

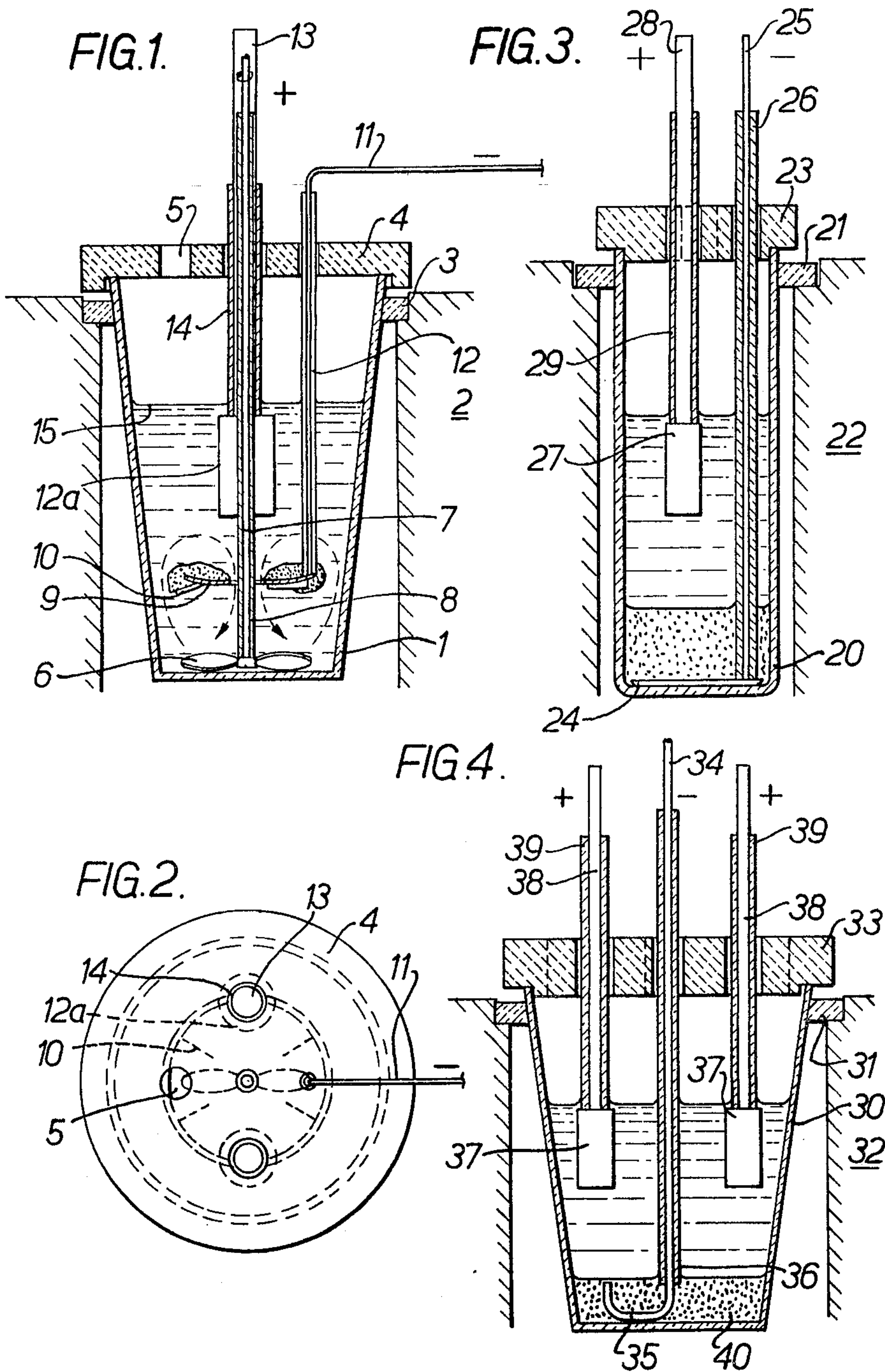
Sept. 13, 1966

A. R. GIBSON ETAL

3,272,726

PRODUCTION OF URANIUM

Filed May 3, 1963



1

3,272,726

PRODUCTION OF URANIUM

Allan Robert Gibson, Harwell, and Ronald George Avery,
Oxford, England, assignors to United Kingdom Atomic
Energy Authority, London, England

Filed May 3, 1963, Ser. No. 277,894

Claims priority, application Great Britain, May 10, 1962,
18,109/62

13 Claims. (Cl. 204—1.5)

The present invention relates to the electrolytic production of uranium metal and its alloys.

