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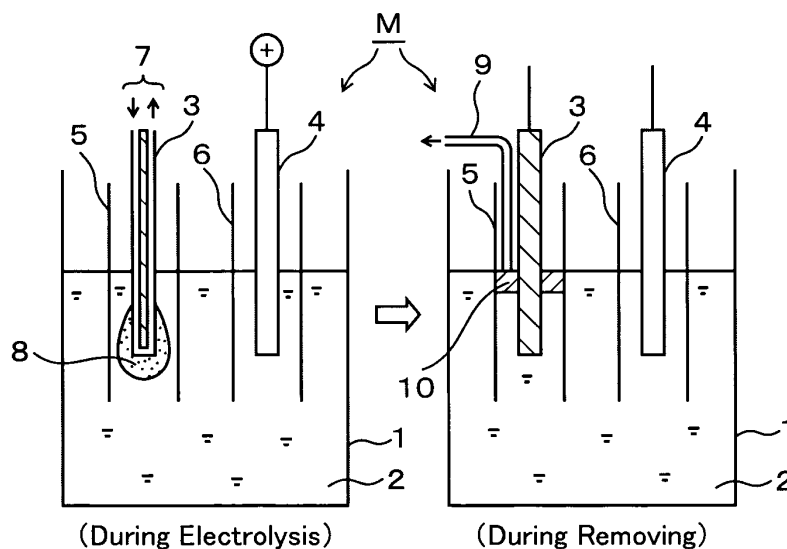
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(54) **APPARATUS FOR PRODUCING METAL BY MOLTEN SALT ELECTROLYSIS, AND PROCESS FOR PRODUCING METAL USING THE APPARATUS**

(57) An apparatus for production of metal by molten salt electrolysis and a method for production of metal using this, in particular, the apparatus and method for production of metal in which metal having solubility in an electrolysis bath can be efficiently produced and recovered are provided. In the method for production of metal,

an electrolysis bath is filled in an electrolysis vessel, positive and cathode are immersed and arranged, metal is deposited on the cathode in which cooling medium can flow inside of the cathode, the solid metal deposited is melted in the electrolysis bath by disconnecting electric current to the cathode, and the molten metal is immediately removed to the outside of the electrolysis vessel.

Fig. 1



Description

Technical Field

[0001] The present invention relates to an apparatus and to a method for production of metal by electrolysis of molten salt, and in particular, relates to a technique for efficient processing for the production of metal that is soluble in an electrolysis bath.

Background Art

[0002] Titanium metal has been conventionally widely used as materials and parts for aviation; recently, demand for this titanium metal has greatly increased for consumer uses, for example, and it has also been anticipated that the supply of titanium sponge, which is a raw material of titanium metal, will need to be increased.

[0003] Conventionally, titanium sponge is industrially produced by the Kroll method, in which titanium tetrachloride is reduced by a reducing metal such as magnesium. However, since the Kroll method is a batch process, there will be a limitation to its efficiency. In addition, it is difficult to greatly reduce the costs of production.

[0004] In Japanese Published Patent Application No. 2002-517613 and Japanese Unexamined Patent Application Publication No. 2005-133195, a technique in which titanium oxide or titanium tetrachloride is continuously reduced by calcium metal in molten salt to generate titanium metal, is investigated. This is a process for production of titanium metal by reducing titanium oxide or titanium tetrachloride by calcium metal. In these methods, calcium chloride, which is a by-product of the reduction reaction, is electrolyzed in molten salt to recover calcium metal again, and calcium metal is reused.

[0005] Since calcium metal is somewhat soluble in molten calcium chloride, it is difficult to efficiently recover calcium metal at high purity by molten salt electrolysis. However, publications say that since the reaction is easily promoted even if calcium chloride is mixed to some extent with calcium metal in the above-mentioned titanium reducing processes, calcium metal is recovered and used containing calcium chloride therein.

[0006] However, from the viewpoint of efficiency of reduction and material handling, it is desirable that calcium metal produced in the molten salt electrolysis be recovered with as high a level of purity as possible.

[0007] Regarding this point, an apparatus for molten salt electrolysis of calcium chloride, such as is shown in Fig. 3, can be considered. In the apparatus, solid calcium metal 8 is deposited on the cathode 3, which is cooled to a temperature of not more than the melting point of calcium metal, the calcium metal 8 is transferred to another container 11, and it is heated to be melted and recovered. However, since another apparatus for recovery is necessary in addition to the electrolysis vessel, the overall process is complicated.

