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(54) ELECTROCHEMICAL PRODUCTION OF RARE EARTH ALLOYS AND METALS COMPRISING A LIQUID ANODE

(57) The present invention disclose a method of recycling rare earth elements, rare earth alloys and/or rare earth metals from permanent magnets and/or scrap metals containing iron (Fe) and rare earth elements in a molten salt electrochemical process. The method comprises steps of: arranging an electrolysis cell comprising an anode compartment in communication with an electric lead of a liquid anode, wherein a cathode and/or a cathode product reservoir is collecting refined rare earth alloys, elements and metals in a solid or liquid state separated by a fluoride based liquid electrolyte.

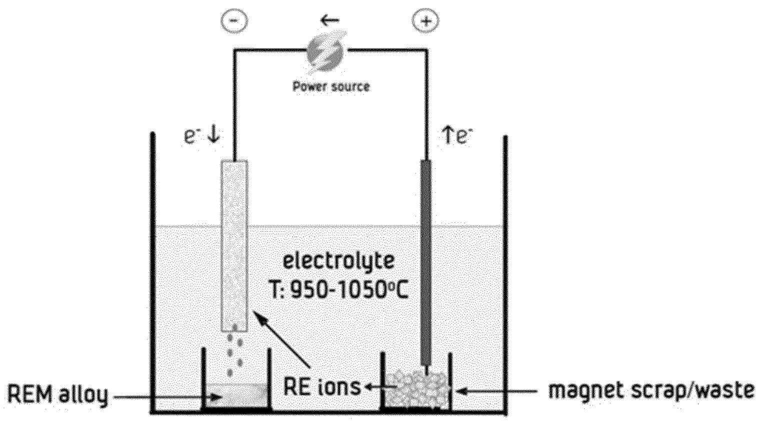

Figure 1

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Description

[0001] The work leading to this invention has received funding from the European Union's Horizon 2020 and Innovation program under Grant Agreement No. 680507.

FIELD OF THE INVENTION

[0002] The present invention is related to electrochemical production of rare earth alloys and metals, and especially to a one-step electro chemical production method comprising a liquid anode.

BACKGROUND OF THE INVENTION

[0003] Rare earth alloys and metals are important ingredients in modern electronic components like semiconductors, but also in products like permanent magnets etc. The Peoples Republic of China is dominating the production of rare earth (RE), and for example, in 2011 the Chinese production covered 97 % of the world market. In addition, the geological availability and distribution of RE is unevenly distributed around the world and it is therefore an international interest in developing alternative second sources of RE materials mitigating any problems related to higher prices and reliable and sustainable delivery of RE alloys and metals.

[0004] This situation has triggered development of methods and systems recovering RE alloys and metals from scrap metals and permanent magnets. A general overview of prior art techniques providing recycling of permanent magnets can be found in the article "Technique for recovering rare-earth metals from spent sinteredNd-Fe-B magnets without external heating" by R. Sasai and N. Shimamura, Journal of Asian Ceramic Societies, 4 (2016) 155-158.

[0005] Prior art electrochemical refining of metals are applied both in aqueous and molten salt electrochemical processes. The refining is commonly based on an impure metal containing anode being refined to a pure cathode. More noble impurities remain in the anode or anode compartment and less noble substances accumulate in the electrolyte.

[0006] An example of prior art is the three layer refining of liquid aluminium dissolved in a copper containing alloy invented by Hoppes and patented in 1925. The refining process takes place in a vertically arranged molten salt cell, wherein the aluminium dissolved in the copper alloy is arranged at the bottom of the cell, and the refined pure aluminium is floating at the top of the electrolyte.

[0007] A common technique in prior art when recycling used permanent magnets and scrap metals comprises a step of oxidizing the permanent magnet and scrap metal materials followed by a purifying step and electrolysis of oxidized materials dissolved in a molten salt.

[0008] An example of prior art is CN 103409649B disclosing a liquid metal and molten salt reduction method and apparatus for extraction and separation of rare earth metals comprising a liquid aluminium cathode and an anode graphite rod added to a heated bath melted as an electrolyte. Lithium aluminium-lithium alloy is dissolved in the liquid aluminium.

[0009] Another example of prior art is J. Lucas, P. Lucas, T. Le Mercier, A. Rollat and W. Davenport, in "Rare Earths. Science, Technology, Production and Use", Elsevier 2015.

