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2,777,809

## PREPARATION OF URANIUM

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No Drawing. Application March 25, 1948, Serial No. 17,101

9 Claims. (Cl. 204—1.5)

This invention relates to a method for preparing metals by electrolysis and more particularly to a method for efficiently preparing substantially pure uranium by the electrolysis of a uranium compound in a fused bath.

In the past, attempts have been made to prepare pure uranium by the electrolysis of uranium compounds in a fused bath, but a number of difficulties were encountered. U. S. Patent 1,821,176, to Frank H. Driggs et al., teaches the production of uranium by the electrolysis of a fused bath of a double halide salt of uranium, but the product is a fine powder. Uranium in this form is useful for some purposes but is readily oxidized, is pyrophoric and is difficult to maintain as pure uranium metal. Moreover, in such a process the electrolysis is carried out at high operating temperatures of the order of 1200° C. to 1300° C. High operating temperatures not only cause low yields because of increased evaporation, but also require the use of special equipment. Some uranium compounds, such as uranium triiodide or uranium tribromide, when used as the source of the uranium, require careful handling because they decompose readily and are quite hygroscopic, either of which properties interfere with electrolysis in a convenient large scale operation.

It is, therefore, the primary object of this invention to provide a simple method for efficiently preparing substantially pure uranium metal from a fused bath.

It is a further object of this invention to provide a method for efficiently preparing substantially pure uranium metal from a used bath containing a stable, relatively non-hygroscopic uranium compound.

It is a still further object of this invention to provide a method for preparing uranium from a fused bath which may be operated at a comparatively low temperature.

It is another object of this invention to provide a method for preparing from a fused bath substantially pure uranium metal in the form of large, ductile, well-developed crystals of uranium which are not pyrophoric and not readily oxidized and which require little further treatment prior to melting to form a slug of substantially pure uranium.

Still further objects and advantages of this invention will appear in the following description.

The objects of this invention are achieved by the process which comprises electrodepositing uranium from a fused bath containing uranium trichloride.

More particularly the bath consists of uranium trichloride and a chloride electrolyte of alkali or alkaline earth metals. It is desirable that the bath have an operating temperature range of 600° C. to 800° C. and preferable that the range be 600° C. to 700° C. When the bath is operated below 600° C. there is a tendency for one or more of the bath metals along with uranium to be the products of the electrolysis. On the other hand, as the temperature of the bath is increased, the evaporation of the salt bath is substantially increased and the yield is correspondingly decreased, the evaporation losses becoming excessive when the bath temperature exceeds 800° C.

The intermediate temperature range permits the forma-

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tion of relatively massive uranium metal in the form of dendritic crystal rather than the fine powders obtained when the bath is operated at a higher temperature such as at 1100° C. Moreover, at a temperature of 600° C. to 800° C. non-porous vitreous or metallic containers may be employed instead of the porous graphite containers which are generally employed for temperatures in the neighborhood of 1100° C. This eliminates the losses due to the porosity of the graphite and reaction therewith to form uranium carbide. The vitreous or metallic containers used must not soften or alloy with uranium. As an example of such containers, containers of Pyrex glass may be used preferably for small scale reduction, and containers of metals, such as tungsten, tantalum, molybdenum, chrome-nickel alloys and silver are advantageously used for large scale reduction.

Alkali or alkaline earth metals or mixtures of such metals are more electropositive than uranium. Thus any of the alkali or alkaline earth halides which melt in the desired range may be used in the bath. For example, a mixture of barium chloride, potassium chloride and sodium chloride may be used because the mixture has a melting point of about 550° C. and is very fluid in temperatures in excess of 600° C.

The uranium halide used in the bath is, of course, of prime importance. Uranium trichloride is used as the source of uranium for electrolysis carried out according to the method of this invention because of its marked superiority over the other previously used uranium halides. Uranium trichloride is of stable composition. It requires few precautions in its handling because it is not very hygroscopic. Moreover, the presence of a small amount of moisture in uranium trichloride exerts no severe detrimental effect during the preparation of the bath for electrolysis, as it does not react with water as readily as the tetrachloride. The trichloride when treated according to the method of this invention yields a product consisting of large, well-developed dendritic crystals of uranium which require little further treatment prior to melting.

