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(54) A METHOD OF ELECTROCHEMICAL PRODUCTION OF RARE EARTH ALLOYS AND METALS COMPRISING A COMPOSITE ANODE, AND A SYSTEM THEREOF

(57) The present invention disclose a method of producing rare earth elements or rare earth alloys in a molten salt electrochemical process, comprising steps of arranging an electrolysis cell with a solid composite anode comprising raw material and a cathode facilitating deposition of rare earth elements, wherein a molten salt electrolyte in the cell comprises chloride compounds.

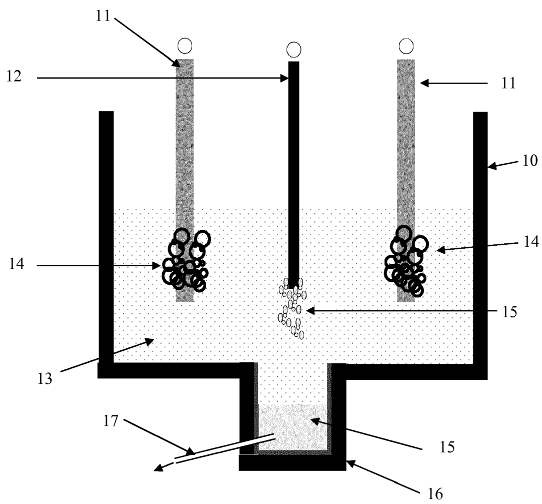

Figure 1

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Description

[0001] A method of electrochemical production of rare earth alloys and metals comprising a composite anode, and a system thereof.

[0002] The work leading to this invention has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 603564.

TECHNICAL FIELD

[0003] The present invention is related to a method and an electrochemical cell thereof providing electrochemical production of rare earth (RE) alloys and metals and especially to a method wherein raw material used in the process is supplied through a rare-earth-oxide-carbon composite anode.

BACKGROUND

[0004] Rare earth (RE) materials are a strategic commodity today, and rare earth elements are important ingredients in most electronic circuitry used in our daily life. China is today the most prominent supplier of rare earth elements, rare earth alloys and rare earth metals. A common method when producing rare earth metals like Nd, Pr, La, Ce as well as some alloys with Fe, for example Dy-Fe, can be produced by electrolysis from molten fluoride based electrolytes using raw materials comprising rare earth oxides. This is the dominant technology in China used in industrial level production of rare earth elements and alloys.

[0005] The report by D. K. Dysinger and J. E. Murphy, "Electrowinning of Neodymium From a Molten Oxide-Fluoride Electrolyte," United States Department of the Interior, Report of Investigations 9504, disclose some of these techniques.

[0006] An electrolytic process may be using a vertical set-up cell comprising graphite anodes, and molybdenum and iron as non-consumable or consumable cathode materials, respectively. Tungsten may also be used instead of molybdenum. The electrolyte may comprise an equimolar REF_3-LiF mixture, and the raw material used in the electrolysis is RE_2O_3. The raw material can be placed as a batch in the electrolyte, or continuously or semi-continuously added at the top of the electrolyte.

[0007] There are some technical challenges operating such a cell. It is necessary to have a good balance between the feeding rate of raw material and oxide consumption. It is necessary that the amount of dissolved oxides match the supply of electrolytic current. For example, if the oxide concentration becomes too low the fluoride electrolyte itself will start to decompose. On the other hand, if the oxide concentration is too high, some of the oxides will settle at the bottom of the cell as sludge instead.

[0008] Therefore, it is a need of an improved electrochemical process when producing rare earth elements, rare earth alloys and rare earth metals.

OBJECT OF THE INVENTION

[0009] In particular, it may be seen as an object of the present invention to provide an electrochemical production method and an electrochemical cell thereof comprising a composite anode-supplying raw material for the production.

[0010] It is a further object of the present invention to provide an alternative to the prior art.