[0010] A further prior art reference is S. Pang, S. Yan, Z. Li, D. Chen, L. Xu and B. Zhao, "Development on Molten Salt Electrolytic Methods and Technology for Preparing Rare Earth Metals and Alloys in China", Chinese Journal of Rare Metals, 35(3) (2011) 440-450.

[0011] Recovering RE alloys and metals from a specific electrochemical process is also subject to cost/benefit assessments in addition to environmental considerations. The cost of recovered RE alloys and metals has to be on a level accepted by end users of the recovered materials. Therefore, there is a need of improved methods recovering compounds comprising rare earth, and/or rear earth alloys and/or rear earth metals.

[0012] An aspect of the present invention is to reduce the number of process steps, and at the same time increase output of rare earth alloys and metals from the process. The present invention is based on an alloy system with high solubility of the actual rare earth metal(s) or rare earth alloy(s).

OBJECT OF THE INVENTION

[0013] In particular, it may be seen as an object of the present invention to provide a method of recycling rear earth (RE) containing permanent magnets and/or scrap metals by providing a liquid anode with dissolved material to be recycled in an electro chemical process in one step.

[0014] It is a further object of the present invention to provide an alternative to the prior art.

SUMMARY OF THE INVENTION

[0015] 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 recycling elements including compounds comprising rare earth (RE), and/or RE alloys and/or RE metals from raw materials including permanent magnets and/or scrap metals containing iron (Fe) and elements to be recycled in an electrochemical process from a molten salt, comprising steps of:

- arranging an electrolysis cell comprising a liquid anode compartment in communication with an electric lead of the liquid anode, wherein a cathode of the electrolysis cell is collecting refined recycled elements in a liquid or solid state separated by a fluoride based liquid electrolyte,
- feeding raw material into the liquid anode compartment,
- the liquid anode is forming a multinary liquid alloy system when dissolving raw materials fed to the anode compartment,
- the liquid anode comprises added Al and Si in quantities providing a melting point temperature of the added materials inside the anode compartment being below the melting point temperature of the raw materials itself,
- the added quantities of Al and Si is further selected to provide a low melting temperature region of Al-Si alloys being able to dissolve Fe, and a maximum or sufficient wt% amount to maintain molten Fe-Al-Si-RE alloys of different compositions,
- collecting refined recycled rare earth metals(s) or rare earth alloy(s) from the cathode.

DESCRIPTION OF THE FIGURES

[0016] The method and system thereof according to the present invention will now be described in more detail with reference to the accompanying figures. The accompanying figures illustrates an example of embodiment of the present invention and is not to be construed as being limiting other possible embodiments falling within the scope of the attached claim set.

Figure 1 illustrates some respective aspects of the present invention.

Figure 2 illustrates further aspects of the present invention.

Figure 3 illustrates an example of embodiment of the present invention.

DETAILED DESCRIPTION OF AN EMBODIMENT

[0017] 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 presented 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. The mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting 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

[0018] The known technology used in China relies on an electrolytic process using a vertically arranged cell comprising consumable carbon anodes and molybdenum or tungsten as inert or iron as consumable cathode materials. The RE or RE alloy is deposited in a liquid form at a temperature around 1050 °C. The electrolyte consists of an equimolar REF_3-LiF mixture, and the RE_2O_3 raw material is applied batch wise or continuously at the top of the electrolyte.

[0019] An example of a prior art liquid anode is the referenced Hoppes method. However, applying Hoppes three layer method when electro-refining rare earth element from for example used permanent magnets would be a challenge due to the high specific densities of the rare earth metals.

[0020] A parameter of interest when designing an electrolysis cell is the kinetics of the electrodes. It is believed that liquid anodes perform better in this respect than an anode consisting of solid chunks of alloys when refining rare earth elements.

[0021] An example of a prior art liquid anode is the referenced Hoppes method. However, applying Hoppes three layer method when electro-refining rare earth element from for example used permanent magnets would be a challenge due to the high specific densities of the rare earth elements and the lack of electrolytes with an intermediate density between the refined element(s) and the composition containing the raw material.

