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## METHOD OF PRODUCING A HARD METAL ALLOY

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This invention refers to a hard metal tool alloy and method of producing the same.

This invention forms a continuation in part of my copending application Ser. No. 727,781, filed May 26, 1934, and of my copending application Ser. No. 743,717, filed September 12, 1934 and issued into Patent No. 2,122,157, which were in turn copending with my application Ser. No. 656,103, filed February 10, 1933 and issued into Patent No. 1,959,879, and my application Ser. No. 625,042, filed July 27, 1932 and issued into Patent No. 2,091,017, which were in turn copending with my application Ser. No. 452,132, filed May 13, 1930.

It is an object of the invention to increase the hardness of such hard metal tool alloys without impairing their toughness.

It is another object of the invention to increase the resistance of such hard metal tool alloys against mechanical wear and chemical effects such as of the oxygen of the surrounding air, or moisture, or a cooling liquid such as water.

It is a further object of the invention to increase the hardness of the alloy without impairing its toughness and the size of hard particles contained therein.

It is another object of the invention to adjust the heat conductivity of the hard metal tool alloy without impairing its hardness or resistance against oxidation.

It is still another object of the invention to increase the speed at which hard alloys of this kind can be used for cutting, drilling, milling, and other machining purposes.

This and other objects of the invention will be more clearly understood when the specification proceeds.

Hard metal tool alloys of the type referred to have been made of tungsten carbide and auxiliary metal taken substantially from the iron group, in amounts from about 3% to 20%. The tungsten carbide has been finely powdered and mixed with the auxiliary metal, and the mixture heated to sintering temperature. Such hard metal tool alloys could be utilized for machining cast iron but do not prove efficient in high speed machining steel and other compositions of metal.

In contradistinction hereto the invention proceeds from fundamentally new considerations. It no longer uses one carbide alone, viz. tungsten carbide, and cements it by auxiliary metal in the heat.

The present invention particularly refers to a method of producing a hard metal composition, comprising a consolidated product consisting sub-

stantially of about 3% to 22% auxiliary metal essentially of the iron group, and at least two carbides of tungsten, molybdenum (i. e. an element of the sixth group of the periodical system), boron (i. e. an element of the third group of the periodical system), silicon, titanium, zirconium (i. e. an element of the fourth group of the periodical system) and vanadium (i. e. an element of the fifth group of the periodical system) and in general of at least two hard carbides of different elements selected from the third through sixth groups of the periodical system. The invention comprises the steps of comminuting, preferably as finely as possible, at least two hard carbides selected from the third through sixth groups of the periodical system, admixing the selected carbides in substantial amounts, including a minimum of 1% of a selected carbide, with auxiliary metal essentially of the iron group in amounts of about 3% to 22%, shaping and preferably pressing the mixture and finally alloying it by sintering it into a hard and tough body and until mixed crystals of selected carbides are formed therein in substantial amounts.

A mixed crystal is a homogeneous solid solution of two (or more) substances capable of dissolving one in the other. Experiments have shown and science has given the rule that the hardness of the mixed crystals is a function of the proportion in which the carbides are present in the mixed crystal, and that this function possesses a maximum. It is particularly advantageous to choose for use in the present invention crystals which lie in, or close to this range of maximum hardness. Let me take first experiments made for instance with  $\text{Mo}_2\text{C}$ ,  $\text{W}_2\text{C}$  and Co, let me increase the amount of  $\text{Mo}_2\text{C}$  while decreasing the amount of  $\text{W}_2\text{C}$ , adding always 10% Co; then (1) 90%  $\text{W}_2\text{C}$  and 0%  $\text{Mo}_2\text{C}$  and 10% Co gives a Rockwell hardness of 55; (2) 81%  $\text{W}_2\text{C}$  and 9%  $\text{Mo}_2\text{C}$  and 10% Co gives a Rockwell hardness of 62; (3) 72%  $\text{W}_2\text{C}$  and 18%  $\text{Mo}_2\text{C}$  and 10% Co gives a Rockwell hardness of 57.5; while (4) with 63%  $\text{W}_2\text{C}$  and 27%  $\text{Mo}_2\text{C}$  and 10% Co the material is brittle. By these few tests it is possible to ascertain the hardest mixed crystal of the respective series.

