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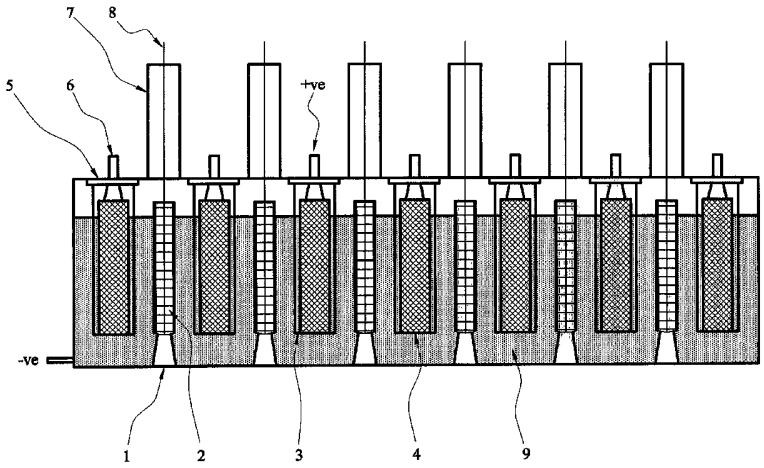
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(54) Title: ELECTROCHEMICAL CELL FOR METAL PRODUCTION



(57) Abstract: The invention provides a process for reducing to metallic form metal oxides, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte whilst controlling the potential of the cathode so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and an apparatus for performing the said process, the said apparatus being free from bolted or screwed fittings and comprising an electrochemical cell which comprises a body or housing, a cathode container, and a cathode connector, wherein said body or housing is maintained as the cathode. The process provides a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen produced as the only by-product, and offers a more practical, efficient and financially viable means for the production of metal from oxides than is available from the prior art. The metallic solid which is produced can be removed or used directly as the feed for an electrorefining process. In an alternative embodiment, the electrolytic ionisation of oxygen and the electrorefining processes are carried out in the same cell and the same salt system.

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ELECTROCHEMICAL CELL FOR METAL PRODUCTION

Field of the Invention

This invention relates to methods for the production of metals from oxides present in spent nuclear fuels and is particularly applicable to the production of actinides, specifically uranium. Methods of the present invention can be used in the treatment of irradiated fuels for producing actinides in metallic form suitable for use as feeds in subsequent electrorefining processes.

Background to the Invention

In the established art, two processes have been developed for the treatment of irradiated nuclear fuel making use of molten salts. As used herein, the term "molten salts" is intended to cover salts such as lithium chloride which melts at an elevated temperature and also ionic liquids which typically are liquid at room temperature or which melt at a temperature up to about 100°C.

The Dimitrovgrad SSC-RIAR process makes use of chemical oxidants (chlorine and oxygen gases) to react with powdered uranium dioxide fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. In an electrochemical cell the uranium compounds are reduced to UO_2 at the cathode, forming a dendritic deposit. This process has both technical and environmental limitations.

The second process, developed by the Argonne National Laboratory (ANL) is fundamentally an electrorefining technology which uses direct current to anodically oxidise uranium to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as dendritic uranium metal.

The ANL process requires a metal feed. If oxide fuels are to be treated, it is necessary to reduce the uranium oxide (usually UO_2 pellets) to the metal. This reduction process is carried out chemically, using lithium metal in a LiCl or LiCl/KCl

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molten salt, or a Li/Cd alloy, at 500 to 600°C. Alternatively, a salt transport process can be used involving a Cu-Mg-Ca alloy and molten $CaCl_2$ salt. However, in both reduction methods the by-products, Li_2O and CaO respectively, need to be recovered from the molten salt phase by an electrolysis step. Effectively this means a two stage process.

A disadvantage of the lithium reduction process for producing a metallic feed from an oxide is the production of Li_2O by-product. This requires recycle to make the process economic, and this is done by an electrolytic recovery of lithium metal. Hence this is a two stage process, comprising a reduction step followed by a lithium recovery stage.

