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HARD METAL ALLOYS AND PROCESS OF
MAKING THE SAME

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The present invention relates to hard metal alloys, and it particularly relates to the alloys including refractory metal carbides which may be utilized for making various types of cutting tools, wear-resisting implements, and so forth.

In the co-pending applications Serial No. 93,717, filed July 29, 1936, Serial No. 93,733, filed July 31, 1936, and Serial No. 93,734, filed July 31, 1936, there are disclosed hard metal alloys in which finely divided particles of refractory metal carbides, preferably tungsten carbides or carbides of other refractory metals, such as titanium, tantalum, vanadium, thorium, molybdenum, uranium, columbium, and chromium, are encased in relatively thin casings or coatings of cobalt, nickel or iron and are cemented together by said casing or coatings into a compact mass.

According to the preferred method of making these alloys, the finely divided carbides, whether of tungsten or other refractory metals, or the finely divided metals themselves and carbon, having a fineness between 150 and 400 mesh, are sprinkled into a relatively concentrated solution of a cobalt, nickel or iron organic or inorganic acid salt or into a slurry of insoluble compounds of these metals with stirring.

The preferred cobalt, nickel or iron salts are the organic water soluble salts, such as the acetates, formates, lactates, rather than the nitrates, chlorides or sulphates.

The solution containing the finely divided refractory metal carbide, or the mixture of the refractory metal itself and carbon, is evaporated to dryness with continued stirring followed by reduction of the pulverized dry mass in a hydrogen atmosphere. After reduction in hydrogen, the alloy produced is compacted and sintered to produce the final hard metal alloy.

Similarly to said co-pending applications, it is among the objects of the present invention to prepare an improved hard metal alloy at low cost and of high quality in respect to strength, hardness and density, which may be made of uniform quality from batch to batch, and which will have a sufficient degree of toughness and density to enable its wide utilization in connection with wear-resisting implements, cutting tools, contact points, and so forth.

Other objects will be obvious and will appear during the course of the following specification.

In accomplishing the above objects of the present invention it has been found most suitable to prepare the alloys of mixtures of at least three finely divided refractory metal carbides, or of

mixtures of at least three refractory metals and carbon.

It is also preferred in certain cases to use mixtures of coating metals by placing at least two coating metal salts in the solution, as for example, cobalt and iron salts, or nickel and iron salts, or all three salts.

Among the preferred refractory metal alloys are tungsten carbide, which should constitute a major proportion of the carbides present, tantalum carbide, which may be present in lesser proportion than the tungsten carbide, and at least one or more of the following carbides in minor proportion: vanadium carbide, thorium carbide, molybdenum carbide, uranium carbide, columbium carbide, and chromium carbide.

These carbides are usually best prepared by obtaining the finely divided metal in pure condition, the metal being preferably prepared by reduction in a hydrogen atmosphere in an electric furnace. These finely divided refractory metals, separately or as mixtures, are preferably carburized by heating them with finely divided carbon, sugar carbon being preferred, in a reducing atmosphere in an electric furnace, which reducing atmosphere may desirably include hydrocarbon gases or vapors of carbon compounds, such as acetylene, ethylene, methane, acetaldehyde, allyl alcohol, and so forth. These finely divided carbides may then be mixed together in the desired proportions to produce the required amount of refractory metals in the final hard metal alloy.

Among the preferred proportions are between 1% to 20% of titanium, vanadium, or chromium carbide, between 58% to 70% of tungsten carbide, between 10% to 30% of tantalum carbide.

Another satisfactory proportion is 2% to 8% titanium or chromium carbide, between 60% to 68% of tungsten carbide, between 15% to 25% of tantalum carbide and between 1½% to 2½% of vanadium carbide.

A less preferred proportion is about 1% to 7% of titanium carbide, about ½% to 2% of chromium carbide, and about 79% to 89% of a mixture of tungsten and tantalum carbides.

