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3,480,410

WC—CrC—Co SINTERED COMPOSITE

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7 Claims

ABSTRACT OF THE DISCLOSURE

A hard metal composition and the method of making the same for use as cutting material, wear parts and the like for cutting tools, dies, and so forth which includes in its composition tungsten carbide, chromium carbide, and cobalt, the chromium carbide being present in the form of particles of an extremely small size below .2 micron and the tungsten carbide is of extremely fine grain size, the resulting metal being much tougher than the average tungsten carbide hard metals and at the same time having a hardness characteristic much higher than that of standard tungsten carbide products with the high range of cobalt included.

This invention relates to a hard metal composition which includes tungsten carbide, chromium carbide, cobalt compositions.

It is an object of the present invention to provide a metal product having a toughness approaching that of conventional tool steel and at the same time a hardness which is comparable to a fine grain tungsten carbide-cobalt composition. While retaining the toughness of high speed steel, the material is much harder than any normal high speed that has practical use. This hardness is also retained at elevated temperatures which may be generated at high speed and high interface temperatures.

In addition, it is an object to provide a hard metal composition which has a high compressive strength and excellent wear resistance coupled with low thermal conductivity and a low co-efficient of friction.

It is a further object to provide a hard metal composition which is adaptable for use at the low speeds of high speed steel and the high speeds of carbide making it ideal for cut-off operations where speed changes with diameter.

In addition, the metal of the present invention has an excellent resistance to interrupted cut operations where the metal is subject to severe shock.

It is a further object of the invention to disclose a method of forming hard metal compositions which have the desirable characteristics mentioned above.

More specifically, the invention relates to a tungsten carbide-chromium carbide-cobalt composition containing from 9 to 20 percent cobalt (preferably 9 to 15 percent) and 0.1 to 2.5 percent chromium carbide (preferably 0.2 to 0.8 percent), the chromium carbide being present in the composition in the form of particles in the size range below 0.2 micron (preferably in the range of 0.01 to 0.05 micron) the percent total carbon in the composition being in the range from [(0.0649) (percent W)+0.12 (percent Cr)] to [(0.0661) (percent W)+0.155 (percent Cr)] and the free carbon being less than 0.1 percent.

The invention further relates to hard metal compositions of the type described, in the form of dense bodies, useful for cutting tools, wear parts, mining tools and dies, said dense bodies having from 0 to 0.06% free carbon, preferably from 0 to 0.02% and more preferably from 0 to 0.01%.

The invention further relates to the process of preparing tungsten carbide-chromium carbide powder compositions useful for preparing the above dense bodies, said

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process comprising the steps of (1) blending a finely divided tungsten powder having a Fischer sub-sieve particle size of from 0.2 micron to 6.0 microns (preferably 0.5 micron to 1.5 microns and more preferably 1.0 micron to 1.5 microns) with (a) a material selected from the group of finely divided chromium oxide or a chromium compound which, when heated to 900° C., is decomposed to a finely divided chromium oxide and (b) finely divided carbon powder and (2) heating the blend to a temperature in the range from 1450° to 1600° C. whereby the carbon reacts with the tungsten to produce tungsten carbide, WC, and with the chromium oxide to produce colloidal sized chromium carbide generally .1 to .2 micron.

In the prior art there have been patents which have recognized that tungsten carbide can be combined with chromium carbide with a cobalt binder to make cutting tools. For example, in the patent to Laise 2,044,853, dated June 23, 1936, there is a disclosure of the use of tungsten oxide to form a tungsten carbide and this patent mentions the possibility of the use of finely divided chromium metal. It is believed, however, that this chromium metal was intended to be a part of the binder to mix with the basic cobalt binder (with which it was mixed) and it did not create a final product having the characteristics of those of the present invention.