Most favorable results have been obtained with mixed crystals of the system  $\text{Mo}_2\text{C}-\text{WC}$ . The maximum hardness is obtained with an alloy containing about 63% of tungsten-monocarbide (WC), 27% of molybdenum carbide and 10% of cobalt; this alloy has a hardness of 69 Rockwell (diamond load=150 kg.). Satisfactory results are obtained with alloys within the com-

position range: 50% to 70% tungsten-monocarbide (WC), 40% to 20% molybdenum carbide and 10% additional metal. When the additional metal is cobalt the hardness varies between 65 and 69 Rockwell for the composition range given. By way of comparison it may be stated that the Rockwell hardness of an alloy containing 90% tungsten-monocarbide and 10% cobalt is 60, whilst that of an alloy of 90% molybdenum carbide and 10% cobalt is 51.

Let me take now the rules given by the science based on the investigations of Kurnakow and Zemczuzny in the "Zeitschrift für anorganische Chemie" 1908, volume 60, page 1, and 1910, volume 68, page 136, referred to in the standard book of Reinglass "Chemische Technologie der Legierungen", second edition, page 52, 53, and in the "Metall-und Legierungskunde" of Dr. M. v. Schwarz, Professor of the College at Munich, second edition (1929), page 49. There is referred to the investigations of Kurnakow and verbatim said: "In an uninterrupted series of mixed crystals the curve of hardness increases with the concentration gradually up to a flat maximum, which lies mostly at the simple atomic composition." If Schwarz says "atomic composition", it is to be considered that he mentions metals and not chemical combinations as carbides. If such combinations are to be used, then instead of "atoms", existing only of the pure metals, the "molecules" are to be taken, because they are in compounds equivalent to the atoms of the single pure metal.

Furthermore, science says that the maximum does not always lie at simple molecular proportions. If one carbide materially exceeds another carbide in hardness, then the maximum of hardness is "shifted" in favor of the harder carbide in the mixed crystal and consequently two (or three) molecules of the harder (or exceedingly harder) carbide form together with one molecule of the softer carbide the mixed crystal of greatest hardness. In other words, the carbides are to be present approximately in integer number ratios of their molecular weights, the higher ratio applying to the relatively harder carbide, if one of the composed carbides is harder than the other. Lastly, if a curve of hardness of mixed crystals is built up depending on the content of the respective carbides, then the maximum of the curve is flat and does not form a tip so that mixed crystals of about greatest hardness are practically also obtained if deviating by about 5% to 10% to both sides from the theoretical molecular proportion corresponding to greatest hardness.

Let me take an alloy having 10% auxiliary metal and therefore 90% carbide. Let me further take that tungsten-carbide and titanium-carbide are to be mixed to form the hardest mixture. Then we have to divide these 90% in the proportion of 60:196, this means that we have to take about 20% (weight) titanium-carbide, about 70% tungsten-carbide and about 10% auxiliary metal.

Let me take molybdenum-carbide and titanium-carbide. Titanium-carbide is exceedingly hard, at least harder than molybdenum-carbide, and is furthermore very light. Consequently the optimum of hardness is to be expected at a proportion of 1:3 (or 1:4). At 1:3 we have about 49.5 (that means less than 50%) molybdenum-carbide and 40.5% titanium-carbide, if 10% auxiliary metal is present. Consequently I have shown in my copending application Ser. No.

575,482 that an alloy containing less than 50% molybdenum-carbide is most advantageous, if the balance is chosen from titanium-carbide and auxiliary metal.

