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METHOD OF PRODUCING HARD CEMENTED CARBIDE COMPOSITES

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My invention relates to a novel hard cemented carbide composite and to a novel process for manufacturing the same, and more particularly; relates to a novel razor blade made of hard cemented carbide composite.

Hard cemented carbide materials have been known for a great many years and have been adapted for many uses where hardness is essential.

Because of their extreme hardness and ability to retain a cutting edge and resistance to corrosion, the desirability of these materials for razor blade edges has long been recognized. Heretofore, however, it has been impossible to manufacture razor blades of these composites due to the extreme difficulty of grinding a thin edge from the material which approaches sapphire in hardness. Attempts to do so have resulted in chipping of the fine edges when the pressure of the grinding or lapping wheel was applied. These difficulties arise from the processes which have heretofore been employed in the production of this composite.

In these processes the hard cemented carbide material is formed by mixing a finely divided or comminuted metallic carbide or carbides with a finely divided metal or alloy of lower melting point. The comminuted powder is then pressed either into the desired shape of the ultimate product or in the form of small billets by subjecting them to pressures in a mold or die. Heat is then applied to the compacted forms in a reducing atmosphere at a temperature which under these circumstances produces a relatively soft composite having sufficient cohesion to permit their further shaping by filing or grinding.

The product is then again heated in a reducing atmosphere to a higher temperature at which the lower melting powdered constituent melts and upon cooling, cements the fine hard particles of metallic carbide in a metal matrix. The first heating operation is commonly called pre-sintering and the later and higher heat treatment is called final sintering.

In this process, the pre-sintering operation is applied at temperatures ranging from 750° to 950° C., and the product which is sought and obtained is soft and easily workable, often likened to the physical attributes of graphite or soapstone. Material in this state when subjected to final sintering becomes smaller in every dimension, the shrinkage being the result of the exclusion of voids by the melting of the lower melting cementing metal and the collapse and pulling together of the unmelted metallic particles.

This process, now well-known, does not, as stated above, lend itself to the manufacture of fine-edged razor blades either in the half-sintered condition or in the full-sintered condition. In the former condition it may be shaped by filing, grinding or cutting with a jeweler's saw but it is too soft and lacks sufficient cohesion to permit working for producing a hard, sharp edge necessary for razor blades. In the latter condition it is too hard to be worked into the fine, hard, sharp edge desired.

I have discovered a novel pre-sintering process which increases the hardness and the cohesion of the compacted powder constituents to an extent which will permit the easy production of razor blade edges from the material in the pre-sintered state. The razor edges, when finally sintered are practically in finished condition, require little or no grinding or lapping and are consequently not subjected to the difficulties of production which have previously prevented the useful application of these materials to razor blades.

Specifically I have found that the physical attributes of pre-sintered, hard cemented carbide materials can be varied within a considerable range of hardness and that similar changes in its cohesion or strength and workability can be produced. I have found that the hardness and strength of pre-sintered hard cemented carbide materials can be increased in a governable manner by varying the compression which is applied to the comminuted powder and that this increase in strength is, in general, proportionate within limits to increasing pressures.

I have further ascertained that increasing hardness and strength result by increasing the oxide content of the cementing metal or metals. I have also found that the hardness of the pre-sintered material increases almost proportionately with the increase in temperature which is applied to it and that at temperatures just short of the final sintering temperature, extreme hardness is obtained.

As a still further means of producing a condition of the material suitable for the ready production of razor blades, I have found that the use of an auxiliary metal or metals having lower melting temperatures than the cementing metal or metals produces by its presence a temporary hardness very desirable for the grinding and lapping of razor blade edges.

The combination and regulation of these means of increasing the strength and hardness of the pre-sintered material results in a physical condition of the end product which enables grind-

ing and lapping thereof in much the same manner as hardened and overtempered steel. By increasing the hardness and strength of the pre-sintered material, the difficulties which have previously precluded its satisfactory grinding into fine razor edges is removed and advantage can be taken of a condition of the material which permits of its being worked into these shapes very much as steel is customarily fabricated into the usual razor blade.

