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CARBIDES OF TANTALUM AND LIKE METALS
AND METHOD OF PRODUCING THE SAME

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My invention relates to new carbides of tantalum and like metals and method of producing the same and has to do, more particularly, with the production of carbides of tantalum or columbium, and multi-carbides having, as a major constituent, tantalum carbide or columbium carbide, and, as a minor constituent, one or more of the carbides of the group of metals consisting of tantalum, columbium, titanium and zirconium, which carbides and multi-carbides differ in chemical and physical characteristics from any combinations of carbon with such metals, that have been heretofore produced.

The principal object of my invention is to produce a novel tantalum carbide, and columbium carbide, and novel multi-carbides, including tantalum carbide or columbium carbide as the major constituent, which are of the greatest value and utility as an ingredient or material for use, in accordance with the principles of powder metallurgy, in the production of hard compositions of matter having greater hardness combined with greater strength than has been attainable heretofore, together with better thermal and electrical conductivity, and other characteristics which enable the hard compositions of matter made from these new carbides and multi-carbides to have very great utility in the construction of metal cutting tools, dies corrosion resisting surfaces and the like.

A further object of my invention is to provide new carbides and multi-carbides, of the character mentioned above, which may be used for the formation of hard compositions of matter of unsurpassed hardness and strength, while incorporating in such hard composition of matter a greater proportion of tungsten than has been possible heretofore, without injuriously affecting the strength of the product.

A further object of my invention is to provide new carbides of tantalum and columbium, and multi-carbides in which tantalum carbide or columbium carbide is the major constituent, and carbides of tantalum, columbium, titanium or zirconium, the minor constituent, which are true chemical combinations of carbon with the respective metals, as indicated by the fact that the carbon therein is in true monatomic ratio to the metal or metals. In this respect, the products constituting my present invention distinguish from the products heretofore known, and erroneously named carbides, which my researches have shown to be no more than carburized metals, the carbon not being present in exact monatomic ra-

tio to the metal and not being uniform throughout the material.

A further object of my invention is to provide new carbides and multi-carbides, of the type heretofore mentioned, of macro-crystalline character, that is to say, having crystals visible to the unaided eye, the term "macro-crystalline" being more specifically defined, for the purposes of this specification, hereinafter. In this respect, my new products differ from the so-called tantalum or columbium carbides heretofore known, which have been of amorphous character, lacking the distinct crystalline character and lustre which is typical of my new products.

A further object of my invention is to provide a method by which these new carbides and multi-carbides can be produced economically and efficiently, and which lends itself particularly to the formation of the multi-carbides above mentioned. A particularly desirable feature of this method is that it lends itself to the production of these valuable and novel multi-carbides from ores containing one or more of the metals above enumerated, as, for instance, tantalite, which contains columbium as a minor constituent, and also columbite ore, which contains tantalum, at times, as a minor constituent. Likewise, there are ores useful in this method, which contain minor percentages of titanium and zirconium together with tantalum and columbium.

Further objects, and objects relating to economies and details of operation and use, will definitely appear from the detailed description to follow. In certain instances, I have accomplished the objects of my invention by the devices and means set forth in the following specification. My invention is clearly defined and pointed out in the appended claims.

A better understanding of my novel products will be had by first considering previous efforts to produce a material including tantalum and carbon. Heretofore, products, which have been called tantalum carbide, have been made in various ways, but none of these prior methods yields a product having the typical metallic lustre, crystalline size, purity and density of my new tantalum carbide. Moreover, these prior products have been far inferior to my new tantalum carbide as an ingredient of, or a material for the production of, hard compositions of matter, in that my new tantalum carbide, when used in accordance with the processes of powder metallurgy, produces a hard composition of matter having combined hardness and strength which surpasses anything

ever attained by the use of the old tantalum-carbon material.

For example, a material, which was called tantalum carbide, has heretofore been made, for subsequent use as an ingredient of hard compositions for tools, by heating tantalum oxide with carbon, in the form of carbon black, at about 2000° C. The product of this process has been described as of a dirty yellow color and having a density of from 13.95 to 14.05. It may be described as "amorphous", in that it does not present crystalline form to the unaided human eye. It does not have the macro-crystalline form of my new tantalum carbide.

For the purposes of this specification, I define "macro-crystalline" as having particles which average greater than .01 mm. in largest cross section dimension and "amorphous" as having particles which average less than .01 mm. in largest cross section dimension. I understand that there is another sense in which all solid bodies may be described as crystalline, and may be shown to have ordered atomic arrangement by X-ray methods, or to have crystalline form which may be seen under the microscope, but I do not use the term in this sense, in this specification.

Another process which has been used for the production of a material called tantalum carbide, for subsequent use in powder metallurgy, consists in heating mixtures of powdered tantalum metal and carbon to about 1800° C. This process also yields a product which is amorphous and not macro-crystalline, and which lacks the characteristics of my new tantalum carbide. The product of this process, or of the oxide process previously described, may be improved somewhat by heating in a vacuum, or by reheating after chemical analysis with the required amount of additional carbon, oxide, or metallic tantalum, to adjust the average carbon content of the mass to about 6.2 per cent carbon, but the products resulting from said processes failed to have the high density, metallic lustre, crystalline form and size, and exact monatomic ratio of carbon to metal, in all parts of the mass, which characterize my new product.

It has also been proposed to produce a material called tantalum carbide by the method described in U. S. Letters Patent, No. 1,928,453, patented September 26, 1933, in which tantalum is heated with carbon to about 1600° C., in an atmosphere of hydrogen. This process, however, likewise fails to yield a product having the purity, uniformity, crystalline form and size, and metallic lustre of my new tantalum carbide. That my new product differs from that disclosed in said patent, is established by the fact that, when the material produced in accordance with said patent is heated, in a good vacuum, in contact with metallic tungsten, the tungsten is carburized, whereas, when my new tantalum carbide is heated under like conditions, in the presence of metallic tungsten, the tungsten is not carburized.

