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HARD METAL ALLOY, ESPECIALLY FOR TOOLS

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This invention relates to a hard metal alloy, especially but not exclusively for tools and other working appliances.

It is an object of the invention to increase the hardness and toughness of such hard metal alloys.

It is another object of the invention to make such hard metal alloys applicable to uses both known so far and new ones.

This application forms a continuation in part of my former application Ser. No. 452,132, filed May 13, 1930, for "Production of hard metal alloys" and my copending applications Ser. No. 575,482, filed November 16, 1931, for "Improvements in or relating to the production of hard metal alloys especially for tools", now Patent 1,925,910, dated Sept. 5, 1933, and Ser. No. 625,042, filed July 27, 1932, for "Tool alloy and method of producing the same", now Patent No. 2,091,017, dated Aug. 24, 1937.

According to the prior art, hard metal alloys had to be made and stored in different grades depending upon the intended use. So, for instance, a certain grade was usable for machining steel, another grade for working semi-steel, and a third grade for machining cast iron. Within the grades themselves differentiations have been established depending upon the composition of the material to be worked. The grades usable for working steel or cast iron could not be used for successfully working glass, or artificial resins, and the great number of grades made the proper and simple handling of them in the manufacture as well as in the distribution very difficult.

According to the invention, a hard metal alloy can be obtained being usable for several purposes. So, for instance, the same hard metal alloy can be used for machining steel and cast iron.

It has been suggested to manufacture hard metal alloys in such way that two or more pure carbides of certain metals, selected especially from the third, fourth, fifth, and/or sixth group of the periodical system, were melted or sintered whereby, however, a body was obtained the composition of which is entirely unknown and indefinite. It may be that in such bodies both separate single carbides, and mixed crystals formed of several carbides were present. In any case, such molten or sintered bodies consisting exclusively of pure carbides and some mixed crystals of them have not succeeded in practical use because of being very brittle.

It has further been suggested to manufacture a hard metal alloy by mixing difficultly and high-melting metals as for instance tungsten and molybdenum with lower and more easily melting metals as for instance iron, cobalt, adding to it an amount of carbon sufficient to carburize the high-melting metals present in the mixture and, afterwards, melting the mixture. Instead of adding the necessary amount of carbon, before melting the mixture, one has molten down the mixture in a carbon crucible and allowed it to take in the necessary amount of carbon from the crucible. It is to be supposed that also in that case some mixed crystals formed, consisting of carbides of the higher melting metals, and of such carbides and the lower melting metals. At all events, no definite mixed crystals of certain carbides alone have formed or have been intended to form. No means were provided to secure the formation of any mixed crystals at all, or of certain mixed crystals in particular.

In Patent 1,959,879 it has further been suggested to manufacture a hard metal alloy containing mixed crystals of certain carbides which are cemented together by lower melting auxiliary metal, preferably taken from the iron group. The inventor is aware of the fact that Patent No. 1,959,879 already discloses and claims mixed crystals made of two or more carbides selected from the third, fourth, fifth, and/or sixth group of the periodical system, and he does not claim such mixed crystals per se in this application.

According to this invention which forms a continuation in part of my co-pending application Ser. No. 625,042, at least two pairs of mixed crystals are to be combined to form a new one, and though the mixed crystal so obtained may come within the scope of protection of the earlier patent referred to, its structure is certainly not disclosed by this earlier patent, but forms the subject of this invention.

According to this invention, at least two mixed crystals of different composition are combined to a new mixed crystal. Taking for instance a mixed crystal consisting of tungsten carbide and molybdenum carbide, and another mixed crystal consisting of molybdenum carbide and titanium carbide, and combining them to form a new mixed crystal, it will contain the three components tungsten carbide, molybdenum carbide, and titanium carbide, and thereby two "binary" mixed crystals have been transformed into a "ternary" mixed crystal. In the same way a binary mixed crystal consisting of tungsten carbide and tantalum carbide, and another binary mixed crystal consisting of molybdenum carbide and titanium carbide, can be combined to a single mixed crystal which contains, however four components, name-

