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PRODUCTION OF HARD METAL ALLOYS, ESPECIALLY FOR TOOLS

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Fig. 1

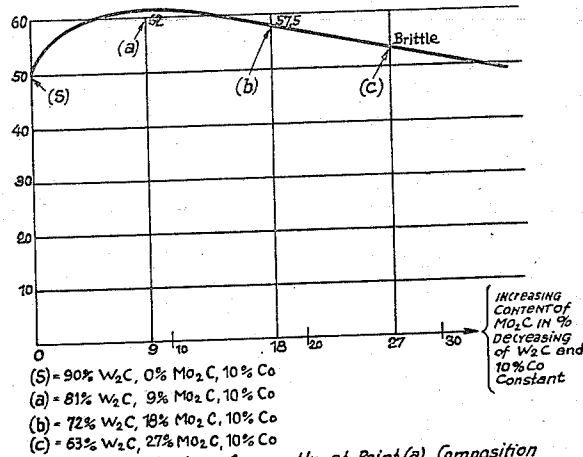
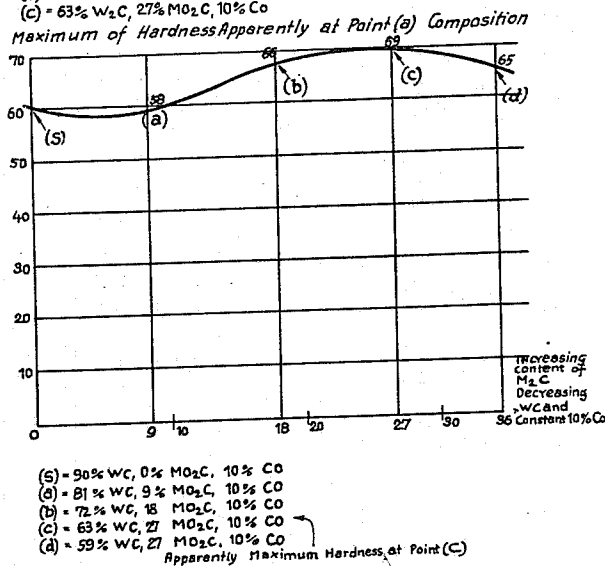


Fig. 2



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UNITED STATES PATENT OFFICE

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PRODUCTION OF HARD METAL ALLOYS,
ESPECIALLY FOR TOOLS.

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Application February 10, 1933, Serial No. 656,103
In Germany May 16, 1929

3 Claims. (Cl. 75-1)

This invention relates to a tool alloy and method of producing the same and forms a continuation in part of my co-pending applications Serial No. 452,132 filed May 13, 1930, for "Production of hard metal alloys" and Serial No. 575,482 filed November 16, 1931, for "Improvements in or relating to the production of hard metal alloys, especially for tools", and Serial No. 625,042 filed July 27, 1932, for "Tool alloy and method of producing the same".

It is known in the production of highly efficient hard tools to employ carbides of tungsten or molybdenum prepared by sintering these components, pulverizing the product and pressing the powder in moulds which are subsequently highly heated. It is also known to add an auxiliary metal to the carbide of tungsten or molybdenum and then to sinter the whole in order to obtain tool materials which, besides being extremely hard, are tough as well.

The present invention relates more particularly to a method of producing a tool alloy comprising a consolidated product containing 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) which are obtained essentially or entirely in the form of mixed crystals by heating to a sufficient extent and the usual addition amounting to about 3 to 20% of one or more metals of the groups containing nickel, cobalt and chromium. A mixed crystal is a homogeneous solid solution of two (or more) substances capable of dissolving one in the other and consequently the product obtained is entirely different from the only fritted products made by processes hitherto known.