As the result of long experience with the methods heretofore known for making so-called tantalum carbides, and extensive study of the literature on the subject, I believe that tantalum carbide has never been produced, prior to my invention, having the macro-crystalline size, the high density, the purity, and the other characteristic features of my new tantalum carbide, and I am satisfied that it is impossible to produce my new tantalum carbide by any of the methods known prior to my invention. As the old methods

have been carried out in practice, the product resulting from the first heating of the initial mixture of tantalum and carbon, or of tantalum oxide and carbon, usually was so grossly imperfect in carbon content that it was customary to make a chemical analysis of each lot heated and to adjust it by adding more carbon, or more tantalum or tantalum oxide, which were more or less imperfectly mixed, reheating as before, again analyzing for carbon, and sometimes repeating the reheating and re-analysis many times until the final product had the carbon content which experience, at that time, had shown to be preferred. In fact, the preferred carbon content, in accordance with these prior practices, was below 6.2 per cent. My invention contemplates a tantalum carbide, in which the carbon content is in monatomic ratio to the tantalum, and the method by which such a product is unfailingly obtained in a single heating process. My invention contemplates, also, columbium carbide and the multi-carbides specified, having similar characteristics as to carbon content and the method of producing them.

While it had been suggested, prior to my invention, that columbium carbide could be made by methods heretofore described, such methods were highly unsatisfactory, and it was impossible to produce columbium carbide, by any of these methods, having any practical utility. The material called columbium carbide, made by these old methods, was amorphous and of a greyish color, and lacked the characteristic macro-crystalline size and other features of my new columbium carbide.

What has been said above, with respect to prior attempts to produce so-called tantalum carbide and columbium carbide, was true likewise of various combinations of carbon with tantalum, columbium, titanium or zirconium. None of these products had the characteristic macro-crystalline size, purity and other features typical of my new products.

The process of my present invention, by which I have been able to produce these novel carbides and multi-carbides, consists essentially of heating a metal of a group consisting of tantalum and columbium, or an alloy, oxide, compound or ore containing said metal or metals, with a menstruum metal or metals, to a temperature above the melting point of the latter, in the presence of a surplus of carbon, or a material containing carbon, and subsequently removing the menstruum metal or metals, and the products containing them, and separating therefrom the pure carbide or carbides produced. My method also comprehends, for the production of multi-carbides, the heating of two or more metals of the group including tantalum, columbium, titanium and zirconium, the metal or metals in major proportion being either tantalum or columbium, or both in sum, or alloys, oxides, compounds or ores containing said metals, with the menstruum metal or metals, to a temperature above the melting point of the latter, in the presence of a surplus of carbon, or a material containing carbon, and subsequently separating the multi-carbide from the mass. I have found aluminum to be the best menstruum metal.

I will refer to the process of making tantalum carbide, as typical of the process of my invention. In such case, metallic tantalum may be dissolved in molten menstruum metal or metals, as, for instance, by dissolving the metallic tantalum in molten aluminum, or by melting a mixture of

metallic tantalum and metallic aluminum. This molten solution of the tantalum and the menstruum metal is then subjected to prolonged heating in the presence of carbon, or a substance containing carbon, or both, the temperature being maintained above the melting point of the solution of metals. I believe that the process can be carried out most expeditiously when the temperature approximates that at which the solution of metals will vaporize, but, of course, from a practical standpoint, the temperature should not be so high that the materials will boil out of the crucible. As the result of this heating of the molten mixture of metallic tantalum and the menstruum metal or metals, in the presence of an excess of carbon, tantalum carbide is formed. At the end of this period of heating, the melt is cooled and subjected to various processes by which the menstruum metal or metals, and the products formed therefrom as a result of the heating, are dissolved or converted into soluble chemical compounds, leaving as solid material the pure tantalum carbide, together with some slight excess of carbon existing in such form that it may be readily separated from the crystals of pure tantalum carbide.

As menstruum metals, I have used aluminum, iron, manganese and beryllium. They may be used separately or in combination. It may be that other metals will also serve the purpose, but I have found that aluminum is particularly satisfactory, as it is readily removable from the resulting mass, either as the metal, as carbide, or in other compounds. In place of aluminum, or the other menstruum metals mentioned, the oxides or other compounds of these metals may be used for, by the process of heating, they are reduced in the presence of carbon and operate with the same effect as if they had been present initially as the pure metals.

The essence of this new method consists in reacting the metal or metals from which the carbides are to be formed, in the liquid phase, with carbon. Inasmuch as the melting point of tantalum metal is considerably above the temperatures which I have found necessary, I believe that the tantalum is dissolved in the molten menstruum and thus put in condition for the liquid phase reaction. Moreover, the melting point of carbon is considerably above the temperatures used and, therefore, I believe that the carbon is dissolved in the molten menstruum, so that it likewise is in condition for the reaction in the liquid phase. As regards columbium, titanium and zirconium, their melting points approximate the temperatures used.

When the desired carbide is formed from the tantalum dissolved in the menstruum metal, the latter may be free to take more metallic tantalum into solution and repeat the process, thus permitting a relatively small amount of the menstruum metal to suffice, when sufficient time is used. I have found that about one and one-half times as much aluminum, as tantalum to be converted into the carbide, is a useful and satisfactory ratio. I have used up to thirty times as much aluminum as tantalum, or other metals to be converted into carbide.

It is not necessary that metallic tantalum, or the corresponding metals in elementary form, be used in this process, because the oxides, or other compounds containing the metal, will be reduced to metallic form due to the heating in the presence of aluminum and carbon.

At the end of the heating period, the result-

ing mass includes the crystals of tantalum carbide, together with the menstruum metal, free carbon, and the products formed by reaction with the menstruum metal or metals. The crystals of tantalum carbide are separated from the mass by various means, as by treating the mass with chemical solutions which react with the menstruum metal or metals, and the products of reaction with the menstruum, producing soluble compounds which are removed in solution form, leaving behind the crystals of my new tantalum carbide. Specifically, I have used hydrochloric acid for this purpose, and other acids, such as nitric acid, sulphuric acid and hydrofluoric acid, which may be used separately and intermittently, or in combination, with the exception of a mixture of hydrofluoric and nitric acids, which reacts with my new tantalum carbide to form a soluble compound. I have also used alkalies, such as sodium and potassium hydroxide, followed by washing with acid solutions. Other means of removing the menstruum metal or metals, or the products of reaction therewith, are by acid vapors or by anodically electrolyzing the mass resulting from the heating process. Finally, I have concentrated my new carbide from the residue left after these treatments, by gravity means, as by "panning" with a liquid such as water or with carbon tetrachloride, and drying the crystals. The gravity concentration removes light impurities, such as graphite, and insoluble products of the menstruum metal.