ly tungsten carbide, tantalum carbide, molybdenum carbide, and titanium carbide, and forms a "quaternary" mixed crystal. The mixed crystals so obtained may then be powdered to any desired degree and mixed with one or more auxiliary metals as for instance cobalt, iron, nickel. The mixture so obtained is then heated till at least part of the auxiliary metal is molten whereby sometimes part of the mixed crystals may be dissolved in the auxiliary metal. Thereupon the mixture is cooled. During cooling some or any one of the mixed crystals dissolved in the melt of the auxiliary metal is precipitated again. In any case, a solid and dense body results. Any known method of manufacturing and shaping such hard metal alloy bodies may be applied. Care is to be taken that the structure of the mixed crystals is substantially maintained or, if any dissolution takes place during heating, a substantial precipitation of the dissolved mixed crystals takes place during cooling. At all events, the amount of mixed crystals added to the mixture before heating must be sufficient in order to secure the wanted amount of mixed crystals in the solidified body after cooling. The amount of carbide being known which may be dissolved, if at all, in a certain quantity of auxiliary metal present, if being heated to a certain temperature and that temperature being maintained for a certain time, also the percentage being known of mixed crystals dissolved which will be precipitated again during cooling of the auxiliary metal forming the solvent for the mixed crystal, it is easy for any one skilled in the art, to determine in advance the amount of mixed crystals to be formed and added to a hard metal mixture according to the invention for securing quantitatively and qualitatively the amount and composition of mixed crystals present in the finished body. So, for instance, if knowing the mixed crystals used are soluble in an auxiliary metal present at the temperature of sintering, one may add to the mixture a surplus of such mixed crystals to such extent that the surplus covers the exact amount of mixed crystals dissolved in the heated auxiliary metal and not being precipitated again while cooling. Or, by using certain auxiliary metals not dissolving a certain mixed crystal or, by observing a certain law of heating the mixture or, by avoiding a certain excessive temperature, or by following two or more of these rules, any wanted composition of the finished body can be obtained.

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 regularly harder than the components if they form mixed crystals at all. 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.

Besides, it is impossible to form mixed crystals of certain components (carbides). While it is impossible to form a mixed crystal of a certain pair of carbides, it might be possible to form a mixed crystal between each of these two carbides and a third one, and the two mixed crystals so obtained may then be transformed into a single crystal because of the presence of this third carbide. So, for instance, titanium carbide and the highly saturated tungsten carbide (WC) are capable of forming a mixed crystal only within certain limits. A certain amount by weight of titanium carbide can only be mixed with a certain fraction of this amount by weight of tungsten carbide. Therefore, a mixed crystal of titanium carbide and tungsten carbide contains titanium carbide in excess. Such amount by weight of titanium carbide is, however, undesired in mixed crystals containing, besides, tungsten carbide because the tungsten carbide is about four times as heavy as titanium carbide. Such large amounts of titanium carbide in a mixed crystal containing also tungsten carbide render for instance a tool not usable for machining cast iron. Tungsten carbide and molybdenum carbide, however, may be mixed in any practical proportion to form a mixed crystal. They are mixable in an uninterrupted series of mixed crystals. In the same way, molybdenum carbide and titanium carbide are capable of forming mixed crystals within the largest range practically desired. If forming mixed crystals, therefore, containing tungsten carbide and molybdenum carbide in a certain proportion, on one hand, and mixed crystals containing molybdenum carbide and titanium carbide in a suitable proportion on the other hand, one may combine these two kinds of mixed crystals to ternary mixed crystals which now contain tungsten carbide, titanium carbide, and molybdenum carbide, in a definite desired proportion. The molybdenum carbide present quasi suffices to form mixed crystals which cannot be otherwise obtained, for the mixed crystal now contains tungsten carbide and titanium carbide in a proportion which could never be present in a binary mixed crystal desired to consist of tungsten carbide and titanium carbide alone but in the same relative proportions. But, of course, in order to obtain such extraordinary proportion of tungsten carbide and titanium carbide in a mixed crystal, also molybdenum carbide must be taken in. As a rule, however, molybdenum carbide behaves quite similarly as tungsten carbide and, regularly, forms a desirable and useful constituent of a hard metal alloy. By similar considerations, the usefulness of a mixed crystal comprising tungsten carbide and molybdenum carbide on one hand, and tantalum carbide and titanium carbide on the other hand, can be understood. It is possible to form in this way a quaternary mixed crystal containing titanium carbide in amounts, for instance, of 16% or more which otherwise could not be combined with the highly saturated tungsten carbide (WC). The invention is not limited, however, to ternary mixed crystals including carbides of different elements, but comprises also ternary mixed crystals including carbides of the same element, but of different composition. So, for instance, a ternary mixed crystal including tungsten monocarbide and tungsten dicarbide comes under the scope of the invention.