[0008] As explained above, a technique in which calcium metal having high purity can be produced by molten salt electrolysis of calcium chloride, is desired.

5 Disclosure of the Invention

[0009] An object of the present invention is to provide a process for production of metal by molten salt electrolysis, and in particular, a process for production of metal, in which metal that is soluble in an electrolysis bath can be efficiently produced and recovered.

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[0010] As a result of research, the inventors discovered that in an apparatus and a method for production of metal by molten salt electrolysis, after a cathode having a flow passage for a cooling medium inside is arranged in an electrolysis bath and solid metal is deposited on the cathode, the solid metal deposited on the cathode is melted in the electrolysis bath by disconnecting the electric current to the cathode, and the molten metal is continuously removed to the outside of the electrolysis vessel to efficiently recover the metal, and thus the present invention was completed.

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[0011] That is, the process for production of metal by molten salt electrolysis of the present invention, in which an electrolysis vessel is filled with an electrolysis bath, and anode and cathode are immersed and arranged in the vessel, is characterized in that metal is deposited on the cathode having a flow passage for a cooling medium inside, electric current to the cathode is disconnected to melt the deposited metal into the electrolysis bath, and the molten metal is continuously removed to the outside of the electrolysis vessel.

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[0012] The present invention is also characterized in that the temperature of the surface of the cathode is maintained at not less than the melting point of the electrolysis bath and not more than the melting point of the deposited metal, and temperature of the electrolysis bath is maintained at not less than the melting point of the deposited metal.

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[0013] Furthermore, the present invention is also characterized in that the cathode wall and the anode wall are immersed and arranged respectively around the cathode and anode.

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[0014] In addition, the present invention is also characterized in that plural electrodes are arranged in the electrolysis bath (hereinafter referred to as a "multiple-electrode electrolysis vessel"), each electrode has a cycle consisting of a connected mode and a disconnected mode of electric current, and molten metal is removed by disconnecting electric current in one electrode during molten salt electrolysis is performed by connecting electric current in another electrode, and by rotating these modes, melt metal can be continuously removed from the multiple-electrode electrolysis vessel.

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[0015] By the present invention, the metal can be produced more efficiently and in an apparatus with simpler structure compared to conventional techniques, and as a result, high efficiency of electric current can be realized.

Brief Description of the Drawings

[0016]

Fig. 1 is a cross sectional view showing a molten salt electrolysis process and metal recovery process in an embodiment of the invention.

Fig. 2 is a plane view showing another embodiment of the invention.

Fig. 3 is a cross sectional view showing a molten salt electrolysis process and a metal recovery process in a conventional molten salt electrolysis.

Explanation for Reference Numeral

[0017]

- 1 Electrolysis vessel
- 2 Electrolysis bath
- 3 Cathode
- 4 Anode
- 5 Cathode wall
- 6 Anode wall
- 7 Cooling medium
- 8 Solid metal
- 9 Tube for removing a molten metal
- 10 Molten metal
- 11 Heating vessel

Best Mode for Carrying Out the Invention

[0018] Embodiments of the present invention are explained below with reference to the drawings. Figs. 1 and 2 show embodiments of an apparatus to perform the present invention. Hereinafter, preferred embodiments are explained by way of these figures.

[0019] Fig. 1 conceptually shows an apparatus M for molten salt electrolysis used in the present invention. The left part of Fig. 1 is a conceptual diagram of the apparatus M for molten salt electrolysis during electrolysis. The apparatus M for molten salt electrolysis includes an electrolysis vessel 1 and an electrolysis bath 2 filled therein, and melt at a temperature not less than its melting point is maintained in the melt condition by a heating means (not shown). In addition, it is desirable that the electrolysis bath 2 be maintained at a temperature greater than the melting point of the metal that is to be deposited.

