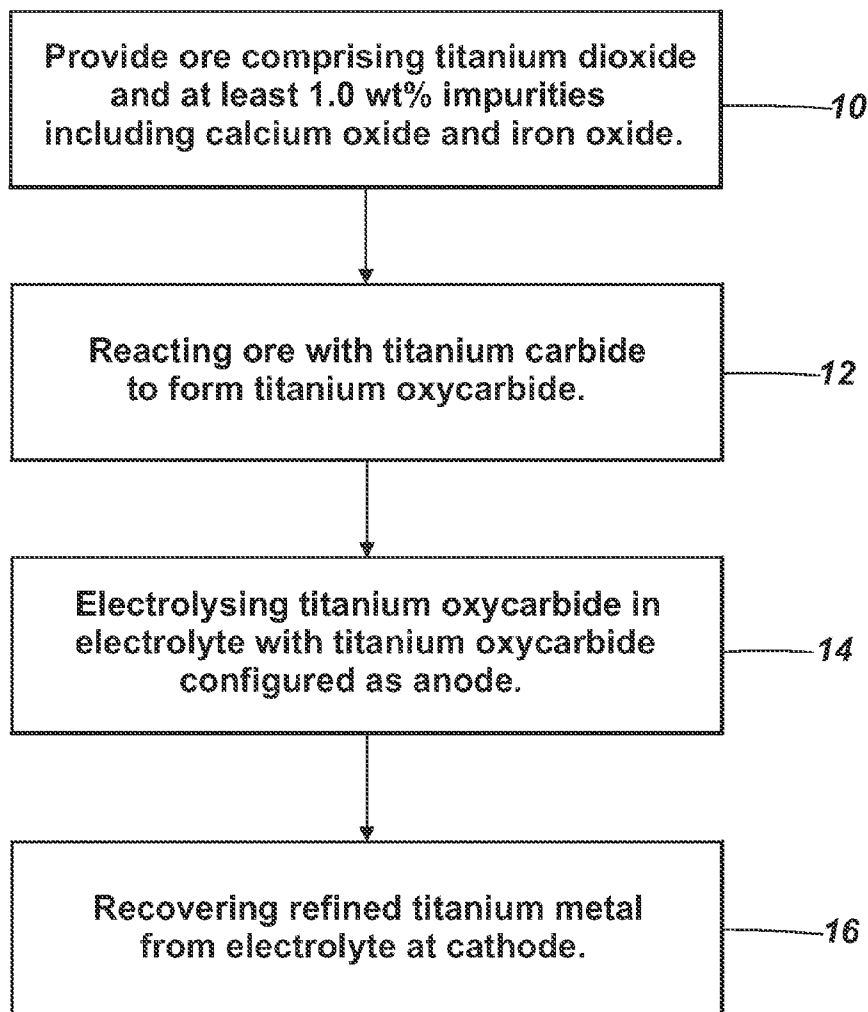(19) **United States**

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(54) **TREATMENT OF TITANIUM ORES**

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Publication Classification

(57) **ABSTRACT**

A method of producing titanium, comprising providing an oxide of titanium having a level of impurities of at least 1.0 wt %, reacting the oxide of titanium to form a titanium oxycarbide; and electrolysing the titanium oxycarbide in an electrolyte, with the titanium oxycarbide configured as an anode; and recovering a refined titanium metal from a cathode in the electrolyte.

Provide ore comprising titanium dioxide
and at least 1.0 wt% impurities
including calcium oxide and iron oxide. —10

Reacting ore with titanium carbide
to form titanium oxycarbide. —12

Electrolysing titanium oxycarbide in
electrolyte with titanium oxycarbide
configured as anode. —14

Recovering refined titanium metal
from electrolyte at cathode. —16

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and at least 1.0 wt% impurities
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to form titanium oxycarbide. ——————12

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electrolyte with titanium oxycarbide
configured as anode. ——————14