It is also possible to use the proportion of about 1% to 3% of chromium carbide, about 29% to 39% of tungsten carbide, and about 48% to 58% of tantalum carbide.

In all cases it is desirable to include, in addition to the tungsten carbide, at least one carbide selected from the group consisting of chromium carbide, titanium carbide, thorium carbide and vanadium carbide, and usually it is also desired to include tantalum carbide.

Generally, the preferred proportions are between ½% to 10% of these three carbides, taken singly or in combination, in addition to the tungsten or tantalum carbides, which may be used in equal proportions or with the tantalum carbide being present in the proportion of from 10% to 25% of the total mixture of carbides.

It has been found particularly desirable to combine these mixtures of at least three carbides, or at least tungsten carbide together with titanium, vanadium and/or chromium carbide, with a saturated solution containing equally molecular proportions of at least two water soluble salts of cobalt, iron and/or nickel. By using a combination of cobalt and nickel or cobalt and iron, or nickel and iron, or all three, it is possible to obtain a satisfactory hard metal with as little as 1% to 5% of coating metal.

Desirably, the salt content of the solution may consist of 50% each of cobalt and nickel acetates or formates, or 33⅓% each of the organic salts of iron, cobalt and nickel. At the same time the carbides are added to the concentrated or saturated aqueous solution of the cobalt, iron and nickel salts, it is also possible to add finely divided refractory metals such as tungsten, titanium, vanadium, chromium, tantalum and so forth, together with finely divided carbon, and also in certain instances it is possible to add finely divided cobalt or nickel directly to the solution before evaporation to dryness or after it has been partly evaporated to dryness.

In the preferred procedure described in said copending applications, the pulverized and finely divided carbide mixture is added to a concentrated solution of cobalt and nickel acetates.

Although the cobalt and nickel salts may be in complete solution in certain instances, the solution may carry suspended particles of cobalt, nickel or iron salts, or even the oxides or hydroxides of these metals.

The proportioning of the refractory metal, of the additional metal such as cobalt, nickel or iron, and of the carbon, is preferably such that the refractory metal will constitute between about 88% to 90% of the alloy; while the additional metal will constitute between about 10% and 11% of the alloy, or in some few instances more than 25% of the alloy; and the carbon will constitute up to 2% to 3% of the alloy, and even up to 10% to 15% in certain instances.

In preparing the alloy from the carbide mixture and solution of the cobalt and nickel acetate, the finely divided carbides are mixed or milled together and are then sprinkled into the cobalt and nickel acetate solution. The liquid is evaporated away with stirring until a dry solid mass is obtained. This solid mass may then be finely ground without decomposition of the cobalt and nickel salts and then subjected to reduction, most desirably in an electric furnace in a hydrogen atmosphere. After this reduction operation has been completed the resultant mass may be formed or pressed to desired shapes and then sintered to form the finished article ready for commercial use in cutting tools, drawing dies, electrical contact points, wear-resisting parts, and so forth.

It is obvious, of course, that it is also possible to utilize iron acetate, formate or lactate in addition to the cobalt and nickel acetates, or to substitute iron acetate either for the cobalt or nickel acetates.

It is also possible to utilize mixtures of different salts such as cobalt acetate and iron formate, or

double salts containing cobalt, nickel and iron, such as various soluble ammonia derivatives or cyanide derivatives. Certain cyanide and ammonia derivatives are particularly helpful in that they form a reducing mixture which produces a hard metal alloy of particularly high quality. These compound salts including ammonia or cyanide groups and also including copper, iron or nickel, may replace part or all of the water soluble organic acid salts, although it is only usually desirable to utilize them in amounts up to about 15% to 50% of the organic acid salts.

The following are several typical examples of carbide mixtures which may be prepared for incorporation with the cobalt and nickel salt solution, said carbides being preferably produced by reduction and/or carburization in a hydrogen atmosphere:

Example 1.—In parts by weight: 5 of titanium carbide, 63 of tungsten carbide, 20 of tantalum carbide, and 2 of vanadium carbide.