Experiments have shown and the 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 Mo_2C , W_2C and Co, let me increase the amount of Mo_2C while decreasing the amount of W_2C , adding always 10% Co; then (1) 90% W_2C and 0% Mo_2C and 10% Co gives a Rockwell hardness of 55; (2) 81% W_2C and 9% Mo_2C and 10% Co gives

a Rockwell hardness of 62; (3) 72% W_2C and 18% Mo_2C and 10% Co gives a Rockwell hardness of 57.5; while (4) with 63% W_2C and 27% Mo_2C and 10% Co the material is brittle. By these few tests it is possible to ascertain by experiment the hardness mixed crystal of the respective series. This is clearly shown in the diagrammatic drawing attached hereto.

Most favorable results have been obtained with mixed crystals of the system Mo_2C -WC. The maximum hardness is obtained with an alloy containing about 63% of tungstenmonocarbide (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 composition range: 50 to 70% tungstenmonocarbide (WC), 40 to 20% molybdenum carbide and 10% additional metal. When the additional metal is cobalt the hardness varies between 65 to 69 Rockwell for the composition range given. By way of comparison it may be stated that the Rockwell hardness of an alloy containing 90% tungstenmonocarbide 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 Messrs. Kurnakow and Zemczuzny in the "Zeitschrift für anorganische Chemie" 1918, volume 60, page 1, and 1920, 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 wordingly 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 combinations as carbides. If such combinations are to be taken, then instead of "atoms", existing only for the pure metals, are to be taken the "molecules" being equivalent for compositions to the atoms of the single pure metal.

Furthermore, the science says, that the maximum does not lie always at simple molecular proportions. If one carbide exceeds another carbide materially on hardness, then the maximum of hardness is "shifted" in favour of the harder carbide in the mixed crystal and consequently

two (or three) molecules of the harder (or exceedingly harder) carbide form together with the softer carbide the mixed crystal of greatest hardness. Lastly, if building up a curve of hardness of mixed crystals 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 about 5% to 10% to both sides from the theoretical molecular proportion corresponding to greatest hardness.

Let me take again the example of 10% auxiliary metal and a mixed crystal of molybdenum-carbide and tungsten-carbide. It is to observe that tungsten-carbide exceeds in hardness the molybdenum-carbide. Therefore the maximum of hardness is not to be obtained at a simple molecular proportion, but I have to take two molecules of tungsten-carbide and one molecule of molybdenum-carbide to form a mixed crystal of greatest hardness. Tungsten-monocarbide (WC) has a molecular weight of 206, molybdenum-carbide (Mo_2C) of about 204 and are therefore about equal. Therefore the 90% of carbide have to be made of two molecules of tungsten-monocarbide and one molecule of molybdenum-carbide. It means that about 60% tungsten-carbide, about 30% molybdenum-carbide per weight are to be chosen for the mixed crystal, while the balance of 10% is formed by the auxiliary metal. The experiments show that the maximum hardness is present at about 27% molybdenum-carbide and therefore 63% tungsten-carbide, if 10% cobalt as auxiliary metal is present. The theory says that the maximum does not form a tip but is quite flat, so that 5 to 10% variation to both sides of the theoretical maximum is possible. Therefore 5% tungsten-carbide more or less and 3% molybdenum-carbide more or less are allowable and the results shown absolutely conform with the theory.

Let me take an alloy having 10% auxiliary metal and therefore 90% carbide. Let me further assume 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 : 206, it means we have to take about 20% (on 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 tungsten-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 (it means less than 50%) molybdenum-carbide and 40.5% titanium-carbide, if 10% auxiliary metal is present. Consequently I have shown in my co-pending application Serial 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 76% tungsten-carbide and about 14% vanadium-carbide, corresponding to the molecular weight of 206 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 for the purpose of lying within the hardest range of mixed crystals formed by these carbides.

Let me take titanium-carbide (TiC) and zirconium-carbide (ZrC), both carbides of the fourth group of the periodical system. Considering that titanium-carbide exceeds in hardness zirconium-carbide, the maximum of hardness of the mixed crystals is to be expected in the proportion one zirconium-carbide and two titanium-carbide. Considering that the molecular weight of zirconium-carbide is 103 and of titanium-carbide 60, I get an alloy of 10% auxiliary metal, about 40% zirconium-carbide and about 50% titanium-carbide.

