

UNITED STATES PATENT OFFICE

2,134,305

METHOD OF MANUFACTURING HARD
METAL ALLOYS

Richard Kieffer, Reutte, Austria, assignor to The
American Cutting Alloys, Inc., New York, N. Y.,
a corporation of Delaware

No Drawing. Application March 27, 1936,
Serial No. 71,183

4 Claims. (Cl. 75—137)

This invention relates to a method of manufacturing hard metal alloys consisting of one or more carbides which form the major portion of the alloy and are cemented by auxiliary metal taken substantially of the iron group and forming the balance of the alloy.

Such alloys are preferably used for tools, or tool elements, and other working appliances which are subjected in operation to mechanical wear.

The carbides involved are preferably those of tungsten, tantalum, columbium, zirconium, boron, silicon, molybdenum, vanadium, chromium which are known as hard and wear resistant while the auxiliary metal substantially taken from the iron group may be supplemented by some chromium.

It is one object of the invention to simplify this manufacture.

It is another object of this invention to render the manufacture cheaper and more efficient.

Up to date the carbides to be used for the hard alloy have been obtained by combining the proper amount of carbon with the desired element.

For this purpose, the element had to be separated from the ores. In general, the elements usable for hard carbides are either present in their ores in form of chemical compounds, and are separated from the ores in such combined form, or if they are present in the ores in a metallic state, they can only be obtained by transforming them in another compound which is then separated from the ores. Regularly, oxide-compounds of the elements are thus obtained which are to be reduced into their metallic state before they can be carburized. These operations rendered the manufacture of the hard alloys difficult and expensive.

According to this invention, at least the carbides to be used in the hard alloy are obtained immediately by proper treatment of the ores in which the elements are contained which are to be carburized. To this effect, the ores are mixed with carbon, or carbon containing substances, in such an amount as to suffice at least for transforming the element if present in the form of a compound in the ores, into its metallic state and immediately afterwards, and in the same operation, into the desired carbide. Consequently, first the state is to be ascertained in which the element to be carburized is present in the ores. The amount of carbon necessary for reducing the element if present in an oxygen-combination is to be ascertained, and then the further amount of carbon necessary for carburizing the

thus reduced element. This total amount of carbon, advantageously with some excess, is then admixed to the ores which are heated so as to separate the elements, or their compounds, from the ores and to reduce them, if they are present in an oxidized state, and furthermore to carburize them. It is done, according to this invention, in a single step, whereupon the carbide so obtained is separated from the remainders of the ores.

One may proceed also in such a way that both the necessary carbon amount, or a slight excess, and the auxiliary metal are admixed to the ores containing the elements to be carburized, and the mixture is then heated to form carbide mixed with auxiliary metal, which is then separated from the remainders of the ores and permitted to solidify.

One may also proceed in such a way that the ores containing the desired element, or elements, to be carburized and ores containing some or all auxiliary metal are mixed, thereupon heated, so that a melt is obtained containing the auxiliary metal and the elements to be carburized, whereby carburization of these elements is done by means of the carbon admixed, whereupon the mixture is separated from the remainders of the ores and permitted to solidify. In case the auxiliary metal is present in its ores also in an oxidized state, additional carbon is to be admixed to the ores sufficient to reduce also the oxides of the auxiliary metal when separating from the ores.

The alloy so obtained is regularly a cast one. It is sometimes advisable to increase its density and toughness thereby that one comminutes the alloy thus obtained to a desired fineness, presses the mixture into a desired shape, and solidifies it again by heat treatment advantageously below melting temperature, i. e., regularly high sintering.

The separation of the oxides contained in the ores may be done at temperatures equivalent to melting temperature or only to a temperature at which these compounds become plastic but ready to combine with the carbon present.