[0020] The electrolysis bath 2 includes a cathode 3 and an anode 4 immersed therein, and a cathode wall 5 and an anode wall 6 immersed therein surrounding respectively around the cathode 3 and anode 4. The lower part of these walls is open, and the electrolysis bath 2 can flow into the inside of the walls. In Fig. 1, the cathode 3 is shown in a perspective view so as to make the inside visible. The inside of the cathode 3 has a structure enabling the flowing of cooling medium 7 to control the temperature of the cathode itself. By cooling the cathode 3 and maintaining the surface of the cathode at a temper-

ature that is not greater than the melting point of the metal by the cooling medium 7, the metal can be efficiently deposited in a solid state.

[0021] Starting the molten salt electrolysis by applying a predetermined voltage between the cathode 3 and anode 4, since the cathode 3 is maintained at a temperature that is less than the melting point of the deposited metal, the metal can be deposited as a solid metal 8 as shown in the left part of Fig. 1. Next, after disconnecting the electric current between the cathode 3 and the anode 4 to terminate the molten salt electrolysis, when the flow of the cooling medium 7 in the cathode 3 is stopped, since the electrolysis bath 2 is maintained at a temperature greater than the melting point of the deposited metal, the metal can be floated to surface of the electrolysis bath as a molten metal 10 as shown in the right part of Fig. 1. The molten metal 10 can be removed to the outside by using a removing tube 9.

[0022] In a case in which the metal deposited by the molten salt electrolysis is calcium metal and the electrolysis bath is calcium chloride, it is desirable that after the deposited metal on the cathode 3 is melted in the electrolysis bath that it be removed to the outside of the electrolysis vessel 1 immediately.

[0023] After the deposited metal on the cathode 3 is melted in the electrolysis bath 2 and is removed to the outside immediately, dissolution and dispersion of the calcium metal into calcium chloride, which is the electrolysis bath, can be effectively restrained.

[0024] The right part of Fig. 1 is a conceptual diagram of the metal removing process of the metal generated in the electrolysis bath 2 after the molten salt electrolysis is terminated. In the right part of Fig. 1, reference numeral 9 is a removing tube for the molten metal, and it is used to recover the molten metal.

[0025] In the present invention, it is desirable that chloride of the deposited metal on cathode 3 be used as the electrolysis bath 2, and that calcium chloride or a complex salt containing calcium chloride be used as the electrolysis bath 2 in a case in which the deposited metal is calcium. In a case of a complex salt containing calcium chloride and potassium chloride as the complex salt, since the decomposition voltage of potassium chloride is higher than that of calcium chloride, it is desirable that a voltage applied to between electrodes of the present invention be not less than the decomposition voltage of calcium chloride and not greater than the decomposition voltage of potassium chloride.

[0026] In the present invention, it is desirable that the surface temperature of the cathode 3 immersed in the electrolysis bath 2 be set at a temperature not less than the melting point of the electrolysis bath 2 and not greater than the melting point of the deposited metal, and at the same time, the temperature of the electrolysis bath 2 be set to a temperature not less than the melting point of the deposited metal. In a case in which the deposited metal is calcium, for example, it is desirable that the surface temperature of the cathode 3 be set at not greater

than the melting point of calcium metal (845°C), and the temperature of the electrolysis bath 2 be set at not less than the melting point of calcium metal (845°C). By setting the temperature in this way and by interrupting the molten salt electrolysis in midstream, the calcium metal once deposited on the cathode in solid state can be melted in the electrolysis bath 2, and thus, the calcium metal in melt state can be efficiently removed to the outside.

[0027] As the complex salt used in the present invention, a complex salt in which potassium chloride is added to calcium chloride is desirable. By adding potassium chloride to calcium chloride in an appropriate amount, the melting point of the electrolysis bath 2 can be decreased compared to a case in which calcium chloride is used alone as the electrolysis bath. In the present invention, it is desirable that potassium chloride be added to calcium chloride in a range of from 5 to 75 mol%.

[0028] As a result, a range of controlling temperature of the cathode can be broadened and operation can be facilitated. In addition, since the operation temperature of the cathode can be set at a lower temperature range compared to the conventional operation, calcium metal can be efficiently deposited on the cathode 3. Furthermore, by using the complex salt consisting of calcium chloride and potassium chloride as the electrolysis bath 2, solubility of the calcium metal in the electrolysis bath 2 can be reduced, and as a result, calcium metal can be efficiently recovered.