Another early patent is U.S. 2,133,867 to Lucas, issued in 1938, which relates to sintered hard metal carbide compositions containing chromium carbide and suggesting the use of cobalt in ranges from 2 to 25 percent. However, this patent does not teach the unusual combination of toughness and hardness that can be achieved with such chemical compositions when the particle size of the chromium carbide is controlled within the colloidal size range. One of the features of the present invention is that the chromium carbide particles are preferably controlled to the size range less than 0.2 micron. This is believed to contribute significantly to the toughness and the hardness of the final composition above referred to.

PROCESS AND INGREDIENTS USED THEREIN

It is believed that the process of handling the ingredients which go to make up the final product is an important factor in achieving the characteristics which have been found to result from the particular combination of ingredients. Also, the selection of the ingredients is significant. The tungsten used in the process of this invention is commercially pure tungsten having an average Fischer sub-sieve particle size .2 micron to about 6 microns. In connection with the production of a fine grain material, it is best to select a tungsten which has a Fischer sub-sieve size of .2 to 1.5 microns, preferably a tungsten of 1.0 to 1.3 microns. It is also preferred that commercially available 99.9 percent pure tungsten powder be selected.

In addition to tungsten carbide, it is also possible to utilize titanium carbide, tantalum carbide, niobium carbide, and vanadium carbide. These carbides have been used as additions to or a substitute for the tungsten carbides of known carbide compounds. These additions may be used as commercially available powders or prepared in accordance with the processes disclosed herein.

As a source of chromium carbide in the process, it is preferred to start with a chromium oxide or a chromium containing composition including solutions of chromium salts which when heated to about 900° C. decompose to chromium oxide Cr₂O₃. The particle size of the chromium oxide then should be in the size range of 0.1 to 0.5 micron. The amount of chromium carbide ordinarily used in compositions of the invention is preferably less than 2.5 percent. Hence a corresponding amount of chromium oxide will be utilized so that ordinarily in the products of the invention, the chromium carbide content will be in the

range from 0.1 to 2.5 percent. The above percentages are in terms of weight.

In the handling of ingredients above described, it is preferable that the chromium carbide be formed in situ. This makes it possible to obtain a very finely divided chromium carbide reaction product, much finer than is available commercially. The presence of the tungsten carbide in the composition is believed to inhibit the grain growth of the chromium carbide and this is a mutual effect in that the chromium carbide inhibits the grain growth of the tungsten carbide. It might be pointed out that the commercially available chromium carbides or chromium metal powders are ordinary in the particle size range of 1 micron and larger and this particle size range is not effective in the compositions of the present invention. Therefore, in order to achieve the desired result, it has been found best to form the chromium carbide in the presence of the tungsten carbide product.

The carbon used in the process to produce the tungsten and chromium carbides is preferably a lampblack, carbon-black or graphite, which materials are conventionally used in the formation of tungsten carbide and other metallic carbides in commerce today. The amount of carbon used in the process of the invention is preferably carefully controlled so that it is just sufficient to convert the tungsten completely to tungsten mono-carbide (WC) and to convert the chromium oxide to chromium carbide.

In carrying out the process, it is important that the compound powders, namely, tungsten, chromium oxide and carbon be intimately mixed together. This can be accomplished by known blending techniques such as ball milling, wet or dry, Muller mixing, or cone blending using an intensifier bar. The mixing time should be sufficiently long that the aggregates of the powder are disintegrated uniformly. The ultimate characteristic of the final powder is dependent upon a complete dispersion of the chromium oxide through the blended mix.

Once the reactants of the powder are blended, the blend is then packed in graphite containers and fired in a non-oxidizing atmosphere such as hydrogen or under vacuum at temperatures of 1450 to 1600° C. for a sufficient length of time to complete the reactions, and more specifically, in the nature of 30 minutes.

As indicated above, it is important that all of the tungsten be converted to tungsten mono-carbide and the chromium oxide converted to chromium carbide inasmuch as the presence of a tungsten di-carbide (W_2C) has a very deleterious effect on hard metals formed from powders containing this compound. The presence of tungsten di-carbide leads to the formation of the well-known eta phase which substantially embrittles the hard metal part. Thus, control of the initial carbon quantities is highly important.