Recovering refined titanium metal
from electrolyte at cathode. ——————16

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6a
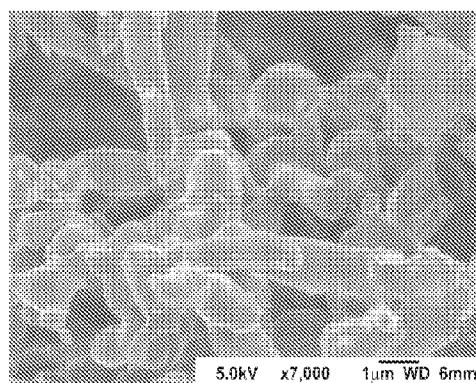
Fig. 6b
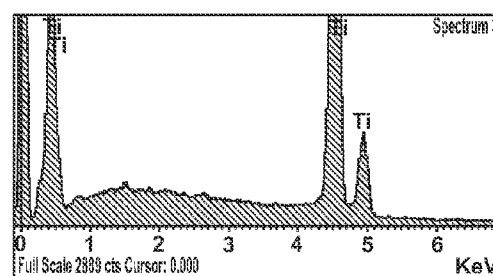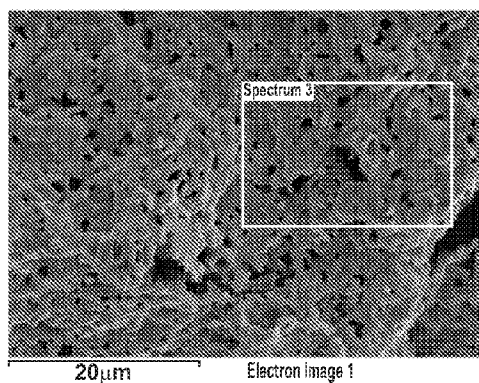
Element	Weight %	Atomic %
Ti K	100.00	100.00
Totals	100.00	

Fig. 7

TREATMENT OF TITANIUM ORES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of U.S. patent application Ser. No. 13/386,891, filed Mar. 2, 2012, which is a continuation-in-part of the national phase entry of PCT/GB2010/051237 which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a method of producing titanium, particularly but not exclusively from an ore comprising titanium dioxide and at least 1.0 wt % impurities including calcium oxide and iron oxide.

BACKGROUND ART

[0003] Titanium is a metal with remarkable properties but its applications are restricted due to the high cost of its extraction and processing. Using the Kroll or Hunter Processes requires high purity titanium tetrachloride which is either reduced with magnesium (Kroll Process) [W. J. Kroll, Trans. Electrochem. Soc., 78 (1940) 35-57] or sodium (Hunter Process) [M. A. Hunter, J. Am. Chem. Soc., 32 (1910) 330-336]. The high purity titanium tetrachloride is produced by carbo-chlorination of the impure titanium dioxide and as all the oxides chlorinate, the impurities are removed by selective distillation of the chlorides. The other way of making high purity titanium dioxide, usually for the pigment industry, is the sulphate route where the impure titanium dioxide is dissolved in sulphuric acid and the iron, which is the major impurity, precipitated as iron oxide. However, there are several sources of titanium oxide which contain impurities or are too fine and render the conventional routes impractical. For example, titanium ores containing significant quantities of calcium oxide form in the carbo-chlorination process, calcium chloride which melts below the temperature of the fluidised bed reactor. This liquid phase de-fluidises the bed. The particle size of some other ore bodies are too fine to remain in a fluidised bed and are simply swept away. Use of the sulphuric acid route results in the formation of stable calcium sulphate when calcium oxide containing ores are leached. It would be advantageous if these materials could be simply converted into high purity titanium.

[0004] As mentioned above, there are two commercial methods, Kroll and Hunter, for the production of titanium using high purity titanium chloride with the vast majority being produced by the Kroll Process. In order to reduce the cost of titanium production, other methods have been investigated, usually starting with high purity oxide. In laboratory and pilot plant scale experiments, titanium dioxide has been reduced using calcium dissolved in calcium chloride (OS Process) [R. O. Suzuki in "Ti-2003 science and technology". Eds G. Lutjering and J. Albrecht, (2004, Wiley-VCH, Weinheim) 245-252.] or electrochemically by electro-deoxidation in molten calcium chloride (FFC Cambridge Process) [G. Z. Chen, D. J. Fray and T. W. Farthing, Nature 407 (2000) 361-364]. In the latter process, the titanium oxide is made the cathode in a bath of calcium chloride and it is found that the cathodic reaction is not the deposition of calcium from the melt but the ionisation of the oxygen in the titanium dioxide, which diffuses to the anode and is discharged. In both these processes, ores containing calcium oxide can be treated as the calcium oxide would simply dissolve in the salt. However,

there would not be any selective removal of the other elements as the final product would be a reflection of the impurities in the original feed material. Other processes, such as the Armstrong Process—'Summary of emerging titanium cost reductions', EHK Technologies. Report prepared for US Department of Energy and Oak Ridge National Laboratory, subcontract 4000023694 (2003) which is a derivative of the Hunter Process, all require high purity titanium tetrachloride as the feedstock.

