

UNITED STATES PATENT OFFICE

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PRODUCTION OF RARE METALS

No Drawing.

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This invention relates to a method of producing refractory metal powders and more particularly to a method of producing tantalum, columbium and vanadium metal powders, substantially free from embrittling compounds containing such gases as hydrogen, nitrogen and the like.

In copending application Serial No. 618,544, filed February 12, 1923, and assigned to the same assignee as the present invention, there is described a process for reducing the difficultly reducible oxides of such rare refractory metals, as uranium, thorium and the like and although reference is made therein to the reduction of vanadium, columbium, tantalum, etc. and suitable results have been obtained by the process as set forth in said application the process as described herein constitutes an improvement upon such prior process.

It has been found that in practicing the process described in the aforesaid application in connection with the reduction of oxides of tantalum, columbium and vanadium, that the resulting metal powder when compacted and sintered in vacuo as described, is usually brittle and cannot be cold worked. It has been determined that this embrittled condition is primarily due to the presence of dissolved gases in the sintered metal body. Such dissolved gases are retained to a high temperature and cannot be completely eliminated from the metal body until fusion in vacuo is obtained.

It was proposed in the aforesaid application to provide in the bomb in which the reduction is effected a small quantity of excess calcium for the purpose of removing the residual air and moisture contained within the bomb after the same was sealed off with a ground stopper. In the normal practice of this method of reduction as by the prior process this excess calcium will effectually clean-up water vapor and residual air, but it is found that such clean-up does not take place

within the bomb normally until at or about the initial temperature at which the oxide reduction reaction commences. The reduction reaction being exothermic is accumulative in heat energy for a short space of time and a relatively high temperature is obtained within the bomb, high enough in the case of metals, such as vanadium, and metals of similar melting points, to be recovered in large size beads. During this relatively unstable reduction period, intermetallic hydrides and nitrides of tantalum, columbium and vanadium may be formed and are subsequently difficult of removal.

In view of the foregoing it is an object of our invention to modify and improve the prior process so that the residual gases, air and moisture, etc., may be substantially eliminated from the reaction chamber at a lower temperature than the initial reduction reaction of the charge and to form compounds with a more electro-positive element than the reduced metal, thereby eliminating the possibility of the reduced metal forming compounds with or dissolving the hydrogen, nitrogen, and the like, during the subsequent reduction reaction.

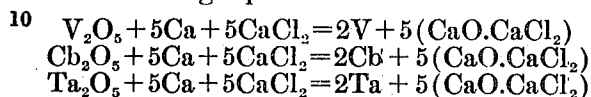
It is also an object of our invention to provide a process for the production of metals, such as tantalum, columbium and vanadium, substantially free from dissolved or combined hydrogen.

A further object of our invention is to provide a process for reducing the oxides of tantalum, columbium and vanadium, whereby pure powders of such metals or beads thereof may be obtained which by suitable heat treatment in vacuo are readily susceptible to cold working.

Another object of our invention is to provide a process for producing tantalum, columbium or vanadium in the coherent homogeneous state which is ductile so that it may be mechanically worked at low temperatures.

Other objects and advantages may be readily seen by those skilled in the art.

In accordance with the present process, the oxides of the rare metals tantalum, columbium and vanadium are mixed with calcium and calcium chloride in the proportions required to effectively reduce them. The proportions used may be expressed according to the following equations:



These proportions as given may be employed advantageously in this process. Other proportions of oxide to calcium and calcium chloride may be used depending upon the heat energy of the reduction reaction that it is desired to obtain. Normally, by varying the calcium chloride content of the charge a wide range in reduction reaction temperature may be obtained, and metal particle sizes consequently may be varied from large beads to fine metal powders. Also, with increase in melting point of the metal, such as tantalum, the calcium chloride content must be appreciably lowered to effect substantial removal of the oxygen from the oxide. Furthermore, although these proportions as given in the reaction expressed above are based upon the use of refractory metal oxides the halides and fluorides may be used with advantage in this method.

