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Yamaguchi et al.(10) **Pub. No.: US 2008/0053838 A1**(43) **Pub. Date: Mar. 6, 2008**(54) **METHOD FOR PRODUCTION OF METAL
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METHOD FOR PRODUCTION OF TITANIUM
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C25C 3/28 (2006.01)(52) **U.S. Cl.** **205/401; 205/398**(57) **ABSTRACT**

A method for production of metal by molten-salt electrolysis is a method for production of metal by molten-salt electrolysis which is performed by filling molten salt of a metal chloride in an electrolysis vessel having an anode and a cathode, and a molten salt which reduces solubility of the metal in the molten salt is used.

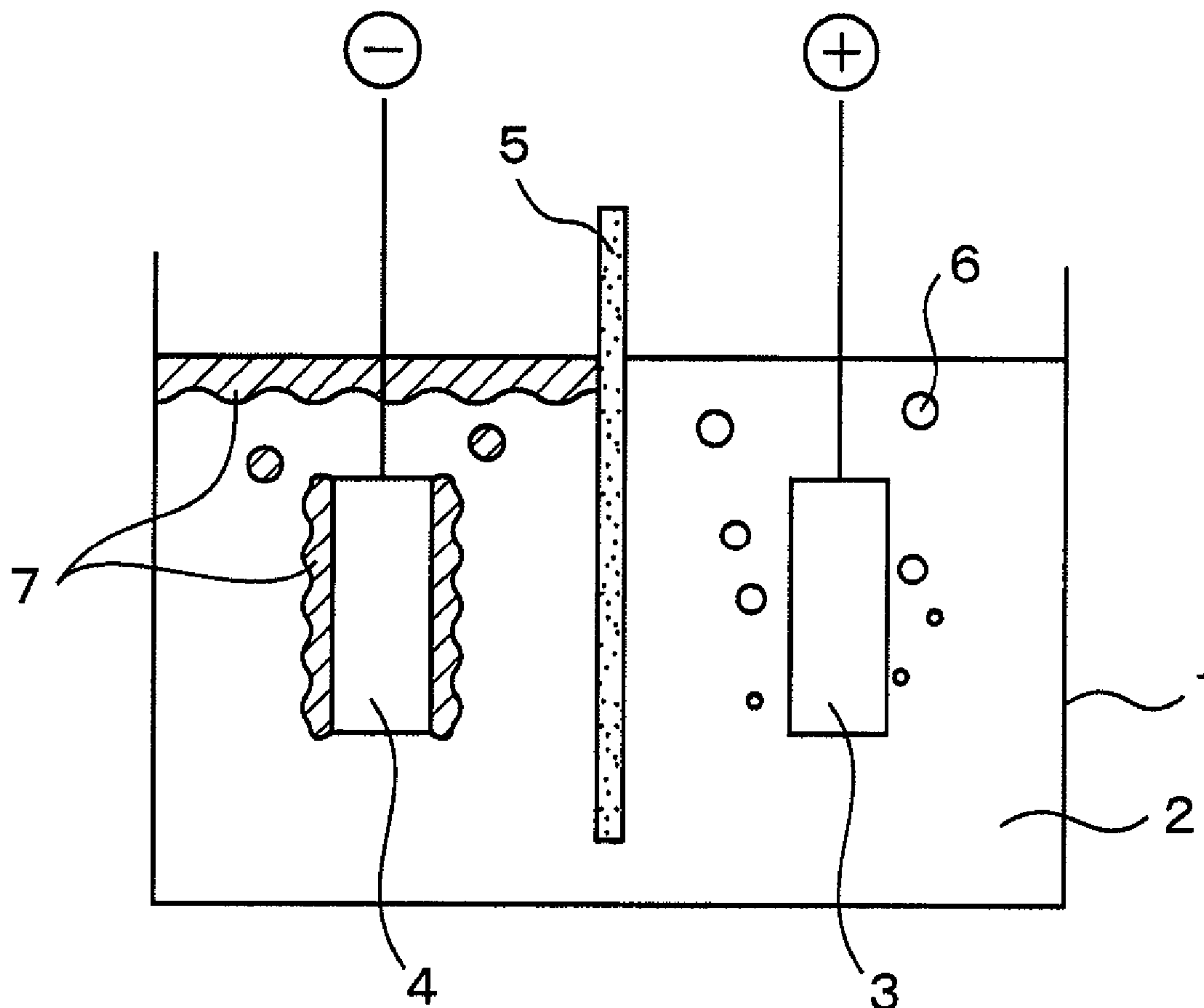
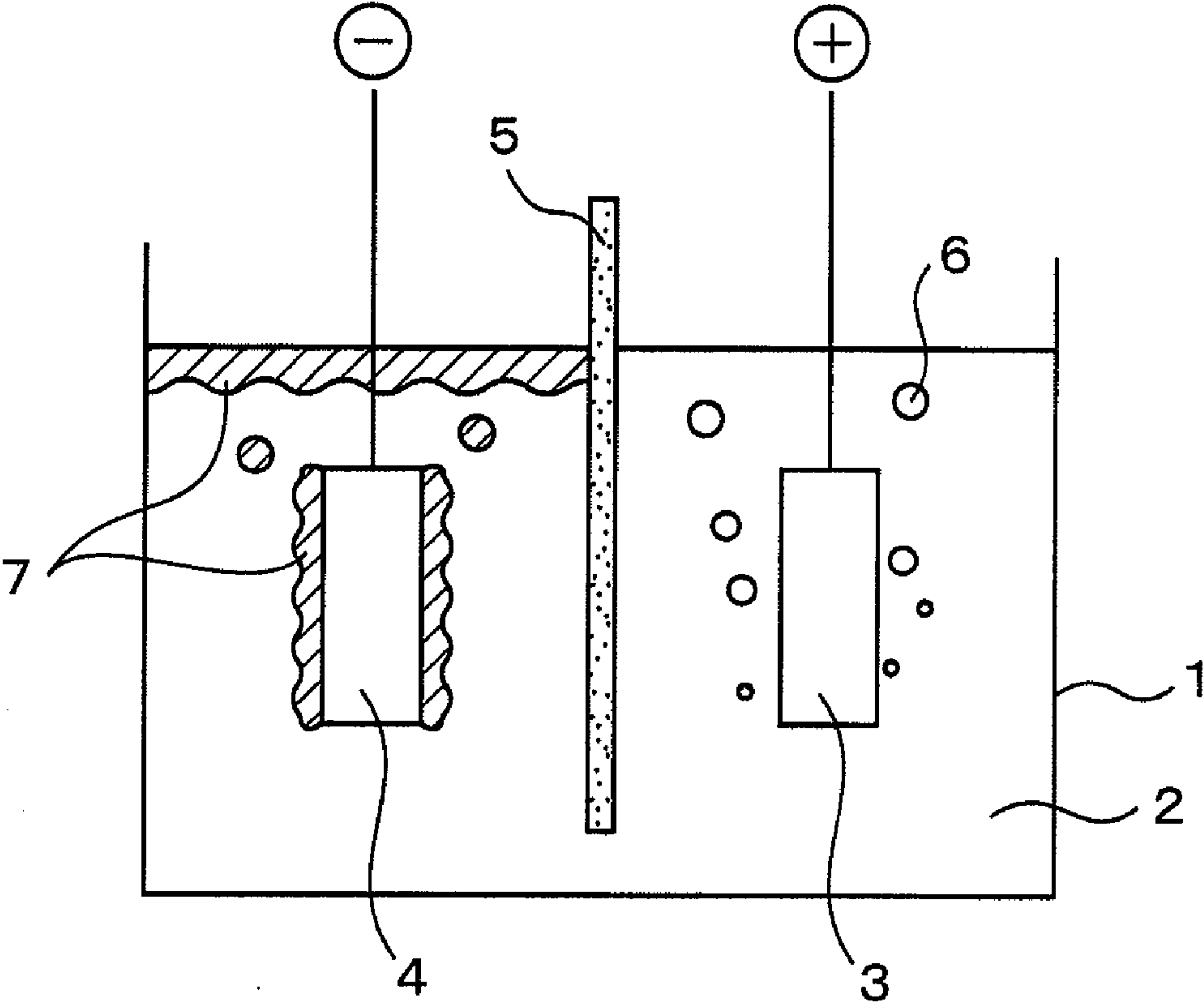


Fig. 1



METHOD FOR PRODUCTION OF METAL BY MOLTEN-SALT ELECTROLYSIS AND METHOD FOR PRODUCTION OF TITANIUM METAL

TECHNICAL FIELD

[0001] The present invention relates to the recovery of metal from a chloride thereof, and in particular, relates to a method for production of metal by molten-salt electrolysis. Furthermore, the present invention relates to a method for production of titanium metal using the metal produced by the method.