[0005] Another process of interest, is that patented by Wainer in the 1950s [U.S. Pat. No. 2,722,509], which describes a process where equimolar amounts of finely divided chemically pure titanium carbide and finely divided chemically pure titanium monoxide were intimately admixed and heated in an argon atmosphere to form a TiC.TiO anode, a mutual solid solution of titanium carbide and titanium monoxide in which the molar ratio of the carbide to the monoxide does not exceed 1. A melt of a chloride salt of an electropositive element is used as an electrolyte and when a voltage is applied, anodic reactions of the following type occur:

$$TiCO = Ti^{2+} + CO + xCO + 2e^-$$
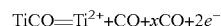
The titanium ions dissolve into the electrolyte, and are reduced at the cathode:

$$Ti^{2+} + 2e = Ti$$
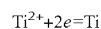
[0006] Withers and co-workers have also investigated thermal and electrochemical processes for production of titanium see WO 2005/019501 and WO 2007/097823. The process involves forming a titanium oxide-carbon composite by mixing titanium oxide with a source of carbon and heating in the absence of air to a temperature sufficient to reduce the plus four valance of the titanium in the TiO_2 to a lower valence and form a titanium suboxide/carbon composite electrode. In the process of forming the titanium suboxide/carbon composite electrode, any iron oxide is reduced to iron and was removed by leaching or complexing the iron in an aqueous solution at ambient temperature. WO 2005/019501 suggests that by incorporating other oxides into the anode, it is possible to reduce these other oxides at the same time, and deposit the cations simultaneously at the cathode to produce an alloy which reflects the composition of the original anode. In the same document, a method of producing high purity titanium is described which uses the same conditions as the previous experiments. These two results are totally inconsistent.

[0007] The present applicant has sought to provide a method of refining titanium from an ore comprising titanium dioxide and relatively high levels (e.g. at least 1.0 wt %) impurities including calcium oxide and iron oxide.

STATEMENT OF INVENTION

[0008] According to a broad aspect, the present invention provides electrorefining of an anode consisting of an oxycarbide to give a pure metallic material at the cathode.

[0009] In accordance with another aspect of the present invention, there is provided a method producing titanium, comprising: providing an oxide of titanium having a level of impurities of at least 1.0 wt %; reacting the oxide of titanium to form a titanium oxycarbide; electrolysing the titanium oxycarbide in an electrolyte, with the titanium oxycarbide configured as an anode; and recovering a refined titanium metal from a cathode in the electrolyte.
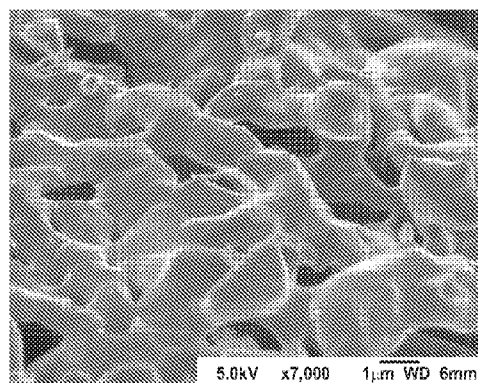
[0010] The present applicant has surprisingly found that by electrolysing the titanium oxycarbide, titanium metal with a

relatively high purity compared to the impurity levels in the oxide of titanium is deposited at the cathode. The refined titanium metal may have a level of impurities of less than 0.5 wt %, i.e. be at least 99.5% pure by weight, and may even be at least 99.8% pure by weight. The present applicant has found that impurities initially present in the oxide of titanium, which might be expected to be deposited at the cathode with the titanium, are retained in the electrolyte.

[0011] The oxide of titanium may be an ore or ore concentrate. The oxide of titanium may comprise impurities selected from the group consisting of oxides of silicon, aluminium, iron, calcium, chromium and vanadium. In one arrangement, the oxide of titanium has impurities including oxides of iron and/or calcium. The presence of such impurities interferes with extraction of titanium using conventional techniques, particularly if the oxides of calcium and/or iron are present in significant quantities. For example, the presence of more than about 0.15 wt %-0.2 wt % calcium oxide may preclude processing in a fluidised bed reactor due to melting of calcium chloride resulting from an earlier carbo-chlorination step. Consequently, an ore containing titanium dioxide and significant levels of calcium oxide and iron oxide has a significantly lower value than other ores with nothing more than minimum or trace levels of calcium oxide and/or iron oxide.