[0022] However, a different cell design according to the present invention with a liquid anode is schematically illustrated in Figure 1. The rare earth containing raw material is placed in the anode compartment 10 from where the RE present in the raw material (for example Nd, Dy, Pr) will be anodically dissolved in the form of ions, which will be discharged at the cathode 11 as metals and/or magnetic rare earth alloys 12. The recovery of REs from the raw material can be extracted, and a valuable product (RE or alloy) can be obtained in one single electrochemical step.

[0023] It is not desirable to work at a high temperature providing a liquid state of the used permanent magnets for example. The melting point of most permanent magnets are about 1400 °C. The high temperature is a challenge since the temperature may enhance corrosion of the cell materials. Therefore, according to an aspect of the present invention, a desired working temperature is below 1100 °C.

[0024] Providing a lower melting point when recycling permanent magnets and/or scrap metal comprising Fe, can be achieved by adding low melting point materials known to achieve such an effect. For example, with respect to a permanent magnet comprising Nd, it is known that Cu forms low melting phases with Nd, but not with Fe. However, using Al the inventors has demonstrated that Al forms low melting areas with Nd and Fe in the Al rich regions. Calculating a ternary phase diagram of Al-Nd-Fe can be achieved with commercially available thermodynamic computer programs like FactSage as known in prior art. The same demonstration has been performed with other RE elements with similar results.

[0025] However, there are further aspects to be taken into consideration when arranging a liquid anode forming a multinary liquid alloy system that fulfils all requirements necessary for an electrochemical process providing necessary efficiency and output of recovered RE elements, alloys and metals from raw materials comprising at least Fe and RE.

[0026] Examples of further requirements are:

- Forming a homogenous liquid phase with raw materials comprising at least Fe and RE.
- Providing a melting point of an anode alloy comprising at least Fe and Re to be around 1050 °C or lower.
- Low vapour pressure at the working temperature, for example at 1050 °C.
- Low cost, non-toxic and abundant materials.

[0027] It is further known that Si forms low melting point alloys with several elements like Cu and Al. When calculating and verifying the calculations in a laboratory test of a phase diagram of Fe-Al-Si, it is possible to observe that the phase diagram reveals a relative large region of molten Fe-Al-Si alloys of different compositions that exist below a temperature of 1050 °C. Further, it is also evident from such calculations and laboratory verifications that the liquid content of Fe at 1050 °C varies from 20 wt% without Si present to a maximum of 50 wt% when Si is present. Further, Al-Si alloys are commercially available, which is an important aspect when considering commercial applications of a liquid anode according to the present invention comprising AlSi.

[0028] According to an aspect of the present invention, AlSi is added to the liquid anode.

[0029] Figure 2 illustrates examples of how liquidus curves of the quaternary system of AlSi-Fe-Nd can be obtained. The same type of illustrations are valid for other RE elements. The cross sections of the AlSi-Fe-RE system from contact lines between the AlSi corner and the Fe-RE (for example Nd) side of the triangle in figure 2 will provide liquidus curves enabling a prediction of melting points of the anode alloy when the electrolysis proceeds and the content of respectively RE and Fe decreases and increases.

[0030] Higher concentration of Si will for example increase the amount of Fe-RE in the liquid phase at 1050 °C when there is a rich Fe composition. If the concentration of RE is high the opposite is observed. However, laboratory verification of this aspect of the present invention confirms a liquid phase with more than 30 wt% of permanent magnet material and scrap metal comprising Fe and RE at 1050 °C.

[0031] Below is a table illustrating non-limiting examples of different anode-alloy compositions when recycling a permanent magnet comprising Fe and RE.

Table 1:

Alloy#	*Al:Si composition* wt%:wt%	*Composition Al:Si:Magnet wt%:wt%:wt%*	*Remarks*
1	70:30	54:23:23	Homogeneous
2	70:30	48:21:31	Homogeneous
3	70:30	44:19:37	Homogeneous
4	90:10	54:6:40	Homogeneous

[0032] According to an example of embodiment of the present invention, a liquid anode is formed of aluminium and silicon and dissolved RE alloys with iron and boron (Al-Si-Fe-RE-B).

[0033] Therefore, the addition of Al and Si lowers the melting point. Further, the liquid anode is forming a multinary liquid alloy system having a larger liquid domain for the RE, RE alloys or RE metals dissolved in the liquid anode. Further, the multinary liquid alloy system is provided with metal elements being more noble than the RE or the RE containing alloy(s) to be recycled.

