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HARD METAL ARTICLE AND METHOD OF MAKING

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This invention relates to the manufacture of articles from hard, unbonded metallic carbides and, more particularly, relates to the making and shaping of tungsten carbide into die, tool, and bearing elements.

It is well known that tungsten carbide is usually processed and shaped by the methods of powdered metallurgy. The refractory nature of this material in powdered form renders it incapable of readily sintering or agglomerating even under conditions of high temperatures and pressures. For this reason, the custom of including some bonding material, which usually takes the form of a metal of lower melting point, such as iron, cobalt, chromium, or nickel, is prevalent throughout this art.

The bonded tungsten carbides, though possessing properties of hardness and toughness, are recognized as being not as hard as tungsten carbide agglomerated without the aid of such a binder. It has been found that some processes in this art have been purportedly productive of unbonded tungsten carbide articles having good physical properties. Examination and analysis have proved that all so-called unbonded articles made by these prior methods included an appreciable amount of iron or other bonding material which is presumed to have been present as an impurity in the initial tungsten or tungsten carbide powder, thought to be pure, or inadvertently added thereto when the tungsten or tungsten carbide powder was pulverized in a ball mill made of iron or stainless steel. While the steel balls of such a mill, and the container itself, act on the powder to pulverize it, the powder, in turn, has an erosive action on the mill elements whereby particles of the latter are mixed into the refractory powder. It appears that the success of prior methods in fabricating unbonded tungsten carbide has been ascribable to the presence of such a bonding agent, accidently or inadvertently included therein.

Hence, the carbides of the prior art have not exhibited the properties of hardness of which they are capable, when pure, and, in consequence of the binders, have been more readily agglomerable than would be the case if no such bonding agents were present.

It is an object of the present invention to produce articles from substantially pure tungsten carbide, which not only have the high degree of hardness attributable to such material, but which are strong, dense, and physically adapted to the various purposes to which they are to be applied, as well.

Although the invention is primarily concerned with tungsten carbide, it is also among the objects to teach a method of processing any of the metallic carbides, nitrides, borides, etc., wherein the ultimate degree of hardness of such material is developed without sacrificing the strength and density of articles fashioned therefrom. Other objects and advantages will become manifest hereinafter as the description develops.

In carrying out the invention, tungsten powder with a maximum impurity content of 0.3% is provided, which has a particle size smaller than is necessary to pass a screen having 325 meshes to the square inch. Powder in the order of 400–600 mesh has been found suitable for the purposes of the invention.

The tungsten powder is then mixed with carbon in finely divided form, such as lamp black, in the proportion that the lamp black amounts to 4–6% by weight of the tungsten powder. The two ingredients are mixed in any suitable manner, one satisfactory method for achieving a thorough admixture being effected by placing the tungsten powder and carbon in a porcelain tumbling mill (without shot or pebbles) and tumbling from two to twenty-four hours. The longer the mixing time allowed, the more intimate the mixture and the more desirable the end product. If the two ingredients are not thoroughly mixed, when working in the higher percentages of carbon, evidences of free carbon will be found throughout the body of the tungsten carbide mass after it has been carburized in a manner about to be described. For this reason, the longer the mixing time, the better will be the final product, particularly when working in the higher ranges of carbon inclusion.

After tumbling, the mixture is carburized by heating in a furnace sealed from the external atmosphere at temperatures ranging from 2300–2700° F. for at least two hours, depending upon the quantity of the charge. In the treatment of a charge weighing in the order of 800 grams, it has been found that by increasing the time factor, lower temperatures, such, for example, as 2100°, for eight hours, can be used if necessary, and higher temperatures, such as 4000° F., for periods of time less than an hour, are admissible. The relationship indicated is that the higher the temperature, or the less the mass under treatment, the shorter the time. However, temperatures in excess of 2700° F. are not recommended since, upon removal from the carburizing furnace, the powder will be found to

have fritted or sintered together, making subsequent handling thereof more difficult.

