Patented Dec. 8, 1931

1,835,025

UNITED STATES PATENT OFFICE

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METHOD OF PREPARING RARE REFRACTORY METALS BY ELECTROLYSIS

No Drawing. Application filed April 4, 1930. Serial No. 441,711.

This invention relates to the art of metallurgy and more particularly relates to the art of electro-metallurgy and has for its object the provision of a method of preparing the rare refractory metals thorium, zirconium and the like group elements (group 4 of the periodic table) by the electrolytic dissociation of their compounds in a fused bath.

Another object of this invention is to provide a suitable fusion mixture for the use in electrolytically preparing thorium, zirconium and the like metals.

Another object of this invention is to provide a method of effecting the electrolytic deposition of metals of the thorium, zirconium group upon a cathode of the so-called floating type, in an adherent sponge-like form.

Other objects and advantages will become apparent as the invention is more fully disclosed.

In copending applications Serial No. 275,264 filed May 4, 1928; 277,096 filed May 11, 1928; 309,682 filed October 1, 1928; 316,624 filed November 1, 1928 and 351,451 filed March 30 1929 by Frank H. Driggs and Frank H. Driggs, et al., there has been disclosed methods which have been devised for the electrolytic extraction of the rare refractory metals from fused baths. The present invention is a continuation in part of these prior filed inventions, and the Frank H. Driggs, co-inventor of the present invention, is the same Frank H. Driggs of the applications above identified. The William C. Lilliendahl, co-inventor of the present invention, is the same co-inventor of application Serial No. 351,451, above identified.

In the applications above identified the various processes and variations in the basic idea originally set forth in applications Serial No. 275,264 and No. 277,096 above identified, in order to adapt the same to the chemical and metallurgical characteristics of the different group elements of the rare refractory metals, have been set forth.

In application Serial No. 275,264 the preparation of the rare refractory metal powders by the electrolytic dissociation of a double alkali fluoride compound in solution in a fused alkali halogen bath is disclosed. Specifically the preparation of tantalum is disclosed and to facilitate the deposition process and to make the same continuous in operation increments of tantalum oxide are added to the bath during the electrolysis process. In this instance the tantalum oxide is soluble in and ionizable in the fusion mixture.

In copending application Serial No. 277,096 above identified the method of preparing uranium metal powder by the electrolytic dissociation of fused baths containing a proportion of a double alkali fluoride compound of uranium is disclosed. Uranium belongs to another group of elements than tantalum and forms oxygen compounds which are not soluble in or decomposed by alkali halogen fusion mixtures. The double alkali fluoride compound KUF_5 employed in this process is substantially oxide free, anhydrous and is highly stable and when fused with alkali fluoride compounds does not tend to interact with atmospheric oxygen to form deleterious oxide compounds.

In copending application Serial No. 309,682 above identified, there is disclosed a method of preparing rare refractory metals by the electrolytic decomposition of a fusion mixture of alkali and alkaline halides having a specific solubility towards the oxide compounds of the rare refractory metal. The invention is specific to the elements of the chromium group and the fusion mixture is comprised specifically of calcium chloride.

In application Serial No. 316,624 a method of effecting an increase in the particle size of the depositing metals in the prior filed applications by adding to the fusion mixture

a proportion of an alkali metal chloride compound, is set forth.

In application Serial No. 351,451 is disclosed a method of effecting the deposition of the rare refractory metals upon what is known in the art as a "floating cathode" by the use of a relatively low melting fusion mixture containing a proportion of an alkali metal halide compound, maintaining the temperature of the bath during deposition of the rare refractory metals, such that the simultaneously depositing alkali metal will be retained adjacent the cathode at least in part as a "metal fog". This condition serves to maintain a "reducing" atmosphere about the cathode. The alkali "metal fog" being the reducing agent thus protects the depositing rare refractory metal from oxidation.

In the application of this latter process to the preparation of the different rare refractory metals it has been found that the fusion mixture to which is added the rare refractory metal compound, must be varied in accordance with the specific chemical and physical properties of the rare refractory metal and the compound from which it is obtained. Tantalum and the metals of the same family group may be obtained from fusion mixtures, such as set forth in copending application 275,264 above identified. Uranium is preferably prepared from the fusion mixture of application 351,451, above identified. Chromium and other members of the same family group may also be prepared using the fusion mixture such as is set forth in application Serial No. 351,451.

It has been found, however, that the metals thorium, zirconium and the like group elements cannot be prepared using either of these fusion mixtures for the reason that the oxygen compounds of the metals are not soluble in either the fused double fluoride compound of the element or in the fusion mixture of alkali and alkaline earth metal halides. Moreover such oxide compounds are not readily reduced by the alkali metal "fog" adjacent the cathode when present in the fusion mixture.

It has also been found that the calcium content of the fusion mixture heretofore employed reacts with the fluorine component of the fusion mixture to form high melting fluoride compounds therewith which increase the melting point of the bath materially when accumulated therein an appreciable amount.

Moreover such compounds being relatively insoluble in water and acid are not subsequently readily removed from the metal powder during the recovery process, and in the case of zirconium, for example, separation of the calcium fluoride from the metal powder by gravity means is impractical.

In order to eliminate these objectional features and to facilitate the electrolytic deposition of the rare refractory metals of the thorium and zirconium group (group 4 of the periodic table), we have employed a mixture of alkali halides rather than a mixture of alkali and alkaline earth halides, and add to this admixture a proportion of an anhydrous oxide free rare refractory metal double halide compound, and effect the deposition of the rare refractory metal from the fusion mixture upon a floating cathode substantially as heretofore disclosed.