In co-pending PCT patent application WO 01/41152 there is disclosed a single step process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt.

The process thereby involves the use of a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen, CO or CO_2 produced as the only by-products. The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of metal (eg Ca) from the cations (eg Ca ions) in the fused salt. Typically, the oxide comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide.

The present inventors have, however, now effected an improvement to the process described in WO 01/41152 which allows a more practical, efficient and financially viable process to be adopted in the production of metals from oxides. The new process is particularly beneficial in that it facilitates the removal of bolted and screwed fittings from the apparatus used for the production of the metal.

Statements of Invention

Thus, according to a first aspect of the present invention there is provided an apparatus for performing a process for reducing to metallic form metal oxides, the said apparatus being free from bolted or screwed fittings, and comprising an electrochemical cell which comprises a body or housing, a cathode container, and a cathode connector, wherein said body or housing is maintained as the cathode.

The body or housing of the cell which comprises the apparatus according to the first aspect of the invention is most conveniently maintained as the cathode by the provision of an electrical connection from a power supply, provided by means of a connector from the cathode terminal to the body or housing of the cell. Typically, said connector comprises a bolted connection, but this is positioned externally to the cell. No bolted or screwed connections are present within the cell, wherein a cathode connector is provided which is affixed to an internal surface of the cell, most preferably the base of the cell, generally by welding. Preferably said cathode connector comprises a cathode rail.

In operation, the body or housing of the cell is maintained as the cathode, and said cathode is brought into contact with the cathode container by means of the cathode connector. Thus, contact is made between the cathode container and the cathode connector in order to facilitate the electrolytic process. Contact may be most conveniently achieved by means of a simple press connection between the two components.

The cathode container preferably comprises a basket, such as a mesh basket, or vessel, typically a metal oxide retaining vessel, and – most preferably – comprises an assembly of such baskets or vessels. In order to effect electrical connection between such an assembly of cathode containers and the cell body during operation of the cell, it is necessary to provide a multiplicity of connectors and to effect contact between individual cathode baskets or vessels and individual connectors, preferably by means of a multiplicity of press connections.

Preferably the oxide is in contact with the cathode container and it is preferred that the cathode is in the form of a mesh basket or, most preferably, an assembly of mesh baskets, with the oxide being contained within the said baskets. In this case, contact between the assembly of cathode containers and the cathode connectors is most simply achieved when the cathode connectors are in the form of a multiplicity of cathode rails which are welded to the base of the cell, allowing press contact to be brought about by the weight of the oxide feedstock in the cathode basket. This represents the most preferred embodiment of the first aspect of the invention. The anode may be any suitable inert anode, such as carbon.

According to a second aspect of the present invention, there is provided a process for reducing to metallic form metal oxides, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte in an apparatus according to the first aspect of the invention, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt.

The molten salt electrolyte may be any suitable molten salt or mixture of such salts, for instance chloride salts, preferably $CaCl_2$ and/or $BaCl_2$.

Preferably, the oxide treated by the process according to the second aspect of the invention comprises an oxide present in spent nuclear fuel. Typically, the oxide comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide, or mixed uranium/plutonium oxides. The uranium oxide is commonly uranium dioxide. Alternatively, the oxide may comprise the oxide of a metal such as zirconium or hafnium.

In such a process, wherein the oxide comprises an oxide present in spent nuclear fuel, the fuel may be first treated mechanically to remove its zircaloy cladding before it is added to the electrolytic cell. Alternatively, the zircaloy cladding may be treated with

the fuel. The fuel may require to be sheared into sections of small length prior to treatment in order to expose the oxide fuel to the molten salt.