The following is a specific example of the preparation of my new tantalum carbide, the procedure given being that which I prefer to use from the commercial standpoint and being the best procedure now known to me for that purpose. I heated 1600 grams of pure aluminum in a crucible of pure Acheson graphite, consisting of a six inch cylinder bored out with a four inch hole to within about two inches of the bottom. When the aluminum was in molten condition, I added to it 1200 grams of Ta_2O_5 . The crucible was covered with a graphite lid, and the crucible and its charge covered with carbon black, and all placed in a high frequency electric heating furnace. I added about 200 grams of additional carbon in the form of graphite rods, so as to provide carbon in addition to that taken up from the crucible itself during the heating process. The crucible was then heated to about $2000^{\circ}C$. for a period of six hours, after which the melt was allowed to cool, the crucible broken open, the contents crushed to the size of grains of wheat and then digested with 10 litres of commercial muriatic acid. This caused a rapid evolution of gas and the solution of the aluminum and aluminum carbide, by conversion to chloride and solution in water. The residue resulting from this treatment with acid consisted of beautiful gold-colored crystals, having a metallic lustre, which were insoluble in the acid. These were rubbed lightly in an agate mortar to remove adherent graphite and other insoluble impurities, concentrated by "panning" with water, digested with hydrofluoric acid for several hours, and the insoluble residue then washed with water and dried. The product showed, upon chemical analysis, a carbon content of 6.22 per cent and was macro-crystalline. I believe it to be substantially pure TaC .

I have also carried out the foregoing method, starting with metallic tantalum and aluminum. In this case, in one specific instance, I melted 425 grams of aluminum in a crucible of pure Acheson

graphite and added to the melt 180 grams of tantalum metal. The rest of the treatment was substantially as described above, with the exception that, since this melt was smaller, the time of heating was only 3 hours and less muriatic acid was required for digesting the cooled mass resulting from the heating.

The product resulting from this treatment also consisted of beautiful gold-colored crystals, having a metallic lustre, and was macro-crystalline. This product also, upon chemical analysis, shows a carbon content of 6.22 per cent and was substantially pure TaC.

The new tantalum carbide, which, in several instances, I have produced by the methods described above, is always of a golden color, has a metallic lustre, and is macro-crystalline. Its crystals average about .04 mm. in largest cross section dimension.

Numerous specimens of this new tantalum carbide, which I have analyzed, show a carbon content of 6.22 per cent. This is in accordance with the theoretical percentage of carbon which should be present in TaC, taking the revised atomic weights of tantalum and carbon as given in the Fifth Report of the Committee on Atomic Weights of the International Union of Chemistry, appearing in the Journal of the American Chemical Society for May 8, 1935, Vol. 57, No. 5, page 787. This report (p. 793) gives, for the atomic weight of tantalum, 180.89. The atomic weight of carbon is also given in said report (page 788) as 12.006. Using these latest revised atomic weights as the basis of calculation, a tantalum carbide, in which one atom of tantalum is combined with one atom of carbon, in true monoatomic ratio, should contain 6.224 per cent of carbon. I have found, by the analysis of a large number of specimens of my new tantalum carbide, that the average percentage of carbon contained therein is 6.225. From this I conclude that my new product is a pure tantalum carbide, in which the carbon is combined with tantalum in the ratio of one atom of carbon to one atom of tantalum, as indicated by the formula TaC. In this respect, my new product differs from the material previously made, and erroneously called tantalum carbide, which contained a smaller percentage of carbon.

A striking demonstration of the soundness of my conclusions in this regard is to be found in the fact that my determination of the percentage of carbon, in specimens of my new tantalum carbide, had been made prior to my knowledge of the revision of the atomic weights of tantalum and carbon, above mentioned. Using the old values for the atomic weights of these elements, the percentage of carbon present in TaC would be 6.205. Notwithstanding this, my tests showed the presence in my tantalum carbide of 6.225 per cent carbon, which I was unable to account for, until the revision in the atomic weights of the elements came to my knowledge, within the last two months.

The materials which have been made prior to my invention, and which have been known under the name tantalum carbide, have had therein from 5 per cent to 6.2 per cent of carbon, the percentage of carbon varying with different heats and 6.2 per cent carbon being the high limit obtainable. Where a high percentage of carbon, within the range, was present in the average of the mass, it was partially present as free carbon, as was especially evident when the high limit was approached, so that it was the

practice to adjust the carbon content to less than 6.20 per cent. These materials, therefore, were not pure TaC. The distinction between my new tantalum carbide, and these prior products, is not wholly academic and theoretical as the purity of the tantalum carbide gives it a thermal and electrical conductivity much higher than that of a material made up of two distinct substances or phases, as, for instance, a mixture of tantalum carbide and carbon or tantalum carbide and tantalum. The presence of free carbon in this old material was detrimental, as it affected the chemical properties of the material, in regard to its reaction with other substances, as well as its physical properties.

I have determined the density of my new tantalum carbide, produced as above described, by standard pyknometric methods and have found it to be 14.445. Heretofore, the material erroneously called tantalum carbide has been of a considerably lower density, having been described as having a density of from 13.95 to 14.05. Density determinations upon my new tantalum carbide have shown a density, in all cases, above 14.05. A remarkable corroboration of the purity and uniformity of my new macro-crystalline TaC has been obtained by the use of the X-ray spectrogram, made from material prepared by me as above described. The compound TaC crystallizes in the NaCl type lattice, and I have had the dimensions between the Ta atoms in my product determined by precision methods, finding it to be 4.445 Angstrom units. The theoretical density may be calculated from the following formula:

$$\frac{A(B+C)D \times 10^{-24}}{(Ex10^{-8})^3}$$

wherein A is the number of molecules in the unit cell, B is the atomic weight of tantalum, C is the atomic weight of carbon, D is the weight of one atom of a hypothetical element having the atomic weight of unity, and E is the observed distance between the Ta atoms in the lattice. Using, in the above formula, the revised atomic weights for tantalum and carbon of 180.89 and 12.006, respectively, the calculation gave, as the theoretical density of my new TaC, 14.47. Since this checks very closely with the density of 14.445, as determined by pyknometric methods, it establishes that this new product is true TaC, in substantially pure form.

The amorphous material, heretofore known as tantalum carbide, was not particularly stable and oxidized rather readily, when exposed to oxidizing conditions. This was a decided objection and presented difficulties in its use in powder metallurgy, inasmuch as the oxidation of the surfaces of the particles tended to interfere with and prevent a good union between them. My new TaC is much more stable than this old material, and not so readily oxidizable, and I believe that this is a factor in the production therefrom of better hard compositions of matter, for use in tools, than have been possible heretofore.