Example 2.—In parts by weight: 4 of titanium carbide, 1 of chromium carbide, and 84 of tungsten carbide.

Example 3.—In parts by weight: 2 of chromium carbide, 35 of tungsten carbide, and 53 of tantalum carbide.

Example 4.—In parts by weight: 38 of titanium carbide, 470 of tungsten carbide, 150 of tantalum carbide, and 15 of vanadium carbide.

Example 5.—In parts by weight: 3 of chromium carbide, 5 of titanium carbide, 5 of thorium carbide, 10 of molybdenum carbide, 20 of tungsten carbide, and 20 of tantalum carbide.

Example 6.—In parts by weight: 30 of titanium carbide, 8 of chromium carbide, and 636 of tungsten carbide.

Example 7.—In parts by weight: 15 of chromium carbide, 260 of tungsten carbide, and 400 of tantalum carbide.

Example 8.—In parts by weight: 1 each of chromium, vanadium, titanium and thorium carbides, 10 of tantalum carbide, and 20 of tungsten carbide.

Example 9.—In parts by weight: 10 of chromium carbide, 10 of vanadium carbide, and 50 of tantalum carbide.

Example 10.—In parts by weight: 10 of molybdenum carbide, 20 of tantalum carbide, and 50 of tungsten carbide.

In each case these carbides have been preferably prepared by carburizing the finely divided, pure metal with sugar carbon in a hydrogen atmosphere for two hours at a temperature of 1200° C. to 1600° C. The metal powders may be separately carburized or they may be mixed together before carburization. These metal powders after carburization are milled for a couple of days, preferably without balls, to give a finely divided mixture having a fineness exceeding 180 mesh.

According to one desirable process of combination, the milled carbide mixture of Examples 1 to 10 is sieved through a 180 mesh screen or sieve and then sprinkled into a solution of 370 parts by weight of equal parts cobalt and nickel acetates in 1,000 parts by weight of water.

Of course, either the cobalt or nickel may be replaced in part or whole by equivalent quantities of iron salts. The solution containing the cobalt and nickel acetates is then evaporated to dryness with constant stirring and the residue is dried for about ten hours and then thoroughly

pulverized so that it may be bolted through a 180 mesh screen.

This powder is then loaded into nickel boats and reduced in a hydrogen atmosphere in an electric furnace according to the following schedule:

Held $\frac{1}{4}$ hour at 20 volts
Held $1\frac{1}{4}$ hours at 50 volts
Held $\frac{1}{4}$ hour at 70 volts
Held $\frac{1}{4}$ hour at 100 volts
Held $1\frac{1}{4}$ hours at 130 volts

The temperature then reaches about 600° C., which is maintained until reduction is complete.

The boats are then pushed into the cooler and allowed approximately fifteen minutes to cool. The final product, which is in the form of a very fine powder, is then formed under pressure to the desired shape. The formed pieces are then placed in carbon tubes and heated in a hydrogen atmosphere in an electric furnace to approximately 1450° C. for thirty minutes or longer, dependent upon the size of the pieces. The tubes are then pushed into the cooler and when cold they are withdrawn.

Although the high temperature treatments, namely the carburizing, the reduction, and the sintering, are carried out in reducing atmospheres, it has been found most suitable to carry out the carburizing in a hydrocarbon atmosphere, while the reduction and sintering operations are carried out in a reducing atmosphere, preferably of hydrogen.

Many other changes could be effected in the particular features of process treatment disclosed, and in specific details thereof, without substantially departing from the invention intended to be defined in the claims, the specific description herein merely serving to illustrate certain elements by which, in one embodiment, the spirit of the invention may be effectuated.