Accordingly, objects of my invention are to provide: a novel hard cemented carbide; a novel process for making a hard cemented carbide; a novel hard cemented carbide razor blade; novel steps in the process of pre-sintering and final sintering; the step of controlling the pre-sintered stage at a point where the composite is sufficiently hard but not too hard and has sufficient cohesion to be worked into fine razor blade edges; the steps of controlling the pressures, temperatures and other conditions of the process of manufacturing hard cemented carbide; a wide range of control of the composite in the pre-sintered and/or final sintered stage; the step in the process which comprises increasing the compacting pressure applied to the comminuted composite previous to sintering; the step of oxidizing the binding metal during mixing; the step of producing an oxide coating of the cementing material around the hard carbide particles; and the employment of an auxiliary binding metal in the process to provide temporary hardness, or any combination of these steps in the process.

There are other objects of my invention which, together with the foregoing, will appear in the detailed description which is to follow.

In practicing my invention, I mix the hard metal carbide and cementing metal or metals in powdered form in a metal rolling barrel filled with metal balls or rods. This is completed in several hours. Heretofore, it has been the practice during this operation to prevent oxidation of the powdered cementing metal by filling the barrel with water or a neutral or reducing gas. In accordance with my invention, I, quite the contrary, contemplate a slight oxidation of the cementing metal. Accordingly, during this mixing, I heat the barrel slightly and introduce oxygen in order to slightly oxidize the binding metal which thus forms an oxide film around the carbide particles. Subsequently, on the application of further heat with a reducing agent as will be described hereinafter, the oxide film will be reduced after compacting and during the pre-sintering treatment will cement the carbide producing a considerable increase in the hardness and strength of the material.

The degree of heat employed and the duration of this oxidizing treatment will vary with the materials used. I have found, however, that using tungsten carbide, for example, as a hard carbide constituent and 10% by weight of metallic cobalt in powdered form as a cementing material that a barrel temperature of from 200° to 400° F. and an oxidizing period of about an hour with the introduction of three liters of oxygen at atmospheric pressure is sufficient to produce satisfactory results.

In compacting, I employ a mold or die of exceedingly heavy construction. It is usually shaped in its internal concavity to form a rough razor blade blank as I prefer to form the compacted materials into such a blank as a means of economy although rectangular billets or other forms can be used. I employ a pressure of from

60,000 to 200,000 pounds per square inch or even greater pressures, depending upon the materials used and the type of blade which is to be made. In the usual practice, pressures of from 10,000 to 60,000 pounds per square inch are used. As a means of furthering the even application of these high pressures, I have found it advisable to employ a lubricant such as paraffin or camphor,—treating the powders with these materials in such carrying mediums as carbon tetrachloride or benzene as is the common practice.

I may, if desired, employ an auxiliary metal of lower melting point than the cementing metal or metals, although this is not always necessary as the other steps of my process are sufficient for the production of blades of some types. In that use, I generally introduce the auxiliary metal in powdered form at the same time as the cementing metal, but it can be added either before or after the oxidizing process just described depending upon the type of the auxiliary metal which is used. The function of this auxiliary metal is to cement the particles of hard carbide and the particles or pellicles of the cementing metal or metals into a transient sintered state which is desirable only for shaping the thin razor edges. Subsequently, during the final sintering heat treatment, this auxiliary metal either alloys with the true cementing metal or metals or is removed by volatilization before the higher melting cementing metal melts and performs its function of producing a metal matrix.

Silver, copper, tin, lead, zinc, antimony or bismuth or such low melting and ductile metals may be used. In selecting them, care must be exercised to combine them suitably with the true cementing metals if they are to remain as an alloy of the ultimate metal matrix. Copper can be used satisfactorily with nickel or cobalt as an auxiliary metal in a cemented tungsten carbide composition for example. In making a composition of this kind I would, for example, mix the following powdered components in the manner which has been described, adding the copper powder after the oxidizing period: tungsten carbide, 90% by weight; cobalt or nickel, 7% by weight; copper, 3% by weight.

I may, on the other hand, employ an auxiliary metal such as silver in conjunction with a true cementing metal such as nickel with which it does not alloy. Or under some circumstances, I may use zinc which melts at a low temperature and is volatile before the melting point of such metals as cobalt or nickel.