As has been stated above, the old amorphous material, known as tantalum carbide, when heated in the presence of metallic tungsten to a temperature of about 1400° C., would carburize the tungsten, surrendering some of its carbon to the tungsten with the formation of a tungsten-carbon material. As a consequence, when this amorphous material was mixed with metallic tung-

sten, for the production of a hard composition of matter, and subjected to heat in the usual processes of powder metallurgy, the tungsten would be carburized in part and, to that extent, would lose some of its characteristic toughness and strength. On the contrary, when my new macro-crystalline TaC is heated to 1400° C., in the presence of metallic tungsten, it does not carburize the tungsten. This, I believe to be an important factor, which enables me to make harder and stronger compositions of matter, using my new TaC as an ingredient.

I have found that hard compositions of matter, made using my new TaC as an ingredient, as will be described hereinafter, have a thermal conductivity considerably in excess of any heretofore obtained with similar compositions, using the old amorphous material as an ingredient. Of course, this is an important factor in cutting tools, as it is desirable to conduct the heat away from the cutting edge as rapidly as possible, in order that the cutting edge may not reach too high a temperature. It is well known to physical metallurgists that pure substances have a much higher thermal and electrical conductivity than impure substances, or materials which consists of a mixture of two or more phases, and I believe that this increased thermal conductivity of the hard compositions of matter, made from my new TaC, is due to the fact that it is substantially pure, whereas the old amorphous material was a mixture of different materials or phases. It is also generally recognized that an improvement in thermal conductivity is accompanied by a corresponding improvement in electrical conductivity, and I believe this to be true in this case also.

The most important characteristic of the new macro-crystalline tantalum carbide of my present invention is that, using that substance as a starting material, and proceeding in accordance with the principles of powder metallurgy, hard compositions of matter can be, and have been, made having a hardness combined with strength, which is far in excess of that of any material heretofore known. I believe that the combination required for better cutting-tool material, comprising tantalum carbide or columbium carbide, or one of my new multi-carbides, is one in which there is to be found united in one material, great hardness, great strength, high thermal conductivity, uniform coefficients of thermal expansion of the substances composing the tool material, and a high softening point when heated. My new carbides and multi-carbides permit me to obtain the desired combination of characteristics to a greater degree, in one or more, or all of these factors, than has been possible with the previously known materials including tantalum and carbon, or columbium and carbon. As already stated, these hard compositions made from my new TaC have good thermal conductivity and they also have a high softening point.

The following is a specific example of the production of my new columbium carbide by the method heretofore described: 100 grams of substantially pure metallic columbium were mixed with 400 grams of molten aluminum and the mixture heated, in a graphite crucible, in the presence of excess carbon, at a temperature of 1800° C. for about six hours. After the melt had cooled, the mass was removed from the crucible and digested with commercial muriatic acid and then with hydrofluoric acid, as previously described in the preparation of tantalum carbide. The residue left from this treatment was sepa-

rated from lighter impurities that were contained therein, by "panning" or other similar methods.

The product obtained by the foregoing method was macro-crystalline and of a lavender color, having a pronounced metallic lustre. Columbium carbide has heretofore been described as a steel-grey, amorphous powder. This new CbC, likewise, has a higher density than previous materials known as columbium carbide, having an observed density of 7.82, instead of 7.56, as reported for products known as columbium carbide, and made by previous processes. The theoretical density of my CbC, produced as above described, was also calculated from the lattice observed in X-ray spectrograms of the material. The observed lattice dimension was 4.457 Angstrom units and, calculating according to the formula given above, a theoretical density of 7.815 was obtained. The latest revised atomic weights for columbium and carbon were used in this calculation. Also, this new product contains from 11.40 to 11.48 per cent carbon, or, as closely as has been determined, 11.44 per cent carbon. This checks with the theoretical calculations, based on the assumption that the product is CbC and using the revised atomic weights for columbium and carbon.

This new columbium carbide is characterized by its macro-crystalline structure, by a content of carbon in monatomic ratio to columbium, by a density higher than the amorphous columbium carbide heretofore known, by the fact that it is more stable and not so readily oxidizable, and by improved thermal conductivity. Hard compositions of matter made from the amorphous columbium carbide, heretofore known, were so lacking in strength as to be useless as metal-cutting tools, but, on the contrary, hard compositions of matter made from my new columbium carbide show about the same combination, of strength and hardness as those made from my new form of tantalum carbide.

I have also found that multi-carbides, of the same general character, may be produced by this same general process, having either tantalum carbide or columbium carbide as a major constituent. For instance, I have produced and tested multi-carbides having TaC as the major constituent and, as a minor constituent, a carbide or carbides of one or more of the metals of the group including columbium, titanium and zirconium. Likewise, I have produced and tested multi-carbides having columbium carbide as the major constituent and, as a minor constituent, a carbide or carbides of one or more of the metals of the group including tantalum, titanium and zirconium. In each instance, I found that these multi-carbides were macro-crystalline and that they had a pronounced metallic lustre, differing therein from the amorphous materials heretofore known and produced by carburization of these metals or their oxides. My calculations showed, in each instance, that carbon and the metals were present in the substance in strict monatomic ratio, and that the densities of the substances were higher than those of the corresponding previously known amorphous materials. The tests showed, also, that these multi-carbides were very valuable as a starting material, or materials, for the production of hard compositions of matter and that, when used in accordance with the principles of powder metallurgy, hard compositions of matter were produced therefrom having, in general, greater combined strength and hardness

than hard compositions of matter made from similar but amorphous materials.

In my investigation of these new multi-carbides, produced in accordance with my invention, I have found that there is a limit to the proportion of minor constituent, which may be present and still retain the desirable characteristics of the product. This limit varies, depending upon the nature of the major and minor constituents, and ranges from 40 molecular per cent to zero. I believe that the carbide or carbides constituting the minor constituent are present in solid solution in the carbide constituting the major constituent, below the said limit. Above that limit, the different carbides may be present in two phases and thus the product forms essentially a mixture of two macro-crystalline carbides. Where the carbides are present in a two-phase system, they seem to lack the high thermal conductivity and some other features, which are especially desirable for making hard compositions of matter, but, in all cases, they have characteristics superior to the similar but amorphous materials heretofore known. In this specification, in the formulas given for these multi-carbides, I have included in parentheses the symbol or symbols for the metal or metals, the carbides of which form the minor constituent.