[0012] The oxide of titanium may have a level of impurities of at least 2.0 wt %, perhaps even at least 2.5 wt %. The oxide of titanium may include at least 0.1 wt % calcium oxide, perhaps even at least 0.5 wt % calcium oxide. Additionally or alternatively, the oxide of titanium may include at least 0.1 wt % iron oxide, perhaps at least 0.5 wt % iron oxide, and perhaps even at least 5 wt% iron oxide. The refined titanium metal may include a lower level of calcium and/or iron than the oxide of titanium.

[0013] The oxide of titanium may substantially comprise titanium dioxide. For example, the oxide of titanium may comprise at least 90wt % titanium dioxide, and possibly even at least 95 wt % titanium dioxide. The titanium oxycarbide may be formed by reacting the oxide of titanium with titanium carbide in relative amounts to form a Ti—C—O solid solution. For example, powders of the oxide of titanium and titanium carbide may be admixed and sintered to form the Ti—C—O solid solution. If the oxide of titanium substantially comprises titanium dioxide, it may be admixed with titanium carbide in relative amounts to achieve a stoichiometric reaction given by

$$4TiC+2TiO_2=3Ti_2CO+CO_{(g)}.$$
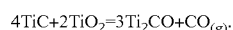
[0014] The electrolyte may be a molten salt, and may comprise a chloride of an alkali or alkali-earth metal. The molten salt may be selected from the group consisting of lithium chloride, sodium chloride, potassium chloride, magnesium chloride and mixtures thereof. The molten salt may comprise a sodium chloride—potassium chloride eutectic or a lithium chloride—sodium chloride—potassium chloride eutectic. Alternatively, the molten salt may be magnesium chloride. Such a salt boils at 1412° C. and is distilled away from the cathodic product; the other salts can only be removed by dissolving in water which causes the titanium to be oxidised. The molten salt may further comprise titanium (II) chloride ($TiCl_2$) and/or titanium (III) chloride ($TiCl_3$). The presence of titanium chloride (perhaps a few percent by weight) may help transportation of titanium ions through the salt.

[0015] The method may further comprise removing impurities from the electrolyte by treating the molten electrolyte with titanium, for example at a temperature of 700° C.

[0016] In accordance with another aspect of the present invention, there is provided a method of refining titanium, comprising: providing a titanium ore or ore concentrate comprising titanium dioxide; reacting the titanium ore or ore concentrate to form a titanium oxycarbide; electrolysing the titanium oxycarbide in an electrolyte, with the titanium oxycarbide configured as an anode; and recovering titanium from a cathode in the electrolyte.

[0017] The titanium ore or ore concentrate may comprise impurities (as defined with the previous aspect). The formation of the titanium oxycarbide may comprise reacting the titanium dioxide with titanium carbide (as defined with the previous aspect). The recovered titanium may have a higher purity (lower level of impurities in relative terms), with the level of titanium increasing from less than 98% by weight in the ore or ore concentrate to at least 99.5% by weight in the recovered titanium, and possibly even at least 99.8% by weight.

BRIEF DESCRIPTION OF DRAWINGS

[0018] An embodiment of the invention will now be described in detail, by way of example, and with reference to the accompanying drawings, in which:

[0019] FIG. 1 is a flow chart illustrating a method embodying the present invention;

[0020] FIG. 2 is an XRD pattern of a Ti—C—O solid solution prepared in accordance with one step of the present invention;

[0021] FIG. 3 is a schematic diagram of an electrorefining cell in accordance with another step of the present invention;

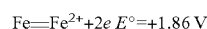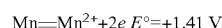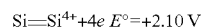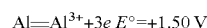[0022] FIG. 4 shows potential profiles during anodic dissolution of Ti—O—C;

[0023] FIG. 5 shows X-ray spectra of the refined titanium metal recovered at the cathode;

[0024] FIGS. 6a and 6b are SEM micrographs of the refined titanium metal recovered at the cathode; and

[0025] FIG. 7 shows EDS spectrum for the refined titanium metal recovered at the cathode.