A suitable composition entailing the use of silver would be: tungsten carbide, 87% by weight; nickel, 7% by weight; silver, 6% by weight. If zinc is used a suitable composition would be: titanium carbide, 87%; nickel, 9%; zinc, 4%. It should be understood that these examples are given for illustration purposes only and that the scope of my invention is not limited to the compositions mentioned.

The selection of the pre-sintering temperature to be used depends upon the character of the blade which is to be produced, the composition of the hard cemented carbide material which has been selected and the auxiliary metal, if any, which is employed in the production of a suitable pre-sintered state of hardness, strength and cohesion.

As the suitable metals have a wide variety of melting points, I prefer an upper limit of just below the melting point of the true cementing metal or alloy. For example, with a cobalt ce-

menting material and tungsten carbide as the metallic carbide in the proportion of say, 94% tungsten carbide to 6% cobalt, the pre-sintering temperature range for this particular composition would be from 2000° F. to 2500° F. With increases in the cobalt percentages these limits would be reduced slightly to from 2000° F. to 2400° F. (Tungsten carbide 87%; cobalt 13%.)

I have found that regulation of the temperature used during the pre-sintering operation is an important means of increasing the hardness, strength or cohesion of the material in this state and that contrary to general knowledge, increasing the pre-sintering temperature results in a proportionate increase in these characteristics up to a temperature at which the binding material melts and cements the hard carbide constituent. It has been recognized for some time that pre-sintered material of the hardness of graphite or soapstone can be produced by treating the compacted comminuted powders at temperatures of from 750° to 950° C. It has not been recognized that increasing the pre-sintered temperature beyond the temperatures which have been mentioned results in greater strength and hardness in almost direct proportion. I accordingly prefer to use pre-sintering temperatures just lower than the temperatures which produce final sintering by the cementing action of the binding or cementing material.

After the razor blade has been produced by grinding and lapping and possibly honing the pre-sintered material into a suitable razor conformation, it is subjected to final sintering which consists in heating it in a reducing atmosphere and suitably protected from oxidation until the binding material melts and sets the hard carbide constituent in a metal matrix. During this operation some shrinking takes place which has a tendency to further increase the sharpness of the razor blade by diminishing the dimensions of its already fine cutting edge.

It will be understood that I have described specific examples of my invention for purposes of illustration and I do not intend to be limited except by the appended claims.

I claim:

1. In the sintering process for producing articles of razor edge sharpness, the steps of controlling the hardness of the presintered composite which comprises mixing hard metal carbides with a cementing metal in powdered form, applying a pressure of more than 60,000 pounds per square inch to the composite, applying a controlled presintering temperature just short of the final sintering temperature and varying in accordance with the hardness desired; working the composite to form fine edge blades; and thereafter applying a final sintering temperature.

2. In the sintering process for producing articles of razor edge sharpness, the steps of controlling the hardness of the presintered composite which comprises mixing hard metal carbides with a cementing metal in powdered form, applying a pressure of the order from 60,000 to 200,000 pounds per square inch to the composite, applying a controlled presintering temperature just short of the final sintering temperature and varying in accordance with the hardness desired; working the composite to form fine edge blades; and thereafter applying a final sintering temperature.

3. In the presintering process of producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which

comprises mixing hard metal carbides with a cementing metal in powdered form, slightly oxidizing the particles of binding metal to form an oxide film around the carbide, applying pressure of more than 60,000 pounds per square inch to the composite at a temperature falling just below the sintering temperature, and thereafter reducing the oxide film in the presintered stage.

4. In the sintering process for producing articles of razor edge sharpness, the steps of controlling the hardness of the presintered composite which comprises mixing hard metal carbides with a cementing metal in powdered form, producing a temporary hardness thereof, applying a pressure of more than 60,000 pounds per square inch to the composite and thereafter applying a controlled presintering temperature just below the sintering temperature to the metal varying in accordance with the hardness of metal desired and working the composite to form fine edge blades.