CHARACTERISTICS OF THE POWDER RESULTING FROM FIRING

The chemical composition of the powder formed during the firing reaction is tungsten mono-carbide (WC) and chromium carbide and when such powders are introduced into the atmosphere, they will chemically absorb trace amounts of oxygen; but aside from this contaminant, the powders are substantially the carbides of tungsten and chromium but in an extremely small relative grain size.

It follows that the tungsten carbide-chromium carbide powders have a relatively high surface area as compared with conventional tungsten carbide and this is believed to be largely due to the fact that the ingredients have a mutually inhibiting effect on each other as far as grain growth is concerned. Specifically, the surface areas of such compositions are greater than 0.5 square meters per gram. This increase in area resulting from the smaller particle size which has been mentioned is thought to be due to the presence of chromium carbide formed in situ.

By methods of this invention, the chromium carbide

has a surface area, by calculation, of about 40 square meters per gram. By way of comparison, commercially available chromium carbides have surface areas in the range of 0.4 square meter per gram which would be a characteristic of a chromium carbide powder having an average particle size of about 2.0 microns. With the particle size of 0.02 micron, the greatly increased area of 40 square meters per gram is obtained. Thus, with the smaller grain size of the tungsten carbide itself and the very small grain size of the chromium carbide, there is a significant increase in the area of the combined composition which is extremely important in connection with the available surface in contact with the binder phase of the completed product.

CONVERSION OF POWDER TO HARD METAL

The next step in the completion of the hard metal composition is the introduction of the binder metal in the form of cobalt powder. This is done by methods which are conventional in the art. The amount of binder used in the form of cobalt powder may vary depending on the nature of the final end product. In order to achieve the toughness desired in the products of this invention, it is further desirable to use a cobalt range of around 9 to 13 percent, by weight. In certain instances where extreme hardness is not a necessary characteristic, it is possible to use up to 40 percent cobalt with the tungsten carbide, chromium carbide powders previously described.

The conventional blending as practiced in the art is by means a ball milling under a liquid vehicle such as naphtha, acetone, kerosene, and so forth for a period of from one to five days. After blending, the wet slurry is screened through a fine mesh screen to remove metal chips or flakes which may result from smearing of aggregate metal particles. The slurry is then dried and wax in the order of 1 to 3 percent may be added as a pressing lubricant and also to inhibit oxidation. The powder is then pressed using conventional procedures and after a pre-sintering, the piece may be cut or modified in size or shape and finally it is sintered in hydrogen or under vacuum at temperatures of the order of 1300 to 1500° C.

The following illustrative examples of actual compounds may be helpful in the understanding of the invention:

Example 1

This is an example of a tungsten carbide-chromium carbide-cobalt composition containing about 0.5% chromium carbide and 10% cobalt, the balance being tungsten mono-carbide.

The powder blend was prepared by mixing the following components:

816.468 parts by weight of tungsten powder,
55.950 parts by weight of lampblack, and
5.823 parts by weight of chromium oxide.

The tungsten powder used was a commercially available tungsten powder having a particle size of a range from 1.0 to 1.3 microns by Fischer sub-sieve analysis. The chromium oxide was nominally Cr_2O_3 . The powders were blended to obtain an intimate mixture. The blend was then carburized at a temperature of 1500° C. For carburization, the powder is packed in a graphite boat and the boat is passed through a carburizing furnace. The powder was heated for about one-half hour at temperature.

Typical analysis of powder obtained in this way indicated 6.20% total carbon. Substantially all of this carbon was combined either as tungsten carbide or chromium carbide.

The tungsten carbide-chromium carbide powder obtained as above described was blended with cobalt powder in the ratio of 90 parts carbide powder to 10 parts of cobalt powder. This blend was ball milled 72 hours under heptane. The balls used in the milling operation were

tungsten carbide-cobalt. The milled powder was wet screened through a 325 mesh screen.