It should be noted that these desirable properties of uranium trichloride overcome the previously encountered shortcomings of a double halide salt of uranium or of other uranium halides such as uranium triiodide or uranium tribromide, mentioned hereinbefore as the source of uranium in the fused baths.

The presently preferred embodiment of the method of this invention is best illustrated by the following example which is given for this purpose only and not the purpose of limiting the spirit or scope of the invention.

### Example

Approximately 150 grams each of C. P. barium chloride, potassium chloride, and sodium chloride are thoroughly dried until all the moisture including the water of crystallization, if any, is removed. Each salt is individually fused and cast in a platinum dish. The salts are then thoroughly ground in a porcelain mortar. 96 grams of barium chloride, 42 grams of sodium chloride, and 62 grams of potassium chloride are thoroughly mixed, fused together, and reground. The salts are placed in a Pyrex container together with 80 g. of anhydrous  $UCl_3$ . A piece of graphite  $\frac{1}{4}$  inch in diameter and a piece of tungsten gauze 1 inch square are respectively connected to the anode and cathode leads which extend through the container. The bath container is sealed and evacuated. Hydrogen which is first purified by passing over platinum asbestos at 300° C. and dried by passing through a calcium chloride and a silica gel drying tower is then introduced. The blanketing flow of hydrogen is continued during the electrolysis to prevent the formation of oxy-chlorides and to convert evolved chlorine gas to hydrogen chlo-

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ride. The mixture of barium chloride, sodium chloride, and potassium chloride is raised slightly above its melting temperature of 550° C. by means of a resistance furnace which surrounds the Pyrex container.

After the uranium trichloride has melted, the anode and cathode are lowered into the fused bath by means of the lead wires, a current of 6 amperes is applied between the anode and cathode, and the temperature is advanced to 650° C. The current and temperature are maintained at these values until the electrolysis is complete. This takes about 3½ hours. The hydrogen, the current, and the furnace are turned off, the major portion of the fused salts are poured off, and the remainder of the fused salts dissolved in water. Bright dendritic crystalline uranium metal remains.

When the electrolysis is operated on this scale, a recovery of 97 percent at 95 percent current efficiency often occurs. Recoveries in almost every case exceed 90 percent. The melting point of the uranium product corresponds to that of pure uranium. The crystals retain their luster for relatively long intervals, they are ductile, they are not readily oxidized, are not pyrophoric, and they may be efficiently and rapidly recovered from the bath.

Small samples of the crystals may be readily consolidated by self-heating in a high frequency induction furnace. The inclusion of oxides in the cast slug may be minimized by washing the crystals in dilute nitric acid. Larger samples are more readily consolidated if they are first compacted under a rather high pressure such as several thousand pounds per square inch. The resultant slug or billet obtained from either small or large scale consolidation is also ductile. The metal may be readily converted to the hydride.

For maximum efficiency, all materials, particularly the uranium trichloride, entering the cell should be thoroughly dry. Excessive moisture present in the cell might result in the formation of a reddish powder, which is probably an oxide, with consequent reduction of yield.

It may be noted that in the example the initial concentration of the uranium trichloride was 28.5 percent by weight. This may, of course, be varied through a rather wide range. When working on a small scale, a high concentration of uranium trichloride causes too great a reduction in the volume of material during the operation. Spray and evaporation losses are also increased with increase in concentration of the uranium. On the other hand, a very low initial concentration will yield poor deposits of uranium. Efficient results may be obtained from a bath containing from 5 to 75 percent by weight of uranium trichloride but the preferred initial concentration is from 15 to 30 percent by weight. It has been found possible to continue electrolysis to the point where virtually no uranium salt remains in the electrolyte. This makes the process valuable as a recovery process as well as a refining process.

Other modifications may also be made. For example, to maintain the non-oxidizing atmosphere, it is possible to use argon and/or helium in place of or along with the hydrogen. The use of hydrogen as a blanket or cover is advantageous in that the hydrogen not only minimizes oxidation, but combines with the chlorine at the anode to form hydrogen chloride which is less corrosive than the chlorine.

The anode used in the example was graphite from which there is very little loss during electrolysis. Tungsten may be employed when it is desirable to eliminate completely the opportunity for carbon contamination. Although the cathode may be of any metal which does not alloy with uranium at the temperature of operation, tungsten or even uranium are preferred metals for the cathode.