BACKGROUND ART

[0002] Conventionally, titanium metal, which is a simple substance, is produced by the Kroll method, in which titanium tetrachloride is reduced by molten magnesium to obtain sponge titanium, and various kinds of improvements have been made to reduce the cost of production. However, since the Kroll method is a batch process in which a set of operations is repeated noncontinuously, there is a limitation to its efficiency.

[0003] To overcome this problem, a method in which titanium oxide is reduced by calcium metal in molten salt to obtain titanium metal directly (see WO99/064638 and Japanese Unexamined Patent Application Publication No. 2003-129268), one in which an EMR method in which a reducing agent containing an active metal such as calcium or an active metal alloy is prepared, and one in which a titanium compound is reduced by electrons from the reducing agent to yield titanium metal (see Japanese Unexamined Patent Application Publication No. 2003-306725) have been proposed. In these methods, calcium oxide, which is a by-product of the electrolytic reaction, is dissolved in calcium chloride, and molten-salt electrolysis is performed to recover and reuse calcium metal. However, since the calcium metal generated during the electrolytic reaction is in a liquid state and is highly soluble in calcium chloride, it dissolves easily in the calcium chloride, and there has been a problem in that the yield of the metal is reduced.

[0004] As explained above, there has been a problem in that it has been difficult to recover metal such as calcium metal efficiently by a conventional method.

DISCLOSURE OF THE INVENTION

[0005] The present invention has been completed in view of the above circumstances, and an object of the present invention is to provide a method for production of metal by molten-salt electrolysis, in which metal used for reducing, such as an oxide or chloride of titanium metal, is efficiently recovered, and another object of the present invention is to provide a method for production of titanium metal in which the metal produced by the method is used.

[0006] The method for production of metal by molten-salt electrolysis of the present invention is a method for production of metal by molten-salt electrolysis which is performed by filling molten salt of a metal chloride in an electrolysis vessel having an anode and a cathode, and a molten salt which reduces solubility of the metal in the molten salt is used.

[0007] In the method for production of titanium metal of the present invention, the metal produced in the above-mentioned method is used as a reducing agent of titanium tetrachloride.

[0008] By the method for production of metal by molten-salt electrolysis of the present invention, since the solubility of the metal in the molten salt is reduced, the metal that is deposited is difficult to dissolve in the molten salt. Therefore, the metal can be effectively recovered.

BRIEF DESCRIPTION OF DRAWINGS

[0009] FIG. 1 is a conceptual cross sectional diagram showing the electrolysis vessel used in the molten salt electrolysis of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0010] Embodiments of the present invention are explained below with reference to the drawings. Here, a case in which the metal is calcium metal, the metal chloride is calcium chloride, and the chloride added to reduce the melting point of the electrolysis bath of the molten salt of the present invention is potassium chloride, is explained.

[0011] FIG. 1 shows a desirable embodiment of the apparatus structure to perform the present invention. In FIG. 1, reference numeral 1 indicates an electrolysis vessel, and an electrolysis bath 2 mainly containing calcium chloride is filled in the vessel. The electrolysis bath 2 is heated to a temperature above the melting point of calcium chloride by a heater, which is not shown, so as to be maintained in a melted condition. As the electrolysis bath 2, a bath of a mixture of calcium chloride and potassium chloride is used. Not only can the melting point of the electrolysis bath 2 be reduced by adding potassium chloride to calcium chloride, but the solubility of calcium metal in the electrolysis bath 2 can also be reduced.

[0012] Reference numeral 3 indicates an anode and reference numeral 4 indicates a cathode, and they are immersed in the electrolysis bath 2. Between the anode 3 and the cathode 4, for example, a dividing wall 5 made of graphite is arranged.