Before completely drying the powder, it is desirable to blend in 2% by weight of paraffin or other known lubricant. The lubricated powder was pressed, using conventional dies with conventional tooling to a part .0918" x .0918" x .0318" thick. These parts were then pre-sintered. Six specimens were cut from the pre-sintered specimens to a size .258 x .318" x .918". After sintering in vacuum at 1500° C. with a time at temperature of ½ hour, the uncut specimens sintered to .765" x .765" x .265". The cut specimens measured .215" x .265" x .765". After grinding the .215" x .265" x .765" specimens to .200" x .250" x .750", specimens were tested for transverse rupture strength. The transverse rupture strength was 450,000 p.s.i., the sintered density 14.50 grams per cubic centimeter, the hardness of 91.5 Rockwell "A," porosity of less than A-1, the average grain size was slightly less than 1 micron, the maximum grains being about 2 microns in size. X-ray examination of the product showed that the chromium carbide particle size was 31 millimicrons.

Example 2

This example is similar to Example 1, except that a part of the tungsten carbide-chromium carbide powder was replaced with tantalum carbide powder. In this way, a composition containing 5% tantalum carbide was prepared. Twenty-five parts of tantalum carbide was added as a 2.0 micron powder to the four hundred and twenty-five parts of tungsten carbide-chromium carbide powder and 50 grams of cobalt powder and milled 72 hours.

Pieces of hard metal pressed and sintered as in Example 1 had a Rockwell A hardness of 91.7, a density of 14.39 gms. per cc. and a transverse rupture strength of 403,000 p.s.i.

Example 3

This example is similar to Example 1, except that 13% cobalt was used instead of 10%. The Rockwell A hardness was 90.5, the density was 14.15 gms. per cc. and the transverse rupture strength was 505,000 p.s.i.

CHARACTERISTICS OF THE HARD METAL PART

The final hard metal composition should contain substantially no free carbon. For certain uses up to 0.06% free carbon can be tolerated, but it is much preferred that the free carbon be in the range of from 0 to 0.02% and more preferably from 0 to 0.01%. The problems connected with free carbon in hard metal compositions are well known in the art.

The hardness of the part depends to a considerable extent on the amount of cobalt used, but for any given cobalt content, the presence of finely divided chromium carbide increases the hardness obtained substantially. For example, the hardness of a tungsten carbide-chromium carbide, 10% cobalt composition is in the range of that nominally obtained with a tungsten carbide, 6% cobalt composition without finely divided chromium carbide.

The solid products of this invention are characterized by having improved hardness at a given tungsten carbide grain size. For the purpose of defining the products of the invention, the hardness index, I, is defined as:

$$I = \left[\left(\frac{Ra}{0.0937 - 0.00030C - 0.0002G} \right) - 1000 \right]$$

where:

Ra=Rockwell A Hardness

C=Percent cobalt

G=Grain size of tungsten carbide in microns

For the products of the invention, the hardness index is greater than 1, and preferably in the range greater than 6, that is, in the range from 6 to 11. Similar products which do not have the finely divided chromium carbide will have a hardness index in the range of -5 to -9. Thus, the

addition of the finely divided chromium carbide increases the hardness index from the range below -5 to the range +1 to +11.

The present invention thus permits a higher cobalt content while maintaining the hardness characteristic. This increased cobalt content increases the toughness characteristic and therefore the resistance to chipping and cracking, thus reducing greatly the possibility of failure in use. Accordingly, the ratio of hardness to strength is extremely good and believed to be greatly superior to known hard metal compounds.

Since the amount of the chromium carbide is generally of the order of .2 to .8 percent, the densities obtainable are nominally the same as one would obtain without the chromium carbide. The critical factor is not really the density, but the lack of porosity. The normal processing techniques which avoid the presence of porosity are practiced in the processes of this invention and normally the products of the invention were substantially free of porosity. By freedom from porosity, is meant that there are substantially no macro or micro pores observable in conventional metallographic examination.

The transverse rupture strength on the products of the invention, like hardness, is a function of the amount of cobalt present. Generally, speaking, products containing about 10% cobalt will have a transverse rupture strength in the range of 400,000 p.s.i. It is not uncommon in the products of the invention to obtain transverse rupture strength in the range of 600,000 p.s.i.