For a long time it has been realised that it might prove to be a cheaper and more satisfactory route for the production of uranium metal (which term includes metallic alloys) if it were possible to do it by means of an electrolytic process and much research has been done on the subject using a molten halide solvent which would appear to be a satisfactory electrolyte under the circumstances.

The uranium salts examined have been the trichloride, the tetrachloride and tetrafluoride in solution in fused alkali or alkaline earth halides. A difficulty associated with the chloride melts is the readiness with which they may be hydrolysed to form uranyl chloride which on electrolysis produces uranium dioxide and not uranium metal as the cathode product.

It has been found possible to electrolyse anodic uranium dioxide intimately mixed with carbon (briquetted) in a complex fluoride melt to yield uranium metal at a temperature above the melting point of uranium.

None of the above routes has proved sufficiently satisfactory to form a production process. A process based on reduction of uranium oxide in an electrolyte which contains no dissolved uranium salts would, if feasible, appear to offer simplicity and economy of operation. The present invention is intended to achieve this object and the oxide used is a product of a process of preliminary purification such as is described in British Patent No. 889,307 or is readily obtained as the product of other purification routes.

According to the present invention there is provided a method for the production of uranium metal or an alloy of uranium, comprising effecting the electrolytic reduction of a suspension of uranium dioxide in a molten alkaline earth metal halide using an anode and a metal cathode which are both unreactive with respect to the molten halide, the temperature being maintained below the melting point of uranium metal.

According to a further aspect of the present invention there is provided apparatus for the production of uranium metal from uranium dioxide, such apparatus comprising a crucible of a refractory material, a refractory lid for said crucible, means to maintain an inert atmosphere within such crucible, said crucible being adapted to contain a molten alkaline earth metal halide electrolyte in which particles of uranium dioxide are suspended, a metal cathode which is unreactive to the electrolyte and to uranium, an anode which is unreactive to the electrolyte and means for stirring the electrolytes.

According to yet a further aspect of the present invention there is also provided apparatus for the production of an alloy of uranium from uranium dioxide, such apparatus comprising a crucible of refractory material, a refractory lid for said crucible, means to maintain an inert atmosphere within such crucible, said crucible being adapted to contain a molten alkaline earth metal halide electrolyte in which particles of uranium dioxide are suspended, a metallic cathode which is unreactive to the electrolyte but which

2

forms an alloy with uranium, and an anode which is unreactive to the electrolyte.

The preferred molten halide electrolyte is calcium or magnesium chloride and the operating temperature is conveniently in the range 850 to 950° C. Under these circumstances the electrolyte must of course be anhydrous.

It will be realised that the cathode should always be "inert" to the molten halide electrolyte but need not necessarily be inert to uranium metal. If it is desired to produce powdered uranium metal then the cathode must of course be inert to uranium metal (the product of the electrolytic reduction) but under certain circumstances it may be desirable to produce an alloy of uranium, for example with aluminum or iron, by using an initial molten pool of metal or alloys as cathode.

If it is desired to produce powdered uranium metal, then the cathode may very conveniently be in the form of a horizontal plate of molybdenum or tantalum and the anode may be arranged above the cathode so that the uranium metal is deposited on the upper surface of the cathode and may be removed with the cathode.

The anode is preferably of graphite as the gases evolved from the electrolyte during electrolysis are firstly chlorine and later carbon oxides.

In order that the invention may more readily be understood, certain embodiments of the same will now be described by way of example and with reference to the accompanying drawing, wherein:

FIG. 1 is a diagrammatic cross section through a cell for the production of uranium metal.

FIG. 2 is a top plan view of the cell of FIG. 1.