The carburizing has been carried out successfully by placing the admixture of tungsten and lamp black in the proportions previously described in a pure graphite cylinder that is sealed with carbon plugs at both ends. This cylinder is then placed in a carbon tube resistance furnace and heated to the desired temperatures for the time allotted in accordance with the above. Since no external atmosphere is admitted into the furnace, the carbon tube at these temperatures furnishes a non-oxidizing or reducing atmosphere therein. If other than a carbon tube furnace is used, the reducing atmosphere, which is desirable, may be otherwise supplied, one preferred way being the passing of hydrogen through the furnace.

Upon removal from the carburizing furnace, the carbon will be found to have combined entirely with the tungsten to form tungsten carbide. In this respect, it is known that there are two forms of tungsten carbide; the single carbide (W_2C), having a combined carbon content of 3.12%, and the double carbide (WC) with a combined carbon content of 6.24%. It is difficult to form the single carbide with any degree of certainty that some of the double carbide is not present. Similarly, it is difficult to form double carbide with the assurance that there is no single carbide present, without running the risk of having a slight excess of carbon, which would be found in uncombined form in the final product, and is undesirable. These considerations are complicated somewhat by the fact that the tungsten carbide picks up a certain amount of carbon from the graphite tube in which it is disposed during the carburizing operation. This pick-up has been found to be about 0.66% where about 3% lamp black has been added to the tungsten powder, and from .25% to .30% where around 6% lamp black has been added to the tungsten powder. The more carbon included at the outset, the less is the amount of carbon picked up.

The prescribed range of admixed lamp black (4–6% by weight) gives a carbide form that is somewhere within the single carbide-double carbide range, and even the higher figure gives a sufficient margin of safety to allow for a .25% pick up without exceeding the amount of combined carbon found in the double carbide form. Since it has been found that in the lower ranges of combined carbon (3.66% to 4.50%), the tungsten carbide tends to be brittle and lack sufficient strength for strenuous service, such as wire drawing dies are subjected to, it is preferable to go to the higher ranges, even though the material having the low carbon content is quite hard. Without sacrificing hardness, the strength of the sintered carbide in the final product has been found to be progressively stronger as the combined carbon content increases. Hence, with all facts considered, the ideal range of combined carbon appears to be from 5–6%, inclusive.

After the powder has been carburized, it is removed from the carbon tube furnace, and from the graphite tube in which it is contained. It will be found in a semi-powdered form, the lumps of which readily crumble between the finger if the temperatures have not been excessive. The higher the temperature, the more stick-like and solid will the charge of the tube become. It is necessary to reduce the material to a small, uniform, particle size before subsequently processing. For this reason, the more easily it reduces to dust at this stage, the better, and hence the recommendation for carrying out the carburizing treatment at the lower temperatures.

The carbide material is ground by placing it in a stainless steel ball mill having stainless steel balls of varying sizes. The balls that have been applied to this purpose vary in diameter from ¼" to ⅝". Although it has been found that uniformly sized balls may be used, the grinding and the thoroughness of the operation is expedited by the use of stainless steel balls that vary in size as indicated. To the carbide powder is added a wetting agent to facilitate the grinding action and to aid in the subsequent handling of the material. Methyl alcohol, carbon tetrachloride, or a high grade naphthalene, have been found suitable for this purpose. The charge of the ball mill is composed of 800 grams of tungsten carbide powder, 400 cubic centimeters of wetting agent, and 5800 grams of the stainless steel balls. The grinding operation is then commenced and continued from fifteen to eighty hours continuously, depending upon the subsequent particle size desired.

In respect to particle size, it has been found that the size of the original tungsten powder determines to some extent the size of the final carbide powder, and that if either is too large (325 mesh or larger), the material, when it is subsequently pressed and sintered, is not as hard as when smaller particles, such as below 325 mesh, are used. The longer the grinding time for the carbide powder, the better are the hardness and density of the final product, and hence the longer grinding times are recommended, up to the maximum time indicated (80 hours). It has been found that when the powder is ground longer than this, it becomes so fine in particle size that during the ensuing pressing and sintering steps it shrinks unduly and is distorted and brittle in consequence thereof.