If it is intended to manufacture a hard metal alloy consisting of a major portion of tungsten carbide (WC or W_2C) and iron, one may start from the ore Ferberite containing approximately 70 to 75% tungsten trioxide and 20 to 25% iron. If the ores contain sulphur, or other impurities, they are advantageously heated up to about $500^\circ C$. whereby the sulphur and other impurities evaporating at, or below, this temperature are

driven off. It is furthermore advisable to comminute or to pulverize the ores although it is not necessary as a rule. To these ores carbon is admixed in sufficient amount to reduce the tungsten trioxide into metallic tungsten and to carburize immediately the metallic tungsten thus obtained. Although it is not correct in the extreme scientific sense one may say that according to this invention the compounds of the elements to be carburized are separated from the ores, reduced and carburized in situ. The great advantage of the invention over all the processes previously used appears therefrom.

It is not only economic but also extremely efficient. In such a way, both WC and W_2C may be formed. In the first case, care has to be taken that the temperature is not elevated so high that the WC decomposes again. It is well known to the art that WC when melted decomposes and therefore temperatures corresponding only to a plastic state of the WC are to be applied. Preferably, temperatures near to about 2000° C. are to be applied.

Regularly, the ferberite is melted at such temperatures, including the iron contained therein. The dross formed is lighter than the metals, or their compounds obtained and swims upon them. Therefore, this dross can easily be removed. One may permit, however, the entire material including the dross also to cool down and to solidify and one may then remove easily the solidified dross.

The process may be performed in an electric resistance furnace, or in an induction furnace, or by an electric arc. The temperature to be applied depends somewhat upon the size of the ores to be treated. If one desires to operate at relatively lower temperatures, the ores are to be comminuted very thoroughly, and heat treated in the presence of carbon containing gases driven into the furnace at preferably substantially elevated pressure. In such case, the tungsten may be carburized already at temperatures between about 1000° and 1200° C., while still in a solid state, and if performing such treatment long enough, through several hours, if need be, then the transformation of the tungsten in a still solid state into the tungsten monocarbide can be performed. At slightly elevated temperature up to about 1400° to 1500° C., also the iron will be melted, so that a desirable alloy containing approximately 74% to 80% tungsten monocarbide and 25% to 20% iron can be obtained. By addition of iron the amount of this auxiliary metal in the alloy can be increased. By addition of another ore containing tungsten but not iron, or iron in a lower proportion, the amount of tungsten carbide in the final alloy can be increased and that of the iron decreased. Due to the presence of the iron in a molten state the melting temperature of tungsten monocarbide formed is materially reduced, from about 2800° C. close to about 2000° C. Consequently, it is advisable not to exceed substantially the temperatures at which this carbide is formed and which lie, in general, above about 1000° C. up to about 2000° C. It is to be understood that the carburization of the tungsten within this temperature range is performed while this tungsten is still in a solid state, and that the carbide formed is also in a solid state in spite of the melted iron present. If raising, however, the temperature substantially above 2000° C., then the tungsten carbide would melt in the presence of the molten iron, and decompose into tungsten dicarbide and free carbon.

Instead of treating the ores in the presence of carbon in a gaseous state, solid carbon such as lamp black may be admixed, or both solid and gaseous carbon may be used.

Hard alloys thus obtained are of a high but not the same purity than other known hard alloys manufactured by cautiously carburizing pure metallic tungsten, mixing it with a pure auxiliary metal and sintering the mixture in a hydrogen atmosphere. However, the hard alloy obtained according to the invention is of sufficient hardness and toughness for use in drills and tool elements for squaring, as stone auger and in all cases in which the tool element is subjected to rough handling. In any case, the material according to the invention can be manufactured at incomparably lower costs than the known ones of somewhat higher purity.

The molten alloy obtained and separated from the ores may be cast in the desired shape. It may also be permitted to solidify, and then be comminuted preferably to a very fine degree, then shaped and sintered at temperatures between 1400° and 1600° C.

Chromium may be added in a metallic state, or while in its ores, if desired. The amount of chromium may be between about 1 to 2%, or more.