The multi-carbide $Ta(Cb)C$, is one which I believe to be of particular value and importance, as it produces hard compositions of matter which are exceedingly good and it can be made readily from the ore known as tantalite, which contains both tantalum and columbium. The following is a specific example of the production of the macro-crystalline multi-carbide, $Ta(Cb)C$, from tantalite ore, in accordance with my invention. I first made a thermit charge of 800 grams of granulated aluminum, 2570 grams of tantalite ore, and 1521 grams of barium di-oxide. This tantalite ore contains about 61 per cent Ta_2O_5 and about 12 per cent Cb_2O_5 . The barium di-oxide was added to the thermit charge in order to provide a material, the heat of reaction of which with the aluminum will supply additional heat necessary for the reduction of the oxides and the melting of the regulus. Ignition of this charge produced a regulus of 1850 grams. Upon heating this regulus with aluminum, in the ratio of 400 parts by weight of regulus to 240 parts of aluminum, adding some graphite sticks or rods, and in a graphite crucible, as before, to about $2000^{\circ}C$., for about six hours, and subsequently treating the cooled mass with muriatic acid, concentrating the residue by mechanical means, and then treating the concentrated residue with hydrofluoric acid, as before, I obtained 897 grams of a macro-crystalline product containing 7.00 per cent carbon and having a density of 12.62. This product was macro-crystalline, had a metallic lustre, and was of a bronze color. As closely as could be determined by analytical methods, the product contained 84 per cent TaC and 16 per cent CbC . This indicated, within the range of analytical error in determining the percentages of tantalum and columbium, that the carbon in the substance was all combined with the metals, as TaC and CbC , respectively.

X-ray spectrographic analysis of this product showed it to be a solid solution of CbC in TaC , and not merely a mixture of TaC and CbC crystals. This is important from the standpoint of the production of hard compositions of matter from this multi-carbide, for I have found that, in the case of macro-crystalline $Ta(Cb)C$, there is a

limit to the solubility of CbC in TaC . I have determined that, for practical purposes, this limit is 25 per cent by weight, that is to say, that the CbC should not exceed 25 per cent by weight of the multi-carbide. This is about 40 molecular per cent. Moreover, I have found that the hard compositions made from the macro-crystalline multicarbide, $Ta(Cb)C$, in which the CbC is less than 25 per cent by weight, are stronger than compositions in which the percentage of CbC exceeds 25 per cent by weight, and are of equal or greater hardness.

The following is a specific example of the method followed in producing a multi-carbide, $Ta(Cb)C$, which proved to be exceptionally valuable as an ingredient of a hard composition of matter for metal-cutting tools: First, I made a thermit charge of 1285 grams of tantalite ore, which contained about 61 per cent Ta_2O_5 and about 13 per cent Cb_2O_5 , 612 grams of granulated aluminum, 742 grams of Ta_2O_5 , in addition to that contained in the ore, and 1014 grams of barium di-oxide. Upon ignition, this charge gave a regulus of metal weighing 1186 grams. This regulus was melted with 1400 grams of aluminum and heated in a graphite crucible, as heretofore described, at about $1900^{\circ}C$. for about seven hours. After the treatment heretofore described for separating the multi-carbide from the mass, a yield of 784 grams $Ta(Cb)C$ was recovered. Chemical analysis showed that this contained 6.68 per cent carbon and that it had a density of 13.223. The major constituent, TaC , constituted 91.26 per cent of the substance and the minor constituent, CbC , constituted the balance, 8.74 per cent. The minor constituent was undoubtedly in solid solution in the major constituent.

This new macro-crystalline multi-carbide, $Ta(Cb)C$, produced in accordance with my invention, is substantially pure, makes hard compositions having high thermal and electrical conductivity, is stable, and does not oxidize readily. Hard compositions may be made therefrom having a combination of strength and hardness which surpasses any made heretofore, from amorphous materials including tantalum, columbium and carbon.

I have tried to make macro-crystalline carbide of titanium and macro-crystalline carbide of zirconium by using a menstruum of aluminum, but have failed to do so. In view of this, it is remarkable that multi-carbides of macro-crystalline form may be made, in accordance with my invention, containing TiC or ZrC , or both of them, as minor constituents.

The following is an example of the method followed by me in producing macro-crystalline $Ta(Zr)C$: A mixture of 1323 grams Ta_2O_5 , 216 grams ZrO_2 , and 1800 grams of aluminum was heated in a graphite crucible, in the presence of excess carbon, at about $1800^{\circ}C$., for about six hours. The resulting mass was treated as previously described, with muriatic and hydrofluoric acids and by concentration, so as to separate the multi-carbide from the mass. As a result of this treatment, I obtained 1047 grams of product consisting of reddish-colored crystals, of macro-crystalline form and size, with metallic lustre, analyzing 6.87 per cent carbon and consisting of 88.35 per cent TaC , and about 11.9 per cent ZrC . This substance had a density of 11.95. The density and the percentage of carbon showed that the carbon contained in the substance was chemically combined with the metals as TaC

and ZrC, and the X-ray spectrogram made from this material showed that the ZrC was present in solid solution in the TaC, and not as a two-phase system. This multi-carbide has high thermal and electrical conductivity compared to previously known amorphous materials containing tantalum, zirconium and carbon, is stable and not readily oxidizable, and hard compositions of matter made from this macro-crystalline multi-carbide, by known processes of powder metallurgy, had such hardness, strength and thermal conductivity as to be exceedingly valuable in metal-cutting tools and the like.

The following is a specific example of the method followed by me in the production of the multi-carbide, Ta(Ti)C, in which TaC is the major constituent, and TiC the minor constituent: 240 grams of TiO₂, 1328 grams of Ta₂O₅, 950 grams of aluminum, and 610 grams of KClO₃ were mixed to form a thermit charge, the KClO₃ being added for the purpose of supplying heat to aid in reducing and melting the metals. The regulus resulting from the ignition of this charge weighed 826 grams. 375 grams of this regulus were heated with 280 grams of aluminum, in a graphite crucible, in the presence of excess carbon, to about 1800° C., for about six hours. The resulting mass was digested with muriatic and hydrofluoric acids and concentrated as previously described, the yield being about 193 grams. This product was macro-crystalline, had a metallic lustre and was of a steel-gray color. This product showed, on analysis, 7.40 per cent carbon and that it was composed of about 8.8 per cent TiC and 91.2 per cent TaC. The density was 12.24. The percentage of carbon and the density indicated that the carbon contained in this substance was chemically combined with tantalum and titanium, as TaC and TiC. I believe that, in this case also, the TiC is in solid solution in the TaC.

The new multi-carbides which may be produced in accordance with my invention, having the characteristic macro-crystalline form, include those in which the minor constituent consists of carbides of two or more metals as, for example, Ta(CbTi)C; Ta(CbZr)C; Ta(TiZr)C; and Ta(CbTiZr)C.