The grain size of the tungsten carbide in the hard metal part is related to the particle size of the tungsten powder used in the preparation of the material. The presence of chromium carbide in a finely divided state as described above restricts grain growth and consequently the grain size of the compositions of the invention will be smaller than those which would be prepared in a similar fashion but without the presence of the finely divided chromium carbide.

The particle size of the chromium carbide in the products of the invention can be determined by X-ray analysis, specifically by the X-ray line broadening technique which is described in the literature. In the products of the invention, the chromium carbide particle size as measured by this technique is less than 2 microns and in the preferred products of the invention, is in the size range from 10 to 50 millimicrons.

USES

Products of the invention are useful as cutting tools, mining tools, wear parts and dies, and other similar applications where hard metal is normally used in commerce. The principal advantage of this invention is a combination of high hardness and high toughness. This is unique because in the ordinary practices of the art, one gets either high hardness with a sacrifice of toughness, or vice-versa. There is obtained, therefore, a combination of high edge strength with a much higher degree of abrasion resistance than is ordinarily obtainable.

What is claimed as new is as follows:

1. A sintered hard metal alloy having a high ratio of hardness to strength with a transverse rupture strength in the range of 450,000 pounds per square inch or higher for use as a cutting tool material with a high edge strength which consists essentially of tungsten carbide, chromium carbide and cobalt substantially free of any free carbon as an impurity, the chromium carbide being present in the amount of 0.1 to 2.5 percent by weight of the finished product, and in the form of a complete dispersion of extremely fine grain size in the range of below 0.2 micron, the cobalt being present in a range of 9 to 20 percent by weight, the remainder of the material being substantially tungsten carbide in the form of tungsten mono-carbide, the average grain size of particles in the alloy being less than 1 micron and substantially free of macro and micro

pores as observable in conventional metallographic examination.

2. A sintered hard metal alloy having a high ratio of hardness to strength with a transverse rupture strength in the range of 450,000 pounds per square inch or higher for use as a cutting tool material with a high edge strength which consists essentially of tungsten carbide, chromium carbide and cobalt substantially free of any free carbon as an impurity, the chromium carbide being present in the amount of 0.2 to 0.8 percent by weight of the finished product, and in the form of a complete dispersion of extremely fine grain size in the range of below 0.2 micron, the cobalt being present in a range of about 10 percent by weight, the remainder of the material being substantially tungsten carbide in the form of tungsten mono-carbide, the average grain size of particles in the alloy being less than 1 micron and substantially free of macro and micro pores as observable in conventional metallographic examination.

3. A sintered hard metal alloy for cutting tools as defined in claim 1 formed from a powder in which the percent total carbon is in the range from [(0.0649) (percent W)+0.12 (percent Cr)] to [(0.0661) (percent W)+0.155 (percent Cr)], any free carbon in the powder present as an impurity being less than 0.1 percent by weight.

4. An alloy for cutting tools as defined in claim 1 in which the grain size range of the chromium carbide is between 10 to 50 millimicrons.

5. An alloy for cutting tools as defined in claim 1 in which the average grain size of the tungsten mono-carbide is in the range of 0.2 to 1.5 microns.

6. An alloy for cutting tools as defined in claim 1 in which hardness index as defined in the formula

$$I = \left[\left(\frac{Ra}{0.0937 - 0.00030C - 0.0002G} \right) - 1000 \right]$$

is in the range of 1 to 11, where *Ra* is Rockwell A hardness, *C* is percent cobalt by weight, and *G* is the grain size of tungsten carbides in microns.

7. An alloy for cutting tools as defined in claim 1 in which hardness index as defined in the formula

$$I = \left[\left(\frac{Ra}{0.0937 - 0.00030C - 0.0002G} \right) - 1000 \right]$$

is in the preferred range of 6 to 11, where *Ra* is Rockwell A hardness, *C* is percent cobalt by weight, and *G* is the grain size of tungsten carbides in microns.

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