The current density may also be varied within rather wide limits. It is difficult to establish accurately the current density because of the growth of dendrites whose area is indeterminate. The size of these crystals can be regulated somewhat by current density to be convenient for handling and subsequent remelting. Moderate in-

crease in current increases the current efficiency, but excessive increase in current is of no benefit and may result in a reduction in recovery because of increased spray loss. A current density of from 5 to 25 amperes per square inch and preferably 15 to 25 has been found to give very good recovery at a rather high current efficiency.

One of the major causes of loss of cathode product in fused bath electrolysis results from reaction of the deposit with anode products such as chlorine. This is particularly true of dendritic cathode deposits which approach the anode. To minimize losses due to this cause and thus to insure maintenance of high current efficiency, it is feasible to increase the distance between the anode and cathode and/or to use special shaped cells such as a V-shaped one with a cathode at the bottom and the anode immersed in the bath at the top.

The process can be carried out on a large scale by modifications well known to those skilled in the art. The cells and the methods of operation can readily be arranged by those skilled in the art so that production is continuous. The process has the advantage of high current efficiency and low operating costs when performed on any desired scale.

The foregoing example and procedures are given for the purpose of illustrating the present invention, but are not intended to be limiting on the scope thereof. Because many widely different embodiments of the invention can be made without departing from the spirit and scope thereof, it is to be understood that this application is not to be limited except as indicated in the appended claims.

What is claimed is:

1. The process which comprises electrodepositing uranium from a fused bath including from 5 to 75 percent uranium trichloride and at least one chloride of a metal of the class consisting of alkali metals and alkaline earth metals at a temperature between 600° C. and 800° C. and in a non-oxidizing atmosphere.
2. The process which comprises electrodepositing uranium from a fused bath including from 5 to 75 percent uranium trichloride and at least one alkali metal chloride at a temperature between 600° C. and 800° C. and in a non-oxidizing atmosphere.
3. The process which comprises electrodepositing uranium from a fused bath including from 5 to 75 percent uranium trichloride and at least one alkaline earth metal chloride at a temperature between 600° C. and 800° C. and in a non-oxidizing atmosphere.
4. The process which comprises electrodepositing uranium from a fused bath including from 5 to 75 percent uranium trichloride and at least one alkali metal chloride and at least one alkaline earth metal chloride at a temperature between 600° C. and 800° C. and in a non-oxidizing atmosphere.
5. The process which comprises electrodepositing uranium from a fused bath containing from 15 to 30 percent uranium trichloride and at least one chloride of a metal of the class consisting of alkali metals and alkaline earth metals at a temperature between 600° C. and 700° C. and in a non-oxidizing atmosphere.
6. The process which comprises electrodepositing uranium from a fused bath containing from 5 to 75 percent uranium trichloride and the balance of barium chloride, potassium chloride and sodium chloride at a temperature between 600° C. and 800° C. and in a non-oxidizing atmosphere.
7. The process which comprises electrodepositing uranium from a fused bath containing from 15 to 30 percent uranium trichloride and the balance of barium chloride, potassium chloride and sodium chloride at a temperature between 600° C. and 700° C. and in a non-oxidizing atmosphere.
8. The process which comprises electrodepositing uranium from a fused bath containing from 5 to 75 percent uranium trichloride and a mixture of 48 percent barium chloride, 31 percent potassium chloride and 21 percent

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sodium chloride at a temperature between 600° C. and 800° C. and in a non-oxidizing atmosphere.

9. The process which comprises electrodepositing uranium from a fused bath containing from 15 to 30 percent uranium trichloride and a mixture of 48 percent barium chloride, 31 percent potassium chloride and 21 percent sodium chloride at a temperature between 600° C. and 700° C. and in a non-oxidizing atmosphere.

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1,597,189

1,821,176

1,842,254

1,861,625

6

### References Cited in the file of this patent

#### UNITED STATES PATENTS

Gero .....	Aug. 24, 1926
Driggs et al. ....	Sept. 1, 1931
Driggs .....	Jan. 19, 1932
Driggs et al. ....	June 7, 1932

#### OTHER REFERENCES

10 Ind. Eng. Chem., vol. 22, No. 5, pp. 516-519, May 1930.