The following is a specific example of the production of Ta(CbTi)C by the method of my present invention: 13,887 grams of tantalite ore, which include about 61 per cent of Ta₂O₅ and about 12 per cent of Cb₂O₅, 5057 grams of aluminum, 4527 grams of TiO₂, and 6084 grams of barium di-oxide were mixed to form a thermit charge. Upon ignition, this thermit charge formed a regulus of metals weighing 10,832 grams. This regulus was melted with aluminum, in the proportion of 1800 grams of aluminum to 1400 grams of the regulus, and heated in a graphite crucible, in the presence of excess carbon, at 1800° C., for about six hours. From the mass resulting, the residue consisting of the macro-crystalline multi-carbide was recovered by digestion with muriatic and hydrofluoric acids, and concentration by gravity means, as heretofore described. The yield for this melt was about 900 grams.

The product was macro-crystalline in form and size, and of a steel-grey color with a lavender cast, having a pronounced metallic lustre. Analysis showed that the product contained 8.40 per cent carbon and that it was composed of 75.42 per cent TaC, 13.62 per cent CbC, and 10.95 per cent TiC. The minor constituents, CbC and

TiC, in this case, constitute a little less than 45 molecular per cent of the substance. This new macro-crystalline multi-carbide has a density higher than the calculated density of a mixture, in the same proportions, of previously known tantalum-carbon, columbium-carbon and titanium-carbon materials. The percentage of carbon and the density show that all of the carbon present in the substance is chemically combined with the metals, tantalum, columbium and titanium, in monatomic ratio, as TaC, CbC and TiC. Furthermore, a study of the X-ray spectrogram, produced from this material, showed that there were two kinds of crystals present and indicated that, while most of the CbC and TiC was in solid solution in the TaC, apparently, some of the TiC existed in a separate phase with CbC and TaC. This product has thermal and electrical conductivity, stability and resistance to oxidation, greatly superior to any amorphous material containing similar proportions of tantalum, columbium, titanium and carbon, and hard compositions made from this product have a combined hardness and strength greatly superior to that of a composition made from such amorphous material or materials. I believe, however, that this product contains too great a percentage of TiC and that its qualities would be still further improved by a slight reduction in the percentage of TiC present, or by substituting more CbC for TiC.

The following is a specific example of the production of Ta(CbZr)C by the method of my present invention: A thermit charge was prepared consisting of 7710 grams of tantalite ore, which included about 61 per cent Ta₂O₅ and about 12 per cent Cb₂O₅, 2750 grams of aluminum, 108 grams of ZrO₂ and 4563 grams of barium di-oxide. Ignition of this charge gave a regulus of 4036 grams. 1345 grams of the regulus was heated with 1742 grams of aluminum, in a graphite crucible, in the presence of excess carbon, to about 1800° C., for about six hours. By the method of separation heretofore described, about 882 grams of macro-crystalline product, of a bronze color and pronounced metallic lustre, were obtained. Analysis showed that the product contained 7.02 per cent carbon and that it had a density of 12.58. Like the other multi-carbides, the carbon contained was chemically combined with tantalum, columbium and zirconium, in the form of TaC, CbC and ZrC.

This product, like the carbides and multi-carbides of macro-crystalline form heretofore described, had characteristics desirable for the formation of hard compositions of matter, which were greatly superior, as compared with those made from amorphous material, including similar proportions of tantalum, columbium, zirconium and carbon.

My researches show, also, that these multi-carbides, of macro-crystalline form, having the characteristics heretofore described, may be prepared by this method, with CbC as the major constituent. An example of this is the multi-carbide, Cb(TaTi)C.

The following is a specific example of the production of the new macro-crystalline multi-carbide, Cb(TaTi)C, by the method of my present invention, and exemplifies the formation of analogous multi-carbides, having CbC as the major constituent and a carbide or carbides of the metals of the group including tantalum, titanium and zirconium as a minor constituent: 5425 grams of columbite ore, which contained

about 52 per cent Cb_2O_5 and about 17 per cent Ta_2O_5 , 650 grams of TiO_2 , 2436 grams of aluminum, and 2028 grams of barium dioxide, were mixed to form a thermit charge, which, on ignition, gave a regulus of metals weighing 3860 grams. 1400 grams of the regulus were heated with 1800 grams of aluminum, in a graphite crucible, in the presence of excess carbon, at about 1800°C ., for about six hours, as heretofore described. After digestion of the resulting mass in muriatic and hydrofluoric acids, and concentration by gravity means, 470 grams of residue was recovered. This was of macro-crystalline form and size, had a metallic lustre, and was steel-grey in color with a lavender cast. Chemical analysis showed that it contained 11.35 per cent of carbon, 72.02 per cent CbC , 17.90 per cent TaC , and 10.08 per cent TiC . The density of the substance was 7.72. I believe that, in this case also, the TaC and TiC are in solid solution in the major constituent, the CbC . This material, also, gave hard compositions of matter having superior qualities to those made from amorphous materials, containing similar proportions of the columbium, tantalum, titanium and carbon. In short, it showed the expected characteristics, when compared with the multi-carbides heretofore described and indicated that it was in the same class with them.

As I have stated heretofore, the most desirable results and the best products seem to be obtained, in the preparation of these multi-carbides, when the molecular percentage of the carbide or carbides, constituting the minor constituent, does not exceed a certain limit. I believe that this limit is the limit of solubility of the carbide constituting the minor constituent in the carbide constituting the major constituent, and that, when said limit is exceeded, you no longer have a single phase system and, therefore, the thermal and electrical conductivity is not as good and the material does not form quite as satisfactory a hard composition for metal-cutting tools. In the case of the multi-carbides of my present invention, in which TaC is the major constituent, I find that the minor constituent should not constitute substantially more than 40 molecular per cent of the entire substance. In the case of these multi-carbides, in which CbC is the major constituent, this is true also.