[0034] According to an example of embodiment of the present invention, a method of recycling rare earth (RE), and/or

RE alloys and/or RE metals from raw materials including permanent magnets and/or scrap metals containing RE and iron (Fe) in an electrochemical process from a molten salt, comprising the steps of:

- arranging an electrolysis cell comprising a liquid anode compartment in communication with an electric lead of the liquid anode, wherein a cathode of the electrolysis cell is collecting refined recycled elements in a liquid or solid state separated by a fluoride based liquid electrolyte,
- feeding raw material into the liquid anode compartment,
- the liquid anode is forming a multinary liquid alloy system when dissolving raw materials fed to the anode compartment,
- the liquid anode comprises added Al and Si in quantities providing a melting point temperature of the added materials inside the anode compartment being below the melting point temperature of the raw materials itself,
- the added quantities of Al and Si is further selected to provide a low melting temperature region of Al-Si alloys being able to dissolve Fe, and a maximum or sufficient wt% amount to maintain molten Fe-Al-Si-RE alloys of different compositions,
- collecting refined recycled rare earth metals(s) or rare earth alloy(s) from the cathode.

[0035] Further, the added specific amounts of respectively Al and Si elements are forming a multinary liquid alloy system having a working temperature below the melting point of the rare earth containing metallic raw material, preferable in the range of 1000-1100 °C.
[0036] Further, the working temperature of the liquid anode may be 1050 °C.
[0037] Further, the cathode may be a Fe cathode and the reactions are as follows:

anode: RE-alloy (liquid) -> RE(III) + alloy anode (liquid) + $3e^-$
cathode: RE(III) + Fe(solid) + $3e^-$ -> RE-Fe (liquid).

[0038] Further, the step of dissolving permanent magnetic material may provide a liquid anode comprising Al-Si-Fe-RE-B.
[0039] Further, the permanent magnets may be Nd based permanent magnets.
[0040] Further, the cathode may be a solid cathode and the step of collecting recycled elements comprises collecting the RE(s) or RE alloy(s) in solid form.
[0041] Further, the step of collecting the RE(s) or RE alloy(s) may comprise collecting liquid iron-RE(s) alloys formed through a reaction on a consumable iron cathode.
[0042] Further, the RE containing permanent magnets and/or scrap metals may be delivered into the liquid anode compartment from a feeding chamber.
[0043] Figure 3 illustrates an example of principles of a functional cell according to the present invention. A tube or canal 20 provides transport of waste material to be recycled into the molten alloy being part of the liquid anode 21 residing in a compartment. An electric lead 22 is connected to a positive electric pole 23 of the power supply. The electric lead 22 is connected to a finger like electrode configuration being arranged inside the molten alloy. The cathode 24 is connected to the negative pole of the power supply and at the bottom of the cell below the cathode a compartment is arranged receiving cathode products.

Claims

1. A method of recycling rare earth (RE), and/or RE alloys and/or RE metals from raw materials including permanent magnets and/or scrap metals containing RE and iron (Fe) in an electrochemical process from a molten salt, comprising the steps of:

- arranging an electrolysis cell comprising a liquid anode compartment in communication with an electric lead of the liquid anode, wherein a cathode of the electrolysis cell is collecting refined recycled elements in a liquid or solid state separated by a fluoride based liquid electrolyte,
- feeding raw material into the liquid anode compartment,
- the liquid anode is forming a multinary liquid alloy system when dissolving raw materials fed to the anode compartment,
- the liquid anode comprises added Al and Si in quantities providing a melting point temperature of the added materials inside the anode compartment being below the melting point temperature of the raw materials itself,
- the added quantities of Al and Si is further selected to provide a low melting temperature region of Al-Si alloys being able to dissolve Fe, and a maximum or sufficient wt% amount to maintain molten Fe-Al-Si-RE alloys of

different compositions,
- collecting refined recycled rare earth metals(s) or rare earth alloy(s) from the cathode.

2. The method according to claim 2, wherein added specific amounts of respectively Al and Si elements are forming a multinary liquid alloy system having a working temperature below the melting point of the of the RE(s) or the RE containing alloy(s), preferable in the range of 1000-1100 °C.