[0013] Starting the electrolysis of the electrolysis bath 2 by connecting the anode 3 and cathode 4 to a direct current power supply, which is not shown, chloride ions in the electrolysis bath 2 are attracted to the anode 3 and donate electrons, forming chlorine gas 6, which is expelled from the system. Calcium ions are attracted to the cathode 4 and accept the electrons, forming calcium metal 7, which is deposited on the surface of the cathode 4.

[0014] It is desirable that the temperature of the electrolysis bath 2 be not less than 650° C. which is a eutectic temperature of calcium chloride and potassium chloride, and that it be not more than 1000° C. In the case in which the target calcium metal is required to be recovered in a solid state, the temperature of the electrolysis bath is maintained at not less than the eutectic temperature of calcium chloride and potassium chloride and at not more than the melting point of calcium metal (845° C.). In the case in which calcium metal is recovered in a melted state, the temperature of the electrolysis bath 2 is maintained at not less than the melting point of calcium metal.

[0015] The temperature of the electrolysis bath is different depending on whether the target calcium metal is to be recovered in a solid state or a melted state, as explained above; however, the bases for improving recovery efficiency

are the same. The upper limit is set at 1000° C.; however, in the case in which the present invention is performed at a temperature not less than the melting point of calcium metal, recovery becomes difficult if solubility of calcium which dissolves in the molten salt is increased. In addition, the vapor pressure of calcium metal increases above 1000° C., and it becomes difficult to recover the calcium metal that is generated. Therefore, in the present invention, the upper limit of the temperature of the electrolysis bath 2 is desirably not more than 1000° C.

[0016] It is believed that the range of temperature of the electrolysis bath 2 is desirably from 650° C. to 850° C. If the temperature of the electrolysis bath 2 is less than 650° C., the electrolysis bath 2 will solidify, as mentioned above. If the temperature of the electrolysis bath 2 is 650° C. or more, it is possible for an electrolysis bath containing a sufficient calcium source to be prepared, and the rate of generation of calcium will be high. In addition, if the temperature is 850° C. or less, the rate of dissolution of calcium in the electrolysis bath 2 will be low, and deterioration of material used for the electrolysis vessel or the like will be low; this temperature range is therefore desirable for practicing the present invention.

[0017] The eutectic composition of the electrolysis bath 2 mentioned above is 25 mol % as a ratio of addition of potassium chloride to calcium chloride. Therefore, it is desirable that potassium chloride in the electrolysis bath 2 also be selected to be not more than 25%. It is desirable that the amount of potassium chloride in the electrolysis bath 2 be low; however, from the viewpoint of reducing the melting point of the electrolysis bath 2, it is desirable that the amount be higher. Therefore, the ratio of the addition of potassium chloride to calcium chloride should be determined while considering the tradeoffs.

[0018] In the case in which the present invention is performed at a temperature not less than the melting point of the electrolysis bath 2 and that not more than 845° C. (not more than the melting point of calcium metal), it is possible for the calcium metal to be deposited near the electrode and to be recovered in a solid state. In the case in which the metal is not deposited, the metal is dispersed in the bath as metal particles, and since the specific gravity thereof is less than that of the bath, the particles float up to the surface of the bath around the cathode. In the case in which the metallic particles are recovered, it is possible to recover them in a mixed condition with the electrolysis bath, and as an embodiment of the present invention, a mixture of the electrolysis bath and solid metal or the metal alone can be recovered.

[0019] On the other hand, also in the case in which the electrolysis is performed at a temperature not less than 845° C. and not more than 1000° C., the solubility of calcium metal in the electrolysis bath 2 can be reduced by controlling the concentration of chlorides added to the electrolysis bath 2. As a result, calcium metal in a solid state is partially deposited at the surface of an electrode and is dispersed in the bath. On the other hand, since the specific gravity of calcium metal partially generated in a melted state is lower than that of the bath, it will ultimately float up near the cathode as a melted metal.

[0020] By recovering the melted metal, the present invention can be performed in the temperature range. During the

recovery, since it would take a long time to separate calcium metal dispersed in the bath and the electrolysis bath 2, it is desirable that the melted calcium and the electrolysis bath 2 be recovered in a mixed state. Apart from these recovery methods, it is possible for the molten salt and calcium to be entirely recovered in a solid state. In the case in which the recovery method is performed, it is possible to use the entire range of the temperature of the present invention.