The reduction charge, after intimately mixing, is placed in an iron bomb, such as shown in the aforesaid application and upon the charge is placed a small piece of alkali metal such as potassium or sodium. The bomb is then sealed so as to exclude air and then the same is heated to a temperature of 900 to 1000° centigrade at which temperature it is held for a sufficient length of time depending upon the particular oxide employed or the proportions used to bring about complete reduction of the refractory oxide.

During the reaction which takes place within the bomb the alkali metal added to the charge, owing to its lower temperature of volatilization than the calcium heretofore employed, is vaporized and combines with the water vapor and residual air in the bomb to form alkali metal compounds. During the subsequent reduction reaction within the bomb of the calcium on the refractory metal oxide or other compound employed the heat energy difference between the stable sodium hydrides, nitrides and the like and the calcium is so small that material reduction of the alkali compounds is not effected. Therefore, the effect produced regardless of what the true theory may be, is substantially that through the addition of the alkali metal to the reaction mixture a prior clean-up of deleterious gases, such as moisture, hydrogen, nitrogen, etc., is effected and these gases are

effectually removed from the reduction reaction and are not absorbed by the rare metal powder produced by the reduction reaction. We have found that ductile bodies of vanadium, for example, in the form of large beads may be obtained directly by this reduction method by raising the heat energy of the reduction reaction only when such alkali metal addition has been made to the charge.

After the reduction reaction has been effected and the bomb and contents cooled to room temperature, the charge must be subsequently disintegrated by washing with water and dilute acid in such a manner as to prevent undue absorption of hydrogen, nitrogen in the rare metal powder. During the disintegration of the charge in water, considerable hydrogen is evolved through the reaction of excess calcium used in the reduction with the water and as such is probably absorbed by the metal powder. Precautions should be taken to prevent undue heating of the solution during such disintegration as the activity of the metal powders at slightly elevated temperatures is very great. The washing of the powder with water and dilute acid removes such reaction products as calcium-calcium oxide and calcium chloride. The powder is permitted to settle, the supernatant liquor is decanted and thereafter the metal powders are washed successively with alcohol and ether to remove the moisture and dried preferably in vacuo for several hours to remove the last traces of alcohol and ether. Thereafter the powder is sieved to remove the coarser particles. The metal powder thus obtained may be pressed into any desired shape and heat treated to coherent metal bodies.

It is preferable in heat treating the compressed bars or discs of tantalum, columbium and vanadium metal to conduct the heating in vacuo or under slightly oxidizing conditions and extreme care must be exercised to remove from the heating chamber and from the metal powder all of the absorbed gases, such as hydrogen, nitrogen and the like, by prolonged evacuation methods as the compacted metal powder, even though maintained in semi-vacuo until ready for heat treating, will absorb large amounts of atmospheric gases. It is also well, after the first evacuation of the treating chamber, to flush the chamber with oxygen or an inert gas, such as argon, neon, etc., to effect substantial elimination of hydrogen, nitrogen, etc. The residual gases also may be removed from the reaction chamber by suitable flashing of a getter, such as misch metal, magnesium and the like, in the treating chamber.

After the chamber has been completely evacuated, a current of electricity may be passed through the bar and the temperature raised in successive stages to such a temperature as will effectively sinter the powdered

particles together. In sintering the bar it is preferable to degasify very slowly, particularly at a temperature low enough so that no reaction can take place between the adsorbed or absorbed gases and the metal powder. Following thorough degasification, the usual sintering method may be employed.

An ingot prepared in accordance with the foregoing process will be found to be substantially free from the embrittling effect of dissolved gases, such as hydrogen, nitrogen, and the like, and amenable to cold mechanical working methods.

Modifications of the process described above may occur to those skilled in the art but such as follow within the scope of the appended claims are contemplated by us as forming part of our invention. As an example, it may be found desirable to produce by this reduction method, alloys of tantalum, columbium or vanadium with themselves or with other metals, such as thorium, zirconium, titanium, tungsten, molybdenum, chromium, iron, cobalt, nickel, manganese, etc., where the preponderant metal will be tantalum, columbium or vanadium in which case the process as described above will be found effective in eliminating the embrittling effect of hydrogen and nitrogen. In the past it has been very difficult to obtain satisfactory ductile alloys of these metals with others as named. By reducing a charge, according to this disclosure, to which has been added the desired amount of alloyed metal, such as thorium in the form of the oxide, an admixed metal powder of tantalum, for instance, containing 5 to 10% thorium or vanadium or chromium may be obtained which can be compacted and heat treated substantially as disclosed in this process.

