of photomicrographs made of a specimen prepared with the commercial tungsten carbide powder. The photomicrograph identified as 4a was taken at 50 power magnification. The

together by binder metal containing the spheroidal powder granules. It will be noted that the granules are packed much more closely together than were the angular granules. The bulk density of the material containing the spheroidal granules is therefore higher. No large open spaces indicating that the powder granules shifted position during infiltration exist. Photomicrograph 5b was taken at 500 power magnification and shows a number of individual spheroidal granules between which bridging has occurred. The third photomicrograph, 5c, was taken at 1500 power magnification and shows the intergranular growth or bridging between the spheroidal particles in still greater detail. It is evident that this intergranular growth or bridging results in a continuous tungsten carbide structure.

The increase in compressive strength obtained by utilizing the spheroidal tungsten carbide powder of the invention in place of angular tungsten carbide powder is shown by the results obtained in a second series of experiments. Test specimens measuring 1 inch in thickness and 1/2 inch in diameter were prepared by infiltrating various tungsten carbide powders with an alloy containing about 55% nickel, 35% copper and 15% tin at a temperature of 2200° F. The infiltration time period ranged from less than 1 minute up to about 16 minutes. The tungsten carbide powder employed included spheroidal powder between about 200 and about 250 mesh in size, produced in a plasma generator as described earlier, and angular powder of various sizes. The specimens were tested in a conventional testing machine to determine the compressive force required to fracture them. The results obtained are shown in the following table.

TABLE I.—COMPARISON OF COMPRESSIVE STRENGTHS

Powder Type	Tungsten Carbide Powder Size Range Tyler Mesh	Infiltration Period, Min.	Compressive Strength, p.s.i.	Remarks
Spheroidal	200-250	<1	239,500	Explosive break, conical fracture.
Do.	200-250	<1	243,000	Do.
Do.	200-250	1.5	261,000	Do.
Do.	200-250	1.5	267,000	Do.
Do.	200-250	4	230,000	Do.
Do.	200-250	8	242,500	Do.
Do.	200-250	8	244,000	Do.
Do.	200-250	16	269,000	Do.
Do.	200-250-70% 325-30%	8	231,000	Do.
Angular	24-32	<1	126,500	Quiet break, 60° fracture.
Do.	60-80	<1	125,000	Do.
Do.	80-100	<1	150,000	Do.
Do.	140-200	<1	192,500	Do.
Do.	170-325	<1	193,000	Do.
Mixture of angular chips and spheroidal powder.	24-32 chips 200-250 powder	4	186,000	Explosive break, conical fracture.

angular carbide powder granules are clearly visible. The large white areas in the upper left and lower right corners of the photomicrograph are carbide chips bonded in place by the binder metal containing carbide powder. It will be noted that the packing of the angular granules between the two chips is very irregular and there are large areas in which no powder granules are visible. Some shifting of the granules as the binder metal infiltrated evidently occurred. Photomicrograph 4b was taken at 500 power magnification and shows an irregularly shaped carbide granule essentially surrounded by binder metal. There is no indication from the photomicrograph that intergranular growth or bridging between granules took place. In photomicrograph 4c, taken at 1500 power magnification, the space between adjacent angular granules is shown. Again there is no evidence of bridging between the granules. Instead, the angular granules clearly exist as the discontinuous phase in the composite product.

FIGURE 5 in the drawing is a series of photomicrographs taken at a specimen prepared with the spheroidal tungsten carbide powder produced in accordance with the invention. Photomicrograph 5a, taken at 50 power magnification, shows two large tungsten carbide chips bonded

The data set forth in the above table show that the specimens prepared with the spheroidal tungsten carbide powder of the invention had significantly greater compressive strengths than did those prepared with the angular powder. In the case of the latter, failure in compression occurred in each instance from the top to the bottom of the specimen along a 60° plane. There was little or no sound when failure occurred. This indicates that the specimens were not homogeneous and that fractures were initiated at the weakest points and then propagated through the specimens. The test specimens prepared with the spheroidal powder, on the other hand, invariably fractured in a conical pattern with a loud explosive report. This latter type of fracture demonstrates that the specimens were essentially homogeneous from the standpoint of compressive strength and that failure of all parts of each specimen occurred almost simultaneously. The greater compressive strength of the material produced from the spheroidal powder is an important advantage for this material.

It will be noted that the strength of the specimens containing spheroidal powder varied with variations in the infiltration period. This is apparently due to the fact that

bridging between the granules depends in part upon the time during which the carbide granules and molten binder metal are in contact with one another. Other tests have indicated that increasing the infiltration period up to a certain point increases bridging and results in greater compressive strengths and that after that point is reached further contact reduces bridging and is accompanied by a reduction in compressive strength.

The data in Table I also shows that the specimens containing the large angular chips and spheroidal powder had about 50 percent more compressive strength than did similar specimens containing only the large angular particles. The use of such a combination of angular chips and the spheroidal powder of the invention results in a material having high wear resistance and is particularly advantageous in hard surfacing applications where angular carbide chips are bonded to tool surfaces to serve as cutting elements.

A further series of experiments was carried out to determine the resistance to erosion of composite materials containing the spheroidal powder of the invention. Small nozzles were prepared by separately infiltrating angular tungsten carbide powder and spheroidal tungsten carbide powder with two different binder metal alloys. One of these was the copper-nickel-tin alloy used in preparing the specimens tested earlier; while the other was an alloy containing about 90% iron and about 10% nickel. The finished nozzles were weighed, subjected to an air stream containing entrained sand particles, and again weighed to determine the weight loss. The weight losses obtained with a 2 minute blast, a 4 minute blast and a 6 minute blast are shown in the following table.