[0021] Calcium metal deposited on the surface of the cathode 4 is partially dissolved in the electrolysis bath 2, and calcium metal partially floats up to the surface of the electrolysis bath. The calcium metal which floated up to the surface of the electrolysis bath may flow to near the anode and will be blocked by the dividing wall 5 to efficiently reduce the back reaction with chlorine gas generated at the anode 3.

[0022] Since calcium metal is soluble in calcium chloride, in the case in which a conventional electrolysis bath consisting of calcium chloride alone is used, the calcium metal deposited will be dissolved in the electrolysis bath. However, in the present invention, since the above-mentioned chloride is added to calcium chloride to reduce the solubility of calcium chloride in the bath, calcium metal alone or the electrolysis bath in which calcium metal is precipitated can be efficiently recovered.

[0023] In addition, by determining the solubility of calcium in the electrolysis bath at not more than 3%, calcium metal generated by electrolysis or a bath containing a large amount of calcium metal can be efficiently recovered. The solubility of calcium metal in the electrolysis bath is more desirably not more than 1.5%, and by selecting the solubility, the recovery efficiency of calcium metal generated by electrolysis can be improved further.

[0024] As a method for reducing the solubility of calcium metal in the electrolysis bath, two methods may be considered. One is a method in which the content of calcium chloride is decreased and the content of potassium chloride, sodium chloride or calcium fluoride is increased to reduce the solubility of calcium metal, and the other is a method in which the temperature of the electrolysis bath 2 is reduced. By each of these methods, the solubility of the calcium metal in the electrolysis bath can be efficiently reduced. It should be noted that the solubility of calcium metal can be efficiently reduced if the temperature of the electrolysis bath is near the melting point of calcium chloride in the case of the bath of calcium chloride alone.

[0025] Calcium metal or the electrolysis bath 2, in which calcium metal is precipitated and recovered in this way, can be used in direct reduction of titanium oxide, for example.

[0026] In the case in which potassium chloride is added to calcium chloride at 5 mol % to 50 mol %, solubility of calcium versus calcium chloride can be reduced to a level of 0.1 % to 0.3%, in a temperature range of 650° C. to 800° C. in the electrolysis bath 2.

[0027] In addition, by adding the above-mentioned chlorides, not only can the solubility of the calcium metal in calcium chloride be reduced, but the melting point of the electrolysis bath can also be reduced. Since the melting point of calcium chloride is 780° C. and the melting point of calcium metal is 845° C., calcium metal in a solid state can be deposited on the cathode 4 in the case in which the

temperature of the conventional electrolysis bath consisting of calcium chloride alone is set at 800° C. In this case, the difference between the temperature of the electrolysis bath and the melting point of the electrolysis bath (780° C.) is only 20° C., and since the electrolysis bath would solidify if the temperature were to go below the melting point, it is necessary that the temperature of the electrolysis bath be controlled precisely.

[0028] However, in the present invention, since the melting point of the electrolysis bath 2 is reduced by mixing the above-mentioned chlorides in the electrolysis bath 2, precise control of temperature is no longer required, and molten-salt electrolysis can be performed reliably. For example, since the electrolysis bath 2 does not solidify even if the temperature of the electrolysis bath 2 is set at around 750° C., calcium metal can be deposited in a solid state on the cathode 4. Practically, by adding potassium chloride to calcium chloride at 5 to 50 mol %, electrolysis can be performed in the electrolysis bath having a temperature about 30 to 140° C. lower than in the case of the bath of calcium chloride alone.

[0029] As explained, in the present invention, since calcium chloride can be deposited in a solid state, dissolution of calcium metal in the electrolysis bath 2 is reduced, and the yield of calcium metal can be effectively improved.

[0030] In the case in which calcium metal is deposited in a solid state, after a certain amount of calcium metal is deposited, supply of electric power to the anode 3 and cathode 4 is stopped, the cathode 4 is pulled out of the electrolysis bath 2, and the calcium metal is scraped off to be recovered. Alternatively, the cathode is transported to a recovery vessel, which is prepared in advance and which is not shown, and calcium metal deposited on the cathode is melted and recovered by heating the recovery vessel to a temperature not less than the melting point of calcium metal.

