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METHOD OF MANUFACTURING HARD
FRITTERED ALLOYS

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The method which is the object of the present invention deals with the manufacturing of alloys consisting of a hard carbide such as tungsten carbide and auxiliary metal of the iron group, preferably cobalt, by means of simple methods which are more rapid than the conventional procedures, although they make it possible to obtain extremely hard and tough materials which resist wear most efficiently.

To make the invention better understood, we will first review the methods that are known at present. The first alloys, consisting of tungsten carbide and cobalt, were obtained by starting with tungsten carbide that was preliminarily prepared in powder form, and with cobalt prepared likewise. These two materials are crushed together for a sufficiently long period, until the cobalt is fixed on the carbide surface. The powder obtained in this manner is then compressed and baked in a neutral or reducing atmosphere, the normal temperature during the baking process being of the order of 1450° C. for alloys titrating between approximately 3 and 15 per cent cobalt, by weight.

A later improvement consisted in prolonging the crushing so as to reduce the dimensions of the hard carbide grains, and to obtain in this manner a frittered alloy whose structural elements are much finer, that would tend to give this alloy a much greater hardness and resistance to wear.

A second improvement comprises the prolonged crushing in the presence of a liquid vehicle, so as to reduce still further the grain dimensions and to improve the hardness and resistance to wear.

All these methods have various shortcomings. First, they are not rational, since one starts with relatively coarse carbide, which must then be made smaller. Another disadvantage is the duration of the crushing, which generally lasts over several days. Such a duration implies the necessity of using a large number of crushers, which wear off during their operation, and which require a more or less important upkeep. It is also disagreeable to lengthen the manufacturing time for several days. Finally, the drying of an exceedingly fine powder in a liquid vehicle is not a very simple operation, for the auxiliary metal offers a very large surface and has a tendency to oxidize. Experience has proved that this drying requires an especially careful procedure.

The method which is the object of the present invention has the purpose of preparing a mixture of tungsten carbide and auxiliary metal that is

from the start prepared in the state of extreme fineness which is required, and which is very intimately mixed, thus avoiding the necessity of any prolonged crushing, be it dry or wet. A short crushing, which is quite optional, is intended to insure the homogeneity of the product, but not to reduce the granulometry.

Applicant's method may be carried out in all cases where it is necessary to agglomerate one or more tungsten carbides and/or molybdenum carbides, the binder being a metal of the iron group, or an alloy of several of these metals, or also an alloy with other metals belonging to different groups. Inasmuch as the procedure remains the same in all cases, the present description will be limited to the simplest, that of tungsten carbide agglomerated with cobalt. This method can be performed with percentages of 2.5 as well as with percentages of 18 or even 20, by weight, of cobalt, the remaining percentage being tungsten carbide. The description will now be given in the case of an alloy having 6 per cent of cobalt by weight.

The principle of the method consists in liberating simultaneously in the nascent state, the auxiliary metal and the metal which is thus to be introduced in a hard constituent. This liberation is accomplished by means of a gas, in such a way that there occurs simultaneously a condensation of the pulverulent materials which will spread out when in contact with the metallic grains, and prevent them from growing. Practically, the simplest way is to accomplish that reduction by means of a carburizing gas, so as to liberate a certain quantity of carbon, which disseminates itself among the grains of cobalt and tungsten and prevents them from growing. In a later stage, the necessary addition of carbon is introduced so as to coagulate the tungsten to the required degree. Experience has proved that it is possible to accomplish that carburation without noticeably increasing the size of the carbide grains. In order to facilitate the understanding of the invention, two examples will now be given.

Example 1

One starts with reducible cobalt and tungsten compounds, for instance, cobalt oxide, CO_3O_4 and a tungsten oxide, for instance, tungstic anhydride.

These two oxides are intimately mixed, preferably by moderate crushing, in a ball mill. The duration of that crushing depends upon the granulometry of the oxides, on the dimensions

and the speed of the mill, its ball loads, etc. Generally, a crushing of a few hours will suffice, which is usually performed in the dry state. However, the wet method may also be used, and under these conditions, one would have to resort to reduction by means of a hydrogen stream or a stream of any other inert gas.