SUMMARY

[0011] Thus, the above described object and several other objects are intended to be obtained in a first aspect of the invention by providing a method of producing rare earth elements or rare earth alloys in a molten salt electrochemical process, comprising:

- arranging an electrolysis cell with a solid composite anode and a cathode facilitating deposition of rare earth elements, wherein a molten salt electrolyte in the cell comprises chloride compounds,
- manufacturing the anode with one or multiple oxygen containing compounds of one or more rare earth elements,
- wherein the electrochemical process results in that the oxygen in the oxide containing rare earth compound(s) are released as oxygen containing gas species and the rare earth element(s) in the anode is(are) electrochemically dissolved as rare earth metal ion(s) in the electrolyte,
- collecting rare earth element(s) or rare earth alloy(s) from the cathode.

[0012] A further aspect of the present invention comprises a composite anode comprising carbon compound(s) mixed with rare earth oxide(s) in amounts such that the molar ratio between carbon and rare earth oxide(s) yields stoichiometric amounts according to a specific electrochemical reaction at a specific operating temperature.

[0013] A further aspect of the present invention comprises an electrochemical electrolysis cell comprising at least one composite anode according to the present invention.

FIGURES

[0014] The method according to the present invention will now be described in more detail with reference to the accompanying figure. The figure illustrates examples of embodiments of the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set. Further, respective examples of embodiments may each be combined with any of the other examples of embodiment.

[0015] Figure 1 illustrates an example of embodiment of the present invention.

DETAILED DESCRIPTION

[0016] Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the present examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference sign in the claims with respect to elements indicated in the figures shall also not be construed as limiting to the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

[0017] According to an aspect of the present invention, production of rare earth elements or alloys containing one or more rare earth elements comprises using a molten salt electrochemical process, more specifically molten chlorides with known low solubility of oxide containing rare earth compounds are used.

[0018] According to an example of embodiment of the present invention, the problem of low oxide solution and sludge formation can be mitigated if the raw material (RE_2O_3) can be supplied through a rare-earth-oxide-carbon composite electrode being a consumable anode.

[0019] If for example RE oxide is mixed with a carbon source, acting as a binder, and formed into a suitable bar or cylinder, and then heated or baked and used as an anode, the expected anode reaction is that during polarisation carbon will react with the oxygen atoms from RE_2O_3 forming carbon oxide or/and carbon dioxide, and RE ions.

[0020] Then the RE ions are electrochemically released and will recombine with halide ions, thus dissolving in the electrolyte as a RE halide complex. For neodymium in a chloride melt, the reactions can be noted stoichiometric in the following way when using a Nd_2O_3 - composite. The same reaction scheme is valid for other rare earths, substituting Nd with another rare earth element(s).

<u>Anode:</u>

[0021]

$$Nd_2O_3 + 3\ C = 2\ Nd^{3+}\ (\text{dissolved}) + 3\ CO\ (g) + 6\ e- \qquad (I)$$

or

$$Nd_2O_3 + 3/2\ C = 2\ Nd^{3+}\ (\text{dissolved}) + 3/2\ CO_2\ (g) + 6\ e- \qquad (II)$$

<u>Electrolyte</u>:

[0022]

$$Nd^{3+}\ (\text{dissolved}) + 3\ Cl^- = NdCl_6^{3-} \qquad (III)$$

Cathode:

[0023]

$$NdCl_6^{3-} + 3\ e^- = Nd + 6\ Cl^- \qquad (IV)$$

with an overall cell reaction:

$$Nd_2O_3 + 3\ C = 2\ Nd + 3\ CO\ (g) \qquad (V)$$

or

$$Nd_2O_3 + 3/2\ C = 2\ Nd + 3/2\ CO_2\ (g) \qquad (VI)$$

with a theoretical standard potential E° = -1.48 and -1.55 volt for reaction (V) and (VI), respectively at 850 °C. The theoretical standard potential for other rare earths varies only slightly from the potential of the reaction with Nd, as all RE elements have standard potential in the same range at given temperatures, as known to a person skilled in the art.