One may also start from wolframite containing about 75% WO_3 and 25% iron. It is to be treated in the same way as described above, rendering a hard alloy, containing between about 70% to 75% W_2C (or WC), balance iron and manganese.

Starting from the ore hybnerite, containing approximately 75% to 77% WO_3 and 23% to 25% manganese, one obtains in the way described above from ferberite an alloy consisting of about 75% to 83% W_2C , or WC, balance manganese.

Due to the fact that tungsten possesses the greater affinity to carbon than iron, or manganese, during the heat treatment tungsten carbide is formed while iron, or manganese, remains uncombined, provided that the amount of carbon admixed, or permitted to pass in gaseous form into the furnace, is properly measured. If adding carbon in such an excess that also the auxiliary metal can be carburized, then an extremely hard but also tough alloy can be obtained.

By the addition of chromium, the hardness of the auxiliary metal cementing the carbides will be increased.

By using nickel, the hardness of the alloy is somewhat decreased but its strength and toughness increased.

In a similar way, other hard alloys may be manufactured. Thus, molybdenum carbide may be obtained out of molybdenum glance. This ore may first be liberated of its sulphur and other impurities by heat treatment at about 500° C. Thereupon carbon is admixed in an amount sufficient to reduce the molybdenum acid (MoO_3) when separating from the ores and to carburize it immediately afterwards (quasi in situ). Iron or cobalt, or nickel, containing ores are to be admixed to the molybdenum glance, if an alloy is to be obtained containing one, or more, of these auxiliary elements. All the ores, after being liberated from impurities by heat treatment up to 500° C. are mixed in such a proportion that the molybdenum carbide and auxiliary metal are present in the desired proportion in the final alloy.

Although the correct amount of carbon can be

calculated, it is better in each of the cases referred to above to establish the proper amounts of carbon by experiment. The contents of the desired element in the ores may differ, so that the experimental way is to be preferred.

One proceeds in a similar way when a hard alloy is to be obtained containing two or more carbides and auxiliary metal. Thereby mixed crystals of the carbide may be obtained. Then, however, the temperatures are to be kept very near to melting temperature, and the treatment to be continued for a sufficient time. The treatment may be shorter if melting of the carbides is permissible.

If starting from ores which contain only the elements, or compounds thereof, to be carburized but no auxiliary metal, then one may obtain also hard bodies consisting only of carbide. They are, as it is well-known to the art, relatively brittle. It is preferable, therefore, to comminute such bodies, and to admix auxiliary metal, and to solidify the mixture in well-known manners.

As outlined above, it is not necessary that all the carbide is obtained immediately out of the ores. It satisfies the invention if only a substantial part of such carbide is obtained in such a way. Furthermore, the auxiliary metal if used, may be either added in a metallic state, or in the form of a compound, or still in its ores.

Furthermore, if more than one carbide is to be included in the alloy, they may be obtained separately, or one carbide together with the auxiliary metal, and then the carbide may be mixed together in the desired proportion and cemented with auxiliary metal.

If a hard alloy is desired consisting, or containing, titanium carbide, one may start, or add, from the ore rutile, or brookite, or anatase, containing approximately 97% to 98% titanium oxide. The amount of carbon necessary for reduction of this oxide and carburizing of the reduced titanium being calculated, or ascertained by experiment, one proceeds in a similar way as outlined above, including the addition of other carbide and auxiliary metal, as the case may be.

If a silicon carbide is to be obtained, or to be added, one starts from a silicate.

If tantalum carbide is desired, one starts from tantalite.

If boron carbide is desired, one starts from borax.

If vanadium carbide is desired, one starts from petronite.

If columbium carbide is desired, one starts preferably from colombsite.

The invention is not limited to any of the examples given herein.

