This invention relates to the production of metals and alloys and has for an object the provision of a new and improved method of obtaining or producing metals and alloys from metal compounds or in some cases direct from their minerals, ores or concentrates, particularly refractory metals of the fourth and fifth groups of the periodic system, such as tantalum, columbium, titanium, zirconium, hafnium and vanadium.

Another object of the invention is the provision of a novel method of producing a metal by the interaction of its carbide with its oxide without melting the metal.

A further object of the invention is the provision and production of a metal alloy wherein the metals are in the same relative proportions as they occurred in the starting material.

Another object of the invention is to simplify and to expedite the production of metals and alloys from their compounds or other sources whereby economically to obtain such metals and alloys in commercial form.

Other objects and advantages of the invention will appear more fully from the following description.

The simplified method of the present invention, briefly described, involves the interaction of metal oxide or oxidized metal and metal carbide or carburized metal at a sub-melting temperature respecting the melting temperature of the metal being produced, whereby to reduce or deoxidize the metal oxide or oxidized metal and to carburize the metal carbide or carburized metal leaving substantially commercial metal.

The carbide and oxide may be made by any suitable methods, or, as will presently appear, we may use the metal ore or any suitable metal-containing mineral or concentrate as the starting material, and prepare or derive either the carbide or the oxide or both the carbide and the oxide therefrom. In proceeding with the description of the invention, we will describe it in connection with the production of tantalum, columbium and the alloys thereof, it being distinctly understood that except as is particularly pointed out the method is similarly applicable to the other metals of the fourth and fifth groups, except where it is apparent from the text that the method is solely applicable to the particular example chosen.

As already suggested, in preparing the carbide we may use as a starting material a pure, finely divided oxide of tantalum and/or columbium made by any suitable method, tantalum and/or columbium ore, or any suitable tantalum- and/or columbium-containing mineral or concentrate. That starting material is carburized by mixing it with sufficient carbon, preferably in the form of lamp black or powdered coal, completely to reduce or to deoxidize the starting material and to convert it into a carbide of the same metal or metals when the mixture is heated to the reducing temperature. When a starting material other than the pure oxide is employed, the carbide so produced is termed an unrefined or ore carbide.

The mixture of the starting material and carbon just described is placed in a suitable container or crucible (e.g., a graphite container or crucible) provided with a vent, and the loaded container is heated to the reducing temperature for the starting material in a molybdenum-wound tube furnace, in a high frequency furnace, or by other suitable heating means whereby to cause the carbon to react with the starting material. The reducing temperature for the starting materials just described above has been found to range from about 1400° to 2000° C.

During the foregoing reaction carbon monoxide gas is evolved and is burned at the vent of the container and the more volatile constituents in case a starting material other than the pure oxide is employed are partially or highly volatilized out of the mixture. The residue where the pure oxide was the starting material is a carbide of tantalum and/or columbium. Where the ore or a starting material other than the pure oxide is employed, the residue is the unrefined or ore carbide which is a carburized mass with a composition depending upon the original composition of the ore or other starting material minus the oxygen and the constituents volatilized during the foregoing heat treatment.

That unrefined carbide is refined by pulverizing the ore carbide and subjecting the pulverulent material to appropriate treatments for removing undesirable constituents. The precise refining treatment or treatments form no part of the present invention, and of course will depend upon the composition of the unrefined carbide and upon the constituents to be removed therefrom. Any suitable treatments including subjecting the pulverulent unrefined carbide to acid baths, leaching treatments, Wilfley Table treatments, etc., may be employed for effecting the desired refinement.