I claim as my invention:

1. A process of preparing hard metal alloys which comprises combining a finely divided mixture of at least three refractory metal carbides and then combining this mixture with a water solution of an organic salt of an additional metal selected from the group consisting of iron, nickel and cobalt, said water solution being concentrated and being evaporated down to dryness while continually stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere, at least two of said refractory metal carbides consisting of tungsten carbide and tantalum carbide and the other refractory metal carbide being selected from the group consisting of vanadium carbide, thorium carbide, molybdenum carbide, uranium carbide, columbium carbide, and chromium carbide.

2. A process of preparing refractory metal alloys which comprises combining a mixture of at least three finely divided carbides of refractory metals with a water solution of an organic acid salt of cobalt, said water solution being concentrated and being evaporated down to dryness while continually stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere, at least two of said refractory metal carbides consisting of tungsten carbide and tantalum carbide and the other refractory metal carbide being selected from the group consisting of vanadium carbide, thorium carbide, molybdenum carbide, uranium carbide, columbium carbide, and chromium carbide.

3. A process of preparing hard metal alloys

which comprises combining a mixture of tungsten, tantalum and vanadium carbides with a water solution of a double ammonia salt of an additional metal selected from the group consisting of cobalt and nickel, said water solution being concentrated and being evaporated down to dryness while subjected to continuous stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere.

4. A process of preparing hard metal alloys which comprises combining a mixture of tungsten, tantalum and chromium carbides with a water solution of an organic acid salt of nickel, said water solution being concentrated and being evaporated down to dryness while subjected to continuous stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere.

5. A process of preparing hard metal alloys which comprises carburizing a mixture of at least three refractory metals, and then combining the mixture with a water solution of at least two organic acid salts selected from the group consisting of the salts of iron, nickel and cobalt, said water solution being concentrated and being evaporated down to dryness while subjected to continuous stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere, at least two of said refractory metal carbides consisting of tungsten carbide and tantalum carbide and the other refractory metal carbide being selected from the group consisting of vanadium carbide, thorium carbide, molybdenum carbide, uranium carbide, columbium carbide, and chromium carbide.

6. A process of preparing hard metal alloys which comprises carburizing tungsten, tantalum and an additional refractory metal selected from the group consisting of titanium, thorium, chromium, molybdenum, vanadium, columbium, and uranium, with sugar carbon, milling the carbides, sifting the carbides through a 180 mesh screen, and combining the carbides with a water solution of an organic acid salt of cobalt, said water solution being concentrated and being evaporated down to dryness while subjected to continuous stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere.

7. A process of preparing hard metal alloys which comprises milling together carbides of tungsten, tantalum and an additional refractory metal selected from the group consisting of titanium, thorium, chromium, molybdenum, vanadium, columbium, and uranium, sifting the carbides through a 180 mesh screen, and combining the carbides with cobalt, said combination being effected by sprinkling the sifted carbides into a concentrated solution of cobalt acetate, evaporating to dryness with agitation, reducing the dried mixture and sintering.

8. A method of making hard metal alloys which comprises combining together at least three finely divided refractory metal carbides selected from the group consisting of titanium, tantalum, tungsten, chromium, uranium, molybdenum, thorium, columbium, and vanadium, and combining said carbides with a water solution of a salt selected from the group consisting of the salts of iron, nickel and cobalt, said water solution being concentrated and being evaporated down to dryness while subjected to continuous stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere.

9. A method of making hard metal alloys

which comprises combining together at least three finely divided refractory metal carbides selected from the group consisting of titanium, tantalum, tungsten, chromium, uranium, molybdenum, columbium, thorium, vanadium, and sprinkling said carbides into a concentrated salt solution, said salt being selected from the group consisting of the salts of iron, nickel and cobalt, evaporating said solution to dryness with agitation, powdering, reducing the powder in a hydrogen atmosphere, forming the reduced powder, and sintering.

