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(54) **METHOD FOR PRODUCING METAL BY
MOLTEN SALT ELECTROLYSIS AND
APPARATUS USED FOR THE PRODUCTION
METHOD**

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(71) Applicant: **SUMITOMO ELECTRIC
INDUSTRIES, LTD.**, Osaka-shi, Osaka
(JP)

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(72) Inventors: **Tomoyuki Awazu**, Itami-shi (JP);
Masatoshi Majima, Itami-shi (JP)

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(57) **ABSTRACT**

Provided is a method for obtaining a particular metal at high purity, with safety, and at low cost, from a treatment object containing two or more metal elements. The present invention provides a method for producing a metal by molten salt electrolysis, the method including a step of dissolving, in a molten salt, a metal element contained in a treatment object containing two or more metal elements; and a step of depositing or alloying a particular metal present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing the dissolved metal element, by controlling a potential of the electrode members to a predetermined value.

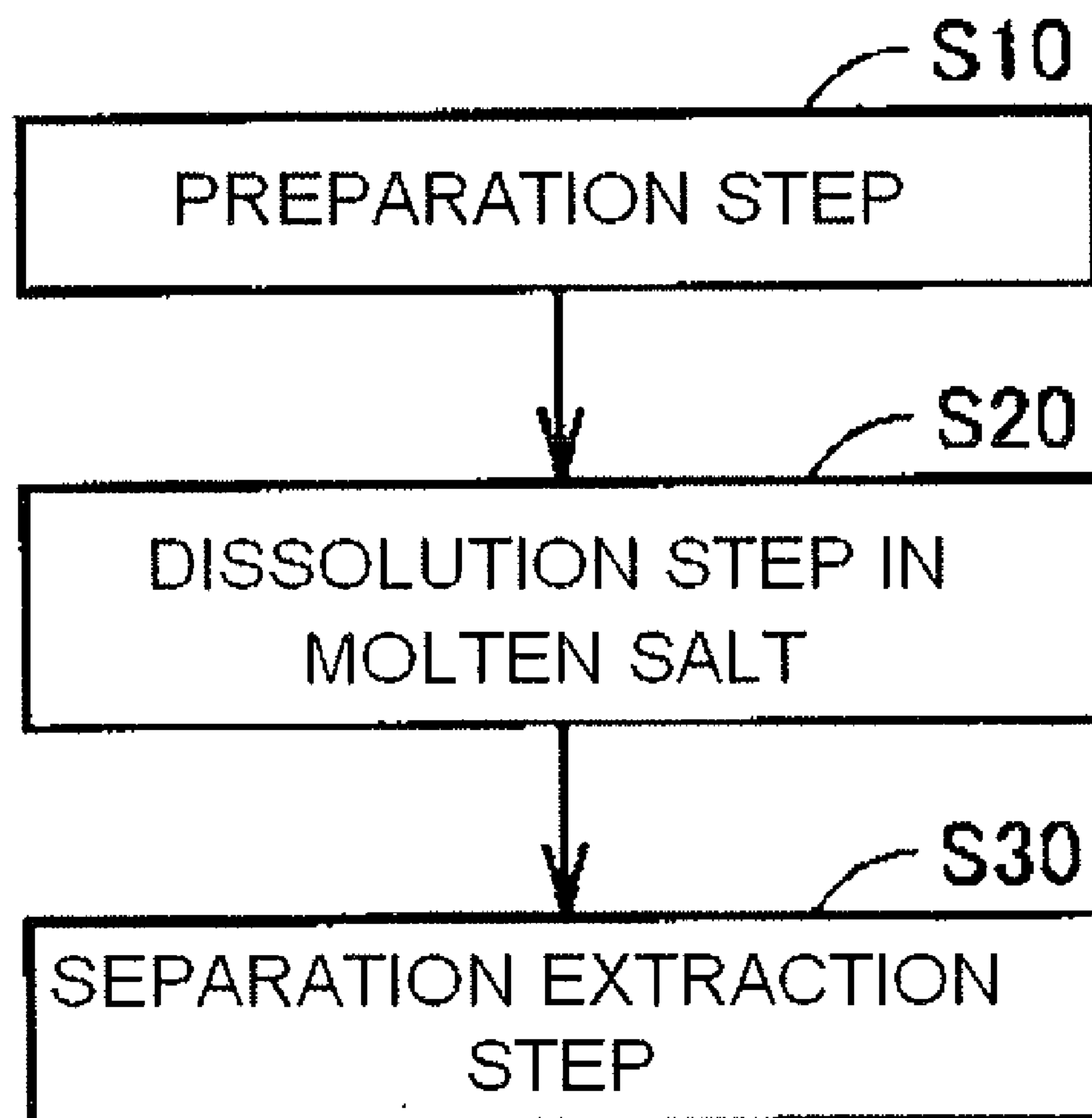


FIG. 1

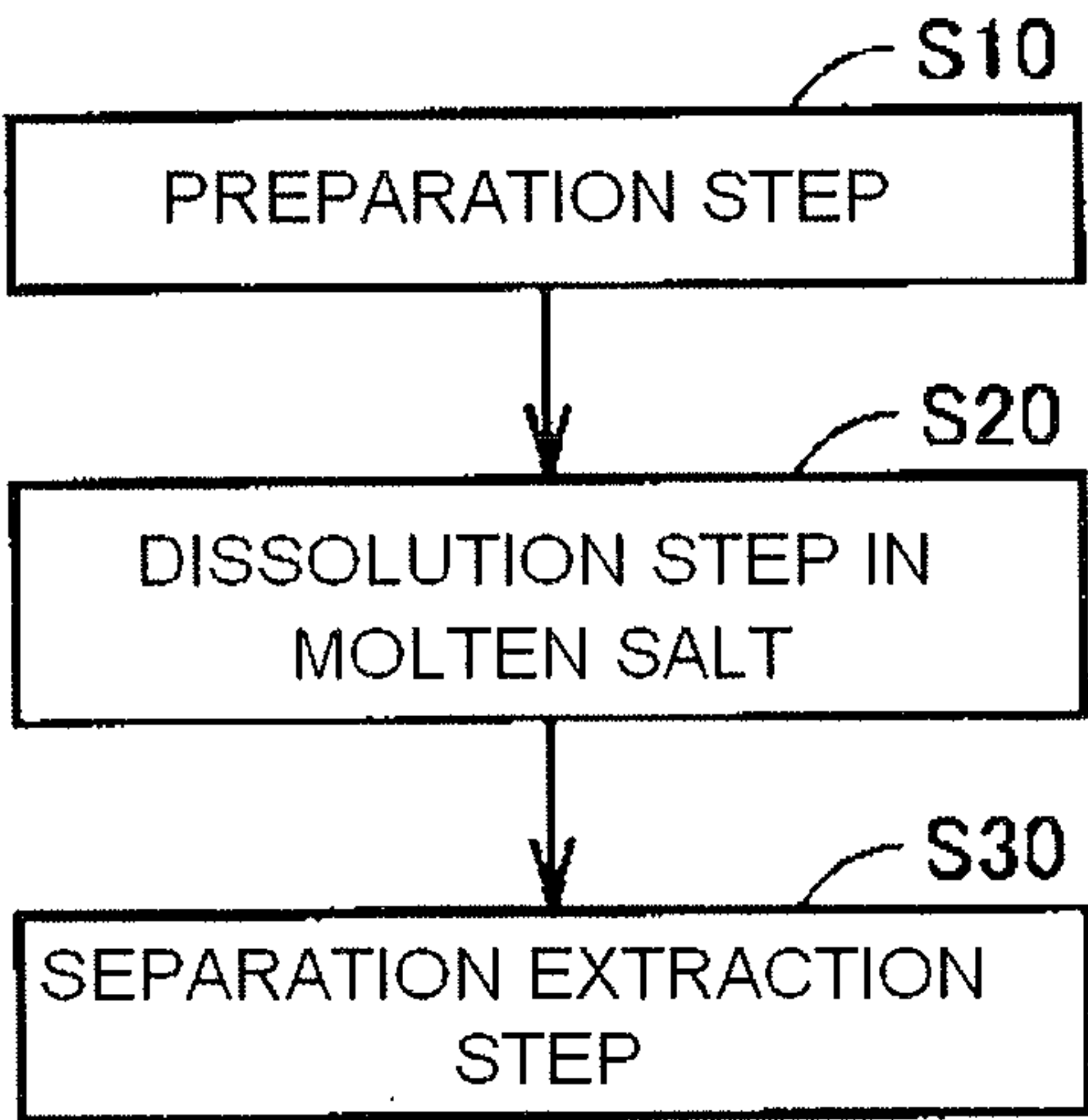


FIG. 2

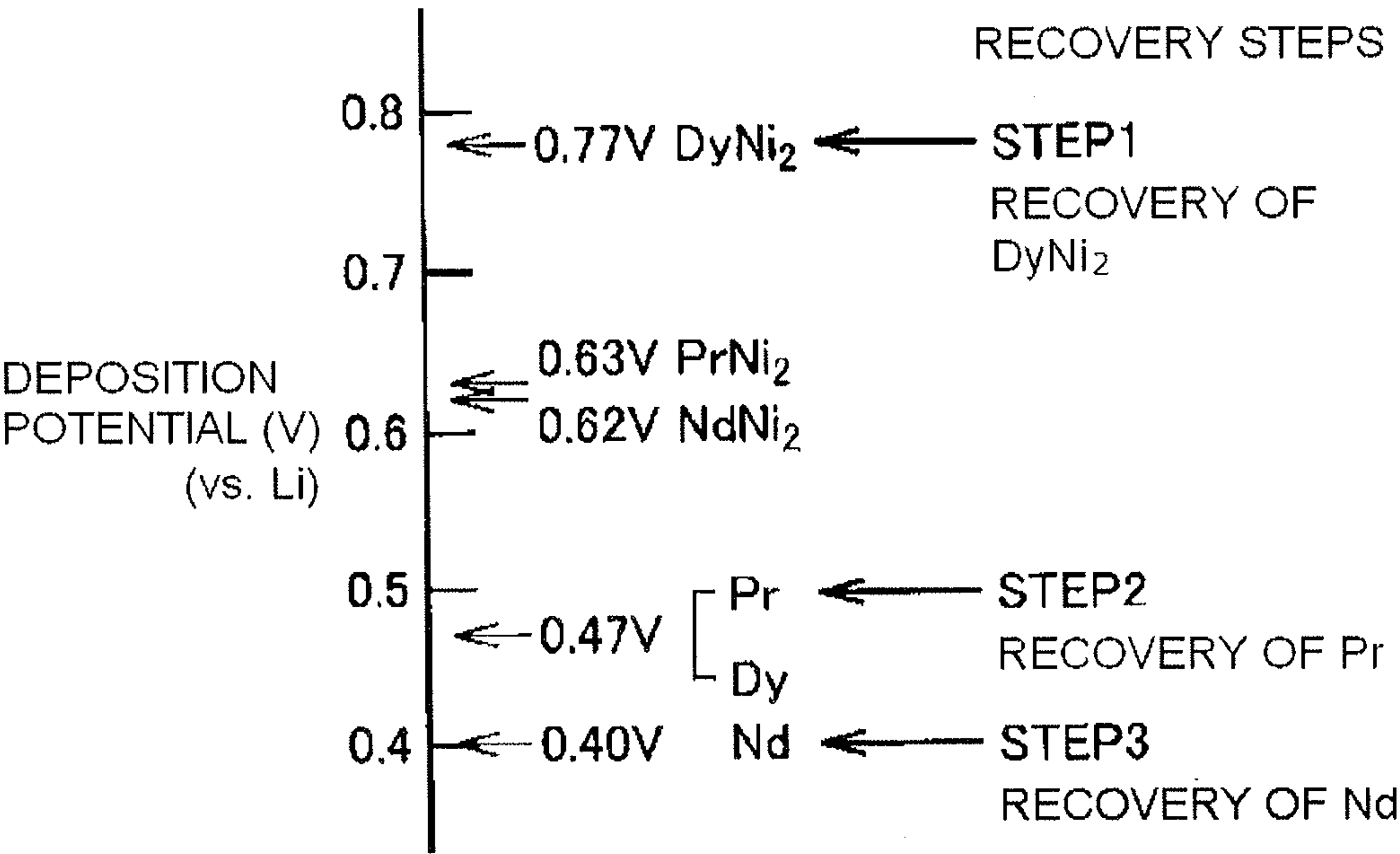


FIG. 3

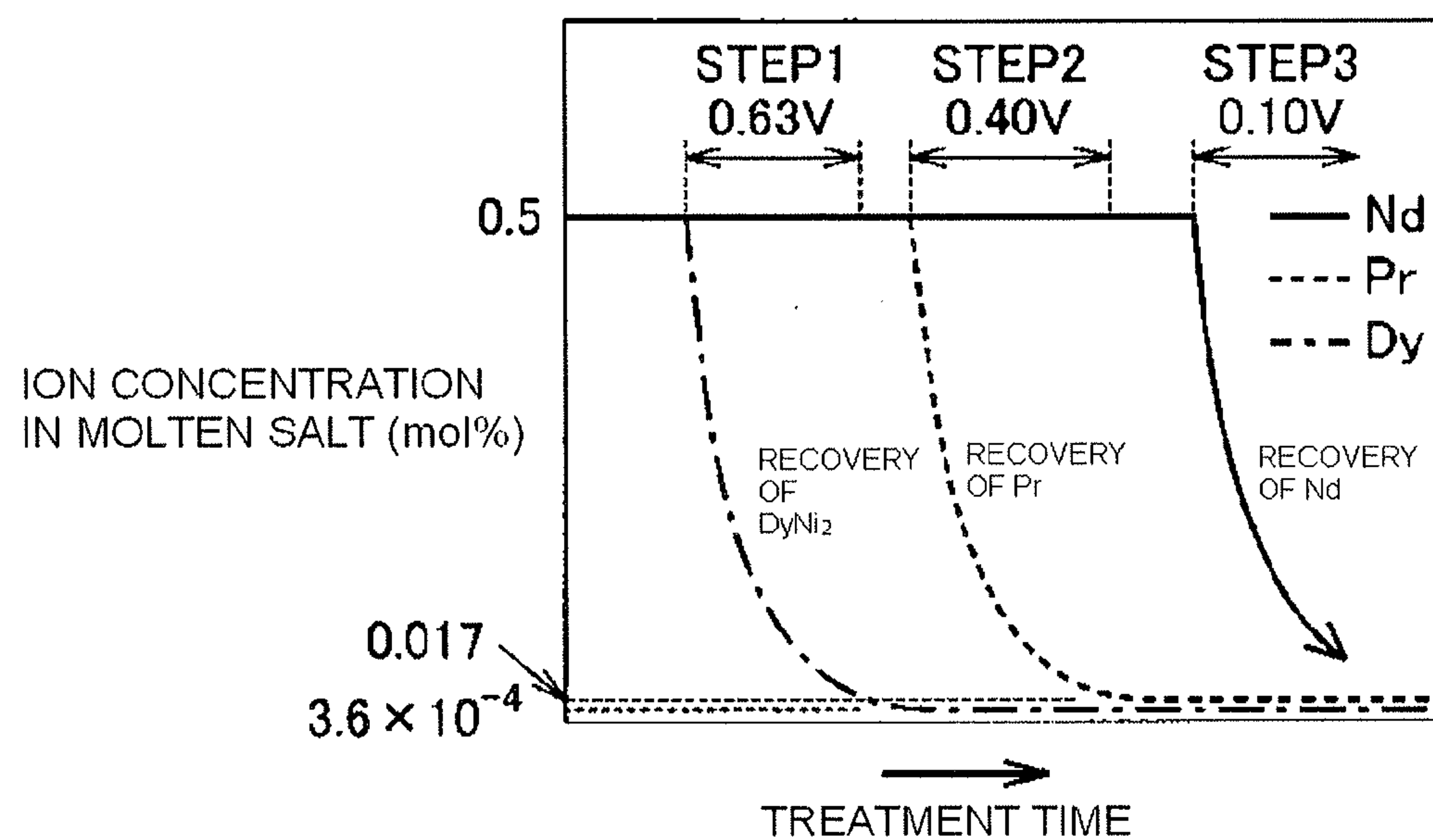


FIG. 4

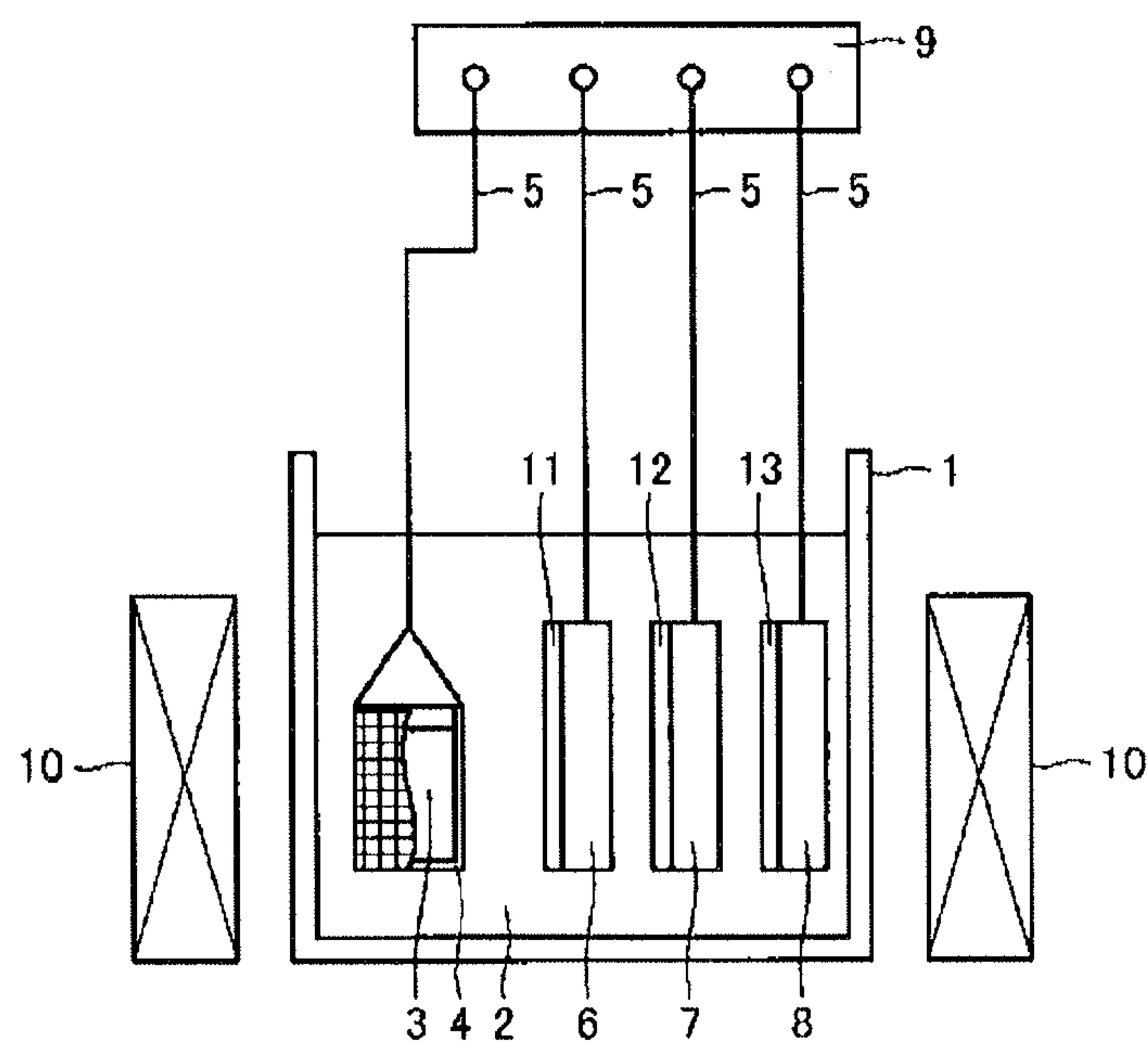


FIG. 5

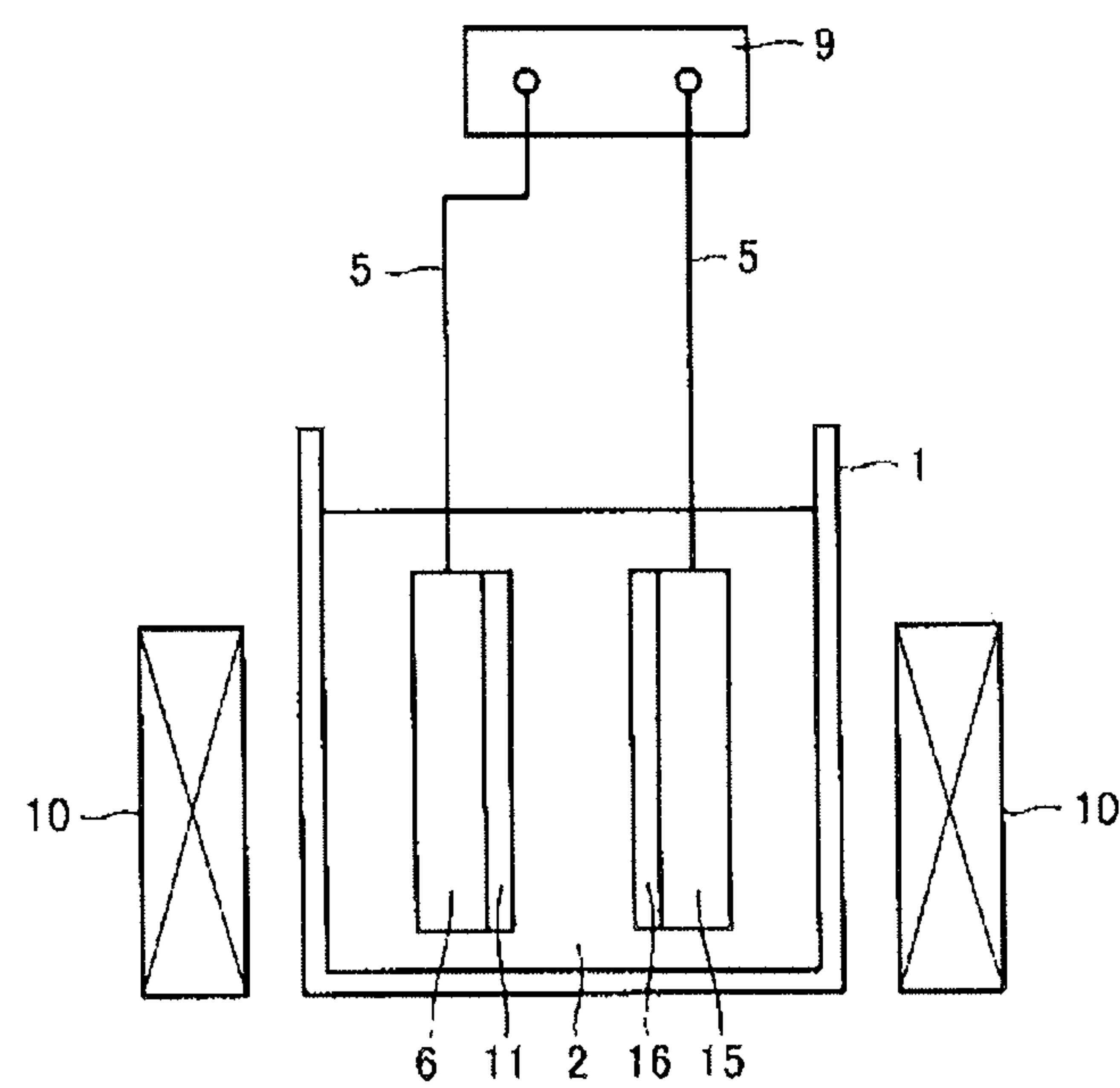


FIG. 6

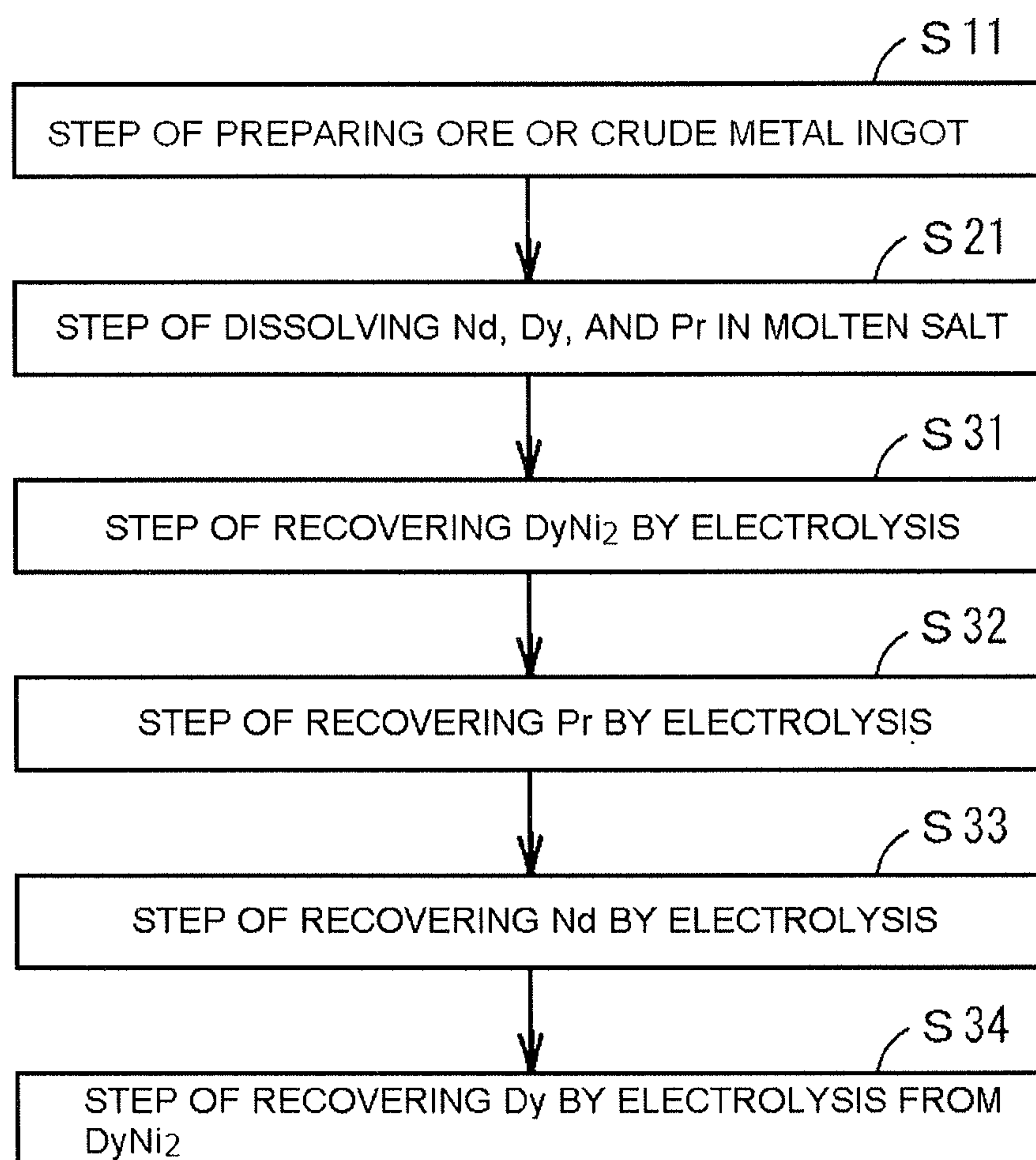


FIG. 7

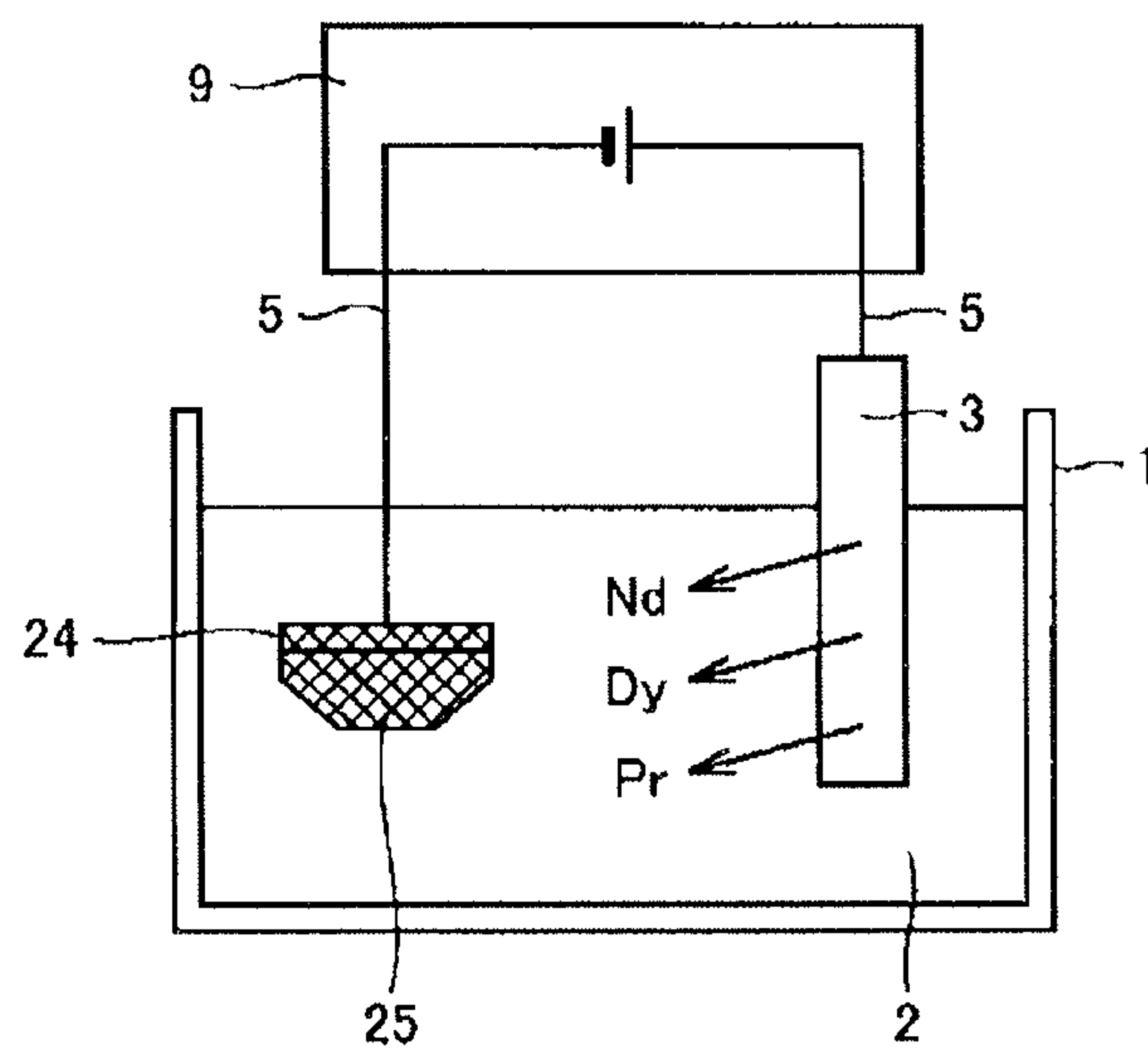


FIG. 8

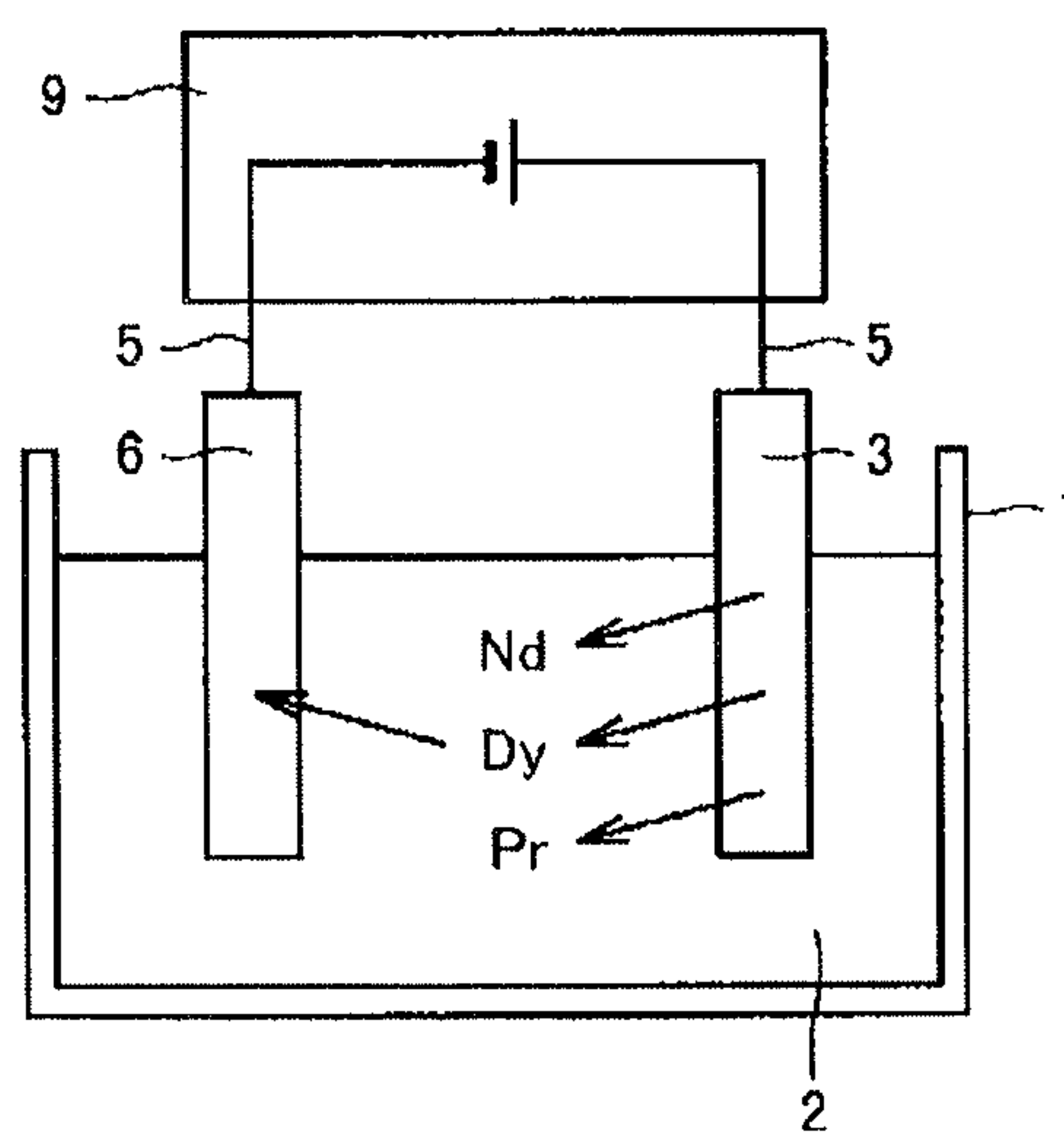


FIG. 9

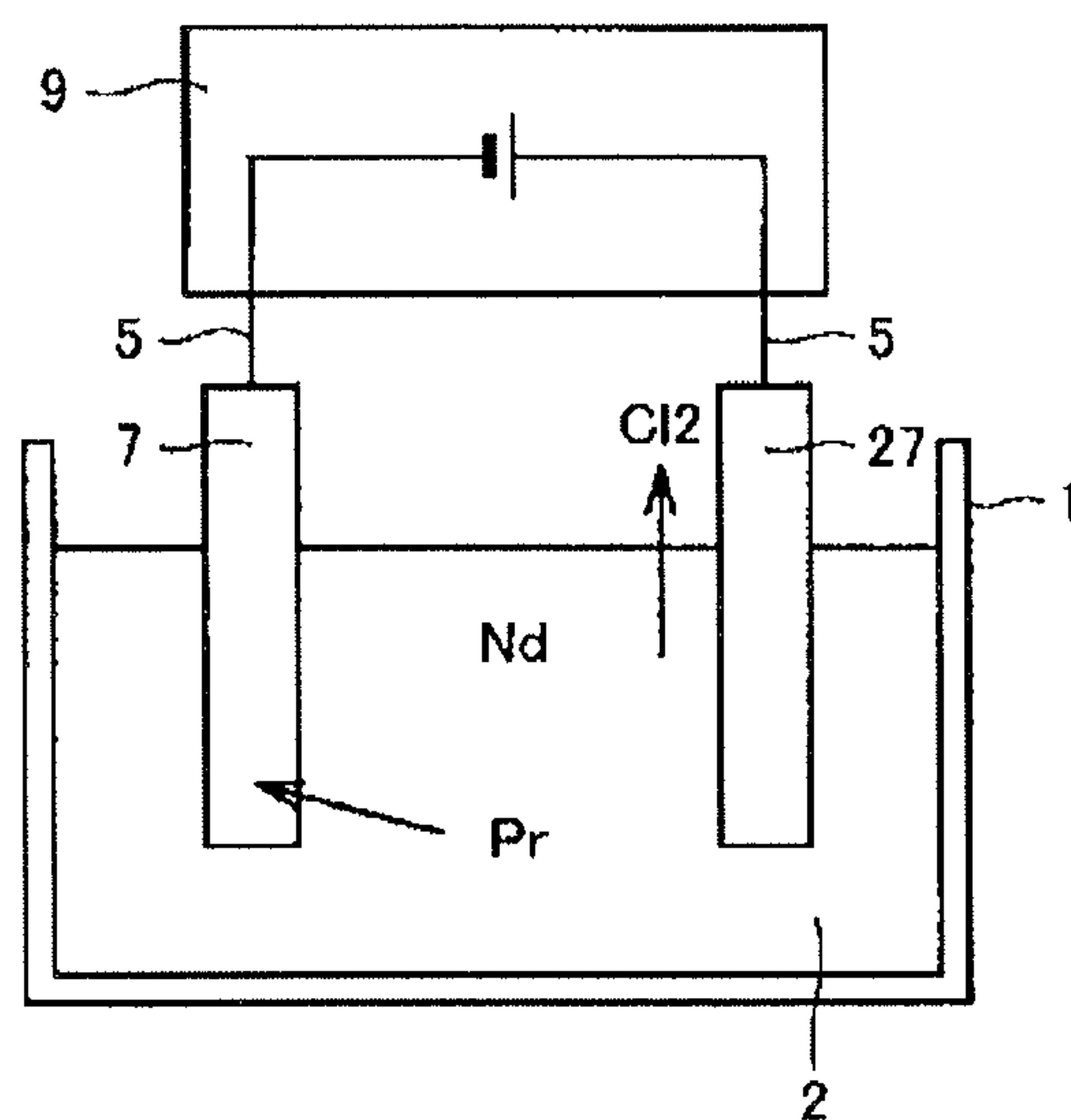


FIG. 10

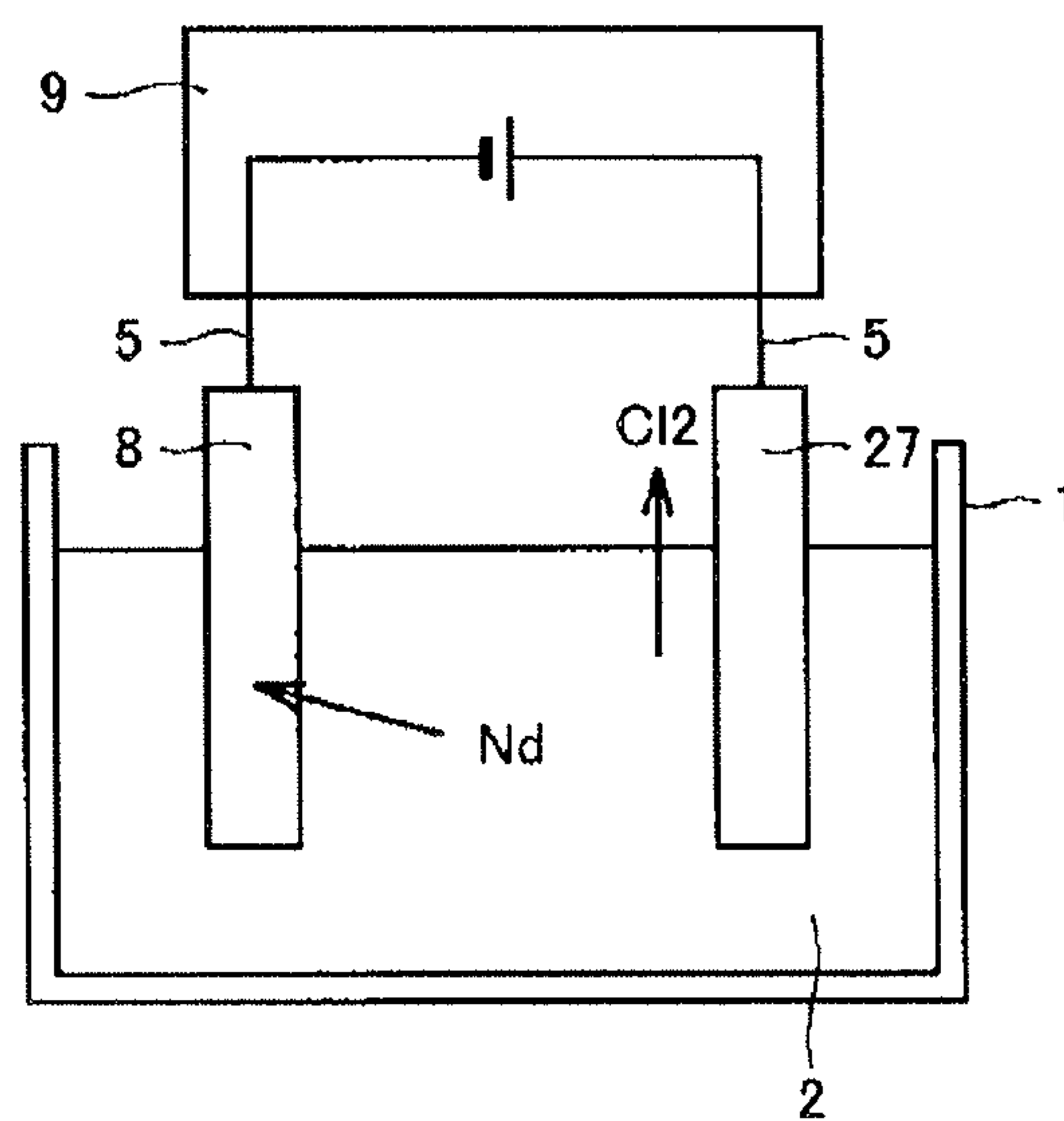


FIG. 11

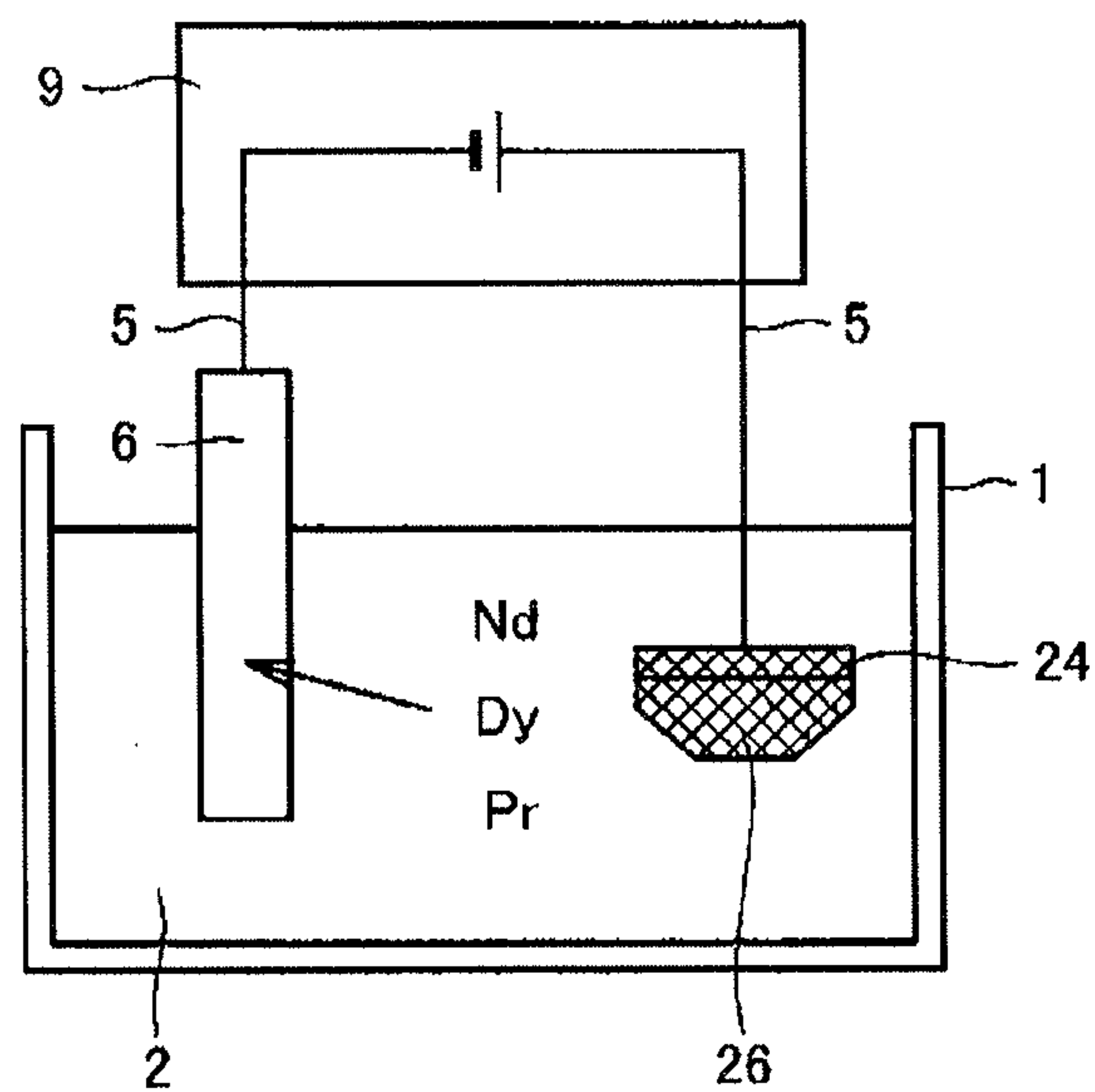


FIG. 12

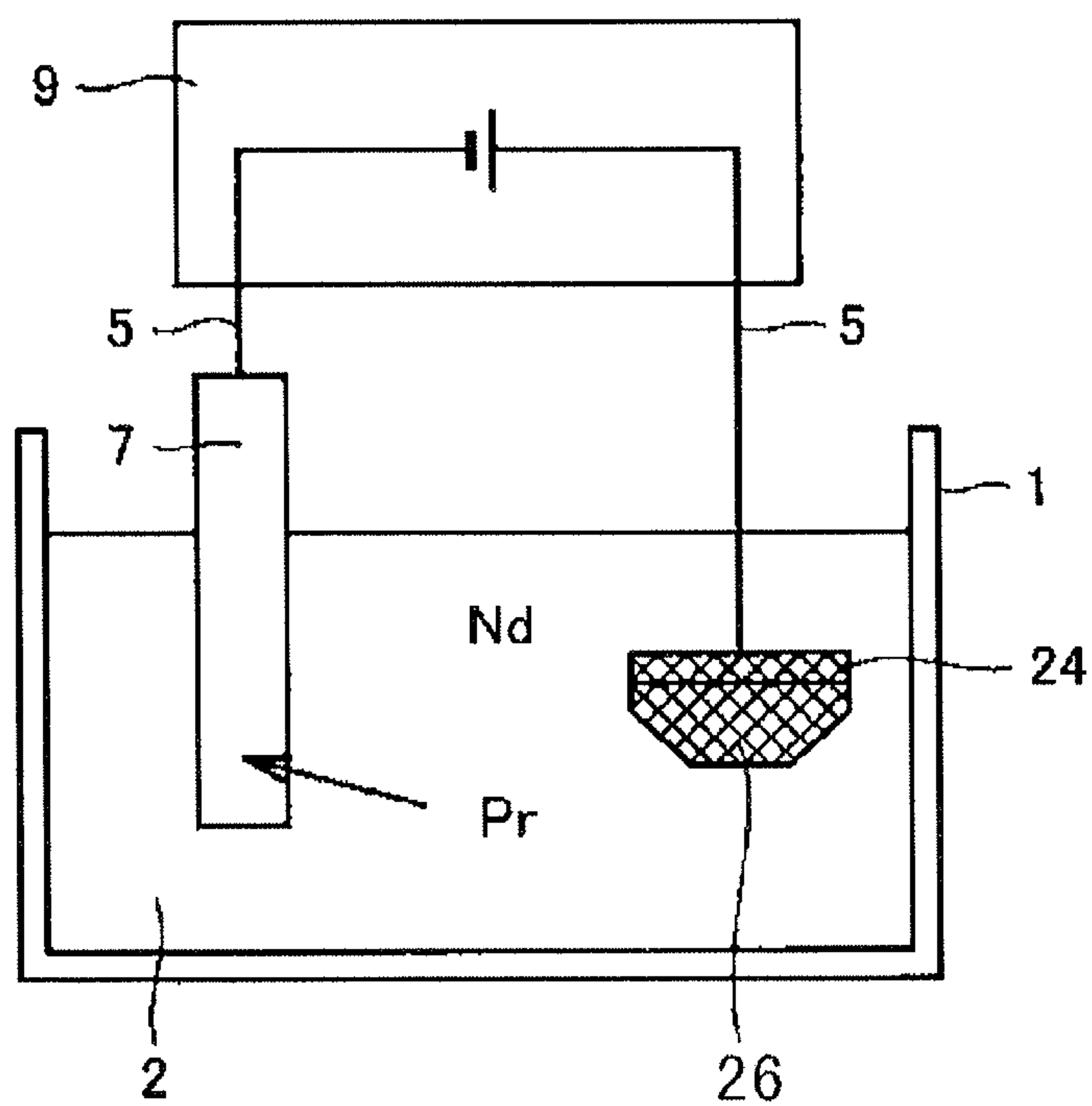


FIG. 13

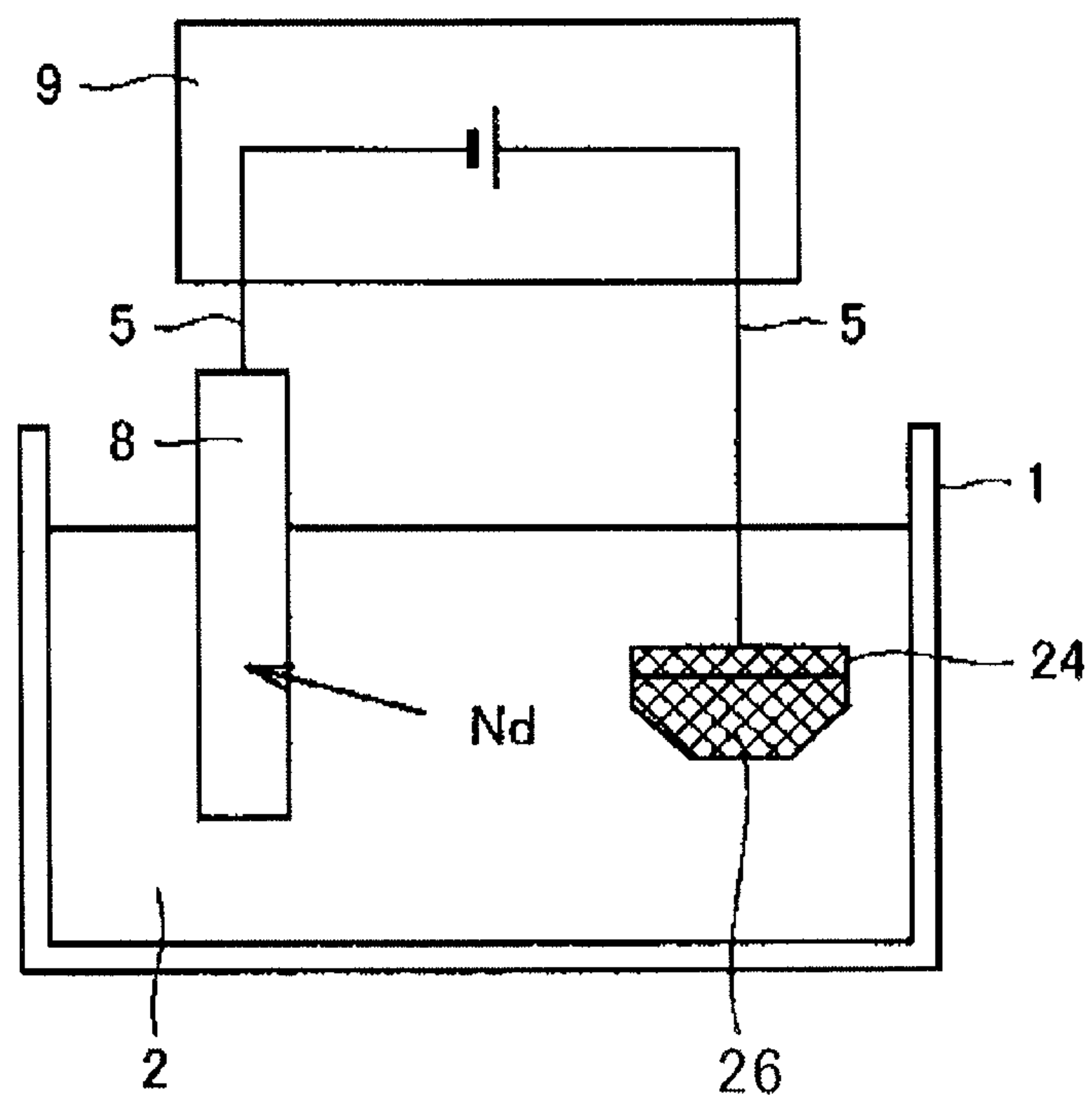


FIG. 14

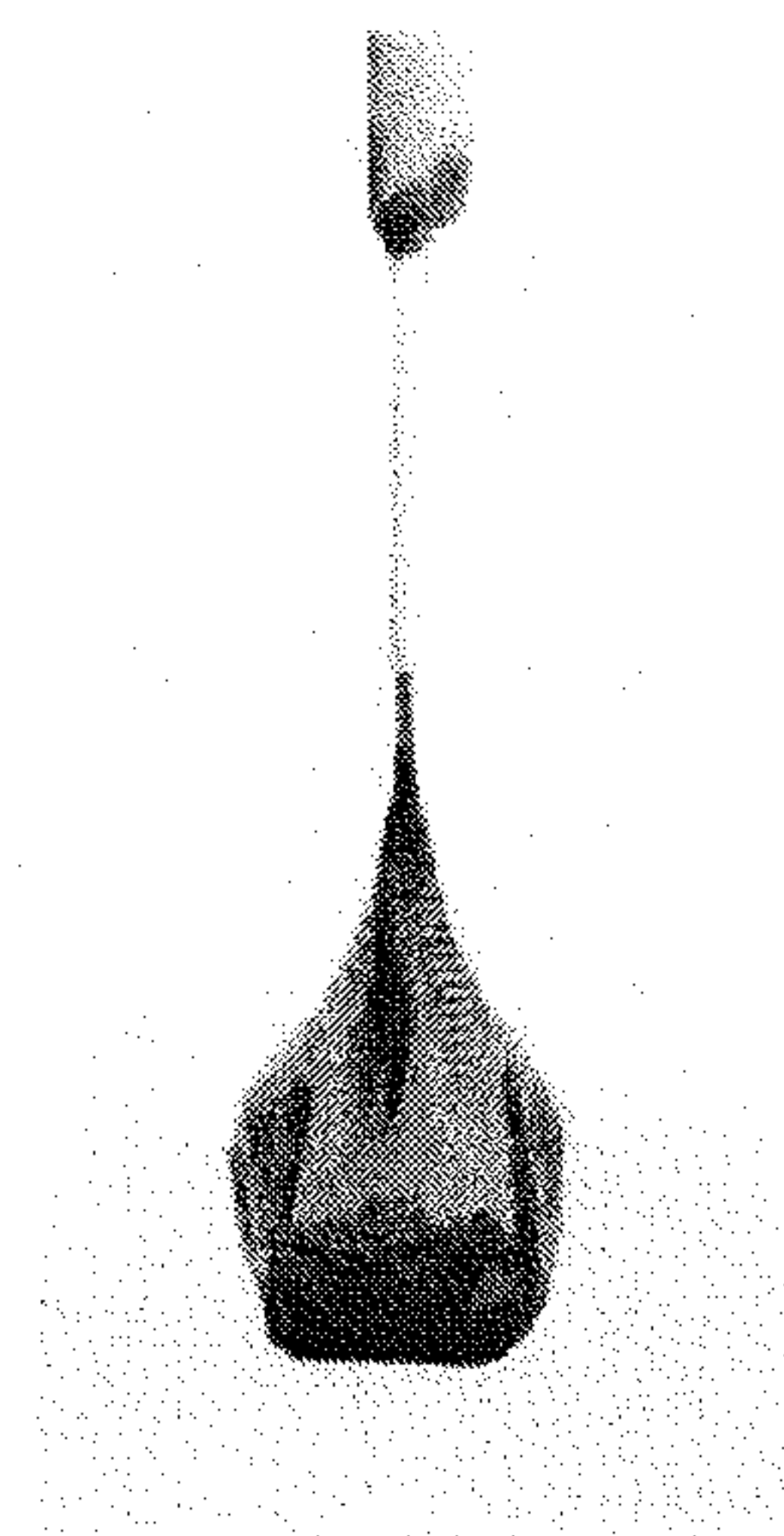


FIG. 15

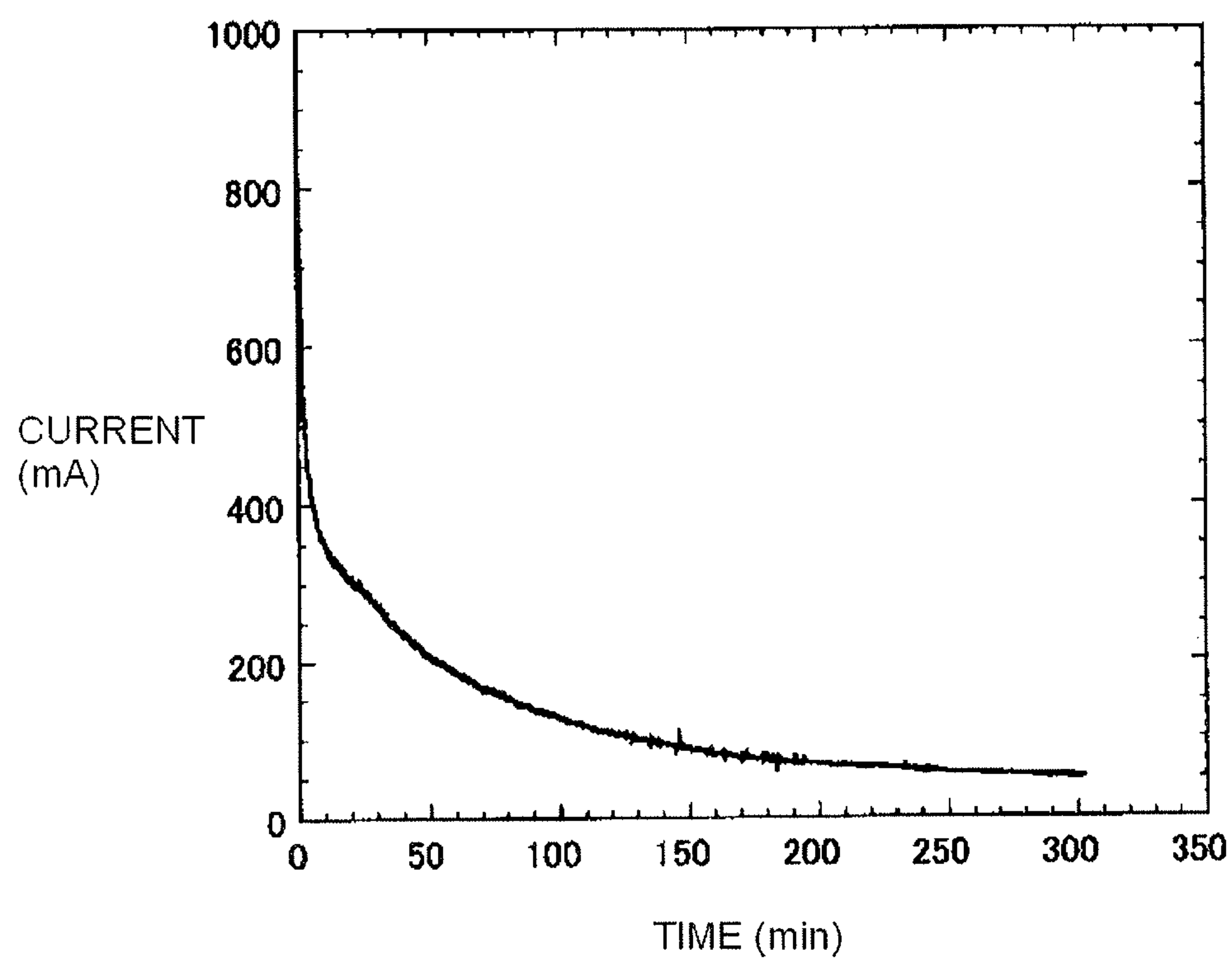