[0024] Obtaining expected results in examples of embodiments of the present invention comprises manufacturing an anode in such a way that the rare earth metal ion(s) is (are) dissolved in a molten salt electrolyte while the oxygen in the oxide containing rare earth compound(s) is (are) released as oxygen containing gas species, most commonly CO or CO_2, as a result of an electrochemical process. The dissolved rare earth element(s) is (are) deposited at the cathode, either in a pure form or as an alloy or as an alloy with the cathode material.

[0025] The advantage of the present invention is that rare earth elements, or alloys containing rare earth elements, can be produced in an electrolyte with low solubility of the oxide.

Example:

[0026] The composite anode can be made by multiple procedures: For example, the carbon compound(s) is (are) mixed with the rare earth oxide(s) in amounts such that the molar ratio between carbon and rare earth oxide(s) yields stoichiometric amounts according to the electrochemical reaction at the operating temperature. An example of method according to the present invention is mixing a carbon based binder, e.g. coal tar pitch, petroleum tar pitch or a synthetic binder, either in solid or liquid form, with the rare earth oxide(s) to yield the stoichiometric composition (equation (V) or (VI) above), when baked or heated to operating temperature. Some of the pitch may be substituted with another carbon source or another carbon containing source, e.g. graphite, carbon black, carbides or oxycarbides of the RE(s). It is advantageous that intimate mixing is achieved avoiding solid particles falling off the anode during use.

[0027] *Electrochemical characterisation, polarisation and gas evolution:* When the anode is polarised, e.g. at 150 mV vs an Ag/AgCl reference electrode, in the molten equimolar NaCl-KCl mixture at 860 °C, the Nd_2O_3 and carbon reacts, evolving CO and/or CO_2 at the anode. Using a gold coated see-through furnace and a quartz container for the electrolysis cell, the gas evolution that occur during the electrolysis can be visually observed. The gas bubbles observed were small and evenly distributed.

[0028] Any other methods of manufacturing the anode providing same operational characteristics as disclosed above is within the scope of the present invention.

[0029] Especially, baked anodes (REO-C anodes) made from a mix of graphite powder, oxide and various amounts of pitch are proven to provide good results with respect to criteria like sufficient electrical conductivity, mechanical stability during electrolysis, even gas distribution, small gas bubbles and enough RE ions that is released during electrolysis.

[0030] Consumable anodes according to the present invention may be manufactured externally and be placed inside an electrochemical cell according to the present invention when production starts. It is also within the scope of the present invention to arrange the step of baking an anode when the anode is placed inside the electrochemical cell, and baking the anode there before or during the production.

[0031] An aspect of the present invention comprises manufacturing an anode which may comprise mixing a binder with the rare earth compounds of the anode, followed by forming the anode into a desired shape by pressing or vibroforming and baking the anode, either in-situ in the cell or in a separate baking furnace forming a solid composite anode.

[0032] Figure 1 illustrates the principle layout of an example of an electrochemical cell being able to support respective method steps of examples of embodiments of the present invention.

[0033] A vessel 10 defines the outer walls of an electrochemical cell according to the present invention. In the example illustrated in Figure 1, two manufactured anodes 11, for example manufactured according to the example disclosed above, is located inside the vessel 10 and are partly submerged into an electrolyte 13 comprising chloride compounds. A cathode 12 manufactured as known in prior art is located in between the two anodes 11. During operation of the cell an electric power source (not illustrated) supplies current to the anodes 11 and the cathode 12. The electrochemical reaction dissolves RE and oxygen containing species 14 as disclosed above. Liquid RE/RE alloy products 15 are collected by the cathode, and below the cathode there is a compartment 16 receiving the liquid RE/RE alloy products 15. A tubing or channel 17 is removing collected liquid RE/RE alloy products from the inside of the compartment 15.