It may be well, however, to illustrate the refining operation by reciting here a refinement of an unrefined carbide to produce substantially...
pure carbide of tantalum and/or columbium. A typical unrefined carbide at this stage of our novel method will contain some silica which was not volatilized during the above described heat treatment, and in addition some iron and manganese which are converted into metal or compounds that are readily attacked by mineral acids. Particles or crystals of tantalum carbide, columbium carbide, or tantalum-columbium carbide do not hold iron, manganese, etc., in solution, and these carbides are therefore produced in a pure condition in the presence of iron, manganese or other impurities which may be contained in the starting material. In other words, the impurities in the unrefined carbides are merely physically mixed therewith and are not chemically combined. Since mineral acids do not react with or attack the carbides of tantalum and/or columbium, the pulverized unrefined carbide is treated with hydrochloric acid, and finally with hydrofluoric acid, to remove iron, manganese, silica, and other such constituents from the unrefined carbide, thus leaving a refined carbide of tantalum and/or columbium, the relative proportions of the tantalum and columbium being the same as they were in the ore or other starting material.

The oxide for reacting with the carbide is preferably an oxide of the metal or metals in the carbide, although the oxide may be of a different metal from that employed in the carbide where it is desired to make an alloy of the metal in the carbide with the metal in the oxide. For example, tantalum oxide may be interacted with tantalum carbide; columbium oxide may be employed for interaction with columbium carbide; and tantalum-columbium oxide may be employed for interaction with tantalum-columbium carbide, although the oxide of either tantalum or columbium may be interacted with the carbide of the other of those metals. The oxide may be some of the pure, finely divided oxide described as a starting material from which the carbide could be made, or the oxide may be prepared by any suitable method.

That oxide may be prepared from some of the refined carbide by directly igniting the carbide and burning out all of the carbon whereby to convert the refined carbide into an oxide of the corresponding metal or metals.

In order to obtain tantalum, columbium, or a tantalum-columbium alloy according to our novel method, the carbide of tantalum and/or columbium and the oxide of tantalum and/or columbium produced as already described, or by any suitable methods, are interacted by subjecting a balanced and an intimate mixture thereof to a temperature sufficient to deoxidize or to reduce the oxide and to decarburize the carbide. Accordingly, the tantalum and/or columbium carbide and the tantalum and/or columbium oxide are intimately mixed, for example by grinding them together in a ball mill in such proportions that the amount of carbon in the mixture is substantially equivalent to the amount of oxygen in the mixture. That is to say, a balanced carbon-oxygen mixture is made by providing about one atom of carbon for every atom of oxygen in the mixture.

That intimately mixed powder is pressed into bars at a pressure of about 5 to about 40 tons per square inch on the face of the bar. A hydraulic or other suitable press may be employed for the pressing operation.

The bars formed as just described are subjected to a heat treatment. The purpose of the heat treatment is to cause the interaction between the carbide and the oxide in each bar, whereby the carbon and oxygen thereof will combine to form carbon monoxide, leaving the de-carburized and the deoxidized metal particles in such intimate association that they will readily combine. We may describe, by way of example, a suitable heat treatment to accomplish that purpose. Each bar is suspended or otherwise supported in a tube or other suitable container made from a material having a melting temperature which is high with respect to the melting temperature of the metal or metals in the bar. For example, such tubes are made of graphite, tantalum, tungsten, etc., and are preferably electrically heated in a suitable electric furnace. For that purpose the ends of the tube may be held by heavy water-cooled copper terminals which pass through insulated sections of the heat-treating furnace. For the production of tantalum or columbium we prefer to use heavy sheet tantalum for the tube.

After inserting a container or tube with a bar therein in the furnace, the furnace is evacuated or hydrogen, argon, helium or other suitable gas is stream through therethrough and the heating is commenced. The atmospheric conditions in the furnace are maintained while the heating is continued. When the temperature of reaction between the carbide and the oxide in the bar is reached there is an evolution of carbon monoxide which may be removed by the vacuum pump or pumps or, as the case may be, with the stream of gas. When the evolution of the carbon monoxide begins to subside, the temperature of the bar is raised but not sufficiently to risk melting the metal. That temperature is maintained until the vacuum gauge or an analysis of the gas stream at the exhaust side of the furnace shows that the carbon monoxide given off by the bar has been substantially entirely removed from the furnace. For the production of tantalum and/or columbium we prefer to use the vacuum furnace. We find that 1,600° C, is a suitable initial temperature of reaction.