FIG. 16

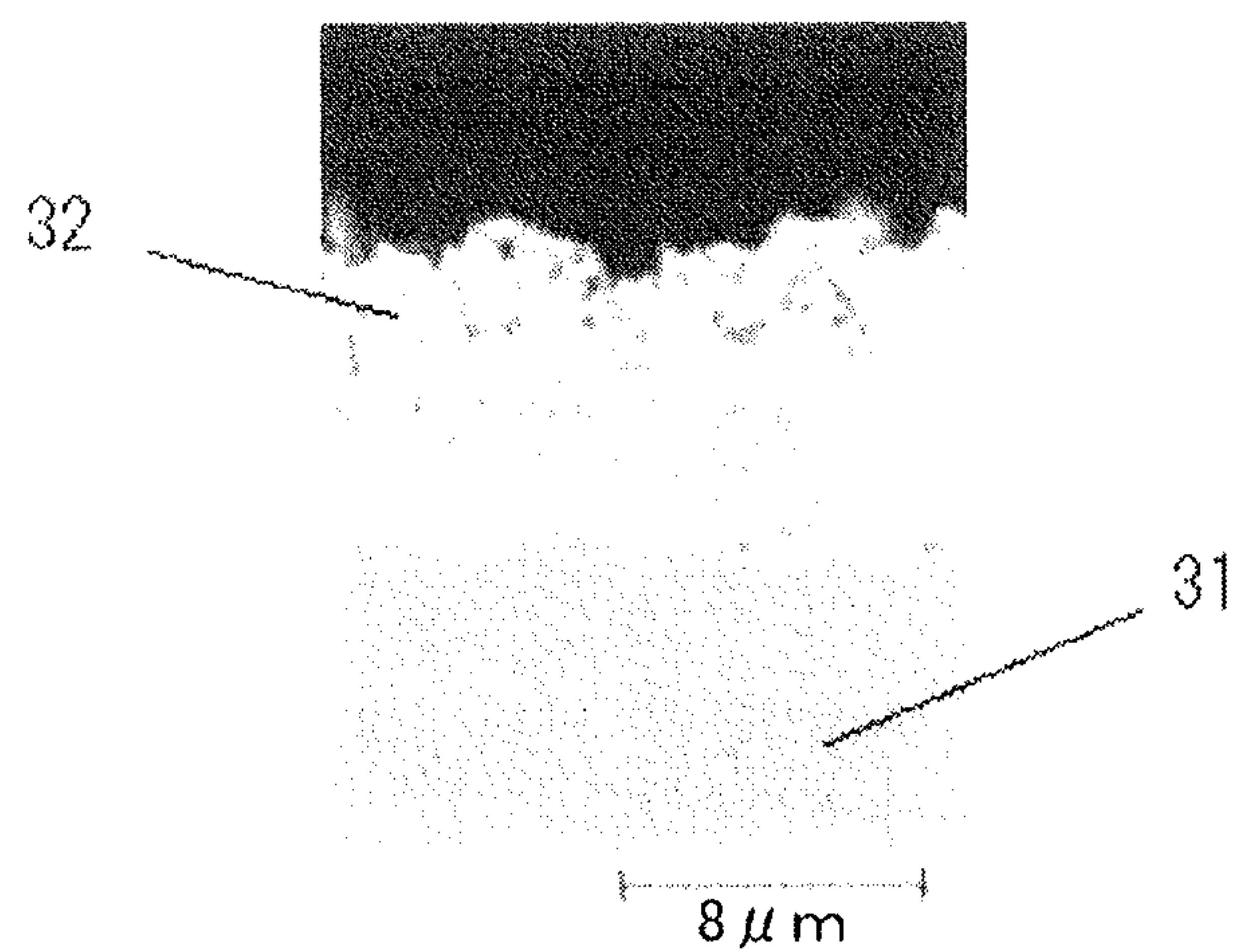


FIG. 17

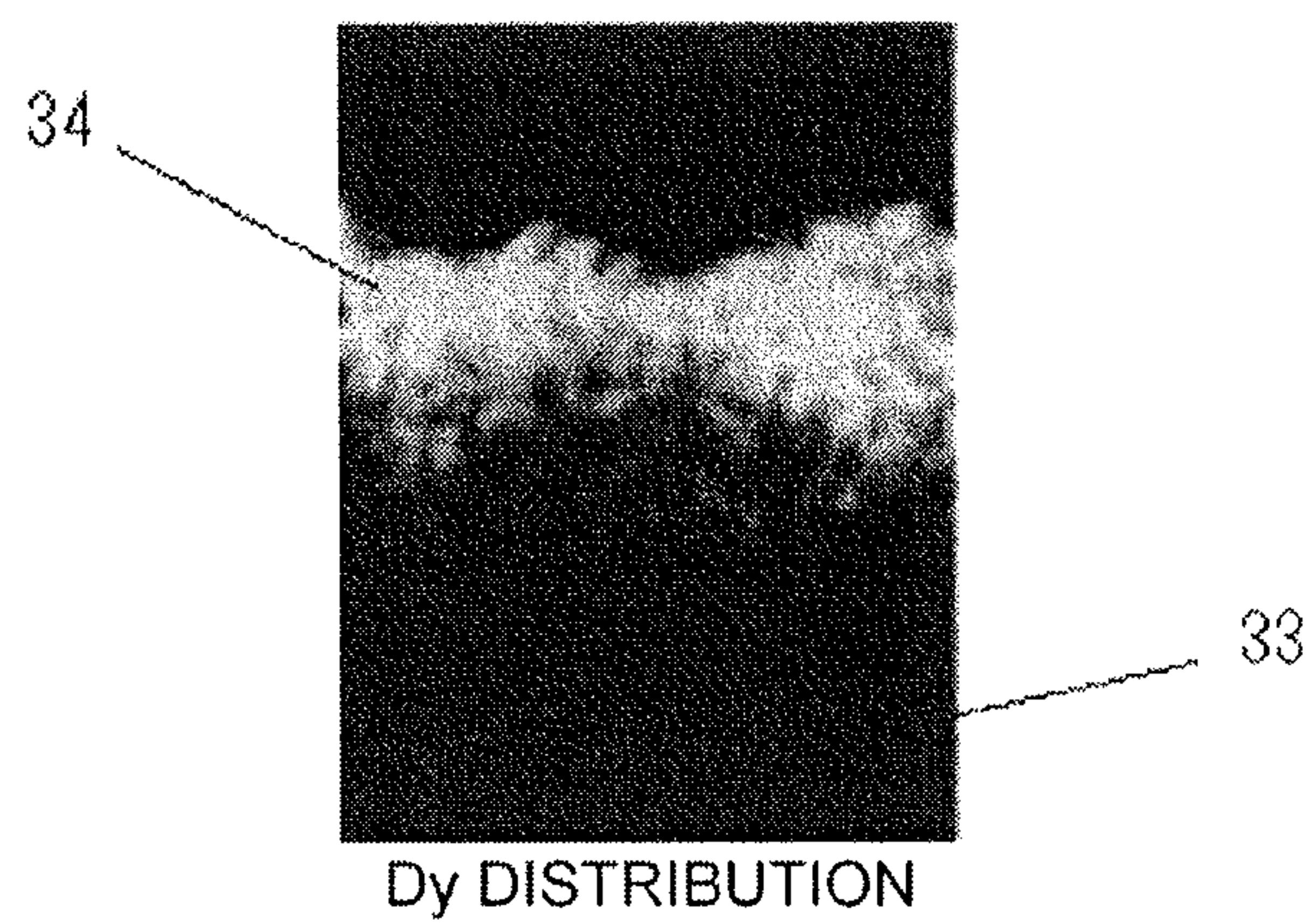


FIG. 18

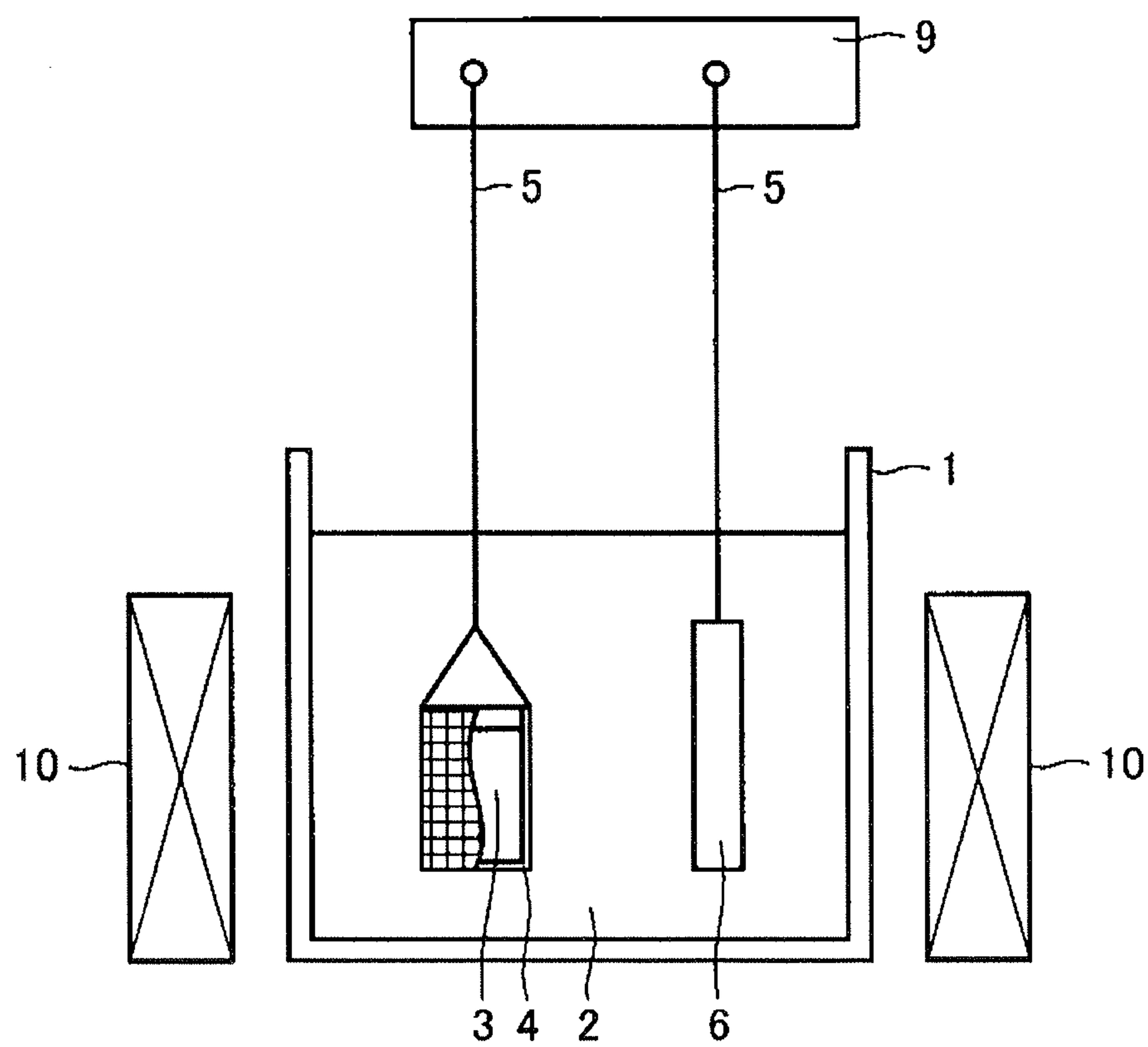
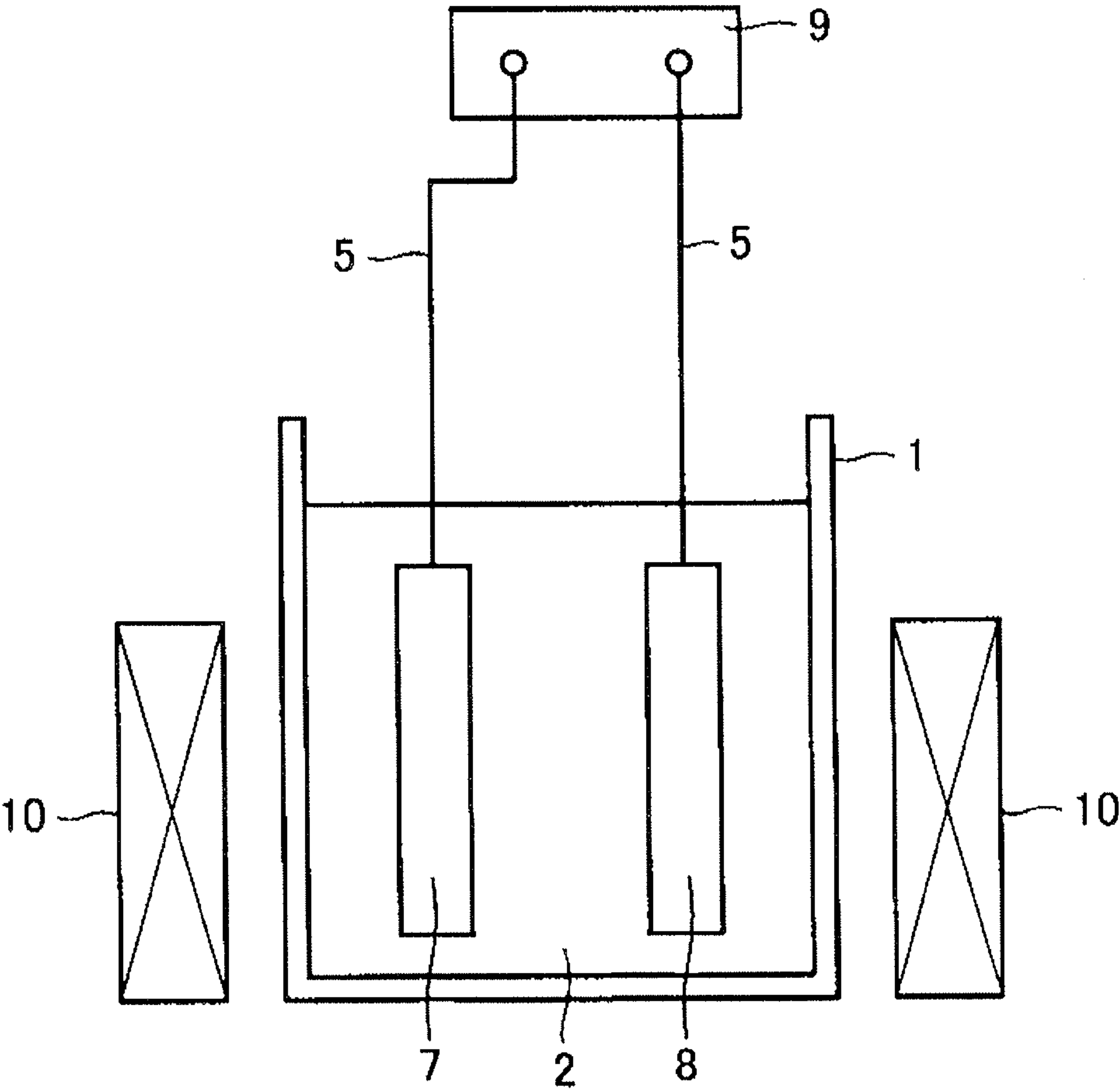


FIG. 19



METHOD FOR PRODUCING METAL BY MOLTEN SALT ELECTROLYSIS AND APPARATUS USED FOR THE PRODUCTION METHOD

TECHNICAL FIELD

[0001] The present invention relates to a method for producing a metal by molten salt electrolysis; and an apparatus used for the production method.

BACKGROUND ART

[0002] Known methods of smelting ores to provide particular metals are pyrometallurgy and hydrometallurgy.

[0003] The pyrometallurgical smelting is a method of melting an ore in a high temperature furnace to separate a target metal. For example, a concentrate, a roasted ore, or a sintered ore is melted in a high temperature furnace, concentrated into a crude metal ingot while gangue, impurities, and the like are separated as slag (Non Patent Literature (NPL) 1, p. 46).