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 60. Taking that the hardness of both carbides is about the same, the mixed crystal has to be made of equal proportions of the molecules, it 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 carbide are to be taken to form the hardest mixed crystal. There may be exceptionally also the medium-proportion of 3:2.

In the samples given, 10% auxiliary metal are chosen only for 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 bigger if lighter mixtures of carbides (e. g. with titanium-carbide) are concerned.

But I have also found that mixed crystals of two or more carbides of the elements of the fourth group, f. i. a mixed crystal of titanium-carbide and zirconium-carbide, are capable of forming very hard and usable crystals.

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

Such solid solutions are used together with auxiliary metals such as nickel, cobalt and chromium singly or in suitable mixtures. Such auxiliary metals are believed to increase the toughness of the alloy or tool produced.

For special purpose, e. g. for heavy cuts, 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.

But I have found also surprising good results by forming substantially mixed crystals of about 30 to 15% molybdenum-carbide (Mo_2C), of the sixth group, and about 65 to 70% titanium-carbide (TiC) of the fourth group, adding hereto as auxiliary metals 8 to 15% nickel and 0 to 7% chromium. Within this range the optimum e. g. for high speed work seems to be at about 8 to 10% nickel and up to 1 to 2% chromium.

Generally, according to this part of my invention, substantially mixed crystals formed of one or more carbides of one or more elements of the sixth group of the periodical system, presenting less than 50% of the body down to about 17% (15%) and below and one or more carbides of one or more elements of the fourth group of the periodical system, such carbides forming from less than 40% of the body up to about 80 and 85%, and one or more auxiliary metals of the sixth or eighth group of the periodical system, or both, such as chromium, nickel, cobalt, are usable, amounting from about 3% to 22%. In every case the amounts of carbides of the fourth group is sufficient to present their advantages e. g. of high resistance against oxidation at elevated temperature, great hardness and relatively small specific weight.

Any suitable known method may be used for the production of the mixed crystals. The carbides, e. g. of tungsten and molybdenum, can be suitably comminuted, mixed and heated up to about 1600° to 2000° C. for about 1 to 2 hours until mixed crystals are formed, which latter are then mixed with the additional metal in powdered form, and the whole is moulded and sintered at a temperature of about 1400 to 1600° C. It is also possible to mix oxides e. g. of molybdenum and tungsten in finely divided form with additions of suitably pulverized carbon and to heat the mixture to a sufficient extent in an electric furnace, whereby, in the example given, a mixed crystal of tungsten-carbide and molybdenum-carbide is obtained.

Another method of preparing the mixed crystals consists therein to mix very finely divided molybdenum and tungsten metal powder and to expose this mixture with a suitable great surface to a current of carbon containing gases at comparatively low temperature, whereby these metals are carbonized but not mixed crystals formed. It is well-known that molybdenum-metal can be carbonized in the presence of carbon containing gases already from 800° C. and tungsten metal already from about 1000° C., so that the treatment in question will be made at about 1000° C. The intimate mixture of carbides of molybdenum and tungsten is now to be transformed in mixed crystals. For this purpose the temperature has to be elevated again up to about 1600 to 2000° C. After this preparation of a mixed crystal the alloying has to be done. For this purpose the selected auxiliary metals or metals are to be added in the wanted quantity, the whole is to be intimately mixed and then to be sintered. If the mixed crystals are too coarse, then the mixed crystals are suitably to be pulverized and to be mixed with the auxiliary metal and then to be sintered. Before or while sintering the

moulding of the powder so obtained takes place, preferably under pressure.

But my invention is not limited to any special process of producing carbides, transforming them in mixed crystals, and also not to any method of consolidating such mixture to or in any shape adapted for the use intended, say as a tool element.