After cooling, the bar is removed from the furnace. If the balance between the carbide and the oxide has been properly adjusted the resulting metal of tantalum, columbium or tantalum-columbium alloy will be substantially free of both carbon and oxygen. Such metals and alloys have been prepared by the foregoing method, which show upon chemical analysis as little as 0.02% carbon and no oxygen.

Tantalum ore as well as columbium ore is frequently tantalite and columbate of iron and manganese with or without small amounts of one or more of such metals as titanium, zirconium, hafnium, vanadium, and other refractory metals, and is conventionally described by the formula (Fe, Mn) (Cb, Ta)₂O₆, although such ores range in fine gradations from the substantially pure columbate to the substantially pure tantalate. By our novel method we therefore produce commercial tantalum or columbium, or a commercial alloy of tantalum and columbium, the amount of either of the mentioned metals with respect to the other metal varying from negligible quantities up to substantially 100% and any of those commercial metals or alloys may include small amounts of one or more of the other refractory metals which were present in the ore or other starting material.

Thus by starting with the ore the resulting...
product will contain tantalum and/or columbium with or without one or more other refractory metals which were present in the ore in their natural proportions, that is to say, in the same relative proportions as they occurred in the ore or other starting material, and due possibly to the very intimate association of the tantalum and columbium throughout the method as well as to the tantalum and columbium respectively being in their natural forms or states, and therefore probably being isomorphous or at least atomically (in contradistinction with aggregatively) intermixed, the resulting material is exceedingly pure.

It is desirable that the metals and alloys produced as described above include as small an amount of carbon as possible. We have discovered that the amount of carbon in the final product may be controlled by varying the grain size or mesh of the carbide which is mixed with the oxide just prior to the pressing operation, and/or varying the pressure for converting the mixed oxide and carbide into bars, and/or by varying the amount of the oxide relative to the amount of the carbide in making the mixture for pressing.

If desired the bar as formed above may be conditioned either by alternate mechanical workings (e.g. hammering) and one or more repetitions of the heat treatment last described above, or by hydrogenating it, pulverizing the hydrogenated bar, and dehydrogenating the pulverized mass as described in our United States Patent No. 2,137,279. In some cases we condition the deoxidized, decarburized product of the heat treatment by a combination of the conditioning operations just described. After such conditioning tantalum bars and columbium bars made as described above have all of the properties of commercial tantalum and columbium respectively. Bars of combined tantalum and columbium have a high resistance to corrosion.

It will thus be seen that by the novel method of the invention commercial tantalum, commercial columbium, and commercial tantalum-columbium alloy may be economically derived from the raw materials used for the starting material and having the properties of the tantalum, columbium, and therefore probably isomorphous or at least atomically (in contradistinction to aggregatively) intermixed, the tantalum and columbium evidently flow together or combine to produce a solid homogeneous product when heated treated as described above.

While we have described certain specific furnace constructions and crucibles in connection with the furnace for interacting the carbide and the oxide, and for heat treating the resulting metal, it will be understood that the method of the invention is by no means limited by the reclamation of such apparatus, the important consideration being to cause tantalum carbide or columbium carbide, to interact either with the oxide of tantalum or the oxide of columbium, or to cause tantalum-columbium carbide to interact with the oxide of tantalum and columbium, whereby to leave tantalum, columbium, or a tantalum-columbium alloy. As pointed out above, the method is applicable to the production of titanium, zirconium, hafnium and vanadium as well as tantalum and columbium, or to any metal or alloy the carbide and oxide of which have an interacting temperature below the melting temperature of the metal and the oxide, and where the oxide has a volatilization temperature sufficiently high to prevent the removal of an appreciable quantity of the oxide as such from the mixture at the interacting temperature.

It will thus be seen that by the novel method of the invention, commercial metal, either as a single metal or as a combination of metals, may be economically derived from metal compounds. Where a plurality of metals is included in the commercial metal or the final product, the metals thereof are present in the same relative proportions as they occurred in the starting materials or compounds.