Let me take the carbide of vanadium of the fifth group of the periodical system, and the carbide of tungsten of the sixth group of the periodical system. Then the correct molecular proportion will be 1:2 because tungsten-carbide exceeds in hardness. Consequently the alloy will contain 10% auxiliary metal, about 70% tungsten-carbide and about 14% vanadium-carbide, corresponding to the molecular weight of 196 of tungsten-carbide (WC) and 63 of vanadium-carbide (VC).

Let me take vanadium-carbide (carbide of the fifth group) and titanium-carbide (carbide of the fourth group). Considering that titanium-carbide exceeds in hardness vanadium-carbide, the molecular proportion is to be chosen with 1:2 and consequently the hard metal will contain 10% auxiliary metal, about 60% titanium carbide and about 30% vanadium carbide in order to remain within the range of hardest mixed crystals formed by these carbides.

Let me take, as last example, boron carbide (of the third group) and titanium carbide (of the fourth group). Boron carbide is known as the hardest carbide and consequently a little harder than titanium carbide. The boron carbide is investigated as  $B_2C$  with a molecular weight of 78. Taking that the hardness of both carbides is about the same, the mixed crystal has to be made of equal proportions of the molecules; this means in the proportion 78:60. Consequently, an alloy will contain 10% auxiliary metal, about 50% boron carbide and about 40% titanium carbide.

I showed by the examples given that either one molecule of each carbide is to be taken, or two molecules of one carbide and only one molecule of the other, or three molecules of one carbide and again one of the other. I must touch the possibility that also two molecules of one carbide and three of the other carbides are to be taken to form the hardest mixed crystal. There may also exist in exceptional cases the intermediate proportion of 3:2.

In the examples given 10% auxiliary metal is chosen only for the sake of uniformity. But the amount of auxiliary metal e. g. of the iron group and chromium can vary between about 3% and 22%. The amount may be smaller if heavy mixtures of carbides (e. g. tungsten-, molybdenum carbide) are concerned and larger if lighter mixtures of carbides (e. g. with titanium carbide) are concerned.

As a consequence of the considerations presented, the following compositions meet my invention regarding the use of the approximately hardest mixed crystal: 10% to 20% vanadium carbide, 85% to 65% tungsten carbide, 5% to 20% auxiliary metal; 50% to 70% titanium carbide, 45% to 25% vanadium carbide, 5% to 25% auxiliary metal; 60% to 40% titanium carbide, 55% to 35% boron carbide, 5% to 25% auxiliary metal; 10% to 25% titanium carbide, 75% to 55% tungsten carbide, 5% to 20% auxiliary metal; 35% to 60% tantalum carbide, 35% to 60% tungsten carbide, 5% to 20% auxiliary metal; 70% to 90% tantalum carbide, 5% to 25% vanadium carbide, 5% to 20% auxiliary metal; 65% to 85% tantalum carbide, 10% to 30% niobium carbide, 5% to 20% auxiliary metal; 25% to

40% vanadium carbide, 55% to 70% niobium carbide, 5% to 20% auxiliary metal.

For special purposes, e. g. for finest cuts or polishing mixtures of titanium carbide and molybdenum carbide in about equal proportions forming substantially mixed crystals of great hardness according to the theory and nickel up to 9% and 15% and chromium up to 1% and 2% as auxiliary metals has been proved.

Whatever be the procedure in the formation of the mixed crystals in any case a body is obtained which is superior in hardness to the elements or carbides alone.

The carbides used according to the invention are extremely hard but require additions, as mentioned before, to increase the toughness of the alloy. As such additions use may be made of one or more of the auxiliary metals such as nickel, cobalt, chromium, either separately or in suitable admixture, and containing sometimes a few per cent (1% to 10%) of carbide as forming one or more (or all) constituents of the mixed crystals.