[0029] For example, in a case in which the temperature of the electrolysis bath 2 is set at 870°C and the surface temperature of the cathode 3 is set at 750°C, calcium metal in a solid state can be deposited on the cathode 3. It should be noted that it is desirable that the difference in temperatures between cathode 3 and the melting point of calcium metal be greater. By using the complex salt having a lower melting point than that of calcium chloride alone as the electrolysis bath 2 as mentioned above, the temperature of the cathode 3 can be decreased.

[0030] In the present invention, after depositing a certain amount of the calcium metal in solid state on the cathode 3, it is desirable that the tube 9 for removing molten calcium metal be inserted into the electrolysis bath 2 between the cathode 3 and the cathode wall 5. In addition, it is desirable that one end of the tube 9 for removing molten calcium metal be connected to a pressure reducing device (not shown) to enable extracting the molten metal to which the other end of the tube 9 for removing molten calcium metal is immersed.

[0031] Next, by disconnecting electric current between the cathode 3 and anode 4, the calcium metal deposited on the cathode 3 can be melted into the electrolysis bath 2. Accompanied by this process, the calcium metal melt in the electrolysis bath 2 can be removed to the outside through the tube 9 for removing molten calcium metal. It should be noted that during removing, the deposited solid metal 8 on the cathode 3 can be smoothly melted by stopping the flow of the cooling medium 7 in the cathode 3.

[0032] Since molten calcium metal has a lower specific gravity than the electrolysis bath 2 and has a tendency to float on the electrolysis bath 2, it is desirable that the cathode wall 5 be arranged around the cathode 3. By arranging the wall 5, dispersion of the molten calcium metal 10 from the cathode 3 can be effectively restrained.

[0033] There can be some cases in which part of electrolysis bath 2 is contained in the molten calcium metal 10 removed through the removing tube 9, and this would not be a problem since reducing reaction of titanium tetrachloride or titanium oxide in a later process would not be interrupted by the electrolysis bath when the calcium metal is used as a reducing agent.

[0034] However, it is desirable that the amount of electrolysis bath 2 contained in the removed metal be as small as possible. To reduce the amount, it is desirable that the depth of the tube 9 for removing molten calcium metal immersed in the electrolysis bath 2 be shallower than the depth of the calcium metal expected on the cathode 3. In this way, calcium metal having high purity and being melted in the electrolysis bath can be efficiently removed.

[0035] Fig. 2 shows another desirable aspect of the present invention. In this aspect, a multiple-electrode molten salt electrolysis apparatus P is constructed by arranging an anode 4 and ten cathodes 3 surrounding the anode in an electrolysis vessel 1. Fig. 2 is a plane view in which the electrolysis vessel 1 is viewed downwardly from its surface to its bottom.

[0036] It is desirable that the anode 4 and the cathodes 3 each be connected in parallel. By connecting electrically in this way, each cathode can be easily set in an electrolysis period and a pause period. The electrolysis period means a period in which calcium metal is deposited in a solid phase on the surface of the cathode, as mentioned above, and the pause period means a period in which molten salt electrolysis is stopped by disconnecting the cathode 3 and a power resource, the solid calcium metal 8 deposited on the cathode 3 is melted in the electrolysis bath, and simultaneously the calcium metal is removed from the electrolysis vessel 1 via the tube 9 for removing molten calcium metal to migrate it to the reduction process.

[0037] By combining the electrolysis period and the pause period of each cathode 3, the calcium metal can be continuously produced by the multiple-electrode molten salt electrolysis apparatus P. The calcium metal produced can be efficiently used as a reducing agent used in a direct reduction of titanium oxide or in a reduction of titanium tetrachloride.

[0038] In addition, calcium chloride, which is a by-product of the reduction process, can be reused as a raw material of calcium metal, which is a reducing agent, by returning it to the electrolysis vessel 1 as shown in Fig. 2. It should be noted that chlorine gas generated in the anode 4 can be used in a chlorination reaction of titanium oxide to produce titanium tetrachloride, which is a raw material of the reduction reaction of titanium.

[0039] Next, desirable aspects of molten salt electrol-

ysis apparatus used in the present invention are explained. It is desirable that the cathode 3 on which calcium metal 8 is deposited be made of metal having electric conductivity, and in particular, be of stainless steel or titanium metal. A cathode 3 made of such material can deposit calcium metal having high purity.