For producing e. g. molybdenum-carbide the following way has been proved as most convenient. Metallic molybdenum and carbon are mixed in the proportion corresponding to the theoretical values, needed for producing the combination Mo_2C . This mixture is powdered and then heated in a reducing atmosphere up to about 1400 to 1600° C. Hereby the combination is produced containing about 5.9% C., the rest being Mo_2 .

Titanium-carbide can be formed in an equal way from metallic titanium and carbon. An advantage consists, however, therein to use titanium-oxide (TiO_2), powdering and mixing it then with carbon, heating the mixture till the carbon is combined with the titanium while the oxygen of the titanium-oxide is expelled in the form of gaseous carbonmonoxide. The product is again mixed with additional carbon and heated up. The treatment is finished if no further carbonmonoxide or titanium-oxide evaporates. Accordingly e. g. about 80 parts titanium-oxide and 33 parts lamp-black may be mixed and about 1 to 2 hours heated in a hydrogen-stream at about 1500 to 1700° C. in a carbon-tube. Such treatment might be more times repeated. The mixture so produced is then further treated in vacuo of 0.1 to 0.0001 millimeters pressure at highly elevated temperatures of about 1900 to 2000° C. The heating in vacuo is advantageously performed by electrical induction (high frequency-treatment). The titanium-carbide achieved in such way is free of oxygen and contains up to about 20% carbon.

In similar ways zirconium-carbide, silicon-carbide, boron-carbide a. s. o. could be produced.

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.

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.

The carbides prepared 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 auxiliary metals such as nickel, cobalt, chromium, either separately or in suitable admixture, and containing sometimes a few percent (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 No. 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 my mentioned application to add such an auxiliary metal, like ferrovanadium, in amounts up to about 10%. Consequently such a hard metal according to my mentioned 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 Mo₂C, as mentioned in my application referred to, then immediately according to the general science existing prior to my invention as reproduced here before, the proportions of the carbide contained can be calculated, namely WC about 60% and Mo₂C about 30%, and the range of such carbide satisfying the science to form hardest mixed crystals lies between about 10% over and down these figures, i. e. between about 54% and 66% WC, 27% and 33% Mo₂C, balance auxiliary metal like ferrovanadium (in the middle 10%).

The mixed crystals of carbides produced are, if needed, powdered again and intimately mixed with the chosen auxiliary metal or metals. Suitable proportions are already 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 in calculation the shrinking which takes place during the following treatment.

The preforming in the moulds may be done also under elevated pressure, up to several atmospheres per square-centimeter, say up to 50 and 75 atmospheres and higher.

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

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

In case, however, difficult forms of the body are to be produced not achievable by usual moulds, or in case sharp edges are wanted, or angles difficultly to be manufactured in such 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 has to be done only in a short period of time, say 1 to 5 to 10 minutes so that the particles are sufficiently fritted together to withstand mechanical treatment without presenting, however, the hardness of the fully sintered body. Such body is then subjected to finishing in any way and then the sintering at the same temperatures is continued till the fully sintered body is achieved.

Another way consists therein to have admixed to the powders ready for preforming glycerine, glycole or other alcohols, shaped this mixture and, if desired, pressed and treated at elevated temperature of about 100 to 200° C. but as best below 180° C., then worked and finished this body of sufficient cohesion whereupon the sintering is possible without any further interruption.

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, silicon, the earth alkalis, the group comprising zirconium and the group comprising the rare earth-metals. Specially the addition of alumina-oxide 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 here mentioned various compositions.

If aluminium-oxide, or similar oxides as mentioned before, are used as additions in small

quantities then the crystals of heavy metal-carbide contained in the body are not materially or not entirely changed, it means increased by heat-treatment, in comparison with the crystals present in the initial untreated material. The crystals are uniformly divided throughout the body. While otherwise some diffusion or solid solution takes place within several carbides and admixed auxiliary metals such alloying seems to be largely or entirely prevented by addition of the mentioned oxides. It helps to increase or to retain largely the toughness of the mass.