SPECIFIC DESCRIPTION OF EMBODIMENT OF INVENTION

[0026] Electrorefining in molten salts is used commercially to produce high purity molten aluminium by dissolving the aluminium into a copper-aluminium alloy. This is made the anode and the aluminium being the most reactive element is ionised into the salt and deposited at the cathode with the impurities remaining in the anode. The ionisation potentials for the pure elements for a chloride melt relative to Na/Na$^+$, at 1173 K, are

$$Al=Al^{3+}+3e \; E°=+1.50 \text{ V}$$

$$Si=Si^{4+}+4e \; E°=+2.10 \text{ V}$$

$$Mn=Mn^{2+}+2e \; E°=+1.41 \text{ V}$$

$$Fe=Fe^{2+}+2e \; E°=+1.86 \text{ V}$$

Manganese should ionise first followed by Al, Fe and Si but as the quantity of manganese is usually very small, aluminium ionises first.

[0027] The same principle can be applied to the refining of titanium but in this invention, the reactions are not the refining of titanium metal but refining metal from metal oxides. A typical composition of an ore is given in Table 1.

TABLE 1

Analysis of a typical commercial Rutile Concentrate	
Element	Assay %
TiO_2	96.5
SiO_2	1.40
Al_2O_3	0.26
Fe_2O_3	0.55
MgO	0.07
CaO	0.66
Na_2O	0.08
K_2O	0.01
P_2O_5	<0.01
MnO	<0.01
Cr_2O_3	0.31
V_2O_5	0.30
LOI	0.07
U_3O_8	0.0004
ThO_2	<0.002
As	<0.001
S	0.03

[0028] If this material is reacted with C to form TiC_xO_y and other oxycarbides, the reactions in Table 2 will occur when the material is made anodic.

TABLE 2

Potentials relative to $Na = Na^+ + e$	
Reaction	Potential relative to Na/Na$^+$ at 1073 K (V)
$TiO + C = Ti^{2+} + CO(g)$	2.85
$CaO + C = Ca^{2+} + 2e + CO(g)$	1.45
$FeO + C = Fe^{2+} + 2e + CO(g)$	1.92
$Cr_2O_3 + 3C = 2Cr^{2+} + 6e + 3CO(g)$	2.47
$MgO + C = Mg^{2+} + 2e + CO(g)$	2.11
$SiO_2 + 2C = Si^{4+} + 4e + 2CO(g)$	2.87

[0029] The order of ionisation should be calcium, iron, magnesium, chromium , titanium and then silicon, ie calcium should be removed as calcium ions, followed by Fe as Fe^{2+}, etc. However these are for pure metal oxides whereas in the ore, it is likely that the oxides form a solid solution and their activities, except for TiO, will be considerably reduced. An activity of 2×10^{-5} will alter the potential by 0.5 V, so that the only firm conclusion is that calcium will ionise first followed by the other elements. Once in the electrolyte, the deposition potentials should be given by Table 3 and the order of deposition chromium, iron, titanium magnesium and, finally, calcium.

TABLE 3

| Potentials relative to $Na^+ + e = Na$	
Reaction	Potential relative to $Na^+ + e = Na$ (V)
$Cr^{2+} + 2e = Cr$	2.07
$Mg^{2+} + 2e = Mg$	0.83
$Ti^{2+} + 2e = Ti$	1.68
$Fe^{2+} + 2e = Fe$	1.99
$Ca^{2+} + 2e = Ca$	−0.18

[0030] Again, these deposition potentials will be influenced by the activities or concentration of the ions in the salt so that if the concentration of the species is low, it will be more difficult to deposit the metal form that species.

[0031] The overall conclusion of these calculations is that it is very likely the calcium, being highly electropositive, will be retained by the electrolyte. Surprisingly, it was found that by electrorefining the oxycarbide, made from an ore with the composition given in Table 1, titanium with a very low impurity content of the other elements was deposited on the cathode.

EXAMPLE

[0032] A broad method of producing titanium from an ore (such as the ore whose composition is given in Table 1) is illustrated in FIG. 1. Having provided the ore at step 10, a titanium oxycarbide is formed at step 12. The titanium oxycarbide is electrolysed at step 14, and refined titanium metal recovered at the cathode at step 16.

[0033] The oxycarbide was prepared (step 12) by mixing an ore of the composition shown in Table 1 in accordance with the stoichiometry given by the equation:

$$4TiC + 2TiO_2 = 3Ti_2CO + CO(g).$$
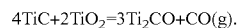
[0034] The powders were pressed into pellets 2 mm diameter and 2 mm thickness using an uniaxial pressure of 2.65 tons cm^{-2}. The pellets were sintered in a vacuum furnace at 1373 K under a vacuum of 10^{-2} Torr. The pellets, after sintering, were homogeneously black and the X-ray pattern (FIG. 2) shows that the pellet was constituted by the Ti—C—O solid solution.