It may be added that the carbon content may also be chosen so that only part of the reduced metal obtained out of the ores is carburized while the balance remains in a metallic state. One may obtain hereby for instance an alloy containing tungsten carbide, molybdenum carbide, molybdenum in a metallic state, and an auxiliary metal. Similar results may be obtained from other ores and other carbides. Thus, for instance, a hard alloy may be made consisting of a major portion of tungsten carbide while the balance consists in metallic tungsten alone.

When hereinbefore a major portion of carbide, comprising one or more carbides, is referred to, it amounts to over 50% by weight of the final alloy, preferably about 60% to over 75%, up to 95% carbide, while the balance con-

sists in metal, particularly in part or entirely of auxiliary metal taken from the iron group and, if desired, a few percent by weight of chromium.

What I claim is:

1. A method of producing a hard body containing auxiliary metal and carbide in desired ratio of one to four elements capable of forming hard carbides, said elements being tungsten, molybdenum, tantalum, titanium, silicon, boron, zirconium, columbium, chromium, comprising the steps of heating auxiliary metal and one to four ores containing oxides of said elements selected in desired ratio, in presence of carbon in an amount sufficient to reduce the oxides of said hard carbide forming elements present in said ores and to convert the reduced elements into carbide, said heating performed to such an extent and temperature as to melt said ores and auxiliary metal and thereby to separate said oxides from said ores, to reduce said oxides and to convert the elements so obtained into carbide, thereupon separating the carbide thus obtained from the remains of said ores, and comminuting and sintering said carbide in desired shape.

2. A method of producing a hard body containing auxiliary metal and carbide of one to four elements capable of forming hard carbides, said elements being tungsten, molybdenum, tantalum, titanium, silicon, boron, zirconium, columbium, chromium, comprising the steps of heating a mixture of auxiliary metal and one to four ores containing oxides of said elements and selected in desired ratio, in presence of carbon in an amount sufficient to reduce the oxides of said hard carbide forming elements present in said ores and to convert the reduced elements into carbide, said heating performed above about 1000° C. and at least at melting temperature of said ores and auxiliary metal but below the melting temperature of carbide to be formed and to such an extent as to separate said oxides from said ores, to reduce said oxides and to convert the elements so obtained into carbide, to melt said auxiliary metal and to alloy it with said carbide, and thereupon separating the alloy thus obtained from the remains of said ores, comminuting said alloy and sintering it into desired shape.

3. A method of producing a hard body containing a major portion of carbide of one to four elements capable of forming hard carbides, said elements being tungsten, molybdenum, tantalum, titanium, silicon, boron, zirconium, columbium, chromium, and about 5% to 30% binding metal selected from a group consisting of iron, nickel, cobalt, chromium, comprising the steps of heating said binding metal and one to four ores selected in desired ratio, in presence of carbon in an amount sufficient to reduce the oxides of said hard carbide forming elements present in said ores and to convert the reduced elements into carbide, said heating performed above about 1000° C. and at least at melting temperature of said ores and binding metal but below the melting temperature of carbide to be formed and to such an extent as to separate said oxides from said ores, to reduce said oxides and to convert the elements so obtained into carbide, and to melt said binding metal, thereupon separating and solidifying the mixture of molten binding metal and carbide thus obtained from the remains of said ores, then comminuting and sintering said mixture in desired shape.

4. A method of producing a hard metal alloy consisting of about 70% to 77% of tungsten car-

bide and the balance substantially iron, comprising the steps of heating between about 1000° C. and about 2000° C. ores containing tungsten oxide and iron selected from the group consisting of ferberite, wolframite and hybnerite in the presence of carbon in an amount sufficient to reduce the tungsten oxide contained in said ore and to convert the tungsten so obtained into the desired carbide, thereby substantially melting said ore and iron contained therein and simultaneously

separating said oxides from said ores, reducing said oxides and converting the tungsten so obtained into carbide, thereupon separating the mass substantially consisting of tungsten carbide and iron thus obtained from the balance of said ore, then allowing said mass to cool and thereupon comminuting and sintering said mass into desired shape.

RICHARD KIEFFER. 11