While we have described a preferred embodiment of the invention, many modifications may be made without departing from the spirit of the invention. The invention is not, therefore, limited to the precise details set forth above, but includes all changes within the spirit and scope of the appended claims.

Having thus described our invention, what we claim as new and secure to be patented by United States Letters Patent is:

1. The improvement in the art of producing refractory metal of the fourth and/or fifth groups which includes pressing, to the form of a coherent bar, a carbon-oxygen balanced powder mixture of carbide and oxide of the metal being produced, furnace heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes, and then, after the reaction is largely completed, raising the temperature of the bar to a point below the melting point of the metal being produced to complete the reaction.

2. The improvement in the art of producing refractory alloys of the fourth and/or fifth groups, which consists in forming a carbon-oxygen balanced mixture of a carbide of intimately associated refractory metals and an oxide of corresponding refractory metals, pressing the powder mixture to the form of a coherent bar, furnace heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes as such, and then, after the reaction is largely completed, raising the temperature of the bar to a point below the least high melting point of the metals constituting the alloy being produced to complete the reaction.

3. The method of producing refractory metal of the fourth and/or fifth groups which consists in forming a carbon-oxygen balanced mixture of carbide and oxide of the metal being produced, and causing the carbide to be decarburized, the oxide to be reduced, and the metal to be formed, by first heating the mixture to a temperature somewhat below the temperature at which substantial volatilization of the oxide as such occurs, and then, after the reaction is largely completed, heating the mixture to a higher temperature below the melting point of the metal being produced, to complete the reaction.

4. The method of producing refractory alloys of the fourth and fifth groups in forming a carbon-oxygen balanced mixture of a carbide of intimately associated refractory metals and an oxide of corresponding refractory metals, and causing the carbide to be decarburized, the oxide to be reduced, and the alloy to be formed, by heating the mixture to a temperature some-
what below the temperature at which substantial volatilization of the oxide as such occurs, and then, after the reaction is largely completed, heating the mixture to a higher temperature below the least high melting point of the metals of the alloy being produced, to complete the reaction.

5. A method of producing refractory metal of the fourth and/or fifth groups, which comprises interacting a carbide and an oxide of the refractory metal being produced, in such proportions that substantially all of the carbon will combine with substantially all of the oxygen to form carbon monoxide, such interaction being accomplished by first heating the carbide and oxide to a temperature below the temperature at which substantial volatilization of the oxide as such occurs, and then, after the reaction is largely completed, heating to a higher temperature which is below the melting point of the metal being produced, to complete the reaction.

6. A method of producing a refractory alloy of the fourth and/or fifth groups which comprises interacting a carbon-oxygen balanced mixture of a carbide of intimately associated metals and an oxide of corresponding metals to remove carbon and oxygen from the mixture, whereby to form an alloy of the metals, such interaction being accomplished by first heating the mixture to a temperature below the temperature at which substantial volatilization of the oxide as such occurs, and then, after the reaction is largely completed, heating to a higher temperature below the melting points of the metals of the refractory alloy being produced, to complete the reaction.

7. The improvement in the art of producing refractory metal of the fourth and/or fifth groups, which includes pressing, to the form of a coherent bar, a carbon-oxygen balanced powdered mixture of carbide and oxide of the metal being produced, and heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes as such.

8. The improvement in the art of producing refractory alloys of the fourth and/or fifth groups which consists in forming a carbon-oxygen balanced mixture of a carbide of intimately associated refractory metals and an oxide of corresponding refractory metals, pressing the powdered mixture to the form of a coherent bar, and heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes as such.

9. A method of producing a refractory metal or alloy of the fourth and/or fifth groups from compounds, ores, minerals and concentrates thereof which comprises carburizing the desired compound or the like with sufficient carbon to form a carbide with substantially all the refractory metal content thereof, purifying the resultant ore carbide to produce substantially all refractory metal carbide, converting a part of the carbide to oxide by direct ignition, mixing the oxide with the carbide to form a substantially carbon-oxygen balanced mixture, pressing the mixture into a bar, furnace-heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes as such, then, after the reaction is largely completed, raising the temperature of the bar to a higher temperature below the least high melting point of the metal or metals contained in the bar to complete the reaction, then hydrogenating the reaction slug to produce brittle hydride of the metal, then crushing the embrittled slug to powder, then dehydrogenating the hydride powder to form metal powder, pressing the metal powder into a bar and sintering the bar to form a dense coherent mass.