[0031] It should be noted that the mixed salt in which sodium chloride or calcium fluoride is added, instead of the potassium chloride mentioned above, can be used as the electrolysis bath 2. The eutectic temperature of the mixed bath in which sodium chloride is added to calcium chloride is 500° C. Furthermore, the eutectic temperature of the mixed bath in which calcium fluoride is added to calcium chloride is 670° C. In each case, the temperature of the electrolysis bath 2 can be effectively reduced compared to the case of the melting point of calcium chloride (780° C.) alone. In addition, the temperature of the electrolysis can also be reduced, and as a result, dissolution loss of calcium metal generated in the electrolysis reaction of the electrolysis bath 2 can also be efficiently reduced.

[0032] While the electrolysis of the molten salt is performed using the electrolysis bath in which potassium chloride is added to calcium chloride, it is desirable that the voltage of the electrolysis be selected so as not to cause deposition of potassium metal. Since the theoretical decomposition voltage of calcium chloride is 3.2 V and the theoretical decomposition voltage of potassium chloride is 3.4 V, a range of from 3.2 V to 3.4 V is desirable. However, if the electrolysis is performed at a decomposition voltage of not less than 3.4 V, potassium metal that is produced will react with calcium chloride to produce calcium metal. Therefore, it may not cause a substantial problem even if the decomposition voltage is high.

[0033] If the voltage applied to the anode and cathode is increased, the amount of electricity supplied to the electrolysis vessel 1 and rate of deposition of metal can be increased. However, according to the increase of the voltage applied, both surfaces of the dividing wall 5 will be polarized. Metal is deposited on the anode-side of the dividing wall 5 and chlorine gas is generated on the cathode-side of the dividing wall 5 when the voltage applied reaches twice the theoretical decomposition voltage. The chlorine gas generated on the cathode-side of the dividing wall 5 could bring the back reaction with calcium metal generated at the cathode 4, reducing the yield of calcium metal. Therefore, the voltage applied to the anode 3 and cathode 4 is desirably an electrolysis voltage which does not produce the polarization of the dividing wall 5. Such a range of voltages is not less than the theoretical decomposition voltage of calcium chloride and is less than twice thereof. Practically, it is from 3.2 V to 6.4 V.

[0034] The anode used in the present invention is required to be made from a material which is durable when exposed to chlorine gas at high temperature. As such a material, graphite is desirable. Not only is graphite durable when exposed to chlorine gas at high temperature, but it is also durable in electrolysis baths at high temperature, and it has appropriate conductivity. It is desirable that the anode be arranged penetrating an upper lid of the electrolysis vessel 1, which is not shown, while being immersed in the electrolysis bath 2. The surface of the anode 3 consisting of graphite and penetrating the upper lid can be coated with a ceramic material. Such a structure can minimize a corrosion of the graphite.

[0035] Since chlorine gas is not generated from the cathode, the cathode, at least, can be made of a material durable to molten salt at high temperature, such as a conventional carbon steel. In the cathode, since there is a possibility of generating carbide when metal is generated, a steel material having a low concentration of carbon is desirable. This carbon steel is desirable since it is durable to molten salt and calcium metal at high temperatures. In addition, it is practical since it is inexpensive and durable.

[0036] The dividing wall of the present invention must be made from a material that is durable to calcium chloride and chlorine gas at high temperature, similar to the case of the anode. Practically, graphite is desirable. The dividing wall itself can be constructed of graphite, or alternatively, an inner part may be constructed of a ceramic and the outer part may be constructed of graphite, and the strength thereof at high temperatures can be maintained for long periods.

[0037] The dividing wall is required to be dense as possible as can; however, some porosities in the wall, which do not allow penetration and migration of calcium metal generated in the cathode 4 to the anode side, do not pose problems in conducting the present invention. Furthermore, it is not necessary for the lower edge of the dividing wall to reach the bottom part of the electrolysis vessel, and it is sufficient for the dividing wall to have a sufficient length so as not to allow calcium metal generated at the cathode 4 or a calcium chloride layer having precipitated calcium metal to migrate to the anode.