[0034] An example of a method according to the present invention comprises steps of:

- arranging an electrolysis cell with a solid composite anode and a cathode facilitating deposition of rare earth elements, wherein a molten salt electrolyte in the cell comprises chloride compounds,
- manufacturing the anode with one or multiple oxygen containing compounds of one or more rare earth elements,
- wherein the electrochemical process results in that the oxygen in the oxide containing rare earth compound(s) are released as oxygen containing gas species and the rare earth element(s) in the anode is(are) electrochemically dissolved as rare earth metal ion(s) in the electrolyte,
- collecting rare earth element(s) or rare earth alloy(s) from the cathode.

[0035] Further, the step of manufacturing the anode may comprise adding at least one or multiple reducing agents participating in the anode reaction when passing direct current through the electrolysis cell.

[0036] Further, the at least one or multiple reducing agents may comprise at least one or multiple carbon allotropes.

[0037] Further, the at least one or multiple reducing agents may comprise at least one or multiple carbon compounds.

[0038] Further, the at least one or multiple reducing agents may comprise a mixture of at least one or multiple carbon allotropes and at least one or multiple carbon compounds.

[0039] Further, the step of manufacturing the anode may comprise mixing a binder with the rare earth compounds of the anode, followed by forming the anode into a desired shape by pressing or vibro-forming and baking the anode, either in-situ in the cell or in a separate baking furnace forming a solid composite anode.

[0040] Further, the electrolyte may comprise a composition of molten halides with low or no solubility of the oxide containing rare earth compounds of the anode.

[0041] Further, the oxygen containing gas species are carbon oxide or carbon dioxide unless other reducing agents in the anode participates in the reaction.

[0042] Further, if sulfur or a sulfur compound is present in the anode and participating in the reaction, the oxygen containing gas species may contain COS or SO_2.

[0043] Further, the deposition of the rare earth elements on the cathode is either in pure form, or as an alloy, or as an alloy with the cathode material.

Claims

1. A method of producing rare earth elements or rare earth alloys in a molten salt electrochemical process, comprising:

   - arranging an electrolysis cell with a solid composite anode and a cathode facilitating deposition of rare earth elements, wherein a molten salt electrolyte in the cell comprises chloride compounds,
   - manufacturing the anode with one or multiple oxygen containing compounds of one or more rare earth elements,
   - wherein the electrochemical process results in that the oxygen in the oxide containing rare earth compound(s) are released as oxygen containing gas species and the rare earth element(s) in the anode is(are) electrochemically dissolved as rare earth metal ion(s) in the electrolyte,
   - collecting rare earth element(s) or rare earth alloy(s) from the cathode.

2. The method according to claim 1, wherein the step of manufacturing the anode comprises adding at least one or multiple reducing agents participating in the anode reaction when passing direct current through the electrolysis cell.

3. The method according to claim 2, wherein the at least one or multiple reducing agents comprises at least one or multiple carbon allotropes.

4. The method according to claim 2, wherein the at least one or multiple reducing agents comprises at least one or multiple carbon compounds.

5. The method according to claim 2, wherein the at least one or multiple reducing agents comprises a mixture of at

least one or multiple carbon allotropes and at least one or multiple carbon compounds.

6. The method according to any claim 1-5, wherein the step of manufacturing the anode comprises mixing a binder with the rare earth compounds of the anode, followed by forming the anode into a desired shape by pressing or vibro-forming and baking the anode, either in-situ in the cell or in a separate baking furnace forming a solid composite anode.

7. The method according to claim 1, wherein the electrolyte comprises a composition of molten halides with low or no solubility of the oxide containing rare earth compounds of the anode.

8. The method according to claim 1, wherein the oxygen containing gas species released at the anode are carbon oxide or carbon dioxide.

9. The method according to claim 8, wherein the oxygen containing gas species released at the anode are carbon oxide or carbon dioxide and other oxygen containing species from other reducing agents that participates in the anode reaction, e.g. sulfur forming COS and/or SO_2 oxygen containing gas species.

10. The method according to claim 1, wherein the deposition of the rare earth elements on the cathode is either in pure form, or as an alloy, or as an alloy with the cathode material.