[0040] It is desirable that the cathode 3 have a structure so that the cooling medium 7 can flow inside the electrode. By such a structure, the surface temperature of the cathode 3 can be efficiently maintained at a temperature not greater than or not less than the melting point of calcium metal.

[0041] That is, the surface temperature of the cathode 3 is maintained at a temperature not greater than the melting point of calcium metal by flowing the cooling medium 7 inside the cathode 3 in a case in which metal is to be deposited on the cathode 3, and the surface temperature of the cathode 3 is maintained at a temperature not less than the melting point of calcium metal by stopping the flow of the cooling medium 7 in a case in which solid metal deposited 8 on the cathode 3 is to be melted in the electrolysis bath 2. As the cooling medium that is flowed in the cathode 3, air or inert gas may be used.

[0042] On the other hand, since chlorine gas is generated on the anode 4, it is desirable that the anode 4 be made of carbon or graphite having corrosion resistance against chlorine gas at high temperature. By the anode 4 being such a material, damage to the anode 4 can be minimized and chlorine gas can be efficiently recovered.

[0043] It is desirable that the cathode wall 5 and anode wall 6 arranged around the cathode 3 and anode 4 respectively be made of ceramic, and silicon nitride is particularly desirable in the present invention. The silicon nitride is desirable as a material in the present invention since it has corrosion resistance against chlorine gas in addition to corrosion resistance against calcium metal and calcium chloride.

[0044] The electrolysis vessel 1 is made of a material having corrosion resistance against calcium chloride or potassium chloride having high temperature, and stainless steel or titanium metal is desirable.

[0045] The tube 9 for removing molten calcium metal of the electrolysis bath 2 can be made of a metallic material having corrosion resistance such as stainless steel, which can be easily replaced when it is corroded.

[0046] By the present invention as explained above, molten calcium metal can be effectively produced. As a result, by using the calcium metal, titanium metal can be produced by effectively reducing titanium tetrachloride or titanium oxide.

Examples

[0047]

1. Construction of apparatus

1) Reaction vessel

Size: inner diameter 150 mm x total length 500 mm
Material: titanium
Shape: cylinder hollow vessel having bottom

2) Cathode

Size: outer diameter 10 mm x length 60 mm
Material: stainless steel (SUS304)
Shape: cylinder solid
Cooling medium: air (maintained at 300°C)
Surface temperature: 750°C

3) Anode

Size: outer diameter 15 mm x length 60 mm
Material: carbon
Shape: cylinder solid

4) Cathode wall

Size: inner diameter 80 mm x thickness 5 mm x length 200 mm
Material: silicon nitride
Shape: cylinder hollow

5) Anode wall

Size: inner diameter 30 mm x thickness 3.5 mm x length 1000 mm
Material: silicon nitride
Shape: cylinder hollow

2. Electrolysis bath

1) Composition: calcium chloride : potassium chloride = 85 : 15 (mol%)

2) Temperature of electrolysis: 870°C

3) Melting point: 713°C

Example 1

[0048] Using the electrolysis apparatus shown in Fig. 1, calcium metal was deposited on the cathode 3. Electric current between the cathode 3 and anode 4 was disconnected and the calcium metal deposited on the cathode 3 was melted in the electrolysis bath 2 while the molten calcium metal 10 was removed to the outside. The calcium metal contained 5% of the electrolysis bath in weight ratio. However, the ratio of the amount of calcium metal recovered and the amount of calcium metal expected from calculation of electric current was 85%, which means a high current efficiency. The electric energy necessary for the electrolysis of calcium metal deposited on the cathode was 6.4 kWh per 1 kg of calcium metal.

Example 2

[0049] Using the multiple-electrode electrolysis vessel in which ten cathodes are arranged in parallel to one anode 4 shown in Fig. 2, molten calcium metal was produced by molten salt electrolysis of calcium chloride. In Fig. 2, molten salt electrolysis was performed by connecting the electric current in the left half area of the electrolysis vessel, and solid calcium metal deposited on the cathode was melted and removed from the electrolysis vessel to supply it to a titanium reducing process by disconnecting the electric current in the right half area of the electrolysis vessel.

[0050] As a result, molten calcium could be substantially and continuously supplied from the electrolysis vessel shown in Fig. 2 to the titanium reducing process. In addition, compared to a case in which ten molten salt electrolysis vessels are individually prepared, initial investment could be reduced by 90%.