[0038] Chlorine gas is recovered from the system, and for example, it can be used in a chlorination reaction of titanium ore. Furthermore, calcium metal can be used in a reduction

reaction of titanium oxide or titanium chloride using molten salt to produce titanium metal. For example, it can be used as the reducing agent of titanium tetrachloride disclosed in Japanese Unexamined Patent Application Publication No. 2005-068540, to produce ingots of titanium metal. Alternatively, it can be used as the reducing agent of titanium metal in the FFC method in which titanium oxide is used as a raw material disclosed in Japanese Application Laid Open No. 2002-517613.

[0039] By using the mixed salt explained above as the electrolysis bath, the melting point of the electrolysis bath can be reduced, which brings to the reduction of the electrolysis temperature, and as a result, the solubility of calcium metal in calcium chloride can be reduced. Furthermore, since the ratio of calcium chloride in the electrolysis bath is decreased by using the mixed salt, the amount of the calcium metal dissolved into the electrolysis bath can be reduced compared to the case in which calcium chloride alone is used as the electrolysis bath.

[0040] It should be noted that sodium chloride or calcium fluoride can be used instead of the potassium chloride mentioned above. In this case, the eutectic composition of sodium chloride to calcium chloride is 54%. Furthermore, the eutectic composition of calcium fluoride to calcium chloride is 20%. Therefore, in the case of using any of the chlorides, the electrolysis bath 2 having the above-mentioned eutectic composition, or a composition not more than that, is desirable.

[0041] In this way, by practicing the present invention, the melting point of the electrolysis bath can be reduced, and the solubility of calcium metal in the electrolysis bath can be reduced. As a result, the calcium metal generated according to the present invention can be efficiently recovered compared to the conventional methods.

EXAMPLES

Example 1

[0042] Using the electrolysis vessel shown in FIG. 1, while maintaining the temperature of the electrolysis bath consisting of calcium chloride at 75 mol % and potassium chloride at 25 mol % at 650° C., and applying a voltage of 4.5 V between an anode 3 made of carbon and the cathode 4 made of carbon steel, the electrolysis of the molten salt of calcium chloride is started. Accompanied by the electrolysis of the molten salt, calcium metal is deposited on the cathode in a solid state. After depositing a predetermined amount of calcium metal on the cathode in a solid state, electric power supply to the positive and cathodes is stopped. After that, the cathode, having deposited calcium metal on its surface, is transferred to a recovery vessel which is heated to a temperature not less than the melting point of calcium metal, and the calcium metal deposited on the surface of the cathode is melted so that it can be recovered. The ratio of the amount of calcium metal actually recovered to the amount of calcium metal generated, calculated from the electric power applied to the electrolysis bath, was 85%. It was confirmed that an electrolysis reaction having high efficiency could be performed.

Example 2

[0043] Using the electrolysis vessel shown in FIG. 1, while maintaining the temperature of the electrolysis bath

consisting of calcium chloride at 85 mol % and potassium chloride at 15 mol % at 730° C., and applying a voltage of 5.0 V between an anode 3 made of carbon and the cathode 4 made of low-carbon steel, the electrolysis of the molten salt of calcium chloride was started. Accompanied by the electrolysis of the molten salt, calcium metal in a solid state floated up to the bath surface around the cathode. The electrolysis bath and calcium metal were drawn off and recovered from the bath surface around the cathode. The recovered calcium content in the electrolysis bath was measured to be 50%. The amount of calcium metal generated was measured from the recovered amount and the concentration, and a ratio was calculated with a theoretical generated amount calculated from the time of electric power supply. As a result, it was confirmed that not less than 75% of calcium metal was recovered. This operation was repeated, and the efficiency was improved.

Example 3

[0044] Using the electrolysis vessel shown in FIG. 1, while maintaining the temperature of the electrolysis bath consisting of calcium chloride at 85 mol % and potassium chloride at 15 mol % at 950° C., and applying a voltage of 5.0 V between an anode 3 made of carbon and a cathode 4 made of low-carbon steel, the electrolysis of the molten salt of calcium chloride was started. Accompanied by molten-salt electrolysis, calcium metal in a melted state floated up to the bath surface around the cathode. The electrolysis bath and melted calcium metal were drawn off and recovered from the bath surface around the cathode. Melted calcium was recovered and the concentration of calcium in the electrolysis bath which was recovered was measured and was 30%. The amount of calcium metal generated was measured from the recovered amount and the concentration, and a ratio with a theoretical generated amount calculated from the time of electric power supply was calculated. As a result, it was confirmed that not less than 60% of calcium metal was recovered. This operation was repeated, and the efficiency was improved. As an additional experiment, the electrolysis bath consisting of calcium chloride at 85% and potassium chloride at 15% was maintained at 950° C. and solubility of calcium in a saturated state was measured, and it was 2.8%.