5. In the presintering process of producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which comprises mixing hard metal carbides with a cementing metal in powdered form slightly oxidizing the particles of binding metal to form an oxide film around the carbide, applying a pressure of more than 60,000 pounds per square inch to the composite, and thereafter applying the presintering temperature.

6. In the presintering process of producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which comprises mixing hard metal carbides with a cementing metal in powdered form slightly oxidizing the particles of binding metal to form an oxide film around the carbide, applying a pressure of more than 60,000 pounds per square inch to the composite, reducing the oxide film and applying thereto a variable temperature in accordance with the desired degree of hardness in the presintered stage.

7. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which comprises mixing a hard metal carbide and a cementing metal in powdered form, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 pounds per square inch depending upon the metals used, and applying a presintering temperature just below the melting point of the cementing metal and reducing the oxides formed in the composite.

8. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which comprises mixing a hard metal carbide and a cementing metal in powdered form, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 pounds per square inch depending upon the metals used; applying a presintering temperature just below the melting point of the cementing metal and reducing the oxides formed in the composite, and working the composite into the desired shape for final sintering.

9. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which comprises mixing a hard metal carbide and a cementing metal in powdered form, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure of from 60,000

to 200,000 pounds per square inch depending upon the material used, and applying a presintering temperature just below the melting point of the cementing metal and reducing the oxides formed in the composite.

5 10. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which comprises mixing tungsten carbide and powdered metallic cobalt, heating the composite in an oxidizing atmosphere, compacting the composite at 10 a pressure above 60,000 pounds per square inch depending upon the metals used, and applying a presintering temperature just below the melting point of the metallic cobalt and reducing the 15 oxides formed in the composite.

11. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which 20 comprises mixing a hard metal carbide and a cementing metal in powdered form, heating the composite to a temperature of 200° to 400° F. in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 pounds per square inch, 25 and applying a presintering temperature just below the melting point of the cementing metal and reducing the oxides formed in the composite.

12. In the presintering process for producing hard cemented carbides, the steps of controlling 30 the hardness of the presintered composite which comprises mixing a hard metal carbide and a first cementing metal in powdered form, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 35 pounds per square inch depending upon the metals used, cementing the metals with a powdered metal added with the first cementing metal and having a lower melting point than the first cementing metal for transient binding before 40 working the composite, and applying a presintering temperature just below the melting point of the first cementing metal and reducing the oxides formed in the composite.

13. In the presintering process for producing hard cemented carbides, the steps of controlling 45 the hardness of the presintered composite which comprises mixing a hard metal carbide and a first cementing metal in powdered form, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 50 pounds per square inch depending upon the metals used, adding together with the first

cementing metal a metal which alloys with the first cementing metal and melts at a lower temperature to bind the composite for working, and applying a presintering temperature just below the melting point of the first cementing 5 metal and reducing the oxides formed in the composite.

14. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which 10 comprises mixing a hard metal carbide and a first cementing metal in powdered form, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 15 pounds per square inch depending upon the metals used, adding together with the first cementing metal a cementing metal which volatilizes below the melting point of the first cementing metal, and applying a presintering temperature just below the melting point of the first cementing metal and reducing the oxides formed 20 in the composite.

15. In the presintering process for producing hard cemented carbides, the steps of controlling the hardness of the presintered composite which 25 comprises mixing a hard metal carbide as tungsten carbide 94% and a first cementing metal in powdered form as cobalt 6%, heating the composite in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 pounds per 30 square inch depending upon the metals used, cementing the metals with a powdered metal added with the first cementing metal and having a lower melting point than the first cementing metal for transient binding before working the 35 composite, and applying a presintering temperature of 2000° F. to 2400° F. and reducing the oxides formed in the composite.

16. In the presintering process for producing hard cemented carbides, the steps of controlling 40 the hardness of the presintered composite which comprises mixing a hard metal carbide and a cementing metal in powdered form, heating the composite to a temperature of 200° to 400° F. for about an hour in an oxidizing atmosphere, compacting the composite at a pressure above 60,000 45 pounds per square inch, and applying a presintering temperature just below the melting point of the cementing metal and reducing the oxides formed in the composite. 50

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