As has already been stated, the tungsten carbide powder, by attrition between it and the mill elements, will pick up impurities comprised of the material of which the mill is made during grinding operations. It is for this reason that a stainless steel mill is employed instead of a pebble mill, because the silica that is ground off a porcelain pebble mill is very difficult to remove from the powder and is very undesirable in the final product in amounts over .5%.

On the other hand, the stainless steel mill specified will contaminate the tungsten carbide powder as, for example, 15% stainless steel impurities are picked up when the carbide powder is ground for forty hours in this type of mill, but the stainless steel impurity can be more readily disposed of than the silica inclusion obtained from a pebble mill, as will now be described.

After the grinding operation, the charge in the mill is removed as a wet sludge and the carbide is left to settle, after which the wetting agent is poured off, leaving the tungsten carbide powder as a wet mass. The tungsten carbide powder is then left to dry, preferably in the air, since attempts to accelerate the drying, as in an oven, sometimes causes rapid oxidation of the finely divided material, which occurs at such a rate as spontaneously to combust in air, leaving a useless mass of tungstic oxide powder. After the powder is thoroughly dry, it is treated to remove the stainless steel impurity by leaching it in a one to one (1–1) mixture of concentrated hydro-

chloric acid and water. This leaching process completely rids the tungsten carbide powder of the stainless steel, while leaving the carbide itself substantially unaffected.

After leaching, the carbide is thoroughly washed in water to eliminate the acid. Since this is not always effective in removing all of the acid, it is desirable to heat the washed powder in a steel cylinder at 1100° F. for one hour, under reducing conditions, thus driving off all traces of the residual acid, and thoroughly drying the powder.

The carbide powder, after the baking step last described, will be found to have caked somewhat, rendering it difficult to pass it through a 325 mesh screen. To restore its particle size, it is customary to return the powder to the ball mill and give it a ten to thirty minute grind in the presence of alcohol. This has been found sufficient to restore the caked carbide to powdery form without being sufficient to reinstate the stainless steel impurity. Thereafter the alcohol is evaporated and the powder is then screened to insure that in particle size it will pass a 325 mesh screen, or smaller. Any lumps failing to pass the screen can be broken up in any suitable manner, as by mortar and pestle.

The powder is then prepared for pressing into final form. This is accomplished by dampening the powder with a liquid vehicle in which a temporary binder is dissolved, such, for example, as carbon tetrachloride and paraffin. Glycerine and alcohol have worked satisfactorily in this same connection. The liquid vehicle is then permitted to evaporate leaving the powder coated with a minute amount of paraffin or glycerine. The purpose of the paraffin or glycerine is to provide a lubricant and a binder for the ensuing pressing operation.

The pressing operation is effected by transferring the powder to appropriate molds and pressing it under pressures varying from 25 to 60 tons per square inch. The temporary binder, such as the paraffin, helps to overcome some of the resistance that the particles of powder exhibit to being pressed, and at the same time holds the particles together after the pressure has been relieved. In the case of pressing nibs for wire drawing dies, a cylindrical mold having an 11° taper, more or less, from top to bottom is preferred in order to afford easy removal of the nib after the pressure has been applied and relieved.

The carbide articles in this preliminary form are then subjected to a pre-sintering treatment at temperatures ranging from 2100–2400° F., which is effected by placing them in a carbon boat and putting them in a cold carbon tube resistance furnace, from which, as soon as the furnace has come up to temperature, they are pushed into a cooling chamber having a water jacket to take the heat away. This is usually effected in about one-half an hour.

The carbide articles in this pre-sintered condition have the consistency of chalk, and while being sufficiently firm are, nevertheless, capable of being turned on a lathe, drilled, or otherwise shaped, without any difficulty. For wire drawing nibs, the taper imparted by the mold is ground off, and the nib is drilled with an ordinary high speed twist drill to whatever hole size is desired. It is customary to grind the ends of the nib at this stage to remove any false tops or chipped edges.