[0004] In smelting, since the specific gravity difference between molten metals is utilized to separate the metals from an ore, the specific gravity difference between the metals to be separated needs to be large. In addition, separation targets need to have low solubility in each other. Since elements that satisfy such conditions between metal materials are limited, target elements separated by pyrometallurgy are limited, which is problematic.

[0005] The hydrometallurgy is a method of dissolving an ore in, for example, an alkaline or acidic solution and separating and extracting a target metal from the solution. A method for separating and extracting the target metal from this aqueous solution is, for example, a method using ion exchange, a method using solvent extraction, or a method using aqueous solution electrolysis.

[0006] In the method using ion exchange, a solid substance that partially has a group of ions allowing ion exchange and is referred to as an ion exchanger is used to perform reversible ion exchange (NPL 1, p. 194).

[0007] Ion exchange, which uses the adsorption capability and exchange capability of an ion-exchange resin, is an excellent treatment. However, since this treatment is performed by repeating of adsorption and dissociation of ions, ion exchange is not suitable for economically and efficiently treating a large amount of substance, which is problematic.

[0008] The method using solvent extraction is a separation method using the difference in the distributions of different solutes in two solvents that are immiscible with each other (NPL 1, p. 199).

[0009] In this solvent extraction, for example, an acid treatment is performed to achieve ionization; and, in separation, a large number of treatment processes need to be performed. In these processes, large amounts of acid and alkali are required and a large amount of wastewater is generated, which is problematic.