[0035] A schematic of the electrorefining cell is shown in FIG. 3. The titanium oxycarbide (Ti—C—O) is configured as the anode and electrolysed in an electrolyte (step 14). The electrolytes that were used were either eutectic NaCl—KCl or eutectic LiCl—NaCl—KCl, containing some $TiCl_2$ and $TiCl_3$. A series of galvanostatic electrolyses were carried out in the current density range from 50 to 100 mA cm^{-2}. From FIG. 4, it can be seen that the potential is essentially constant but rises to the decomposition potential of the bulk salt when the anode had been consumed and the lead wire was acting as the anode.

[0036] The anode and cathode current efficiencies were calculated assuming that the valency of the titanium ion in the solution was 2.5. It was assumed that the following electrochemical reactions took place during the electrorefining:

Anode: $Ti = Ti^{3+} + 3e$ and $Ti = Ti^{2+} + 2e$

Cathode: $Ti^{3+} + e = Ti^{2+}$ and $Ti^{2+} + 2e = Ti$

TABLE 3

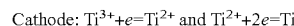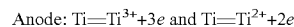| Experiment Sequence	Temperature (°C.)	Cell voltage (V)	Anode Remaining (%)	Anode current efficiency (vs Ti$^{2.5+}$)*	Cathode Current Efficiency (vs Ti$^{2.5+}$)*
1	570	1.6	2.1	88.3	38.6
2	570	1.8	3.2	82.6	42.1
3	620	1.6	—	94.2	50.6
4	620	1.8	1.7	87.6	39.5

4

TABLE 3-continued

Experiment Sequence	Temperature (° C.)	Cell voltage (V)	Anode Remaining (%)	Anode current efficiency (vs Ti$^{2.5+}$)*	Cathode Current Efficiency (vs Ti$^{2.5+}$)*
5	670	1.6	3.4	80.5	44.3
6	670	1.8	3.8	81.8	47.6

*Anode and cathode current efficiencies on the assumption that the electrolyte contains a 50/50 mixture of Ti^{3+}/Ti^{2+}.

[0037] From Table 3, it is clear that most of the titanium and some of the impurities dissolved in the salt. However, the high Ti^{3+} concentration lowered the current efficiency at the cathode.

[0038] Metal deposited at the cathode during electrolysis (step **16**) was collected. Such metal was physically broken and washed and FIG. **5** shows the X-ray spectra, FIG. **6**, the microstructure, and FIG. **7**, the EDS spectrum. This conclusively shows that relatively pure titanium was deposited at the cathode.

[0039] The impurities of the cathodic product were analysed by inductively coupled plasma. The electrorefined product as described above was prepared from the ore concentrate, presented in Table 1. It can be seen (see Table 4), compared to their composition in the ore concentrate, that the main metal elements have been reduced to a very low level (typically by about one order of magnitude or more) except iron. The relatively high iron composition in the cathodic product could be partly because a steel bar was used as a cathode, which contaminated the cathodic product when physically removing from the electrode.

TABLE 4

The composition of the impurities in the starting and end products.

	Sample				
	Al (%)	Ca (%)	Cr (%)	Fe (%)	Si (%)
Concentrate	0.232	0.782	0.350	0.660	1.540
Electrorefined Product	0.032	0.079	0.029	0.130	<0.001

[0040] As can be seen, there has been a reduction in a significant number of the elements so the quality of titanium has increased from 96.44% (in the concentrate) to 99.73% which is a substantial increase.

[0041] An Induction Coupled Plasma Unit (ICP) was used to analyze the impurities in the molten salt after the experiments. The cell contained 260 g of the NaCl—KCl electrolyte and for every electrolysis, around 0.326 g of Ti—C—O anode was used and electrolysis was performed under a cell voltage of 0.6V. After electrolysis around 1 g salt was taken out from the bulk electrolyte and dissolved in high purity water. The concentration of the impurities was analyzed by ICP and the results are shown in Table 5.