We prefer, without being specifically limited thereto, to employ the double fluoride compounds of the rare refractory metals in the practice of the present invention, for the reason that they may be most readily and conveniently prepared on a commercial basis, and when prepared may be kept indefinitely without substantial deterioration.

In the preparation of thorium, for example, a fusion mixture of equal parts potassium chloride (KCl) and sodium chloride (NaCl) is employed. The melting point of this admixture is well under 750 to 800° C., the limits within which the alkali metal is retained adjacent the cathode as a metal "fog" in accordance with the invention set forth in copending application Serial No. 351,451 above identified.

To this fusion mixture is added a proportion of an anhydrous double thorium potassium fluoride having the empirical formula K_1ThF_5. This compound may be most readily prepared by adding potassium fluoride to a solution of thorium nitrate.

The proportion of the double thorium potassium fluoride salt that may be added to the fusion mixture of alkali chlorides varies between 5% and 25%. It is preferable to add the minimum amount and to add increments of the double compound as the electrolysis proceeds.

It is also preferable to frequently change cathodes as it has been found that in the metals of this class there is apparently a limit as to the thickness of deposit of the sponge metal that may be built up on the cathode. This limit is believed due to the fact that the deposition of the sponge metal is such that the electrical conductivity from one particle to another is relatively poor. As the deposit builds up the resistance increases and the current efficiency thereby decreases.

It has been found, for example, that substantially the same weight deposit of thorium is obtained upon a cathode at the end of an hour as was obtained at the end of the first 15 minutes. By inserting a fresh cathode in the cell each 15 minutes four times the weight of the deposit obtained on a single cathode was obtained.

The cathode is preferably comprised of molybdenum and in its preferred form is comprised of molybdenum strip. The anode may be comprised of carbon and if desired the con-

tainer for the fusion mixture may be comprised of graphite or carbon and be employed as the anode.

A specific example of the practice of my invention may be set forth as follows:

Fusion mixture

	Grams
NaCl	500
KCl	500
K_1ThF_5 (anhydrous)	60

Fused in graphite crucible approximately 3½ inches diameter by 5½ inches deep.

Temperature of bath 750° to 800° C.

Anode the crucible.

Cathode-molybdenum strip approximately 10 mil thick by 1" width and 4" immersed length.

Cathode current density approximately 7–8 amperes per square inch.

Voltage across cell approximately 6 volts.

About every 15 minutes a fresh cathode should be inserted and fresh additions of K_1ThF_5 to replace that deposited out should be made. The current efficiency is about 43 per cent. The percent yield is about 53 per cent.

In the electrolytic preparation of zirconium there is no specific variation from the bath composition or in the method of depositing the metal powder. The fifty-fifty admixture of sodium and potassium chlorides is employed to which is added between 5% and 25% zirconium potassium fluoride K_2ZrF_6. The electrolysis of the fused mixture is conducted similarly to that above set forth for thorium.

Having broadly and specifically set forth the nature and scope of the present invention it is apparent that there may be many departures and variations made from the specific embodiment herein disclosed without departing essentially from the nature and scope of the invention as is set forth in the accompanying claims.

What is claimed is:

1. The method of preparing rare refractory metals of group 4 of the periodic table which comprises electrolytically depositing the same from a fused bath comprised of alkali metal halides containing a proportion of a double halide compound of the rare refractory metal.

2. The method of preparing rare refractory metals of group 4 of the periodic table which comprises electrolytically dissociating a fused double alkali metal-rare metal halide compound in a bath comprised substantially of fused alkali metal chloride compounds.

3. The method of preparing rare refractory metals of the thorium, zirconium class which comprises electrolyzing a fusion mixture comprised of alkali metal chloride compounds containing a proportion of an anhydrous oxide free double halide compound of the rare refractory metal.

4. The method of preparing rare refractory metals of the thorium, zirconium class which comprises electrolyzing a fusion mixture comprised of alkali metal chloride compounds containing a proportion of a double alkali metal-rare metal fluoride.

5. The method of preparing thorium which comprises electrolytically depositing the same from a fused bath comprised of alkali metal halides and a proportion of a double halide compound of thorium.

6. The method of preparing thorium which comprises electrolytically depositing the same from a fused bath comprised of alkali metal chlorides and a proportion of an anhydrous oxide free double fluoride compound of thorium.

7. The method of preparing thorium which comprises electrolytically despositing the same from a fused bath comprised of sodium and potassium chlorides containing a proportion of oxide free double fluoride compound of thorium.

8. The method of preparing metal powders of rare refractory metals of group 4 of the periodic table which comprises electrolytically depositing the same upon a cathode from a fused bath comprised of alkali metal chlorides containing a proportion of double halide compound of the rare refractory metal.

9. The method of preparing thorium which comprises electrolytically depositing thorium metal powder upon a cathode from a fused bath comprised of a mixture of alkali metal chlorides containing a proportion of an oxide free double fluoride compound of thorium, the temperature of said bath being maintained at a temperature of from 600° C. to 800° C.

10. The method of preparing zirconium which comprises electrolytically depositing the same from a fused bath comprised of alkali metal halides and a portion of a double halide compound of zirconium.

11. The method of preparing zirconium which comprises electrolytically depositing the same from a fused bath comprised of alkali metal chloride and a portion of anhydrous oxygen free double fluoride compound of zirconium.

12. The method of preparing zirconium which comprises electrolytically depositing the same from a fused bath comprised of sodium and potassium chloride containing a portion of oxygen free double fluoride compound of zirconium.

In testimony whereof, we have hereunto subscribed our names this 2nd day of April, 1930.

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