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# UNITED STATES PATENT OFFICE

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## METHOD OF PREPARING RARE REFRACTORY METALS

No Drawing. Application filed October 1, 1928. Serial No. 309,682.

This invention relates to the art of metallurgy and more particularly to the art of electro-metallurgy and comprises essentially a method of producing the rare refractory metals by the electrolysis of fused baths. More particularly the invention is directed to the provision of a suitable fused bath from which certain of the rare refractory metals may be produced by electro-chemical means which metals have been heretofore unobtainable or difficultly obtainable by such means.

In copending applications Serial No. 275,264, filed May 4, 1928 and Serial No. 277,096, filed May 11, 1928, both by Frank H. Driggs and assigned to the same assignee as the present application, are described two methods for the production of rare refractory metals by electrolytic dissociation of their fused salts. One of these methods is particularly applicable to the production of tantalum and similar metals and the other process is specifically directed to the production of uranium although not limited to this metal.

In the production of the rare refractory metals of the group known as chromium, tungsten, molybdenum and also uranium, by electro-metallurgical methods, difficulty is experienced in preventing the formation of highly refractory and highly inert and insoluble oxide compounds. The usual fused bath heretofore employed in the electrolysis of these metals has been non-reactive with respect to these oxide compounds and care must be taken to utilize compounds of these metals therein which are highly stable at elevated temperatures and non-decomposable to such oxygen carrying compounds. Such suitable compounds have been described in the above identified copending application Serial No. 277,096.

Whereas the process as described in the said copending application is specifically successful in preparing the rare refractory metals by electrolysis the preparation of the anhydrous, non-oxygen carrying compounds $KUF_5$ or $K_3CrF_6$ to utilize therein introduces an added step in the process which it is one of the objects of this invention to eliminate.

Another object of the present invention is to provide a fused bath which is reactive with the oxygen containing compounds of the rare refractory metals of this particular group.

Another object of this invention is to provide an electro-metallurgical method for the production of these metals from a fused bath containing oxygen-carrying compounds of said metals.

Another object of this invention is to provide a relatively cheap economical and highly efficient means of preparing the substantially pure rare refractory metal powders of the chromium, uranium, tungsten, and molybdenum group, so that they may subsequently be compacted, sintered into coherent ingots and mechanically deformed to desired shapes and sizes.

Other objects and advantages may be apparent as the invention is more fully disclosed.

In accordance with our invention we utilize as the fused bath, an alkaline earth metal halide, such as calcium chloride, to which we may add in various proportions, depending upon the particular metal of the group being prepared, the particular compound employed, the temperature of the bath, and other factors; a compound of the refractory metal, such as the oxide, a double alkali metal halide, such as the double potassium chromium chloride or fluoride, or the halogen compound (anhydrous) or any desirable mixture of the above mentioned compounds.

This fused bath is then decomposed by the passage of an electric current therethrough and the rare refractory metal component deposited therefrom. Subsequently the cooled fused bath is lixiviated with water and the calcium chloride dissolved away and the metal powder remaining digested with suitable acid solvents to remove deleterious impurities. The metal powder is then dried with alcohol and ether and subsequently compacted and sintered into a coherent metal body. If desired, the process may be made a continuous one by frequent additions to the fused bath of additional amounts of the

rare refractory metal compound as the content thereof is exhausted.

According to the disclosure in copending application Serial No. 277,096, it is extremely difficult to prevent the formation of oxygen-carrying compounds of chromium and uranium during the electrolytic dissociation of their fused salts and that it is essential to employ a highly stable nonoxygen carrying double halogen compound such as the double potassium uranium fluoride, having the formula $KUF_6$, prepared by the method as disclosed in a copending application Serial No. 168,826, entitled Preparation of an oxide-free halide of a rare refractory metal, and assigned to the same assignee as the present application.