3. The method according to claim 2, wherein the working temperature of the liquid anode is 1050 °C.

4. The method according to claim 1, wherein the cathode is a Fe cathode and the reactions are as follows:

anode: RE-alloy (liquid) -> RE(III) + alloy anode (liquid) + $3e^-$
cathode: RE(III) + Fe(solid) + $3e^-$ -> RE-Fe (liquid).

5. The method according to any claim 1-4, wherein the step of dissolving raw material is providing a liquid anode comprising Al-Si-Fe-RE-B.

6. The method according to any claim 1-5, wherein the raw material is Nd based permanent magnets.

7. The method according to claim 1, wherein the cathode is a solid cathode and the step of collecting refined recycled elements comprises collecting the RE(s) or RE alloy(s) in solid form.

8. The method according to claim 1, wherein the step of collecting the RE(s) or RE alloy(s) comprises collecting liquid iron-RE(s) alloy(s) formed through a reaction on a consumable iron cathode.

9. The method according to claim 1, wherein raw materials are delivered into the liquid anode compartment from a feeding chamber.

10. An electrochemical production cell arranged to support a method according to any claims 1-8.

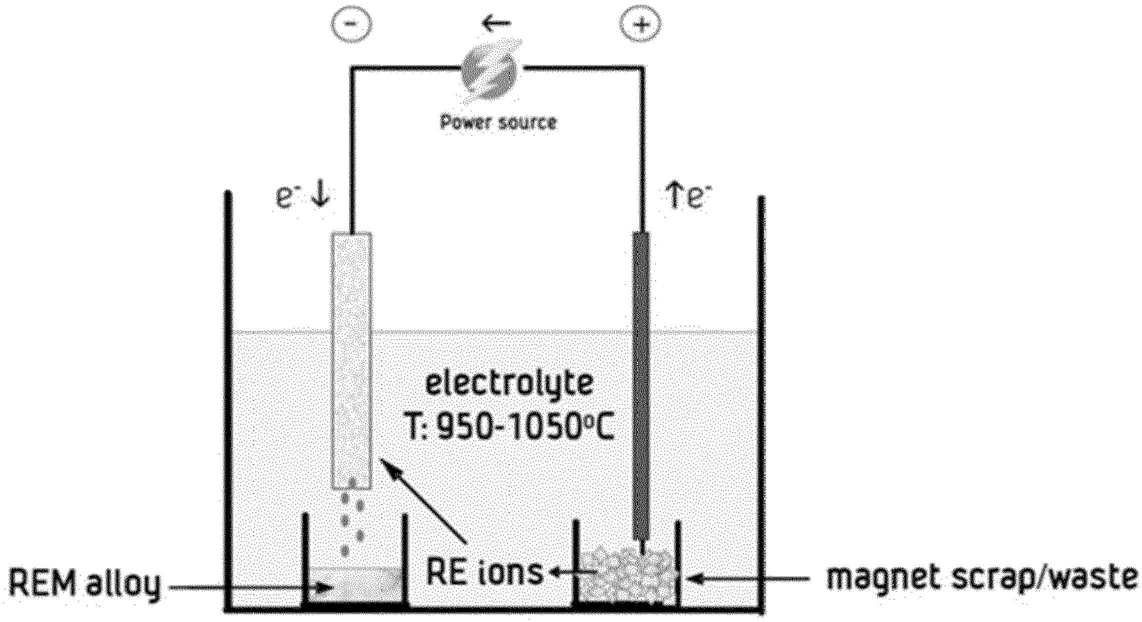
Power source
e⁻ ↓
↑e⁻
electrolyte
T: 950-1050°C
REM alloy
RE ions
magnet scrap/waste