The principal use for these novel carbides and multi-carbides, of macro-crystalline form and size, is as one of the starting ingredients in the manufacture of hard compositions of matter intended to be used for metal-cutting tools, dies, corrosion resisting surfaces and the like. These new macro-crystalline carbides and multi-carbides are to be used, in accordance with the known processes of powder metallurgy, for the formation of hard compositions, but the macro-crystalline character of the carbide enters into and so modifies these known processes that a result is achieved, which differs materially from anything possible using amorphous combinations of carbon with tantalum, columbium, titanium or zirconium. Heretofore, it has been the practice, in preparing hard compositions from the amorphous tantalum-carbon material, for example, to grind or comminute said material, with proper proportions of tungsten, in a ball mill and under non-oxidizing conditions, the mill using nickel balls which, by erosion, contribute the desired proportion of nickel to the mixture. This finely comminuted mixture is then formed into pieces of the required shape, by pressure, and the pieces

thus formed are heated under a vacuum to about 1400°C ., for about forty minutes. As the result of this treatment, a hard composition is formed, in which it is probable that the tungsten and nickel serve to effect a union or bond between the particles of tantalum-carbon material. While it has proved possible, by this method, using the amorphous tantalum-carbon material, to produce very hard compositions, they lack the strength which is desirable for materials to be used in metal-cutting tools, dies and like situations. Furthermore, if, in an effort to increase the strength, additional nickel is employed as an ingredient of the composition, the hardness decreases to such an extent that the product is not desirable for use as a metal-cutting tool. The same is true when other metals, such as cobalt, are added to increase the strength of the composition. Furthermore, using the amorphous tantalum-carbon material as a basis for the composition, there is a limit to the amount of tungsten that can be employed as an ingredient, and still have the necessary strength, for, if excess tungsten be added to the composition, it becomes brittle and breaks under a much lower load.

If, instead of amorphous tantalum-carbon material, my new macro-crystalline carbides, or multi-carbides, are used as the starting ingredient, comminuted in a ball mill, under non-oxidizing conditions, with the desired proportions of tungsten and nickel or other metals, and the resulting comminuted mixture treated as heretofore, a hard composition will be produced which is fully as hard, if not harder, than those heretofore made by the old processes, using the amorphous material, and which, combined therewith, has a much greater strength, thus rendering the product more desirable for use in metal-cutting tools, dies and the like. Moreover, the composition has a higher thermal conductivity, with the result that heat is conducted away from the cutting edge much more effectively and this, too, is a very desirable feature from a commercial standpoint. I have discovered that the greater strength and higher thermal conductivity of these compositions, made from the macro-crystalline carbides or multi-carbides, is due to the fact that, after comminution of the macro-crystalline material, it presents a greater area of freshly fractured surface, free from oxidation, as a result of which a more nearly perfect union of the carbide particles is effected.

I have also found that, when my new macro-crystalline carbides or multi-carbides are used as an ingredient of a hard composition of matter, it is possible to include a larger percentage of tungsten in the composition, and this is highly desirable from the standpoint of increasing the strength of the composition at the temperatures developed therein by use in metal-cutting, and also because it assists in raising the thermal conductivity of the composition.

A further advantage of these macro-crystalline carbides and multi-carbides resides in the fact that, by comminuting them for greater or lesser times or under different conditions, the particles may be reduced to different grades of fineness, so that the carbide, in different degrees of fineness, may be mixed for forming a hard composition of matter. I believe that this practice improves the strength of the resulting composition. This, of course, is impossible with amorphous material.

Each of the macro-crystalline carbides and multi-carbides herein described has a very high

melting point, it being, in each instance, above 3400° C. Each of these carbides and multi-carbides is also extremely resistant to acids and alkalis. In fact, the only solvent which I have found for them is a mixture of hydrofluoric and nitric acids.

In the specification and claims, I have used the term "phase" in the usual physical chemical sense, as defined, for example, by J. L. R. Morgan, in his "Elements of Physical Chemistry", 5th ed., page 137, (1914): "A phase is a physically distinct, mechanically separable portion of a system; it need not however be chemically simple." Whenever I have referred to a single phase system or body, I mean a body or substance containing but one such phase.

The hard compositions of matter made from these macro-crystalline carbides or multi-carbides and the method of making such compositions of matter are not claimed herein, being claimed in U. S. Patent No. 2,093,844, dated September 21, 1937, based upon my application Serial No. 39,505, filed September 6, 1935, in U. S. Patent No. 2,093,845, dated September 21, 1937, based upon a divisional application thereof Serial No. 66,707, filed March 2, 1936, and in U. S. Patent No. 2,123,574, U. S. Patent No. 2,123,575, and U. S. Patent No. 2,123,576, each dated July 12, 1938, based upon applications Serial No. 127,558, Serial No. 127,559, and Serial No. 127,560, respectively, each filed February 24, 1937, as divisional applications of said application Serial No. 39,505.

The present application is directed to the carbides and multi-carbides themselves, and the process of making the carbides or multi-carbides.

I am aware that the invention disclosed herein, both as regards the product and the process, is susceptible of considerable variation without departing from the spirit thereof, and, therefore, I claim as my invention broadly as indicated by the appended claims.

What I claim is:

1. The new product of reaction between a metal of the group consisting of tantalum and columbium, with carbon, produced in the presence of a molten metallic menstruum differing from the reactants, said product consisting of macro-crystalline carbide of the group of carbides consisting of TaC and CbC, characterized by its metallic lustre, crystalline form, and a combined carbon content in monatomic ratio to the metal present.

2. The new product of reaction between tantalum and carbon, produced in the presence of a molten metallic menstruum other than tantalum, consisting of macro-crystalline TaC, characterized by a golden color, metallic lustre, crystalline form and a combined carbon content in monatomic ratio to the tantalum content.

3. The new product of reaction between tantalum and carbon, produced in the presence of a molten metallic menstruum other than tantalum, consisting of macro-crystalline TaC having a density between 14.3 and 14.6.

4. The new product of reaction between columbium and carbon, produced in the presence of a molten metallic menstruum other than columbium, consisting of macro-crystalline CbC characterized by a lavender color, a metallic lustre, crystalline form, and a combined carbon content in monatomic ratio to the columbium content.

5. The new product of reaction between columbium and carbon, produced in the presence of a molten metallic menstruum other than columbium, consisting of macro-crystalline CbC having a density between 7.7 and 7.9.

6. The new product of reaction between a metal of the group consisting of tantalum and columbium, in a major proportion, and metal, in a minor proportion, selected from the group consisting of tantalum, columbium, titanium and zirconium, other than the metal selected from the first-named group, with carbon, produced in the presence of a molten metallic menstruum other than the selected metals, and consisting of particles characterized by metallic lustre, crystalline form and a combined carbon content in monatomic ratio to the metals present.

7. The new product of reaction between metals selected from the group consisting of tantalum, columbium, titanium and zirconium, with carbon, consisting of particles composed essentially of a carbide of a metal of the group consisting of tantalum and columbium, as a major constituent, and, as a minor constituent in solid solution in the major constituent, material selected from the group consisting of the carbides of tantalum, columbium, titanium and zirconium other than the carbide selected from the first-named group, produced in the presence of a molten metallic menstruum other than the selected metals, said particles being characterized by metallic lustre, crystalline form and a combined carbon content in monatomic proportion to the metals present.

