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HARD SINTERED MATERIALS

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This invention relates to sintered hard materials consisting mainly of alumina.

Such materials can be used with advantage as cutting tools, but their resistance either to flank wear or to cratering is not very good. Our object is to provide a material in which both properties are good. We have found that if the resistance to flank wear is to be good the grain size of the alumina in the sintered material should be as small as possible, and if the resistance to cratering is to be good the grains should be well bonded together by the other materials present. Now the problem is complicated by the fact that as the sintering temperature increases the grain size increases also, but that to ensure good wetting of the particles of alumina by a constituent included for bonding purposes the sintering temperature should be high.

We have found that by using a novel bonding agent, namely a mixture of titanium nitride and a sub-oxide of titanium, we can produce materials in which the resistance to flank wear and the resistance to cratering are both good.

A material according to the invention is made by sintering a homogeneous mixture consisting by weight of from 87 to 96% alumina with the remainder (except for impurities) titanium nitride and sub-oxide of titanium and containing at least 2% titanium nitride and at least 2% sub-oxide of titanium. By a sub-oxide of titanium we mean a compound of titanium and oxygen with or without carbon, having the titanium atoms arranged in a face-centred cubic lattice whether or not carbon is present. The oxygen and carbon atoms occupy lattice sites between the titanium atoms. Carbon, if present, may amount to up to 10% and preferably from 5 to 7% by weight of the titanium and oxygen.

In general the sintering temperatures of compositions consisting essentially of alumina lie within the range of 1400 to 1800° C. In making materials according to the invention the sintering is effected within a limited range of temperature, namely from 1600 to 1750° C., and preferably at 1650° C. at least. In order to obtain the best results so far as bonding is concerned, the temperature must be correlated with the precise composition of the mixture. As the amount of sub-oxide of titanium increases, the sintering temperature decreases. As the amount of titanium nitride increases, the sintering temperature increases. A given amount of titanium nitride involves a rather greater increase in sintering temperature than the decrease required by the same amount of sub-oxide of titanium. When the sub-oxide contains carbon, the sintering temperature should be higher (by up to 50° C.) than for the same amount of sub-oxide free from carbon.

Since a low temperature is desirable for a fine grain size, the facts just given suggest the use of the minimum amount of titanium nitride and of a sub-oxide of titanium free from carbon. However, the bonding is improved with increase in the titanium nitride content. Moreover, the sintering temperature cannot be controlled in practice with the precision that would be desirable, and the use of a sub-oxide of titanium containing carbon allows greater latitude in the sintering temperature required to obtain optimum results. We prefer, therefore, to compromise, and to make the composition of the powder mixture

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approximately 91% of alumina, 3% of titanium nitride and 6% sub-oxide of titanium with carbon amounting to 6.7% of the sub-oxide. The best sintering temperature for this composition is 1700° C.

Examples of other compositions and the most suitable sintering temperatures are as follows.

Alumina	Nitride	Sub-oxide	Temperature, °C.
87	2	11 (6.7% carbon content)-----	1,700
87	2	11 (without carbon)-----	1,650
87	11	2 (without carbon)-----	1,740
96	2	2 (6.7% carbon content)-----	1,650

Naturally the particle size of the alumina in the composition before sintering should be as small as possible, and in practice the alumina must first be thoroughly ball-milled.

If the ball-milling is performed with balls, e.g. of tungsten carbide, which themselves wear away in the process, grinding detritus may be present in the powder which is sintered, that is to say, this powder may not consist solely of the homogeneous mixture.

The sub-oxide may be made by any convenient method, for example by heating a mixture of titanium dioxide and titanium hydride in a vacuum at a temperature of about 1500° C. Preferably the ratio of dioxide to hydride is between 8 to 5 and 8 to 7 parts by weight. Again the sub-oxide can be made by heating a mixture of titanium dioxide and titanium.

If the sub-oxide is to contain carbon it may be made by heating a mixture of titanium dioxide and titanium carbide in a vacuum to about 1500° C. The ratio of titanium dioxide to titanium carbide in the mixture may be between 1 to 2 and 8 to 3, preferably between 3 to 4 and 4 to 3, these ratios being parts by weight. Alternatively, a mixture of titanium dioxide and carbon may be used.