TABLE II.—COMPARISON OF WEAR AND EROSION RESISTANCE

Nozzle	Composition	Percent Weight Loss in—		
		Two Minutes	Four Minutes	Six Minutes
A.....	250-325 Mesh Spheroidal WC Powder; Cu-Ni-Sn Binder.	0.28	0.47	0.68
B.....	175-325 Mesh Angular WC Powder; Cu-Ni-Sn Binder.	0.55	1.16	1.89
C.....	250-325 Mesh Spheroidal WC Powder; Fe-Ni Binder.	0.26	0.48	0.66
D.....	175-325 Mesh Angular WC Powder; Fe-Ni Binder.	0.50	1.34	1.79

It can be seen from the data in Table II above that the weight loss with the nozzles containing the spheroidal tungsten carbide powder was only about a third that with the nozzles prepared from the angular powder. The fact that the weight losses were about the same with the two different alloys indicates that the powdered carbide employed was primarily responsible for the differences noted. The increased resistance to erosion obtained with the spheroidal powder permits substantial improvements in tools and other articles normally fabricated or hard surfaced by infiltrating powder tungsten carbide with a metallic binder.

What is claimed is:

1. A process for preparing an improved tungsten carbide composition which comprises heating tungsten carbide consisting essentially of mon tungsten carbide and ditungsten carbide to an elevated temperature in excess of about 5000° C. and thereafter cooling molten droplets of said tungsten carbide to a temperature below the melting point of tungsten carbide at a rate sufficient to prevent the dissipation of normally unstable constituents formed at said elevated temperature.

2. A process for preparing an improved tungsten carbide composition which comprises heating a non-oxidizing gas stream to produce a plasma, injecting powdered tungsten carbide consisting essentially of mon tungsten carbide and ditungsten carbide into said plasma, cooling said entrained droplets of said tungsten carbide at a rate sufficient to preserve normally unstable constituents present in

the molten tungsten carbide, and recovering solidified spheroidal tungsten carbide granules.

3. A process as defined by claim 2 wherein said non-oxidizing gas is a reducing gas.

4. A process as defined by claim 2 wherein said non-oxidizing gas is an inert gas.

5. A tungsten carbide powder comprising spheroidal granules containing mon tungsten carbide, ditungsten carbide, and a third constituent containing tungsten and carbon which is characterized by X-ray diffraction peaks at 2θ values of about 36.6 and about 42.5 degrees.

6. A tungsten carbide product comprising spheroidal tungsten carbide granules between about 100 and about 400 Tyler mesh in size, said product being characterized by the presence of prominent X-ray diffraction peaks at 2θ values of about 36.6 and about 42.5 degrees.

7. A process for the production of an improved tungsten carbide composition which comprises passing angular granules of powdered tungsten carbide consisting essentially of mon tungsten carbide and ditungsten carbide through a plasma having a temperature sufficient to melt said granules, cooling the molten granules to a temperature below the melting point of tungsten carbide at a rate sufficient to preserve normally unstable constituents present in said molten granules, and recovering spheroidal tungsten carbide granules characterized by the presence of prominent X-ray diffraction peaks at 2θ values of about 36.6 and about 42.5 degrees.

8. A process as defined by claim 7 wherein said angular granules range between about 100 mesh and about 400 mesh on the Tyler screen scale.

9. A process as defined by claim 7 wherein said plasma

is produced by the partial ionization of a gas comprising argon.

10. A process for the production of an improved composite material containing tungsten carbide which comprises infiltrating a mass of spheroidal tungsten carbide granules with a binder metal melting at a temperature between about 1750° F. and about 2500° F. and having the ability in the molten state to wet said spheroidal tungsten carbide granules, said carbide granules being characterized by X-ray diffraction peaks at 2θ values of about 36.6 and about 42.5 degrees.

11. A process as defined by claim 10 wherein said binder metal is a copper-nickel alloy.

12. A process as defined by claim 10 wherein said binder metal is an iron-nickel alloy.

13. A process as defined by claim 10 wherein said spheroidal granules range between about 100 and about 400 mesh in size.

14. A composite material containing spheroidal tungsten carbide granules characterized by X-ray diffraction peaks at 2θ values of about 36.6 and about 42.5 degrees, and a metallic binder present in the pores between said carbide granules.

15. A material as defined by claim 14 wherein said metallic binder is a nickel alloy.

16. A process for the production of an improved erosion resistant material containing tungsten carbide which comprises placing spheroidal tungsten carbide granules characterized by X-ray diffraction peaks at 2θ values of

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about 36.6 and about 42.5 degrees in a refractory mold, infiltrating said carbide granules with a molten nickel alloy melting at a temperature between about 1750° F. and about 2500° F. and in the molten state having the ability to wet said carbide granules, and thereafter cooling said mold and its contents to a temperature below the melting point of said nickel alloy.

17. A process as defined by claim 16 wherein said alloy is a copper-nickel-tin alloy.

18. A tool comprising a ferroalloy body, a matrix containing a metallic binder and spheroidal tungsten carbide granules bonded to said body, and a plurality of particulate cutting elements embedded within said matrix, said granules being characterized by X-ray diffraction peaks at 2θ values of about 36.6 and about 42.5 degrees.

19. A tool as defined by claim 18 wherein said cutting elements are diamonds.

20. A tool as defined by claim 18 wherein said cutting elements are tungsten carbide particles between about $\frac{1}{32}$ and about $\frac{1}{2}$ inch in size.

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