The powder thus obtained is arranged in containers so that it forms a rather thin layer of uniform thickness, for instance, 8 to 30 mm. The reduction is accomplished here by means of illuminating gas, which preferably should be dried prior to its usage. The heating is accomplished gradually, up to about 900° C. The cobalt is the first part to be reduced, after which it intervenes as a catalyzer and facilitates the reduction of the tungstic oxides that are formed in succession with the gradual rise of the temperature. At the same time, the cobalt intervenes as catalyzer in regard to the carbon monoxide which is always contained in illuminating gas, and this catalyzation liberates carbon in noticeable quantities, which however, remains dispersed throughout the alloys. The results remain satisfactory as long as the percentage of carbon remains below that required for the final composition of the alloy.

When the reduction is complete, and if the velocity of the gas flow and the temperature-rise curve have been suitably adjusted (the gas velocity and the temperature rise being variables which depend evidently on the quantity to be treated, on the furnace dimensions, and the composition of the illuminating gas, etc.) one obtains a very fine mixture of these two metals with carbon that is nearly chemically pure. This mixture is made homogeneous in a sample and the carbon that it contains is determined by means of a standard apparatus, such as used in siderurgical laboratories. If it is desired to prepare saturated tungsten carbide, the final composition must have 6 per cent of cobalt and 5.75 per cent of carbon. Assuming that the analysis has given 2.75 per cent carbon, it is obvious that 3 are missing in order to obtain the saturated carbide. This additional carbide is introduced in powder form, for instance, very pure lamp-black. The mixture is homogenized by a few hours' treatment in a dry ball mill, after which the carburizing is performed.

In the case of the classic procedures, the carburizing requires very high temperatures, generally of the order of 1400 and 1500° C. Experience has proved that in the presence of cobalt, the carburizing may be accomplished at much lower temperatures, for instance, of the order of 1150 to 1300° C. This is the additional advantage of the method. The carburizing is performed in a hydrogen stream, so that the hydrogen attacks the free carbon and transforms it into methane. As a result, it is now methane which intervenes actively in the carburizing process. The carburizing lasts several hours; generally it is completed after one or one and a half hours. As a measure of safety, it may be extended by at least one-half hour.

After the carburization, the mass has been undergoing a slight frittering, but it can be easily loosened up; to this end, it is treated in a ball mill for about ten hours. This crushing, which is performed in the dry state and for a short time, has the sole purpose of homogenizing the materials, and of separating the grains which the sintering has agglomerated; but it has not the purpose of reducing the size of the carbide crystals. Therein lies an essential difference from the former methods.

Once the crushing is completed, the powder is ready for the compression. However, it is preferable, although quite optional, to pass it through a screen, so as to eliminate the grains which the crushing has not separated, and which still cling together. The manufacture is terminated as in the conventional methods, that is to say, by the compression, amounting to 1 to 5 tons per sq. cm. for instance, and then by agglomeration by a complete frittering between 1400 and 1550° C. or also, by incomplete frittering, between 600 and 900° C. followed by machining and final frittering at a higher temperature, say 1400 to 1550° C. One can also fritter under a relatively low pressure, provided the temperature and the compression are brought into play simultaneously.

Example 2

Sometimes, illuminating gas is subjected to certain variations which are likely to entail irregularities in the alloys. One may overcome these differences by mixing illuminating gas with a certain proportion of hydrogen, for instance, one-third or one-half of its own volume. One may also carburize the hydrogen by dispersing within the hydrogen atmosphere a carefully regulated quantity of some hydrocarbon or similar carburizing substance.

Good results have been obtained with hydrocarbons which were let to fall drop by drop, by means of a regulating device, into the pure and dry hydrogen stream which flows through the reduction furnace. One may use benzene or its homologues, for instance, solvent naphtha, or petroleum ether. The output of liquid hydrocarbon must be regulated depending upon the nature of that product, so as to obtain a carbon deposit under the same conditions as mentioned in the preceding paragraph. This regulation must be performed in accordance with the velocity of the hydrocarbon flow, and as a function of the furnace charge. Good results have been obtained, for instance by incorporating in the hydrogen quantities of liquid toluene in the amount of 20 to 60 cu. cm. per cu. m. of gas.