The powder mixture may be formed into cutting tools by any appropriate powder-metallurgical process such as the processes well-known in the manufacture of sintered hard metals. For instance pure alumina may be mixed with the titanium nitride and sub-oxide of titanium by ball-milling in a liquid for several days. The liquid used for ball-milling can in some cases be water, for example when carbon-containing sub-oxide is used, but in other cases a non-aqueous liquid such as acetone is desirable. The milled powder can be dried, sieved, mixed with a lubricant and pressed. The shaped cutting tools are sintered in a vacuum.

Two examples will now be given, all proportions expressed as parts or percentages being by weight.

Example 1

A mixture was made of 8 parts of titanium dioxide and 6 parts of titanium hydride, both being in powder form. The mixture was heated in a tungsten crucible in a vacuum at 1500° C. for 30 minutes to yield a sub-oxide of titanium which thereupon was ball-milled into a fine powder. X-ray diffraction tests showed that the titanium atoms were arranged in a face-centred cubic lattice.

1820 grams of pure alumina of the kind known by the trade name of "Cera," 60 grams of titanium nitride, and 120 grams of the sub-oxide of titanium prepared as described above, and consequently carbon-free, were charged into a stainless steel ball-mill. Acetone was added and ball-milling with tungsten carbide balls continued for 7 days. The resulting mixture, after being separated from the balls, was dried and sieved through a 100 mesh sieve. The powder was lubricated with 5% of paraffin wax by adding it as a solution in carbon tetrachloride, and after evaporation of the solvent the powder

was pressed in a die under a pressure of 10 tons per square inch. After removing the wax by heating in a hydrogen atmosphere at a temperature of 500° C. to 550° C., the pressings were ground to a shape suitable for cutting tools. They were placed in a tungsten crucible and heated in a vacuum in a high-frequency electric furnace to a temperature of 1700° C. for 30 minutes.

The sintered pressings had a hardness of 1700 diamond pyramid hardness. They were used for machining a low-alloy steel under the following conditions:

Speed—1000 to 1800 surface ft. per minute

Feed—.010 inch per revolution

Depth of cut—.050 inch

After cutting times of 1 to 5 minutes, the flank wear and cratering were less than with commercially available sintered alumina tools.

It was found that a slight rise of sintering temperature caused the pieces to have a coarser grain-size and hence to show a greater rate of flank wear when used for machining.

Example 2

A mixture of 4 parts of titanium dioxide and 3 parts of titanium carbide was made, and then heated in a carbon crucible in a vacuum furnace at 1550° C. for 30 minutes. The surface of the charge, after heat treatment, was differently coloured from the bulk and was scraped off and discarded. The bulk-remainder was broken up and sieved through a 30 mesh sieve.

Analysis showed that the product contained 5.9% of carbon, and X-ray diffraction tests showed that the titanium atoms were arranged in a face-centred cubic lattice.

The quantities 1820 grams of "Cera" alumina, 60 grams of titanium nitride and 120 grams of the carbon-containing sub-oxide charged into a stainless steel ball-mill. Distilled water was added and the charge was milled with tungsten carbide balls for 7 days. The resultant powder, after being separated from the balls, was dried in a vacuum oven, sieved, lubricated and pressed to

shape. The pressings, after removal of the wax by heating in a hydrogen atmosphere, were sintered in a vacuum in a high-frequency electric furnace at a temperature of 1700° C. for 30 minutes.

The hardness and resistance to flank wear and cratering were substantially the same as with the pressings described in Example 1. The sintering temperature was however appreciably less critical.

The sub-oxide may be made and the milled powder may be sintered in an atmosphere which is neutral to the substance being heated, instead of in a vacuum.

Although the invention is particularly useful in the manufacture of tools for machining metals, it is not limited to this, as materials according to the invention can also be used for making parts which are required to have resistance to wear.

What we claim is:

1. A process for producing hard sintered objects comprising forming a homogeneous mixture consisting essentially of from 87% to 96% alumina, at least 2% titanium nitride and at least 2% sub-oxide of titanium in which the titanium atoms are arranged in a face centered cubic lattice, pressing the homogeneous mixture into the shape of the objects and sintering said shaped mixture at a temperature of 1600° to 1750° C. in an inert ambient medium.

2. A method according to claim 1 in which the sub-oxide of titanium contains from 5 to 7% carbon by weight of the titanium and oxygen.

3. A method according to claim 1 in which the sintering temperature is at least 1650° C.

4. A sintered hard object consisting essentially of from 87 to 96% alumina, at least 2% titanium nitride and at least 2% sub-oxide of titanium.

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