We have determined that alkaline earth metal chlorides, particularly calcium chloride, has a sufficient solubility for oxide compounds of the above identified group of metals and particularly for uranium oxide and chromium oxide compounds so that it may be successfully employed as the fluxing agent of an electro-metallurgical bath instead of or as substantially replacing the mixture of alkaline and alkaline earth metal fluorides heretofore employed.

We have also determined that the use of this particular fluxing agent in the specific production of this group of metals by electrolysis, provides a means of obtaining the metals in this group in a cheaper, simpler and more efficient manner than heretofore possible.

The electrolysis may be carried out in a carbon, graphite or nickel crucible or the crucible may be comprised of any material or alloy which is substantially non-reactive with the alkaline earth metal chloride, but it should be preferably sufficiently conductive to act as the cathode of the cell.

As a specific embodiment of the nature of our invention we will describe the invention as applied to the production of the rare refractory metal chromium although we have been equally successful in the application of the basic principle of the invention in the production of the other metals of the same family group.

We first form a fused bath of calcium chloride in a carbon, graphite or preferably nickel crucible, to which is added in amounts sufficient to saturate the bath, a suitable chromium compound such as chromium chloride, chromium potassium chloride ($K_3CrCl_6$), chromium potassium fluoride ($K_3CrF_6$) or chromium oxide ($Cr_2O_3$) or any desirable combination of these compounds. We may add, for instance, to the fused bath, chromium potassium chloride in amounts up to 20 percent or so and thereafter to the fused bath add sufficient chromium oxide to saturate the bath. Or we may add to the bath the chromium oxide alone, in which case we have found that the calcium chloride will dissolve approximately 2 percent of its weight of chromium oxide. The specific components of the bath we prefer to employ contains the following ingredients:

| | Grams |
|---|---|
| Calcium chloride | 150 |
| Chromium oxide | 7 |
| Or chromium chloride | 14 |
| Or chromium potassium chloride | 20 |
| Or chromium potassium fluoride | 18 |

When the bath is nicely fused and at a temperature approximating 900° C., the electrolysis may be started. In the electrolysis we prefer to employ a carbon or graphite anode and insert the same centrally in the fused bath, utilizing the crucible as the cathode.

With a bath of the above composition the break-down voltage will be approximately 10 volts, and to effect deposition of the chromium, a current of 15 amperes may be applied.

The electrolysis may be allowed to continue until all of the chromium content has been dissociated into metal and if desired, may be made a continuous one through the addition from time to time of fresh chromium oxide, chromium chloride or other fusible and ionizable chromium containing compound. By calculating the current equivalent factor for the particular chromium compound utilized and then adjusting the ampere hours to be greater than this equivalent, the bath at the conclusion of the run may be made substantially free of chromium oxide.

At the conclusion of the run the fused bath is allowed to cool to room temperature and then washed with distilled water to remove the soluble calcium chloride. The deposited metal powder, which will be found accumulated along the side of the cathode crucible, is then successively washed with dilute nitric acid, water, alcohol and ether and then thoroughly dried in vacuo. The resultant metal powder should then be sieved through a fine mesh screen, compacted into suitable shapes and sizes and sintered by well known metallurgical means into a coherent ingot. Thereafter the ingot may be reduced to desired shapes and sizes by well known mechanical deformation methods.

Whereas we have specifically described the invention as relates to the production of metallic chromium powder it is obvious that many departures may be made from the specific embodiment without essentially departing from the nature of the invention and all such departures and variations are anticipated as may fall within the scope of the following claims.

What is claimed is:

1. The method of preparing the rare re-

fractory metals of the group known as tungsten, molybdenum, chromium and uranium, which comprises electrolytically decomposing a fused bath containing dissociable compounds of the rare refractory metal, said bath being comprised in major part of a chemical compound having a solubility towards the oxygen carrying compounds of said rare refractory metals to form compounds therewith substantially dissociable by the electric current.