As I stated already in my copending application Serial Number 452,132, also ferrovanadium may be used as auxiliary metal. Ferrovanadium contains about 20% iron and melts like iron or cobalt between about 1450° to 1500° C. I suggested in the above mentioned application to add such an auxiliary metal, like ferrovanadium, in amounts up to about 10%. Consequently such a hard metal according to my copending application comprises up to about 10% auxiliary metal melting between about 1450° and 1500° C., and about 90% carbide. If choosing the range of hardest mixed crystals formed e. g. by WC and Mo<sub>2</sub>C, as mentioned in my application referred to hereinbefore, then immediately according to the general science existing prior to my invention as presented hereinbefore, the proportion of the carbide contained can be calculated, namely WC about 60% and Mo<sub>2</sub>C about 30%, and the range of such carbide satisfying the science to form hardest mixed crystals lies between 54% and 66% WC, 27% and 33% Mo<sub>2</sub>C, balance auxiliary metal like ferrovanadium (on an average 10%).

The carbides produced are, if needed, powdered again and intimately mixed with carbide, if desired, and the chosen auxiliary metal or metals. Suitable proportions have already been mentioned before. The mixtures are then preformed by pressing in suitable moulds to a shape similar to the desired shape. There is to be taken into calculation the shrinking which takes place during the following treatment.

An electric furnace can be employed for effecting the heating and sintering; the sintering may also be carried out by means of high frequency currents. In some cases particularly good results are obtained by carrying out the heating or sintering in a vacuum.

If mixed crystals of more than two carbides are to be contained in the composition, one proceeds with advantage in such a way that first at least two groups of binary crystals in solid solution are formed, each group comprising different carbides, whereupon these groups are combined into ternary or quaternary mixed crystals in solid solution and then compacted with auxiliary metal. Those groups of mixed crystals, and the mixed crystals combined of the groups, are preferably formed before addition of substantial amounts of auxiliary metal. The latter may be added, however, in substantial or even in their entire amount

to the groups of mixed crystals before final compacting or sintering.

Auxiliary metal may be added in trifling amounts to the original carbides when forming the binary mixed crystals, and either small amounts or the entire amount of the auxiliary metal may be added when forming the quaternary mixed crystals, the latter formation occurring simultaneously with final sintering of the composition.

There exist several ways of explaining the surprising result of the invention, although the inventor declines to limit the invention or to base it on any theory.

According to the theory applying to mixed crystals, the mixed crystal is harder than the components. If, therefore, two mixed crystals are caused to permeate each other to form a new ternary or quaternary mixed crystal, it can readily be expected that the mixed crystal so formed is harder than the components. This means that the combined mixed crystals are harder than the "parent mixed crystals" and because of the fact that the latter ones are harder than the single carbides from which they are obtained, the final mixed crystal has to be harder also than the carbides themselves.

It is satisfactory for the invention if only substantial amounts of such mixed crystals are present. According to experience already about 10% of the hard metal alloy formed by mixed crystals are capable of considerably improving the properties of the hard metal. If about half of the present carbides or more are transformed into mixed crystals, a decisive improvement can be ascertained. Besides, auxiliary metal may be present in amounts of from about 3% to 25%. The amounts of mixed crystals of carbide of elements taken from the third, fourth, fifth, and/or sixth group of the periodical system may conveniently amount to at least from about 35% to 45% of the alloy, up to about 75% to 95% of it, and auxiliary metal preferably taken from the eighth group of the periodical system, and especially from the iron group, in amounts from about 5% to about 25% by weight of the alloy.

It is quite difficult to mention any minimum amounts of carbide to be present, because 5% titanium-carbide occupy a space four times as large as 5% by weight of tungsten-carbide. Nevertheless, the minimum amount of carbide to be present and forming part of a mixed crystal according to the invention, has to be substantial and, as a minimum, about 1% by weight of the alloy.

The preforming or shaping of the initial mixture containing two or more hard carbides and auxiliary metal according to the invention in finely divided, or as finely divided a form as possible, in the moulds may be done also under elevated pressure, up to several atmospheres per square centimeter, say up to 50 to 75 atmospheres and higher.