It is not necessary, according to the invention, that the hard metal alloy contains solely at least ternary mixed crystals as far as the carbides present are concerned. It is satisfactory, however, 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 at least ternary mixed crystals are capable of considerably improving the properties of the hard metal. If about half of the carbides present or more are transformed into such ternary 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 ternary, quaternary, and so on, 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, the remainder being formed by binary and/or simple carbide of the same or other elements taken from the same or other groups of the periodical system, 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 ternary, and so on, mixed crystal according to the invention, has to be substantial and, as a minimum, about 1% by weight of the alloy. In manufacturing the alloy, the carbides are to be chosen so that they readily form mixed crystal pairs (binary mixed crystals) and that further, the mixed crystals so obtained are capable of forming again mixed crystals, i. e. to permeate each other and to form a so-called solid solution. In the same way, the auxiliary metal is to be chosen so that the mixed crystals formed are not dissolved and separated again into their constituents or mixed crystal-constituents in any undesired and uncontrollable way.

Carbides usable for the invention are in the first place those of silicon, boron, titanium, zirconium, vanadium, tantalum, columbium, molybdenum, tungsten. But also elements of the eight group as chromium, cobalt, nickel, iron, may sometimes be chosen to form carbides to be combined with those of other elements to form mixed crystals. These carbides have in common the properties of being sufficiently hard and refractory, i. e. they do not decompose under the influence of water and/or air at elevated temperatures. Hard metals are used in the first place as tool implements for high speed work. Thereby the temperature of the hard metal and at least of its working edge is raised by several hundred centigrades and cooling water is to be applied. Therefore among all carbides of elements belonging to the third to sixth group of the periodical system only those are suitable and consequently to be chosen for the purposes of the invention which are refractory in the sense just defined and which is meant also by the use of the term refractory in the appended claims.

In practice for instance the following alloy has proven to be most advantageous: About 60% to 75% tungsten carbide, either in the form of W_2C, or W C, or of a mixture of both; about 10% to 25% titanium carbide; about 1% to 25% molybdenum carbide; about 5% to 25% cobalt, nickel and/or iron. In such a mixture titanium carbide may particularly be present in amounts of from about 12% to 15%, molybdenum carbide in amounts of from about 1% to 5%. In manufacturing the hard metal alloy, first two groups of mixed crystals are formed, one group consisting of molybdenum carbide and tungsten carbide, the other group of titanium carbide and tungsten carbide, whereupon these two groups are combined to a single group of substantially ternary mixed crystals, containing tungsten carbide, titanium carbide, and molybdenum carbide. The formation of mixed crystals may occur by heating the chosen amounts of the carbides up to from about 1600° to 2000° C., preferably in a neutral or carbon-containing atmosphere. In the same way the ternary (and so on) mixed crystals can be obtained by heating the previously obtained mixed crystals up to the same range of temperature, or a higher one, up to about 2600° C. The temperature to be applied depends on the melting temperature of the carbides themselves, on their mutual solubility, and on the time of heating. If applying the heat within a range of about 1600° to 2000° C., a heating of from 1 to 4 hours regularly suffices. The mixed crystals so obtained are then powdered and mixed with the auxiliary metal preferably powdered to about the same degree and then the so-called sintering has to be done within a range of temperature of above 1300° C. up to about 1400 to 1600° C.

While any man skilled in the art can proceed to practice the invention described, there may be given, nevertheless, a few further examples of making hard metal tool alloys according to the invention.