TABLE 5

The composition of the impurities in salt after electrolysis (the electrolyte was used four times)

	Sample				
	Al (ppm)	Ca (%)	Cr (%)	Fe (%)	Si (%)
Blank	0	0	0	0	0
After 1st electrolysis	0.00176	0.33831	0.00558	0.00104	—
After 2nd electrolysis	0.00122	0.76268	0.03040	0.00098	0.04148
After 3rd electrolysis	0.00166	1.38767	0.03570	—	0.05111
After 4th electrolysis	0.00219	1.62361	0.03753	0.00407	0.05483

[0042] It can be seen that most of the impurities have been anodically dissolved into molten salt where they remain. In general, the quantity of impurities increases with use of the electrolyte but the increases are not uniform. This may be due to heterogeneity in the composition of the pellets. The elements Ca, Cr, Fe and Si build up as ions in the salt whilst the Al is lost from the melt as aluminium chloride which has a very high vapour pressure. Calcium has too high a deposition potential to deposit whilst titanium is depositing and for the other elements it can be assumed that the very low concentrations lead to low concentration gradients and hence low mass transfer in the melt. Cr, Fe and Si could be removed by treating the melt with titanium where the following reaction will occur.

$$MCl_2 + Ti = TiCl_2 + M$$

where M is either Cr, Fe or Si or a portion of the electrolyte removed and discarded

[0043] Treatment of the electrolyte with titanium at 700° C. removes many of the impurities down to very low levels, such as Cr 0.003 wt % Fe 4×10^{-6} wt %, Si 6×10^{-9} wt % which will give a titanium product with an even lower level of impurities.

[0044] In accordance with yet another aspect of the present invention, there is provided a method of extracting a metal or semi-metal from an ore comprising an oxide of the metal or semi-metal, comprising the steps of providing the ore; reacting the ore to form a product comprising an oxycarbide, a carbonitride or an oxynitride of the metal or semi-metal; electrolysing the product in an electrolyte, with the product configured as an anode; and recovering the metal or semi-metal from a cathode in the electrolyte.

[0045] The metal or semi-metal may be selected from the group consisting or: zirconium, silicon, aluminium, scandium, vanadium, chromium, yttrium, tantalum, titanium, uranium, hafnium and niobium. Each such metal or semi-metal is capable of forming an oxycarbide so the extraction method defined above may help to simplify the production of the metal or semi-metal. During electrolysis, the metal/semi-metal oxycarbide (MCO) is oxidised at the anode as follows:
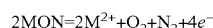
$$MCO = M^{2+} + CO + 2e^-$$
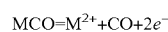
[0046] with the metal ions (M^{2+}) dissolving into the electrolyte. At the cathode, the metal ions are reduced as follows:

$$M^{2+} + 2e^- = M$$
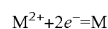
[0047] Forming the oxycarbide may be relatively straightforward, for example by reacting the oxide (MO) with a carbide of the same metal or semi-metal (MC). In some instances, it may be possible (and even useful in the case of

niobium and tantalum) to form a carbonitride or an oxynitride instead of the oxycarbide. Such carbonitrides and oxynitrides will be electrically conducting, just like the oxycarbide, making them suitable for use as an anode during electrolysis. Where carbonitrides and oxynitrides are used the anodic reaction will be:

$$2MCN = 2M^{2+} + 2C + N_2 + 4e^-; \text{ or}$$

$$2MON = 2M^{2+} + O_2 + N_2 + 4e^-$$
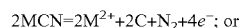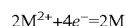
[0048] with the metal ions (M^{2+}) dissolving into the electrolyte. At the cathode, the metal ions are reduced as follows:

$$2M^{2+} + 4e^- = 2M$$

[0049] The ore may comprise impurities of at least 1.0 wt %, possibly at least 2.0 wt %, and possibly even at least 2.5 wt %. The metal or semi-metal recovered from the cathode may have a level of impurities of less than 0.5 wt %, and possibly less than 0.2 wt %. In other words, the method the metal or semi-metal is refined during extraction.

[0050] The electrolyte may be a molten salt, and may comprise a chloride of an alkali or alkali-earth metal. The molten salt may be selected from the group consisting or lithium chloride, sodium chloride, potassium chloride, magnesium chloride and mixtures thereof. The molten salt may comprise a sodium chloride-potassium chloride (NaCl—KCl) eutectic, or a lithium chloride-sodium chloride-potassium chloride (LiCl—NaCl—KCl) eutectic. The molten salt may further comprise a chloride of the metal or semi-metal being extracted. For example, the molten salt may further comprise silicon chloride if silicon is the semi-metal being extracted from silica.