2. The method of preparing the rare refractory metals of the group known as tungsten, molybdenum, chromium and uranium, which comprises electrolytically decomposing a fused bath containing dissociable compounds of said rare refractory metals, said bath being comprised in major part of an alkaline earth metal halide reactive with respect to the oxygen carrying compounds of said rare refractory metals to form compounds substantially dissociable by the electric current.

3. The method of preparing chromium metal powder which comprises electrolytically decomposing a fused bath containing dissociable compounds of chromium, said bath being comprised in major part of an alkaline earth metal halide reactive with respect with oxygen carrying compounds of chromium to form compounds therewith which are substantially dissociable by the electric current.

4. The method of preparing chromium metal powder which comprises electrolytically decomposing a fused bath comprised in major part of calcium chloride and containing a proportion of a halogen compound of chromium together with approximately 2% chromium oxide.

5. The method of preparing chromium which comprises electrolytically decomposing a fused bath comprised in major part of calcium chloride and containing a proportion of a dissociable chromium compound and adding thereto at frequent intervals increments of additional dissociable chromium compounds such as chromium oxide.

6. The method of preparing rare refractory metal powders of the tungsten, molybdenum, chromium and uranium class which comprises electrolytically depositing said metal powders from a fused bath comprised in major part of calcium chloride to which have been added a proportion of a dissociable rare refractory metal compound fusible and soluble in said calcium chloride, prolonging the time of said electrolytic deposition by means of adding thereto at frequent intervals additional amounts of said rare refractory metal compound, continuing said electrolysis until substantially all of the oxygen carrying compounds of said refractory metal has been decomposed and removed from said fused bath, thereafter cooling the fused bath to room temperature, effecting a separation of said electrolytically deposited metal from the aqueous and acid soluble residual component of said bath, and collecting the remaining refractory metal powder.

7. The method of preparing chromium metal powder which comprises electrolytically depositing said metal powder from a fused bath comprised in major part of calcium chloride containing a proportion of a dissociable chromium compound soluble in and ionizable in said calcium chloride, replacing said chromium compound as decomposed by means of frequent additions to the fused bath of a chromium compound soluble in said bath, continuing the electrolytic decomposition until the oxygen compounds of chromium are substantially all decomposed, thereafter cooling the fusion and recovering the deposited metal powder from the cooled fused mass by dissolving away the water and acid soluble impurities in any desired manner.

8. The method of preparing the rare refractory metal powders of the tungsten, molybdenum, chromium, uranium group which comprises electrolytically depositing the rare refractory metal powder from a fused bath comprised of an alkali earth metal chloride containing a proportion of a double halide compound of said rare refractory metal.

9. The method of preparing the rare refractory metal powders of the tungsten, molybdenum, chromium, uranium group, which comprises electrolytically depositing the rare refractory metal powder from a fused bath comprised of calcium chloride containing a proportion of a double halide compound of said rare refractory metal.

10. The method of preparing the rare refractory metal powders of the tungsten, molybdenum, chromium, uranium group, which comprises electrolytically depositing the rare refractory metal powder from a fused bath comprised of calcium chloride containing a proportion of a double halide compound of said rare refractory metal and a proportion of an oxygen containing compound of the rare refractory metal.

11. The method of preparing chromium metal powder which comprises electrolytically depositing the metal in powder form from a fused bath comprised of calcium chloride containing a proportion of an ionizable chromium compound.

12. The method of preparing chromium metal powder which comprises electrolytically depositing the metal in powder form from a fused bath comprised of calcium chloride containing a proportion of a double halide compound of chromium.

13. The method of preparing chromium metal powder which comprises electrolytically depositing the metal in powder form from a fused bath comprised of calcium chloride containing a proportion of a double ha-

lide compound of chromium and a proportion of a chromium oxide compound.

14. The method of preparing chromium metal powder which comprises electrolytically depositing the metal in powder form from a fused bath comprised of calcium chloride containing a proportion of chromium oxide.

In testimony whereof, we have hereunto subscribed our names this 28th day of September, 1928.

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