The special tool alloy described hereinbefore and containing tungsten carbide, titanium carbide, molybdenum carbide, and auxiliary metal taken from the eighth group of the periodical system, may be manufactured in about the following way: 5% by weight of MO_2C and 4% by weight of TiC are powdered, intimately mixed, preferably in a ball mill, for about 20 to 30 hours, and then heated up to about 1600 to 2000° C. in a crucible and preferably by induction for about one to two hours, whereby mixed crystals of them are obtained. About 65% by weight of W_2C and about 12% by weight of TiC are powdered preferably in a ball mill for about 20 to 36 hours and then heated in the same way, up to about 1600–2000° C. for one to four hours. Both kinds of mixed crystals so obtained are then intimately mixed again and powdered preferably in a ball mill by treating them for about 10 to 40 hours therein and heated again up to about 1600–2000° C. for about one to four hours. Thereby new mixed crystals are obtained comprising the two kinds of mixed crystals which have been intimately mixed together before. To this mixture is then added auxiliary metal in amounts of about 14%, consisting for instance of 13% nickel and 1% chromium. This material is once more intimately mixed preferably in a ball mill by treating it for about 4 to 24 hours therein, whereupon the powder so obtained may be pressed to a desired shape and heated up to about 1400–1600° C. for about 1 to 4 hours and cooled in any desired way, that is, rapidly or slowly, or first rapidly and then slowly, or first slowly and then rapidly.

This material will be suited to work steel, semi-steel, and cast iron in a very superior way.

Another composition may be obtained from two groups of mixed crystals, one group consisting of about 8% TiC and 35% TaC, the other group of 8% TiC and 35% W_2C, this group of mixed crystals being manufactured in an analogous way as described before in the body of the specification,

whereupon the two groups are intimately mixed and again heated up to about 1600 to 2000° C. or more, whereby new mixed crystals of them are obtained. After adding auxiliary metal, the mixture may be shaped and sintered.

Also a group of mixed crystals may be formed, however, consisting of about 8% TiC and 10% MO_2C, and another group consisting of 60% W_2C and 15% MO_2C, whereupon these two groups are combined to form ternary mixed crystals, to which are then added about 7% cobalt as auxiliary metal. This mixture is then shaped and sintered.

Apparently, in the three examples the binary mixed crystals pertaining to the two groups to be combined subsequently, present a hardness which is higher than that of the single carbides constituting the respective mixed crystals, because the amounts of the carbides to be combined in a mixed crystal are chosen accordingly. If two of such mixed crystals are combined to a single new one, its hardness will surpass that of the constituent binary mixed crystal. Furthermore, in such way amounts of certain constituents as for instance the very important titanium carbide can be incorporated into the final body which otherwise are difficult to incorporate and, furthermore, an extraordinarily uniform distribution of all the constituent carbides throughout the body and their thorough permeation of each other is secured.

It must be understood that the detailed description of choosing and combining carbides to form mixed crystals and especially such of greatest hardness as explained in Patent 1,959,879, relates to this invention in the same way as all other detailed descriptions contained therein as to manufacture of carbides, forming mixed crystals thereof, choosing and adding auxiliary metal, shaping and consolidating a desired body.

What I claim is:

1. A hard metal for tool elements and other working appliances consisting of at least three different hard and refractory carbides of elements selected from the third, fourth, fifth, and sixth group of the periodical system and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25% by weight, substantial amounts of said carbides forming mixed crystals.

2. A hard metal for tool elements and other working appliances consisting of at least four different hard and refractory carbides of elements selected from the third, fourth, fifth, and sixth group of the periodical system and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25% by weight, substantial amounts of said carbides forming mixed crystals.

3. A hard metal for tool elements and other working appliances consisting of at least three different hard and refractory carbides of elements selected from the third, fourth, fifth, and sixth group of the periodical system and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25% by weight, at least about 10%, by weight of the final body, of said carbides forming mixed crystals.

4. A hard metal for tool elements and other working appliances consisting of at least four different hard and refractory carbides of elements selected from the third, fourth, fifth, and sixth group of the periodical system and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25% by weight, at least about 10%, by weight of the final body, of said carbides forming mixed crystals.

5. In a hard metal as being claimed in claim 3, the carbides present amounting from about 75% to 95% by weight of the final body and forming mixed crystals amounting from about 35% up to 75% and 95%.

6. In a hard metal as being claimed in claim 4, the carbides present amounting from about 75% to 95% by weight of the final body and forming mixed crystals amounting from about 35% up to 75% and 95%.

7. A hard metal as being claimed in claim 1, the auxiliary metal being chosen from the eighth and sixth group of the periodical system.

8. A hard metal as claimed in claim 2, the auxiliary metal being chosen from the eighth and sixth group of the periodical system.

9. A hard metal as claimed in claim 1, containing carbide of at least one element of the eighth group in substantial amounts besides hard and refractory carbides of elements of the third to sixth group of the periodical system.