Said oxide may be in any physical form, and this is generally dependent on the particular chemical nature of the spent nuclear fuel and the processing to which the material has previously been subjected. For example, the fuel may comprise a powder, an amorphous mass, or a dense solid agglomerate. In any event, the material may be treated according to the method of the second aspect of the present invention by connection to an electrical circuit such that it serves as the cathode during electrolysis; as previously disclosed, connection to the circuit may be conveniently effected by the use of a cathode basket, into which the material is placed.

The process provides a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen produced as the only by-product. The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of metal (eg Ca) from the cations (eg Ca ions) in the fused salt.

The process according to the second aspect of the invention provides a more practical, efficient and financially viable means for the production of metal from oxides. The electrical continuity of the system which is provided is effective since all the components are held in the cathodic potential region and are, therefore, metallic in nature.

Detailed Description of the Invention

In order to carry out an embodiment of the process according to the second aspect of the present invention, using a metal oxide which comprises spent nuclear fuel, an electrolytic cell is assembled which has a carbon anode, a mesh basket cathode and a cathode rail connector welded to the base of the cell. Irradiated oxide fuel is placed in the mesh basket. The electrolyte consists of a molten salt or a mixture of such salts comprising, for example, chloride salts such as $CaCl_2$ or $BaCl_2$. A voltage is applied between the cathode and the anode. At the cathode the reaction involves the

diffusion of oxygen atoms to the surface of the solid, followed by ionisation according to the reaction:

$$O_2 + 4e^- \rightarrow 2\,O^{2-}.$$

The oxide ions which are produced dissolve in the electrolyte and are transferred to the anode where they are re-oxidised to produce oxygen, CO or CO_2 gases. The potential at the cathode may be controlled, via a third reference electrode, to ensure that the reaction occurring at the cathode is oxygen ionisation and not deposition of eg Ca metal from the cations in the fused salt. Electrolysis at elevated temperatures results in an increased rate of oxygen diffusion, thereby also encouraging ionisation rather than metal deposition.

After electrolysis the irradiated fuel is left in the form of a metallic solid at the cathode. This metallic solid, which contains fission products, can be removed or used directly as the feed for an electrorefining process. The remaining components of the cell may be re-used immediately without the need for any cleaning.

In an alternative embodiment in accordance with the present invention the electrolytic ionisation of oxygen and the electrorefining processes are carried out in the same cell and the same salt system. In such cases a second cathode, or cathode assembly, may be required.

It is to be emphasised that the advantage of the apparatus and process of the present invention is that they facilitate the performance of an effectively single stage process which provides advantages over the prior art in terms of practicality, efficiency and cost. The process is advantageously used for the treatment of irradiated oxide nuclear fuel, possibly in the form of pellets and, most particularly, is applied to fuels such as uranium oxide, and mixed uranium and plutonium fuels.

In order to fully illustrate the above and other features of the apparatus according to the first aspect of the invention, without in any way limiting the scope of the

invention, a preferred embodiments will now be described with reference to the drawing.

Description of the Drawing

Figure 1 shows an apparatus according to the first aspect of the invention which comprises a series of electrolytic cells, the bodies and housings of which are, in use, connected by means of cathode rails 1 to cathode baskets 2. The cells also comprise anodes 4, surrounded by anode protective sleeves 3, and connected to an electrical supply by means of electrical connections 6, these being protected by insulation shrouds 5.

In operation, the cathode baskets 2, which are equipped with basket handles 8, cooled by means of cooling chambers 7, are loaded with spent nuclear fuel pellets and lowered into the electrolyte 9 to a point at which contact is made with cathode rails 1 and, thereby, with the cell housing, which is maintained as the cathode, thereby allowing processing to commence.

CLAIMS

1. An apparatus for performing a process for reducing to metallic form metal oxides, the said apparatus being free from bolted or screwed fittings and comprising an electrochemical cell which comprises a body or housing, a cathode container, and a cathode connector, wherein said body or housing is maintained as the cathode.