Figure 1

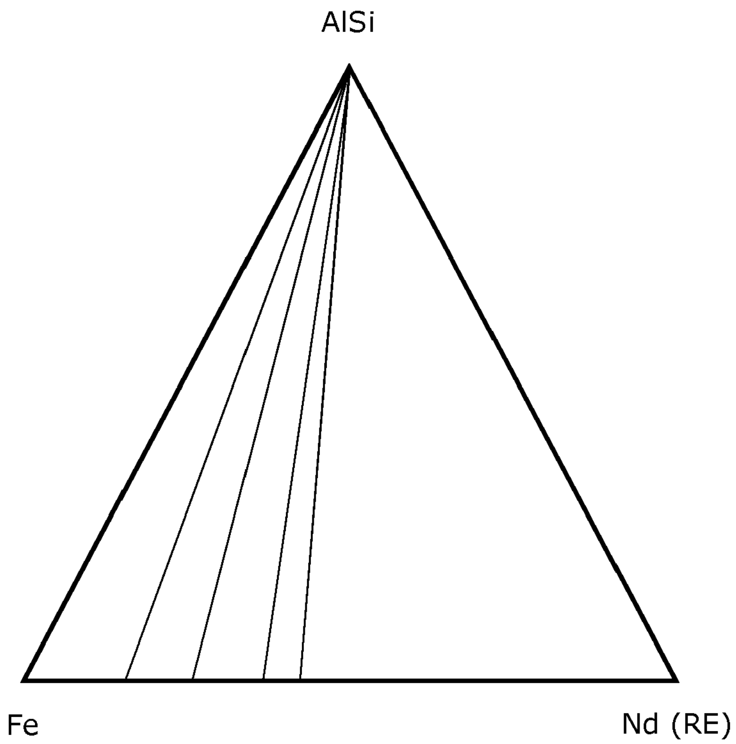

Figure 2

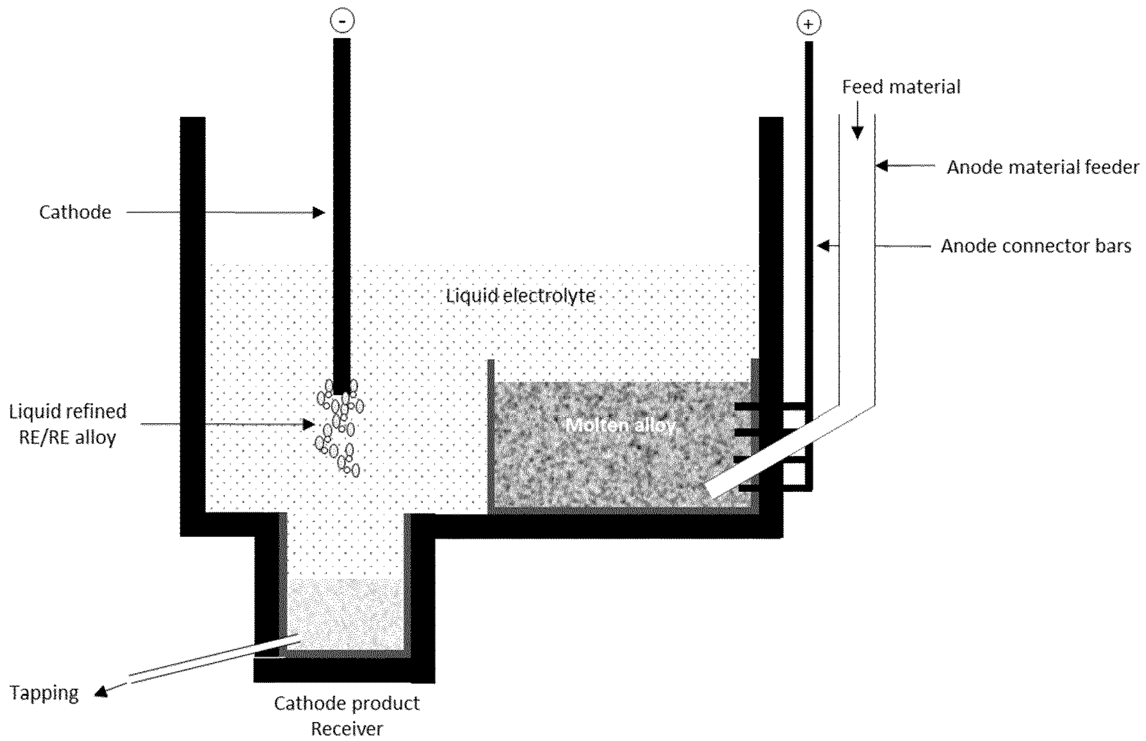
-
+
Feed material
Anode material feeder
Cathode
Anode connector bars
Liquid electrolyte
Liquid refined
RE/RE alloy
Molten alloy
Tapping
Cathode product
Receiver

Figure 3

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EUROPEAN SEARCH REPORT

Application Number
EP 16 20 5757

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	28 June 2017	Hammerstein, G

CATEGORY OF CITED DOCUMENTS

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