In this condition, the carbide articles, to which has been imparted their final form, are ready for the final sintering operation. This may be accomplished by placing them in a carbon boat, and re-introducing them into the carbon tube furnace for heating from 3000–4000° F. for one hour, after which they are pushed into the cooling zone at the rear of the furnace, where they remain until cooled. The temperature range is necessary because the exact temperature depends upon the type of powder used, and its particle size, the finer powder sintering at the lower end of the range, and the coarser powder sintering at the upper end of the range.

After the sintering, the carbide articles are ready for any finishing steps found to be necessary or desirable. Referring again to the example of the wire drawing nibs, it is customary to grind the circumference by running the nibs on centers and using a diamond wheel. Thereafter, the nibs may be placed in a jig and the ends ground true so they are rectangular with respect to the sides and vertical axis thereof. The finished article is then ready to be checked for hardness.

The hardness measurements are taken on a Rockwell superficial hardness tester, which employs the 30 N scale. The articles made in accordance with the foregoing will be found to vary in hardness from 90 to 94 on this scale. An average hardness, however, of from 91 to 92 on the 30 N scale will be realized. This corresponds to 72 and 76 on the Rockwell C scale. When compared with the bonded carbides, the best reading of which does not exceed 90, and, more frequently, occurs around 88 to 89, the hardness of the carbide articles of this invention compares very favorably. As to strength, the carbide articles formed in accordance herewith may be handled, mounted and used, for all intents and purposes, just like the bonded carbide article.

It will be appreciated that, although tungsten carbide has been used throughout this specification for purposes of illustration, the invention will find application in the treatment of other metallic refractories by powdered metallurgical methods. Thus, the specification should be regarded in an illustratory and not a limiting sense, since other substances, e. g., tantalum, zirconium, boron, etc., and their oxides, nitrides, borides, carbides, etc., in so far as they may be applicable, come within the purview of the invention as is defined in the following claims.

I claim:

1. The method of making articles from substantially pure tungsten carbide powder which includes carburizing tungsten powder of a size that will pass a 325 mesh screen, grinding the tungsten carbide powder, leaching the ground powder with a solvent that will remove solids of lower melting point therefrom but which will not deleteriously affect the tungsten carbide; thereafter freeing the tungsten carbide powder of the solvent, treating the powder with a temporary binder-lubricant, pressing the powder into a compact mass, and heating the compact mass to drive off the lubricant binder and to integrate autogenously the powder particles of the mass.

2. The method of making articles from substantially pure metallic carbide powder which includes carburizing metallic powder of a size that will pass a 325 mesh screen, grinding the metallic carbide powder, leaching the ground powder with a solvent that will remove solids of a low melting point therefrom but which will not deleteriously affect the metallic carbide; thereafter freeing the metallic carbide powder of

the solvent, treating the powder with a temporary binder-lubricant, pressing the powder into a compact mass, and heating the compact mass to drive off the lubricant-binder and to integrate autogenously the powder particles of the mass.

3. The method of producing articles from self-bonded pure metallic carbide powder which includes providing metallic carbide powder of a particle size not greater than 325 mesh, treating said powder to remove any impurities of lower melting point than the metallic carbide, infusing the powder with a binder-lubricant, pressing the powder into a concrete mass, and sintering the resultant mass autogenously to unite the powder particles.

4. The method of producing articles from self-bonded pure tungsten carbide powder which includes providing tungsten carbide powder having a carbon content up to 6.25% by weight of the tungsten, and of a particle size that will pass a 325 mesh screen, treating said powder to remove any impurity of lower melting point than the tungsten carbide, infusing the powder with a binder-lubricant, pressing the powder into a concrete mass, and sintering the resultant mass autogenously to unite the powdered particles.

5. An article of manufacture resulting from the method set forth in claim 1.

6. An article of manufacture resulting from the method set forth in claim 2.

7. An article of manufacture resulting from the method set forth in claim 3.

8. An article of manufacture resulting from the method set forth in claim 4.

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