It may be mentioned that the formation of such oxides is also possible during the heat-treatment if adding to the initial mixture also the wanted small amounts of the metals like alumina, silicon a. s. o. and having then combined them with the oxygen freed during heat-treatment.

Generally, the body according to my invention is consolidated by using auxiliary metals of the kind and in the amount as mentioned before and treating it at elevated temperature, say in the range up to about 1400 to 1600° C.

I disclosed already in my copending application Serial No. 575,482 the use of a material containing 15 to 30% molybdenum-carbide, up to 65 to 70% titanium-carbide, and auxiliary metal, like nickel, in the range from 8 to 15% and chromium in the range from zero to 7%. It means that the minimum of auxiliary metal present is 8%, the maximum (nickel plus chromium) 22%. Consequently, as I expressed in the claims attached to this copending application, the titanium-carbide in a body containing 15% molybdenum and 8% nickel must amount to 77%, it means about 80% as upper limit.

But I mentioned in the same copending application an equal amount of molybdenum-carbide and titanium-carbide besides of 9 to 15% nickel and 1 to 2% chromium as auxiliary metals. It results in as minimum 83% carbide, and consequently half of it is 41.5% titanium-carbide. Considering in connection herewith, however, that in the same application 15% nickel and 7% chromium, i. e. 22% auxiliary metal, is mentioned besides of carbide, and that the same amount of auxiliary metal is principally usable also, according to my disclosure and the claims in the mentioned copending application, if molybdenum-carbide and titanium-carbide are present in about equal amounts, it results that titanium-carbide may amount also to the half of 78%, i. e. about 39%. Consequently I am entitled to claim in the appending claims an alloy containing less than 40% up to about 80% titanium-carbide, auxiliary metal up to about 22%, while molybdenum-carbide may be present in amounts less than 50%, as mentioned in the appending claims to the copending application, down to about 15%. Indeed, if using 9% nickel and 1% chromium while molybdenum-carbide and titanium-carbide are present in about equal proportions then about 45% molybdenum-carbide results being less than 50%.

For sake of clearness I expressly state that the consolidation of the body can be done in the presence of auxiliary metals being heated and alloying, as 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.

5 In the accompanying drawing is shown diagrammatically: in Figure 1 a scale of hardness for certain alloys containing mixed crystals of Mo_2C , W_2C and Co, and

10 Figure 2 is a similar scale for different compositions of the alloys.

What I claim is:

1. In a method of producing a hard metal for tool elements containing at least two carbides in substantial amounts of elements selected from the third, fourth, fifth and sixth group of the periodical system and auxiliary metal substantially of the iron group in amounts from about 3 to 22%, forming substantially mixed crystals of said carbides by mixing them and heat-treating the mixture at a temperature between about 1600 and 2000° C., consolidating the mass so obtained with the auxiliary metal by treatment at elevated temperature up to about 1400 to 1600° C.

2. In a method of producing a hard metal for tool elements containing at least two carbides in substantial amounts of elements selected from

the third, fourth, fifth and sixth group of the periodical system and auxiliary metal substantially of the iron group in amounts from about 3 to 22%, forming substantially mixed crystals of said carbides by mixing them and heat-treating the mixture at a temperature between about 1600 and 2000° C., mixing the mass of mixed crystals so obtained with the auxiliary metal and sintering this mixture at elevated temperature up to about 1400 to 1600° C.

3. In a method of producing a hard metal for tools or tool elements containing at least two carbides in substantial amounts of two elements selected from the third, fourth, fifth and sixth group of the periodical system and auxiliary metal substantially of the iron group in amounts from about 3 to 22%, forming mixed crystals of said carbides by mixing them and heat-treating the mixture at a temperature between about 1600 and 2000° C., finely powdering the mass so obtained and intimately mixing the powder with powdered auxiliary metal and sintering this mixture at elevated temperature up to about 1400 to 1600° C.

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30	105
35	110
40	115
45	120
50	125
55	130
60	135
65	140
70	145
75	150