The body so preformed and advantageously still under pressure is now to be sintered. It is done by electrical current led through the body itself or around the body through the mould. Any other kind of heating is applicable.

The temperature of the body is to be elevated to about 1400° to 1600° C. and this heat-treatment is to be continued for about one or several hours, or parts of them, till the wanted structure of the body is achieved.

Generally, the body according to my invention is consolidated by using auxiliary metals of the

kind and in the amounts as mentioned before and sintering it at elevated temperature, say in the range up to about 1400° C. to 1600° C.

In case, however, difficult forms of the body are to be produced not achievable by usual moulds, or in case sharp edges are desired, or angles difficultly to manufacture in such a way, so that the mechanical working or finishing of the hard metal body is needed after sintering, then the following ways are preferable.

The pressed and preformed body is to be submitted to sintering temperatures as mentioned before, but such sintering should be done during a short period of time only, say for 1 to 5 to 10 minutes so that the particles are sufficiently fritted together to withstand mechanical treatment without presenting, however, the hardness of a fully sintered body. Such a body is then subjected to finishing in any way and then the sintering at the same temperature is continued until the fully sintered body is achieved.

Surprising results have been further achieved by adding oxide of metals or metalloids not being reducible by hydrogen and not, or only at high temperatures, forming carbides. Such oxides are presented by alumina, silica, the earth alcalis, the group comprising zirconium and the group comprising the rare earth metals. Especially the addition of alumina in the finest divided form in relatively small amounts, say up to about 0.5% has caused the formation of most suitable alloys of the herein mentioned various compositions.

When I refer in the appended claims to carbide of elements selected from the third, fourth, fifth and sixth group of the periodical system, I mean carbides adapted for use in hard tool elements, having a suitable hardness and not being dissolved by water or other liquid employed for cooling or similar purposes at operation temperatures. Such carbides are boron-carbide (belonging to the third group), titanium-carbide, silicon-carbide, zirconium-carbide (belonging to the fourth group), vanadium-carbide, niobium-carbide, tantalum-carbide (belonging to the fifth group), and tungsten-carbide, molybdenum-carbide and chromium-carbide (belonging to the sixth group).

For the sake of clarity, I expressly state that the consolidation of the body can be done in the presence of auxiliary metals being heated and alloyed, as a whole, with the carbides present, or alloying only, more or less superficially with one or all carbides present, or not alloying at all with them as the case may be due to the relative properties of the auxiliary metals and carbides present.

Tool alloys prepared according to the invention are, as a rule, not used for the production of the entire tool, but merely for the part of the tool which in practice is used directly for cutting, drilling, etc. and which is subject to wear.

From the above description it appears that the carbides to be cemented by auxiliary metal may be transformed into mixed crystals entirely or in substantial amounts before substantial amounts of auxiliary metal are added. The mixed crystals are formed by heat treatment. Growth of crystals (re-crystallization) is either prevented by the presence of auxiliary metal or can be prevented through addition of traces of alumina, silica, etc., as explained hereinbefore. It has also been found that mixed crystals resist re-crystallization to a large extent. Thereby finest grain of carbides present in the alloy including mixed crystals is retained, and a tough

and very efficient, clean cutting material is obtained.

If carbides highly resistant to oxidation are combined with mixed crystals and other carbides less resistant to oxidation, the resistivity of those mixed crystals against oxidation surpasses that of the carbide of originally lower resistivity. However it has been found, that the mere presence of carbide of higher resistance to oxidation in finely divided form close to carbides of lower resistivity suffices to increase that resistance against oxidation for the entire alloy beyond the individual lower degree of resistance of carbides present. That most finely divided state of carbides seems to be the requirement for the last mentioned effect.