10. A process of producing refractory metal alloys which comprises combining together at least three finely divided refractory metal carbides, and then combining this mixture with a water solution of the double cyanide salts of cobalt and nickel, said water solution being concentrated and being evaporated down to dryness while subjected to continuous stirring, the dry material being pulverized and sifted and then reduced in a reducing atmosphere, at least two of said refractory metal carbides consisting of tungsten carbide and tantalum carbide and the other refractory metal carbide being selected from the group consisting of vanadium carbide, thorium carbide, molybdenum carbide, uranium carbide, columbium carbide, and chromium carbide.

11. A refractory metal alloy containing about 1% to 10% of at least one carbide selected from the group consisting of titanium carbide, molybdenum carbide, vanadium carbide, uranium carbide and chromium carbide, about 58% to 70% of tungsten carbide, about 10% to 25% of tantalum carbide, and about 5% to 15% of an additional metal selected from the group consisting of cobalt, iron and nickel, each of the carbide particles being encased in and cemented together by a coating of said additional metal, said alloy being prepared by mixing the carbides with a salt solution of the encasing metal followed by evaporating, drying, pulverizing, reducing, compressing and sintering.

12. A hard metal alloy consisting of about 2% to 8% of titanium carbide, about 60% to 68% of tungsten carbide, about 15% to 25% of tantalum carbide, about 1½% to 2½% of vanadium carbide, and the residue additional metal from the group consisting of cobalt, iron and nickel, each of the carbide particles being encased in and cemented together by a coating of said additional metal, said alloy being prepared by mixing the carbides with a salt solution of the encasing metal, followed by evaporating, drying, pulverizing, reducing, compressing and sintering.

13. A hard metal alloy comprising about 1% to 7% of titanium carbide about ½% to 2% of chromium carbide, about 79% to 89% of tungsten and tantalum carbides, and the residue being an additional metal selected from the group

consisting of cobalt, iron and nickel, each of the carbide particles being encased in and cemented together by a coating of said additional metal, said alloy being prepared by mixing the carbides with a salt solution of the encasing metal, followed by evaporating, drying, pulverizing, reducing, compressing and sintering.

14. A hard metal alloy comprising about 1% to 3% of chromium carbide, about 29% to 39% of tungsten carbide, and about 48% to 58% of tantalum carbide, and the residue in additional metal selected from the group consisting of nickel, iron and cobalt, each of the carbide particles being encased in and cemented together by a coating of said additional metal, said alloy being prepared by mixing the carbides with a salt solution of the encasing metal, followed by evaporating, drying, pulverizing, reducing, compressing and sintering.

15. A hard metal alloy comprising about 90% of a mixture of at least two hard metal carbides including tantalum and tungsten carbides, and about 10% of a mixture of nickel and cobalt, the particles of the carbide being each encased in and cemented together by a coating of nickel and cobalt, said alloy being prepared by mixing the carbides with a salt solution of the encasing metal, followed by evaporating, drying, pulverizing, reducing, compressing and sintering.

16. A hard metal alloy comprising about 90% of a mixture of at least two hard metal carbides including tantalum and tungsten carbides, and about 10% of a mixture of nickel, iron and cobalt, the carbide particles being each encased in and cemented together by said last mentioned mixture, said alloy being prepared by mixing the carbides with a salt solution of the encasing metal mixture, followed by evaporating, drying, pulverizing, reducing, compressing and sintering.

17. A process of producing a hard metal alloy which comprises evaporating a slurry containing finely divided cobalt and nickel acetates and at least one hard metal carbide including tungsten carbide, reducing the mixture, forming and sintering, the carbide particles being each encased by cobalt acetate before reduction.

18. A hard metal alloy consisting of finely divided tungsten, tantalum and chromium carbides, the particles of which are each encased in, and cemented together by, a coating of an additional metal selected from the group consisting of iron, cobalt and nickel, said alloy being prepared by mixing the finely divided tungsten and tantalum carbides with a solution of a water soluble salt of the additional metal to form a slurry, followed by reduction to dryness with constant agitation, reduction of the dried mixture in hydrogen, and sintering.

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