FIG. 3 is a section similar to FIG. 1 through a cell designed for the production of uranium-aluminum alloy, and

FIG. 4 is a view similar to FIG. 1 through a cell designed for the production of uranium-iron alloy.

Referring now to FIGS. 1 and 2 of the drawings, the apparatus comprises a conical flat bottomed alumina crucible 1 located in a furnace 2, an insulating ring 3 serving to support the crucible 1 in the bore in the furnace 2. The upper end of the crucible is closed by a refractory lid 4 e.g. made of pyrophyllite, which is provided with an aperture 5 for the supply of argon to maintain an inert atmosphere within the cell and through which uranium dioxide may be fed in the cell.

A molybdenum impeller 6 is carried by a stainless steel shaft 7 and is located close to the base of the crucible 1, the shaft being surrounded by an alumina sheath 8 and being provided at its upper end with means for attachment to a stirrer motor (not shown). The cathode 9 is in the form of a circular plate of molybdenum of area 3.6 sq. ins. and is provided with four louvres 10 to permit the circulation of the electrolyte and the uranium dioxide therein, under the influence of the stirrer 6. The cathode 9 is supported by a tungsten rod 11 which is provided with an alumina sheath 12 and which also functions as the cathode lead.

Two graphite anodes 12a are also provided and are located above the cathode 9, each of these anodes being carried at the end of a graphite rod 13 and each of these rods being protected by an alumina sheath 14, at least as far as the melt level indicated at 15. Suitable holes are provided in the lid 4 for the passage of the anode rods, cathode lead and stirrer rod.

The cell shown in the drawing is designed for small scale experimental work with a charge of 850 gms. of

anhydrous calcium chloride, the capacity being of the order of 750 ml.

In one experiment that was carried out using the cell that has been described the details of the run were as follows—

Time	Temp., ° C.	Volts	Amps.	Amp./Hrs.	UO ₂ added, gms.	Remarks
0.00-----	930	5.5	25.0	-----	25.0	Started.
0.30-----	960	5.6	25.0	12.5	-----	
0.45-----	950	5.6	25.0	18.75	50.0	
1.00-----	950	5.75	25.0	25.0	-----	
1.30-----	950	5.8	25.0	37.5	75.0	
2.00-----	955	5.8	25.0	50.0	-----	Stopped agitator. Stopped run.
2.12-----	960	5.8	25.0	55.0	-----	

It is to be noted that the rotation of the impeller 6 was stopped before the end of the run and this expedient was adopted in order to ensure that as far as possible any uranium dioxide lodged on the cathode was reduced.

In order to minimise attack by the atmosphere a suitable cover was provided over the lid 4 and argon was used as an inert atmosphere to protect the cathode deposit. This deposit was found to be substantially pure uranium in the form of a powder and a relatively large amount of melt was found to be entrained with the powder on removing the cathode. However, the discharged metal may be removed from the cathode, leached and dried when a fine grey crystalline powder is obtained which is not pyrophoric at room temperature. This powder was successfully compacted without a binder in a 1/2" diameter die.

The yield in the experiment above described was approximately 55 gms. of uranium metal corresponding to approximately 1 gm./amp. hr. thus giving a current efficiency of approximately 45% on tetravalent uranium. Visual examination showed no appreciable residue of uranium dioxide and the slight loss of metal probably occurred during the leaching and washing procedure.

It is important to observe that a suitable quality of uranium dioxide must be employed and we prefer to use either electrolytic dioxide (for example prepared by the method of British Patent No. 889,307) or hydrogen precipitated oxides. These oxides are appreciably coarser than hydroprecipitated material which did not prove to be satisfactory. It is further important to emphasise that effective agitation must be employed in this process of powder production, in order to maintain a stream of uranium dioxide over the cathode face. Mechanical agitation has been proved greatly superior to gas injection in the melt.