The method according to Example 2, is carried out exactly as in the preceding case. Once the reduction is terminated, the carbon present is determined, the desired addition of carbon is incorporated, and the carburizing is accomplished in a stream of pure and dry hydrogen. The carburizing temperature is below that of the conventional methods, just as in the case of Example 1.

In its large outlines the new method described is similar to that followed at the beginning of the industry of hard frittered alloys. The crushing was always performed in the dry state, not lasting very long. However, in contrast to these old methods, alloys with a much finer grain are obtained, which can withstand wear much better, especially in the case of machining on hard castings and special castings. For the same chemical composition, the alloys in accordance with the former methods, without crushing, permit one lathe pass, having a length of 20 to 150 mm. on a hard casting cylinder with a Brinell hardness of 500 units, and for certain conditions of feeding speed (22 meters per minute, 0.6 mm. per revolution) and cutting depth (1 mm.). Under the same conditions the alloys prepared in conformity with the invention have made possible passes ranging between 500 and 1200 mm. The 500 mm. passes correspond to alloys manufactured without much precaution, whose fine-

ness is not of the best, whereas the longest passes correspond to alloys which have been manufactured with great care, and where every operation was carefully supervised and performed according to the laws of physical chemistry.

It has been noted also that the process may be carried out just in the same manner after one substitutes for the cobalt some of its alloys, for instance alloys of cobalt and nickel. In this case, it suffices to start with a mixture of the oxides of these two metals, instead of starting from the oxide of cobalt alone. It has been also pointed out in the preceding paragraphs that the raw materials which are to be reduced are the oxides Co_3O_4 and WO_3 (tungstic anhydride). It is evidently possible to start from a lower oxide of tungsten, such as W_2O_5 or WO_2 , for instance. One may also start from another reducible cobalt compound besides cobalt oxide, for instance an organic compound or a cobalt carbonate. Certain organic compounds, such as acetate, have the advantage of freeing hydrocarbons during the reduction and, consequently, of facilitating the deposit of carbon which is necessary for the successful operation.

Finally, it has been observed that it is possible to carburize hydrogen with other substances besides those that have been indicated, for instance with mineral essences, lower alcohols, volatile ketones, etc.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. A method for preparing a finely divided mixture of the powdered ingredients employed in the manufacture of sintered hard metal compositions, said method comprising mixing an oxide of a refractory metal and an oxide of a lower melting point metal, reducing said mixture

in a carburizing medium, adding sufficient carbon to the mixture to permit the desired carburization of the refractory metal constituent of said alloy and heating the mixture at a temperature of about 1150 to 1300° C. in a hydrogen atmosphere.

2. A method for preparing a finely divided mixture of powdered ingredients employed in the manufacture of sintered hard metal compositions, said method comprising mixing an oxide of a refractory metal and an oxide of a lower melting point metal, reducing said mixture in a carburizing medium at a temperature below the carburizing temperature of the refractory metal to thereby deposit on the reduced metals a quantity of carbon less than that required to effect complete carburization of said refractory metal, thereafter adding sufficient carbon to permit complete carburization of the refractory metal and heating the mixture at a temperature of about 1150 to 1300° C. in a hydrogen atmosphere to effect complete carburization of said refractory metal.

3. A method for manufacturing sintered hard metal compositions consisting of one or more refractory carbides and auxiliary lower melting point binder metal, said method comprising mixing an oxide of a refractory metal with a reducible compound of said lower melting point binder metal, reducing said mixture in a carburizing medium, adding sufficient carbon to the mixture to permit complete carburization of the refractory metal constituent of said alloy, heating the mixture at a temperature of about 1150 to 1300° C. in a hydrogen atmosphere to effect complete carburization of said refractory metal and thereafter crushing the mixture.

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