What I claim is:

1. In a method of producing a hard metal alloy, in particular for tools and parts thereof, the steps of mixing auxiliary metal substantially of the iron group in amounts from about 3% to 22% and at least two hard and refractory carbides in substantial amounts of elements selected from the third, fourth, fifth and sixth group of the periodical system, said carbides present in finely divided state and in suitable proportions to yield approximately hardest mixed crystals when alloyed, such approximate proportions indicated by integer number ratios between and including 1:1 to about 1:3 of the molecular weights of the contained carbides, shaping the mixture and alloying said carbides and metal by sintering at temperatures between about 1400° C. to 1600° C. until said mixed crystals are formed in substantial amount.

2. In a method of producing a hard metal alloy, in particular for tools and parts thereof, the steps of mixing auxiliary metal substantially of the iron group in amounts from about 3% to 22% and at least two hard and refractory carbides in substantial amounts of elements selected from the third, fourth, fifth and sixth group of the periodical system, said carbides present in finely divided state and in suitable proportions to yield approximately hardest mixed crystals when alloyed, such approximate proportions indicated by integer number ratios between and including 1:1 to about 1:3 of the molecular weights of the contained carbides, shaping and pressing the mixture and alloying said carbides and metal by sintering at temperatures between about 1400° C. and 1600° C. until said mixed crystals are formed in substantial amount.

3. In a method of producing a hard metal alloy, in particular for tool elements and other working appliances, the steps of comminuting as finely as possible at least two hard carbides of different elements selected from the third through sixth group of the periodical system, admixing the selected carbides in substantial amounts, including a minimum of 1% of a selected carbide, with auxiliary metal substantially of the iron group in amounts of about 3% to 22%, shaping said mixture and finally alloying it by sintering into a hard and tough body and until mixed crystals of said selected carbides are formed therein in substantial amount, including a minimum of about 10%.

4. In a method of producing a hard metal alloy, in particular for tool elements and other working appliances, the steps of comminuting as finely as possible at least two hard carbides of elements selected from the third, fourth, fifth and sixth group of the periodical system, admixing said selected carbides in substantial

amounts, including a minimum of 1%, of a selected carbide, with auxiliary metal essentially of the iron group in amounts of about 3% to 22%, shaping said mixture and finally alloying it by sintering into a hard and tough body and until mixed crystals of said selected carbides are formed in substantial amount, including a minimum of about 10%, the hardness of which exceeds that of any carbide contained in said mixed crystals.

5. In a method of producing a hard metal alloy, in particular for tool elements and other working appliances, the steps of comminuting as finely as possible at least two hard carbides of elements selected from the third, fourth, fifth and sixth group of the periodical system, admixing said selected carbides in substantial amounts, including a minimum of 1% of a selected carbide, with auxiliary metal essentially of the iron group in amounts of about 3% to 22%, shaping and pressing said mixture and finally alloying it by sintering into a hard and tough body and until substantial amount, including a minimum of about 10%, of said selected carbides form mixed crystals, the hardness of which exceeds that of any carbide contained therein.

6. In a method of producing a hard metal alloy, in particular for tool elements and working appliances, the steps of comminuting as finely

as possible at least two hard carbides of elements selected from the third through sixth group of the periodical system, admixing said selected carbides in substantial amounts, including a minimum of 1% of a selected carbide, and in proportions suitable to yield approximately hardest mixed crystals, with auxiliary metal essentially of the iron group in amounts of about 3% to 22%, shaping said mixture and finally alloying it by sintering into a hard and tough body and until said mixed crystals are formed in substantial amount, including a minimum of about 10%.

7. In a method of producing a hard metal composition, in particular for tool elements and other working appliances, the steps of finely comminuting at least two hard carbides of different elements selected from the third through sixth group of the periodical system, admixing the selected carbides in substantial amounts, including a minimum of 1% of a selected carbide, with auxiliary metal substantially of the iron group in amounts of about 3% to 22%, shaping and pressing said mixture and finally alloying it by sintering into a hard and solid body and until mixed crystals of said selected carbides are formed therein in substantial amount, including a minimum of about 10%.

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