10. A hard metal as claimed in claim 1, containing carbide of at least one element of the eighth group in amounts from about 1% to 5% besides hard and refractory carbides of elements of the third to sixth group of the periodical system.

11. A hard metal for tool elements and other working appliances consisting of at least three different carbides selected from a group comprising molybdenum carbide, mono-tungsten-carbide, di-tungsten-carbide, titanium carbide, tantalum carbide, boron carbide, vanadium carbide, columbium carbide, and auxiliary metal substantially of the eighth group of the periodical system in amounts of about 3% to about 25% by weight, the minimum amount of a selected carbide to be 1% and substantial amounts of said carbides forming mixed crystals.

12. A hard metal for tool elements and other working appliances, comprising about 60% to 75% by weight selected from a group comprising tungsten monocarbide and tungsten dicarbide, about 10% to 25% titanium carbide, about 1% to 25% molybdenum carbide, and about 3% to 25% auxiliary metal, at least three different carbides present forming mixed crystals in substantial amounts.

13. A hard metal as being claimed in claim 12, the mixed crystals formed of at least three carbides amounting to at least 45% to 50% by weight of the body.

14. A hard metal as claimed in claim 12, the mixed crystals present and being formed of at least three carbides amounting to about 75% to 95% by weight of the body.

15. A hard metal as claimed in claim 12, the auxiliary metal being selected from the sixth and eighth groups of the periodical system.

16. A hard metal for tool elements and other working appliances consisting of titanium carbide, tantalum carbide, tungsten carbide and auxiliary metal substantially of the eighth group of the periodical system in amounts of about 3% to about 25% by weight, the minimum amount of a selected carbide to be 1% and substantial amounts of said carbides above about 10%, forming mixed crystals.

17. A hard metal for tool elements and other working appliances consisting of molybdenum carbide, tantalum carbide, titanium carbide and

auxiliary metal substantially of the eighth group of the periodical system in amounts of about 3% to about 25% by weight, the minimum amount of a selected carbide to be 1% and substantial amounts of said carbides above about 10%, forming mixed crystals.

18. In a method of producing a hard metal for tool elements and other working appliances containing at least three hard and refractory carbides of elements selected from the third, fourth, fifth, and sixth group of the periodical system, and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25%, transforming substantial amounts of said carbides into at least two groups of mixed crystals, each group containing different carbides, mixing substantial amounts of mixed crysta's of said groups and forming from this mixture ewly combined mixed crystals, and consolidatin the mass so obtained with the auxiliary me.' by treatment at elevated temperatures up to about 1400° to 1600° C.

19. In a method of producing a hard metal for tool elements and other working appliances containing at least three hard and refractory carbides of elements selected from the third, fourth, fifth, and sixth group of the periodical system, and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25%, transforming by heat treatment at above about 1600° C. substantial amounts of said carbides into at least two groups of mixed crystals, each group containing different carbides, mixing substantial amounts of mixed crystals of said groups and forming from this mixture newly combined mixed crystals by heat treatment at above about 1600° C., and consolidating the mass so obtained with the auxiliary metal by treatment at elevated temperatures up to about 1400° to 1600° C.

20. In a method of producing hard metal for tool elements and other working appliances containing at least three hard and refractory carbides of elements selected from the third, fourth, fifth and sixth group of the periodical system and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25%, transforming substantial amounts of said carbides into at least two groups of mixed crystals, each group containing different carbides, mixing substantial amounts of mixed crystals of said groups and forming from this mixture newly combined mixed crystals, adding thereto a substantial amount of at least one of said carbides and auxiliary metal, and consolidating the mass so obtained by treatment at elevated temperatures up to about 1400° to 1600° C.

21. In a method of producing hard metal for tool elements and other working appliances containing at least three hard and refractory carbides of elements selected from the third, fourth, fifth and sixth group of the periodical system and auxiliary metal substantially of the eighth group of the periodical system in amounts from about 3% to 25%, transforming substantial amounts of said carbides into at least two groups of mixed crystals, each group containing different carbides, mixing substantial amounts of mixed crystals of said groups and forming from this mixture newly combined mixed crystals by heat treatment at above about 1600° C., adding thereto a substantial amount of at least one of said carbides and auxiliary metal, and consolidating the mass so obtained by treatment at elevated temperatures up to about 1400° to 1600° C.

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