[0051] In accordance with yet another aspect of the present invention, there is provided a method of extracting a metal from a nuclear fuel comprising uranium; comprising the steps of: providing the nuclear fuel; reacting the nuclear fuel to form a product comprising an oxycarbide, a carbinitride or an oxynitride of at least the uranium; electrolysing the product in an electrolyte, with the product configured as an anode; and recovering the metal from a cathode in the electrolyte.

[0052] The nuclear fuel may comprise uranium metal (U-235 and/or U-238) or may comprise an oxide, carbide or nitride of uranium. In one embodiment, the metal extracted from the nuclear fuel may comprise or consist of uranium. The nuclear fuel may also comprise a radioactive metal other than uranium, which may have been created directly or indirectly by uranium fission, for example plutonium (e.g. Pu-239). If so, the metal extracted from the nuclear fuel may be uranium or something other than uranium, for example plutonium. The nuclear fuel may contain a variety of fission products, and the method helps useful metals such as uranium and/or plutonium to be separated therefrom, with electroreduction and electrorefining advantageously taking place simultaneously during electrolysis.

[0053] The electrolyte may be a molten salt and may comprise a chloride of an alkali or alkali-earth metal. The molten salt may be selected from the group consisting of lithium chloride, sodium chloride, potassium chloride, magnesium chloride and mixtures thereof. The molten salt may comprise a sodium chloride-potassium chloride (NaCl—KCl) eutectic, or a lithium chloride-sodium chloride-potassium chloride (LiCl—NaCl—KCl) eutectic. The molten salt may further comprise a chloride of the metal being extracted. For example, the molten salt may further comprise uranium chloride if uranium is being extracted from the nuclear fuel.

1. A method of extracting a metal or semi-metal from an ore comprising an oxide of the metal or semi-metal, comprising the steps of
   providing the ore;
   reacting the ore to form a product comprising an oxycarbide, a carbonitride or an oxynitride of the metal or semi-metal;
   electrolysing the product in an electrolyte, with the product configured as an anode; and
   recovering the metal or semi-metal in a refined form from a cathode in the electrolyte.

2. A method according to claim 1, in which the metal or semi-metal is selected from the group consisting of: zirconium, silicon, aluminium, scandium, vanadium, chromium, yttrium, tantalum, uranium, hafnium and niobium.

3. A method according to claim 1, in which the ore comprises impurities of at least 1.0 wt %.

4. A method according to claim 3, in which the metal or semi-metal recovered at the cathode has a level of impurities of less than 0.5 wt %.

5. A method according to claim 1, in which the electrolyte is a molten salt.

6. A method according to claim 5, in which the molten salt comprises a chloride of an alkali or alkali-earth metal.

7. A method according to claim 6, in which the chloride of the alkali or alkali-earth metal is selected from the group consisting of lithium chloride, sodium chloride, potassium chloride, magnesium chloride and any mixtures thereof.

8. A method according to claim 7, in which the molten salt comprises one of a sodium chloride-potassium chloride eutectic and a lithium chloride-sodium chloride-potassium chloride eutectic.

9. A method according to claim 8, in which the molten salt further comprises a chloride of the metal or semi-metal being extracted.

10. A method of extracting a metal from a nuclear fuel comprising uranium, comprising the steps of:
    providing the nuclear fuel;
    reacting the nuclear fuel to form a product comprising an oxycarbide, a carbonitride or an oxynitride of at least the uranium
    electrolysing the product in an electrolyte with the product configured as an anode: and
    recovering the metal from a cathode in the electrolyte.

11. A method according to claim 10, in which the metal being extracted is uranium.

12. A method according to claim 11, in which the nuclear fuel comprises uranium oxide, uranium carbide or uranium nitride.

13. A method according to claim 10, in which the nuclear fuel further comprises a radioactive metal other than uranium, with the metal being extracted being the radioactive metal other than uranium.

14. A method according to claim 10, in which the electrolyte is a molten salt.

15. A method according to claim 14, in which the molten salt comprises a chloride of an alkali or alkali-earth metal.

16. A method according to claim 15, in which the chloride of the alkali or alkali-earth metal is selected from the group consisting of lithium chloride, sodium chloride, potassium chloride, magnesium chloride and any mixtures thereof.

17. A method according to claim **16**, in which the molten salt comprises one of a sodium chloride-potassium chloride eutectic and a lithium chloride-sodium chloride-potassium chloride eutectic.

18. A method according to claim **17**, in which the molten salt further comprises a chloride of the metal being extracted.

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