10. A method of producing a refractory metal or alloy of the fourth and/or fifth groups from compounds, ores, minerals and concentrates thereof which comprises carburizing the desired compound or the like with sufficient carbon to form a carbide with substantially all the refractory metal content thereof, purifying the resultant ore carbide to produce substantially all refractory metal carbide, converting a part of the carbide to oxide by direct ignition, mixing the oxide with the carbide to form a substantially carbon-oxygen balanced mixture, pressing the mixture into a bar and furnace-heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes as such. Then, after the reaction is largely completed, heating the mixture to a higher temperature below the temperature of the bar to cause interaction of the carbide and oxide as such occurs, then, after the reaction is largely completed, raising the temperature of the bar to a higher temperature below the least high melting point of the metal or metals contained in the bar to complete the reaction, then hydrogenating the reaction slug to produce brittle hydride of the metal, then crushing the embrittled slug to powder, then dehydrogenating the hydride powder to form metal powder, pressing the metal powder into a bar and sintering the bar to form a dense coherent mass.

11. A method of producing a refractory metal or alloy of the fourth and/or fifth groups which comprises interacting a carbon-oxygen balanced mixture of a carbide of intimately associated metal or metals and an oxide of corresponding metal or metals to remove carbon and oxygen from the mixture whereby to form an alloy of the metals, such interaction being accomplished by first heating the mixture to a temperature below the temperature at which substantial volatilization of the oxide as such occurs, and then, after the reaction is largely completed, heating to a higher temperature below the melting points of the metals of the refractory alloy being produced, to complete the reaction.

12. A method of producing a refractory metal or alloy of the fourth and/or fifth groups which comprises interacting a carbon-oxygen balanced mixture of a carbide of intimately associated metal or metals and an oxide of corresponding metal or metals to remove carbon and oxygen from the mixture whereby to form an alloy of the metals or a metal, such interaction being accomplished by first heating the mixture to a temperature below the temperature at which substantial volatilization of the oxides as such occurs and then, after the reaction is largely completed, heating to a higher temperature below the melting point of the metal or metals of the refractory alloy being produced, to complete the reaction, thereafter hydrogenating the reaction mass to produce a brittle hydride of the metal or metals, then crushing the embrittled mass to powder, then dehydrogenating the hydride powder to form metal powder, pressing the metal powder into a bar and sintering the bar to form a dense coherent mass.

13. The improvement in the art of producing refractory metals or alloys of the fourth and/or fifth groups which consists in forming a carbon-oxygen balanced mixture of a carbide of refractory metal or intimately associated refractory metals and an oxide of the corresponding refractory metal or metals, pressing the mixture to the form of a coherent bar, heating the bar to a temperature below the temperature at which substantial volatilization of the oxide as such occurs and then after the reaction is largely completed, heating to a higher temperature below the melting point of the metal or metals of the refractory alloy being produced, to complete the reaction and thereafter hydrogenating the reaction slug to produce brittle hydride of the metal or alloy, then crushing the embrittled slug to
powder, then dehydrogenating the hydride powder to form metal powder, pressing the metal powder into a bar, and sintering the bar to a dense coherent mass.

14. The improvement in the art of producing refractory metal of the fourth or fifth group, which includes mixing an oxide of the desired metal with sufficient carbide to form a carbide with substantially all the refractory metal content thereof, mixing the carbide with sufficient oxide to form a substantially carbon-oxygen balanced mixture, forming a coherent bar from said mixture, heating the bar to cause interaction of the carbide and oxide at a temperature below the temperature at which the oxide volatilizes as such, and then after the reaction is largely completed, heating to a higher temperature below the melting point of the metal being produced, to complete the reaction.

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