If it is desired to produce an alloy of uranium and aluminum, for possible use in a nuclear fuel element, it is convenient to use the apparatus illustrated in FIG. 3. This apparatus comprises a deep cylindrical alumina crucible 20 which is supported by an insulating ring 21 in a furnace 22, the crucible being closed by a pyrophyllite lid 23. The cathode in this arrangement is in the form of a pool of molten aluminum in which is immersed a stainless steel disc 24, the disc 24 being located close to the bottom of the crucible 20 and connected to a stainless steel rod 25 which acts as the cathode lead, this rod being protected by an alumina sheath 26. The anode is in the form of a rod of graphite 27 connected to a smaller graphite rod 28 and this latter rod is protected by an alumina sheath 29, the anode and cathode leads passing through the lid 23 which is also provided with a gas vent (not shown).

Unlike the previous embodiment, no stirrer is provided for we have found that it is advisable not to stir either the electrolyte, which is desirably anhydrous calcium chloride, or the cathode alloy which is in a pool above the cathode 24. The reason for this is that the compound UAl₂ has a melting point of 1590° C. and it is

considered that it would be impracticable to operate the cell at a temperature at which this alloy is molten due to the high vapour pressure of calcium chloride at this temperature and the difficult conditions that would be imposed on the cell. At the start of the electrolysis there-

fore the cathode pool is formed by 7.5 gms. of aluminium (which melts at 660° C.) whilst the charge in the cell is 100 gms. of calcium chloride and 25 gms. of uranium dioxide. Details of a typical run using the cell are as follows—

Time	Temp., ° C.	Volts	Amps.	Amp./Hrs.	Remarks
0.00-----	875	7.1	10.0	-----	Started.
0.30-----	900	6.0	10.0	5.0	
1.00-----	900	5.5	10.0	10.0	
1.30-----	910	5.5	10.0	15.0	
2.00-----	910	5.5	10.0	20.0	
2.25-----	910	5.5	10.0	24.0	Run stopped.

It will be apparent from the phase diagram of the alloy that the mean temperature of electrolysis being 900° C. and the melting point of aluminium being 660° C., after a very short period of electrolysis the cathode alloy would become so enriched in uranium that its melting point would be above 900° C. and so it would be impossible to stir the alloy. Instead it has been found that the process of diffusion is sufficient to obtain a substantially homogeneous alloy which in the above experiment contained 74.2% by weight of uranium corresponding to an alloy of UAl₃. On removing this alloy and leaching with water the product proved to consist of discrete particles of coarse powder.

In order to produce the UAl₂ alloys a sample of this UAl₃ powder was heated in an alumina boat in a furnace at 1500° C. under a vacuum of 1×10⁻⁵ mm. of mercury. The initial charge to the furnace in one experiment weighed 11.7 gms. and the product weighed 9.5 gms. giving a loss of 2.2 gms. of aluminium. An analysis of the product showed that it had a uranium content of 79% by weight and was substantially pure UAl₂. It was successfully fused in an argon arc furnace.

The process of the invention, when applied to the preparation of uranium/iron alloy, necessitates modification of the technique used for the uranium/aluminium alloy. From the phase diagram of the uranium/iron system, it can be seen that a eutectic containing approximately 12.5% iron is molten well within the practical working range of the calcium chloride electrolyte. Initial attempts to electrolyse uranium from reduced UO₂ into such an alloy without agitation of the alloy proved impracticable, uranium being deposited as solid metal particles above the cathode pool without being incorporated in the alloy. Continuous stirring of the molten metallic alloy proved to be effective in producing a homogeneous alloy. Consequently the apparatus of FIG. 4 was devised and as can be seen it comprises a conical alumina crucible 30 supported by an insulating ring 31 in furnace 32, the upper end of the crucible being closed by a pyrophyllite lid 33. The cathode lead is in the form of a tungsten rod 34 the lower end of which is bent to form a U-shaped stirrer 35. The straight vertical portion of the tungsten rod is protected by an alumina sheath 36. Two

graphite anodes 37 are provided and graphite anode leads 38 are protected by alumina sheaths 39.