Comparative Example 1

[0051] As shown in Fig. 3, after the cathode 3 having solid calcium metal deposited on its surface was once moved to the outside, it was moved to a heating vessel 11 to obtain the molten calcium metal. In this case, additional electric energy (52.7 kWh per 1 kg of calcium metal) to melt the metal, which was not necessary in Example 1, was necessary.

[0052] As mentioned above by way of Examples and the Comparative Example, by producing calcium metal by the present invention, the apparatus is easy to use compared to a conventional one, and energy for melting calcium metal deposited on the cathode can be reduced about 88%.

Claims

1. An electrolysis apparatus for production of metal, comprising:

an electrolysis vessel;
an electrolysis bath filled in the electrolysis vessel;
a cathode and an anode immersed in the electrolysis bath;
a wall arranged between the two electrodes; and
a removing tube for removing metal generated, wherein a flow passage of a cooling medium is formed inside the cathode.

2. The electrolysis apparatus for production of metal, according to claim 1, wherein an anode wall and a cathode wall are arranged respectively surrounding the anode and the cathode.

3. The electrolysis apparatus for production of metal,

according to claim 1, wherein plural cathodes are arranged surrounding the anode.

4. A method for production of metal using the electrolysis apparatus according to one of claims 1 to 3, comprising:

depositing the metal in solid state on the cathode;

disconnecting electric current to the cathode to melt the solid metal in the electrolysis bath, while the molten metal is removed continuously to the outside of the electrolysis vessel.

5. The method for production of metal, according to claim 4, wherein a surface temperature of the cathode is maintained at a temperature not less than the melting point of the electrolysis bath and not more than the melting point of metal deposited, and wherein temperature of the electrolysis bath is maintained at a temperature not less than the melting point of the metal.

6. The method for production of metal, according to claim 4, wherein the electrolysis bath is contained in the molten metal removed to the outside of the electrolysis vessel.

7. The method for production of metal, according to claim 4, wherein a wall is immersed and arranged around the cathode.

8. The method for production of metal, according to one of claims 4 to 7, wherein plural electrodes are held in the electrolysis bath (hereinafter referred to as a multiple-electrode electrolysis vessel), each electrode has a different cycle of connection period and disconnection period of electric current so that molten salt electrolysis is performed by connecting electric current of one electrode while molten metal is removed by disconnecting electric current of another electrode, to continuously remove the molten metal from the multiple-electrode electrolysis vessel.

9. The method for production of metal, according to claim 4, wherein the molten metal removed is used as a reducing agent of titanium tetrachloride or titanium oxide.

10. The method for production of metal, according to one of claims 4 to 9, wherein the molten salt is a complex salt consisting of calcium chloride and potassium chloride.