2. An apparatus as claimed in claim 1 wherein said cathode connector is affixed to an internal surface of the cell.

3. An apparatus as claimed in claim 2 wherein said cathode connector is affixed to an internal surface of the cell by means of welding.

4. An apparatus as claimed in any one of claims 1, 2 or 3 wherein an electrical connection from the cathode container to the body or housing of the cell is provided by means of a cathode connector.

5. An apparatus as claimed in claim 4 wherein said electrical connection is provided by means of a press connection.

6. An apparatus as claimed in any preceding claim wherein said cathode connector comprises a cathode rail.

7. An apparatus as claimed in claim 6 wherein said rail is welded to the base of the cell.

8. An apparatus as claimed in any preceding claim wherein the cathode container comprises a mesh basket or metal oxide retaining vessel.

9. An apparatus as claimed in any preceding claim wherein the cathode container comprises an assembly of cathode containers.

10. An apparatus as claimed in claim 9 wherein said assembly comprises an assembly of mesh baskets or metal oxide retaining vessels.

11. An apparatus as claimed in any preceding claim wherein the anode is a carbon anode.

12. An apparatus as claimed in any preceding claim wherein the body or housing of the cell is maintained as the cathode by the provision of an electrical connection from a power supply to the body or housing of the cell.

13. A process for reducing to metallic form metal oxides, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte in an apparatus as claimed in any one of claims 1 to 12, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt.

14. A process as claimed in claim 13 wherein the body or housing of the cell is maintained as the cathode and is brought into contact with the cathode container by means of a press connection between said container and a cathode connector.

15. A process as claimed in claim 13 or 14 wherein the oxide comprises the oxide of zirconium or hafnium.

16. A process as claimed in claim 13 or 14 wherein the oxide comprises an oxide present in spent nuclear fuel.

17. A process as claimed in claim 16 wherein the oxide comprises an actinide oxide.

18. A process as claimed in claim 17 wherein the actinide oxide comprises uranium oxide, irradiated uranium oxide or mixed uranium/plutonium oxide fuel pellets.

19. A process as claimed in claim 18 wherein the uranium oxide comprises uranium dioxide.

20. A process as claimed in any of claims 13 to 19 wherein the oxide is located in a mesh basket which forms the cathode.

21. A process as claimed in any of claims 13 to 20 wherein the molten salt electrolyte comprises at least one chloride salt.

22. A process as claimed in claim 21 wherein the chloride salt is $CaCl_2$ or $BaCl_2$.

23. A process as claimed in any one of claims 16 to 22 wherein the fuel is treated together with its cladding.

24. A process as claimed in any one of claims 16 to 22 wherein the cladding is removed from the fuel prior to treatment.

25. A process as claimed in any of claims 13 to 24 wherein the metal resulting from the process is used as the feed for an electrorefining process.

26. A process as claimed in claim 25 wherein the electrorefining process is carried out in the same electrolytic cell as the electrolytic reduction process.