As it is intended that the cathode pool should be molten the whole time and as the temperature of electrolysis is in the region of 900° C., it is obviously impracticable to start with pure iron as the cathode alloy for the melting point of iron is 1535° C. Therefore an initial alloy (approximating to the eutectic) was made up by mixing together 183.35 gms. of uranium and 26 gms. of iron and heating the mixture under vacuum to 1300° C. when 209 gms. of an homogeneous alloy was obtained. The whole of this alloy was placed in the apparatus of FIG. 4 to form a cathode pool 40 in which the stirrer 35 was immersed, and the charge to the cell was completed by 125 gms. of anhydrous calcium chloride and 24 gms. of uranium dioxide. The details of one particular experiment are as follows—

Time	Temp., ° C.	Volts	Amps.	Amp./Hrs.	UO ₂ added, gms.	Remarks
0.00-----	930	6.1	10	-----	8	
0.30-----	925	6.0	10	5	16	
1.00-----	935	5.9	10	10	24	
1.30-----	935	5.8	10	15	-----	

The homogeneous alloy ingot was removed from the cell at the end of the electrolysis and was found to weigh 231 gms. giving a current efficiency of approximately 66%. This alloy analysed to show 89% uranium as compared with 87.55% uranium in the initial cathode pool. The addition of iron to the molten cathode pool will restore the same to its initial composition thus providing a route for the formation of the master alloy at the eutectic composition containing 12% of iron whereby a continuous production process is possible.

It should be mentioned that in all the experiments described above very little attack on the cell materials took place except in the case of the formation of the uranium aluminum alloy which attacked the crucible to some extent.

We claim:

1. A method for the production of a uranium containing material selected from the group consisting of uranium metal and alloys of uranium comprising the steps of suspending particles of uranium dioxide in an electrolyte consisting essentially of a molten alkaline earth metal chloride, effecting electrolysis in an electrolysis cell containing an anode and a metal cathode which are both unreactive with respect to the molten chloride, and maintaining the temperature of the molten chloride below the melting point of uranium.

2. A method for the production of uranium metal comprising the steps of suspending particles of uranium dioxide in an electrolyte consisting essentially of a molten alkaline earth metal chloride, effecting electrolysis in an electrolysis cell containing a metal cathode which is unreactive to both the said molten chloride and to uranium metal and an anode which is unreactive to the molten chloride, stirring the molten chloride during electrolysis

and maintaining the temperature of the molten chloride below the melting point of uranium metal.

3. A method according to claim 2 in which the cathode is made of molybdenum.

4. A method according to claim 2 in which the anode is made of graphite.

5. A method according to claim 2 in which the molten alkaline earth metal chloride is selected from the group consisting of calcium chloride and magnesium chloride.

6. A method according to claim 5 in which the electrolyte is maintained at a temperature in the range 850–950° C.

7. A method for the production of an alloy of uranium comprising the steps of suspending particles of uranium dioxide in an electrolyte consisting essentially of a molten alkaline earth metal chloride, effecting electrolysis in an electrolysis cell containing an anode which

is unreactive to the said molten chloride and a cathode chosen from the class consisting of an alloy of uranium and a metal which forms an alloy with uranium, said cathode being unreactive with respect to the molten chloride, and maintaining the temperature of the said electrolyte below the melting point of uranium.

8. A method according to claim 7 in which the anode is made of graphite.

9. A method according to claim 7 in which the cathode is formed by a pool of molten aluminum.

10. A method according to claim 7 in which the cathode is formed by a pool of molten iron-uranium alloy.

11. A method according to claim 10 in which the iron-uranium alloy contains approximately 10–12.5% by weight of iron.

12. A method according to claim 11 in which the iron-uranium alloy is continuously stirred.

13. A method according to claim 7 in which the molten alkaline earth metal chloride is selected from the group consisting of calcium chloride and magnesium chloride.

References Cited by the Examiner

UNITED STATES PATENTS

2,519,792	8/1950	Rosen	204—1.5
2,773,825	12/1956	Newcombe	204—243
2,781,304	2/1957	Wilhelm et al.	204—1.5
2,951,793	9/1960	Hansen	204—1.5
3,079,324	2/1963	Allen et al.	204—246

OTHER REFERENCES

AECD-3687. The Electrolytic Process for the Manufacture of Uranium, by J. W. Marden et al. June 24, 1946, pages 34, 35, 36, 37, 43, 54, 78, 80, 81, 82, 83.

REUBEN EPSTEIN, Primary Examiner.