What is claimed is:

1. The method of preparing tantalum, vanadium and columbium metal powder free from hydrogen and nitrogen, which comprises heating a mixture containing an oxide of these metals, calcium and calcium chloride in a sealed or evacuated container in the presence of an alkali metal.

2. The method of preparing tantalum, vanadium and columbium free from hydrogen and nitrogen, which comprises heating to the reaction temperature in the absence of air, a mixture consisting of an oxide of one of said metals, an alkaline earth metal and an alkaline earth halide, said heating being effected in the presence of the vapor of an alkali metal.

3. The method of forming a hydrogen and nitrogen free powder of columbium, tantalum or vanadium which comprises forming a mixture of the oxide of one of said metals, an alkaline earth halide and an alkali metal, enclosing said mixture in a bomb, placing upon said mixture a small portion of the alkali metal, sealing said bomb to exclude the

atmosphere therefrom, raising the mixture to reaction temperature, permitting the bomb to cool, and then recovering the rare metal powder.

4. The method of preparing tantalum, vanadium and columbium free from impurities affecting the workability thereof which comprises heating a mixture of an oxide of one of such metals, calcium and calcium chloride to reaction temperature and simultaneously therewith removing residual gas and water vapor by vaporizing a substance capable of combining therewith at a temperature lower than the reaction temperature of said mixture, said substance forming compounds non-reducible by the metal subsequently reduced by calcium.

5. The method of producing vanadium capable of being cold-worked which comprises heating to reaction temperature a mixture of vanadium oxide, calcium and calcium chloride in the presence of an alkali metal in the vaporized state, removing the metal thus produced, pressing, sintering in vacuo and mechanically working to desired form.

6. The method of producing ductile alloys of columbium, vanadium and tantalum, which comprises heating to reaction temperature a mixture of the oxides of the metals desired to be alloyed, calcium and calcium chloride in the presence of an alkali metal in the vaporized state, removing the metal alloy thus produced, pressing, sintering in vacuo and mechanically working to desired form.

7. The method of producing a metal of the tantalum group of metals substantially free of deleterious gaseous impurities which comprises reducing the oxide compound of said metal in an hermetically sealed container with an alkaline earth metal in the presence of a flux comprised of an alkaline earth halide and prior to the initiation of the reducing reaction, removing from the hermetically sealed container the deleterious residual gases therein by means of combining said gases with a highly reactive metal forming compounds therewith substantially stable at the temperature of reduction of the main body of the charge and non-reducible by the rare refractory metal produced by the reducing reaction of the main body of the charge.

8. The method of producing refractory metal powders substantially free of deleterious gaseous impurities which comprises effecting the reduction of the oxide compound of said refractory metal with calcium in the presence of calcium chloride in an hermetically sealed container and substantially effecting removal of the residual atmospheric gases within said container by supplying to the charge therein a proportion of a highly reactive metal, volatile at a temperature below the reduction temperature of the main

body of the charge and capable of forming with the residual atmospheric gases therein compounds which are stable at the reducing temperature of the main body of the charge and non-reducible by the refractory metal produced by the main reducing reaction.

9. The method of producing refractory metal alloys containing one of the metals of the tantalum, columbium and vanadium group, which comprises forming a mixture of metal powders of the constituents of said alloy substantially free of deleterious gaseous impurities by means of simultaneously reducing in an hermetically sealed container the oxide compounds of said alloy constituents admixed in the desired proportions, with calcium and a flux comprised of calcium chloride, and effecting removal of the residual gases within said hermetically sealed container prior to the reduction reaction by means of alkali metal vapor added as a proportionate member of the charge and thereafter recovering the reduced metal powders, and sintering the same in vacuo.

25 In testimony whereof, we have hereunto subscribed our names this 18th day of February, 1927.

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