Example 4

[0045] Except that 20 mol % of calcium fluoride was added to calcium chloride instead of potassium chloride, electrolysis tests were performed under the same conditions as those of Example 3. Calcium metal recovered in this Example 4 was 70% of the theoretical value.

Example 5

[0046] A molten salt in which the added ratio of potassium chloride to calcium chloride was 25 mol % was prepared, and calcium metal corresponding to 10 wt % of the total of all the molten salts was added to the molten salt to perform heating and melting testing. In the testing, the heating temperature was set at several levels to determine the effects on the recovery ratio of calcium metal. As a result, as shown in Table 1, there was a tendency for the recovery ratio of calcium metal to continuously decreased with increasing temperature in a range of heating temperature of 800° C. to 1000° C. However, when the heating temperature was above

1000° C., a strong tendency for the recovery ratio of calcium metal to decrease was observed. The reason for this is estimated to be that both the evaporation loss of calcium metal and the solubility of calcium metal in the molten salt are increased by increasing the bath temperature. Furthermore, similar testing was performed in the cases of combinations of sodium chloride and calcium chloride, and combinations of calcium fluoride and calcium chloride, and results similar to those in the case of potassium chloride were obtained.

TABLE 1

Mixed salt	Temperature					Unit: wt %
	800° C.	900° C.	1000° C.	1010° C.	1050° C.	
CaCl ₂ —KCl (25)	95	70	60	45	30	
CaCl ₂ —NaCl (54)	97	75	65	50	40	
CaCl ₂ —CaF ₂ (20)	92	66	55	40	25	

*Values in parentheses are eutectic compositions.

Comparative Example 1

[0047] An electrolysis bath consisting of calcium chloride alone was maintained at 900° C., a voltage of 4.5 V was applied to an anode made of carbon and a cathode made of carbon steel, so as to begin an electrolysis of a molten salt of calcium chloride. At this time, little melted calcium metal was observed at the surface of electrolysis bath. The electrolysis bath around the surface was drawn off to analyze the concentration of calcium metal, and the concentration of the calcium metal was 1%. In addition to the electrolysis examination, the solubility of calcium in a saturated state in calcium chloride at 900° C. was measured, and it was 3.2%.

[0048] As explained above, metal used for reduction of oxides or chlorides of titanium can be efficiently recovered by the present invention.

1. A process for production of a metal by molten-salt electrolysis, the process comprising a step of filling metal chloride in an electrolysis vessel having an anode and a cathode,

wherein a molten salt which reduces solubility of the metal in the molten salt is used.

2. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein the metal generated by the electrolysis is recovered alone or as a mixture of the molten salt and the metal.

3. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein the molten salt contains at least one selected from calcium chloride, potassium chloride, sodium chloride, and calcium fluoride.

4. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein the molten salt is a mixed salt of calcium chloride with potassium chloride, sodium chloride, or calcium fluoride, and

a composition of the potassium chloride, sodium chloride, or calcium fluoride versus the calcium chloride is a eutectic composition or is not more than the eutectic composition.

5. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein the metal is calcium, potassium, or sodium.

6. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein the temperature of the molten salt is not less than the eutectic temperature of a mixed salt of calcium chloride with potassium chloride, sodium chloride, or calcium fluoride and is not more than 1000° C., and

wherein the metal generated by the electrolysis is generated alone or as a mixture of the molten salt and the metal.

7. The process for production of a metal by molten-salt electrolysis according to claim 6,

wherein the solubility of metal in the molten salt is not more than 3%.

8. A process for production of titanium metal comprising a step of using the metal produced in the method according to claim 1, as a reducing agent of titanium tetrachloride.

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