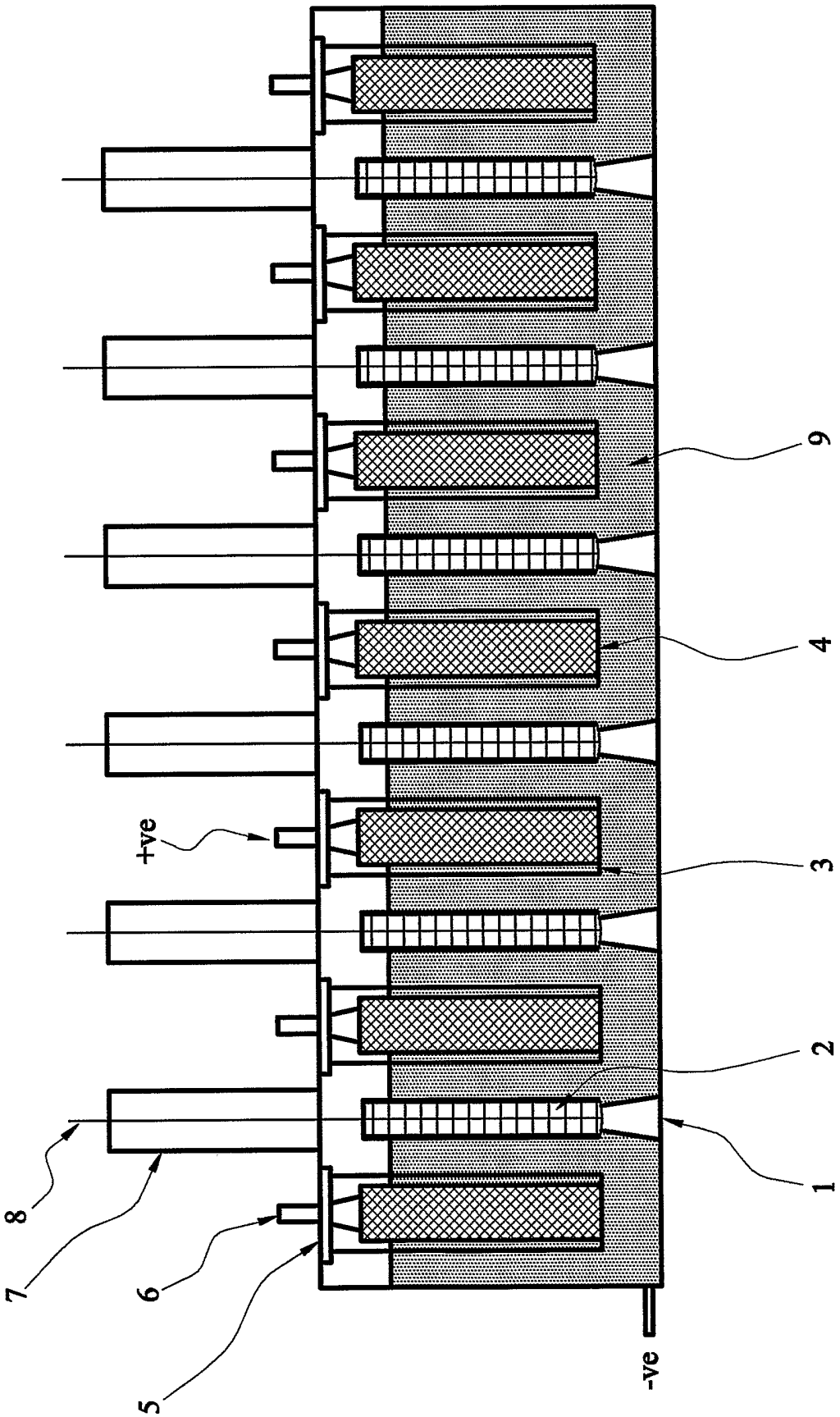


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/00792

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G21C19/42 C25C3/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G21C C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 378 325 A (DASTOLFO JR LEROY E ET AL) 3 January 1995 (1995-01-03) column 6, line 49 -column 6, line 60; figure 3 ---	1
A	WO 00 40782 A (NORA VITTORIO DE ;MOLTECH INVENT SA (LU)) 13 July 2000 (2000-07-13) page 15, line 32 -page 15, line 39 ---	1-26
A	US 5 650 053 A (GAY EDDIE C ET AL) 22 July 1997 (1997-07-22) abstract; figure 1 ---	1-26

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2003	12/08/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lohberger, S

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 160 367 A (PIERCE R DEAN ET AL) 3 November 1992 (1992-11-03) abstract	1-26
A	US 3 982 928 A (CHIOTTI PREMO ET AL) 28 September 1976 (1976-09-28) abstract	1-26
E	US 6 540 902 B1 (GOURISHANKAR KARTHICK ET AL) 1 April 2003 (2003-04-01) column 2, line 5 -column 7, line 35; figures 1-5	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

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