11. The method for production of metal, according to one of claims 4 to 7, wherein the metal is calcium metal.

Fig. 1

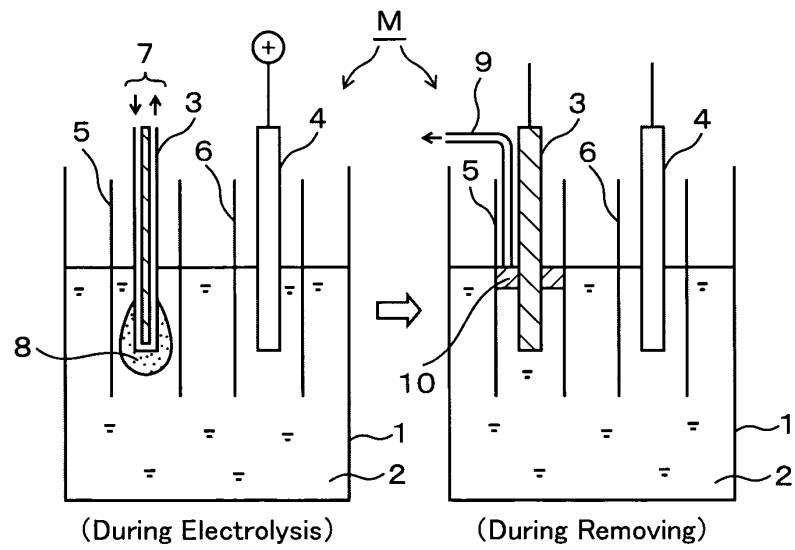


Fig. 2

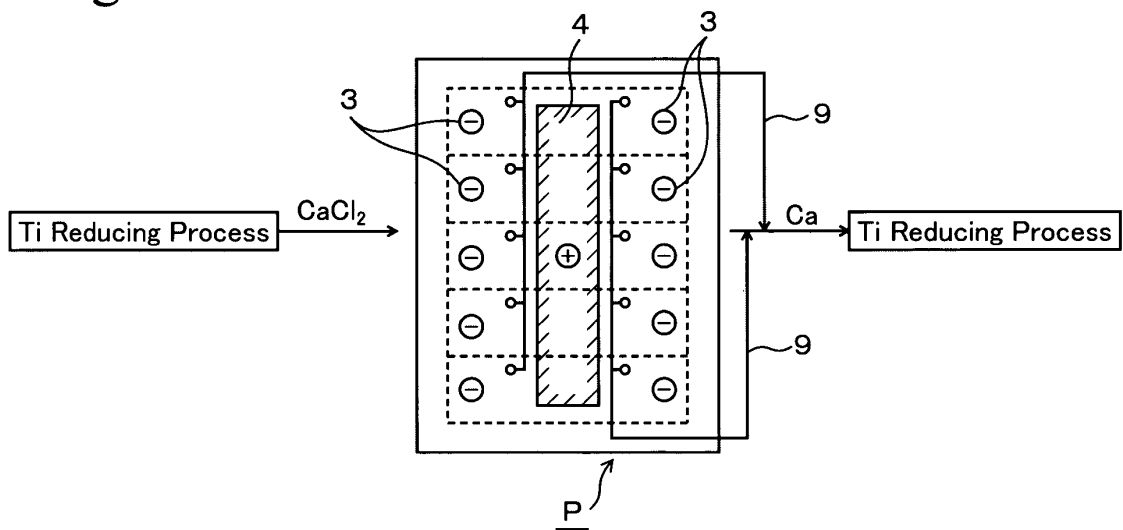
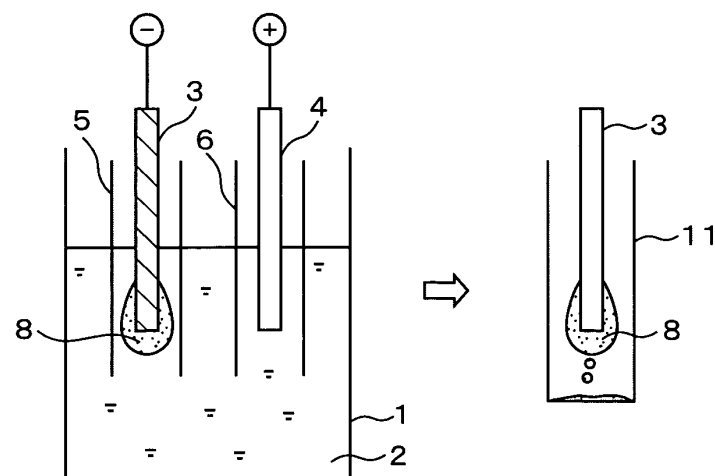


Fig. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/000060

A. CLASSIFICATION OF SUBJECT MATTER

C25C7/02(2006.01)i, C22B34/12(2006.01)i, C25C3/02(2006.01)i

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)

C25C7/02, C22B34/12, C25C3/02

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	WO 2006/003864 A1 (Toho Titanium Co., Ltd.), 12 January, 2006 (12.01.06), Par. Nos. [0015], [0016]; Fig. 1; Par. No. [0033]; Fig. 3 & EP 1785509 A1	1, 2, 4-7, 9-11 3, 8
Y	JP 2-13031 B2 (Sumitomo Light Metal Industries, Ltd.), 03 April, 1990 (03.04.90), Column 5; Figs. 1 to 3 (Family: none)	1, 2, 4-7, 9-11

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

24 April, 2008 (24.04.08)

Date of mailing of the international search report

13 May, 2008 (13.05.08)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/000060

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 54-43811 A (Asahi Glass Co., Ltd.), 06 April, 1979 (06.04.79), Claims; page 2, lower right column; page 3, upper left column to upper right column; Figs. 1 to 3 (Family: none)	1, 2, 4-7, 9-11

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- JP 2005133195 A [0004]