8. A multi-carbide existing as a single phase body, consisting essentially of, as a major constituent, a carbide of a metal of the group consisting of tantalum and columbium, and, as a minor constituent in appreciable amount up to 40 molecular per cent of the multi-carbide, material other than the major constituent selected from the group consisting of the carbides of tantalum, columbium, titanium and zirconium, produced in the presence of a molten metallic menstruum other than the selected metals, and characterized by metallic lustre, crystalline form and a combined carbon content in monatomic proportion to the metals present.

9. A multi-carbide consisting of, as a major constituent, a carbide of a metal of the group consisting of tantalum and columbium, and, as a minor constituent in solid solution in the major constituent, material, other than the major constituent, selected from the group consisting of the carbides of tantalum, columbium, titanium and zirconium, produced in the presence of a molten metallic menstruum other than the selected metals, and characterized by metallic lustre, crystalline form, and a combined carbon content in monatomic proportion to the metals present.

10. The method of producing carbides which comprises the reacting of metal selected from the group consisting of tantalum and columbium, with carbon, in a molten metallic menstruum selected from the group consisting of aluminum, iron, manganese and beryllium, at a temperature above the melting point of the menstruum, solidifying the resulting mass, and separating the carbide therefrom.

11. The method of producing carbides which comprises dissolving in a molten metallic menstruum a metal selected from the group consisting of tantalum and columbium, as a major constituent, and, as a minor constituent, a metal selected from the group consisting of tantalum, columbium, titanium, and zirconium other than the metal selected from the first-named group, reacting said solution with carbon, solidifying the resultant mass, and separating the carbide therefrom.

12. The method of producing carbides which

comprises the reacting of metal from the group consisting of tantalum and columbium, with carbon, in a molten metallic menstruum differing chemically from the metal from which the carbide is to be formed, at a temperature above the melting point of the menstruum, solidifying the resulting mass, and separating the carbide therefrom.

13. The method of producing carbides which comprises dissolving a metal selected from the group consisting of tantalum and columbium in a molten metallic menstruum other than tantalum or columbium, subjecting said menstruum solution of the metal to prolonged heating, at a temperature above the melting point of the menstruum, in the presence of carbon, solidifying the resulting mass, and separating the carbide therefrom.

14. The method of producing carbides which comprises the reacting of metal from the group consisting of tantalum and columbium, in solution in a molten menstruum formed of a metal other than tantalum or columbium, with carbon, at a temperature exceeding the melting point of the menstruum solution, solidifying the resulting mass, and separating the carbide therefrom.

15. The method of producing carbides which comprises dissolving metal from the group consisting of tantalum and columbium in a molten menstruum of metal from the group consisting of aluminum, iron, manganese and beryllium, subjecting said molten menstruum solution to prolonged heating, in the presence of carbon, at a temperature exceeding the melting point of the menstruum solution, solidifying the resulting mass, and separating the carbide therefrom.

16. The method of producing carbides which comprises the reacting of metal from the group consisting of tantalum and columbium, in solution in molten aluminum, with carbon, solidifying the resulting mass, and separating the carbide therefrom.

17. The method of producing tantalum carbide, which comprises the reacting of tantalum in a menstruum selected from the group consisting of aluminum, iron, manganese, and beryllium, with carbon, at a temperature exceeding the melting point of the menstruum metal and below the melting point of tantalum, solidifying the resulting mass, and separating the tantalum carbide therefrom.

18. The method of producing tantalum carbide, which comprises the dissolving of tantalum in molten aluminum, subjecting said solution to prolonged heating, in the presence of carbon, at a temperature exceeding the melting point of said solution and below the melting point of tantalum, solidifying the resulting mass, and separating the tantalum carbide therefrom.

19. The method of producing columbium carbide, which comprises the reacting of columbium in a menstruum metal selected from the group consisting of aluminum, iron, manganese and beryllium, with carbon, at a temperature exceeding the melting point of the menstruum metal, solidifying the resulting mass, and separating the columbium carbide therefrom.

20. The method of producing columbium carbide, which comprises the dissolving of columbium in molten aluminum, subjecting said solution to

prolonged heating, in the presence of carbon, at a temperature exceeding the melting point of said solution, solidifying the resulting mass, and separating the columbium carbide therefrom.

21. The method of producing multi-carbides of metals, which comprises the solution, in a molten menstruum selected from the group consisting of aluminum, iron, manganese and beryllium, of a metal selected from the group consisting of tantalum and columbium, as a major constituent, and, as a minor constituent, metal selected from the group consisting of tantalum, columbium, titanium and zirconium, other than the metal selected from the first-named group, subjecting said menstruum solution to prolonged heating, in the presence of carbon, at a temperature exceeding the melting point of the menstruum solution and below the melting point of tantalum, solidifying the resulting mass, and separating the multi-carbide therefrom.

22. The method of producing multi-carbides of metals, which comprises the solution in molten aluminum of a metal selected from the group consisting of tantalum and columbium, as a major constituent, and, as a minor constituent, metal selected from the group consisting of tantalum, columbium, titanium and zirconium, other than the metal selected from the first-named group, subjecting said solution to prolonged heating, in the presence of carbon, at a temperature exceeding the melting point of the solution and below the melting point of tantalum, solidifying the resulting mass, and separating the multi-carbide therefrom.

23. The method of producing multi-carbides, which comprises preparing a thermit charge embodying an ore containing a metal selected from the group consisting of tantalum and columbium, in a major proportion, and metal in a minor proportion selected from the group consisting of tantalum, columbium, titanium, and zirconium, other than the metal selected from the first group, igniting said thermit charge, melting the regulus of metals obtained thereby with menstruum metal selected from the group consisting of aluminum, iron, manganese and beryllium, subjecting said melt to prolonged heating, in the presence of carbon, at a temperature exceeding the melting point of the menstruum metal, solidifying the resulting mass, and separating the multi-carbide therefrom.

24. The method of producing carbides which comprises reacting metal selected from the group consisting of tantalum and columbium in the presence of a molten metallic menstruum other than said selected metal, with carbon, solidifying the resulting mass, digesting the material of said mass with hydrochloric acid and then with hydrofluoric acid, and separating the residue insoluble in said acids.

25. The method of producing carbides which comprises reacting metal selected from the group consisting of tantalum and columbium in the presence of molten aluminum, with carbon, solidifying the resulting mass, digesting the material of said mass with hydrochloric acid and then with hydrofluoric acid, and separating the residue insoluble in said acids.

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