11. A composite anode to be used in a method according to any claim 1-10, wherein the composite anode comprises carbon compound(s) mixed with rare earth oxide(s) in amounts such that the molar ratio between carbon and rare earth oxide(s) yields stoichiometric amounts according to a specific electrochemical reaction at specific operating temperature.

12. An electrochemical electrolysis cell comprising at least one anode according to claim 11.

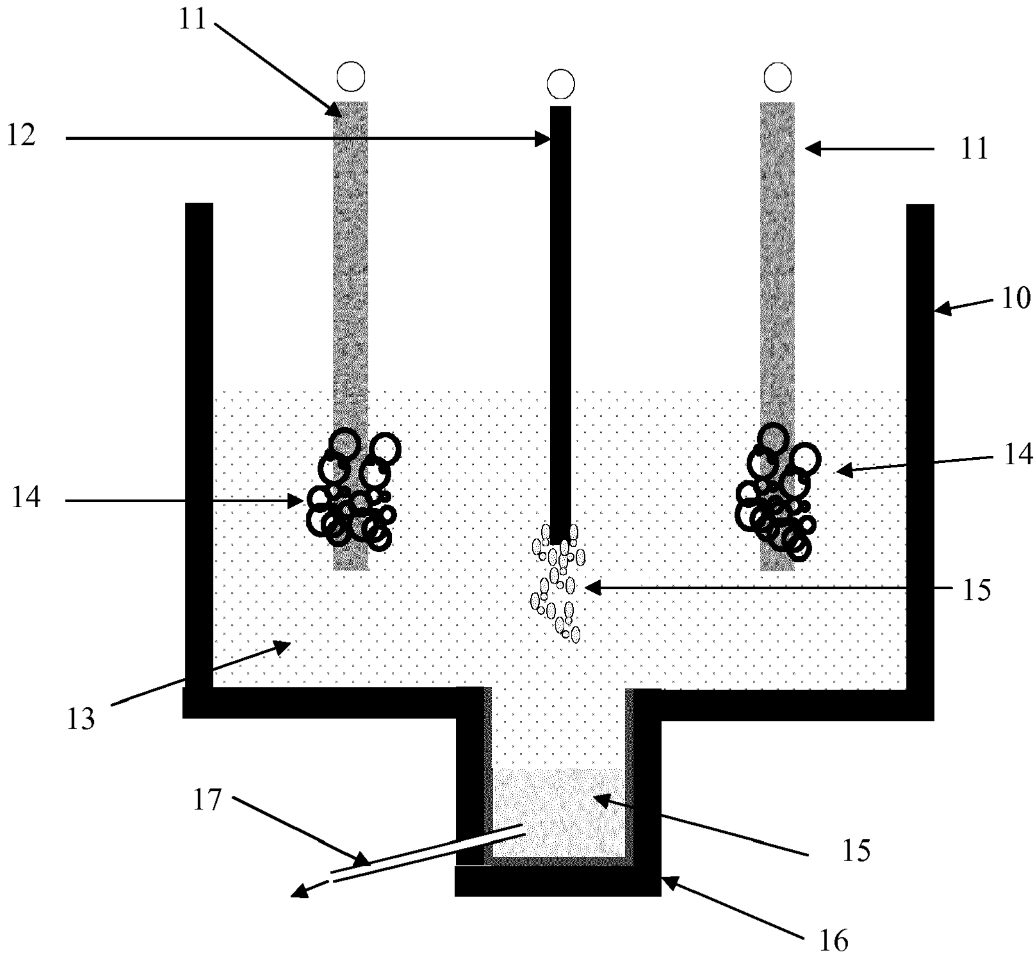

Figure 1

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EUROPEAN SEARCH REPORT

Application Number
EP 16 19 6270

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A	US 2016/102411 A1 (FRIEDRICH BERND [DE] ET AL) 14 April 2016 (2016-04-14) * paragraphs [0004], [0005], [0020], [0021] * ----- -/--	1-12	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	6 April 2017	Hammerstein, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 16 19 6270

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 16 19 6270

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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