[0010] In the method of electrolysis smelting using aqueous solution electrolysis, the presence of a difference between elements in tendency for anode dissolution or cathode deposition is used and a pure metal is produced. Simultaneously, in the electrolytic solution used, reactions of generating slightly soluble salts from impurity ions are also used (NPL 1, p. 219).

[0011] However, metal elements that can be separated and deposited by purification using aqueous solution electrolysis

are limited. For example, deposition of rare earth materials cannot be theoretically achieved, which is problematic.

[0012] Regarding Al, electrolytic smelting utilizing molten salt electrolysis is also known. In this method, three layers of Al (purification target material) alloyed so as to have a decreased melting point, a molten salt, and the recovered metal, are formed and the specific gravity difference is utilized to perform smelting. Since the specific gravity difference is thus utilized, smelting needs to be performed while all the three layers are melted (NPL 1, p. 254).

[0013] The target metal of this method is Al. In addition, when the potential of an impurity present with the purification target metal is close to the potential of the purification target metal, entry of the impurity into the deposited target metal occurs, which is problematic.

[0014] On the other hand, a method for recovering tungsten is described in, for example, NPL 2 as follows.

[0015] Hard scrap or soft scrap of cemented carbide tools is made to react with sodium nitrate molten salt and then dissolved in water to produce an aqueous solution of sodium tungstate. The aqueous solution of sodium tungstate is treated by an ion-exchange method using an ion-exchange resin to produce an aqueous solution of ammonium tungstate. From the aqueous solution of ammonium tungstate, ammonium paratungstate (APT) is crystallized. After that, the thus-crystallized ammonium paratungstate is calcined, reduced, and carbonized to provide tungsten carbide.

[0016] The hard scrap collectively denotes pieces of scrap still having the shapes of products. The soft scrap denotes powder-form scrap such as powder dust and cutting dust generated during processing for producing cemented carbide tools.

[0017] Patent Literature (PTL) 1 proposes, in the production of sodium tungstate by oxidizing hard alloy scrap and/or heavy metal scrap in a molten salt bath, use of a molten salt containing 60 to 90 wt % of sodium hydroxide and 10 to 40 wt % of sodium sulfate. PTL 1 also proposes that the reaction between such scrap and the molten salt is performed in a rotary kiln that is operated as batch processes and can be directly heated.

[0018] However, in the above-described method described in NPL 2, the reaction between hard scrap or soft scrap of cemented carbide tools and sodium nitrate molten salt occurs very vigorously. Accordingly, the reaction is difficult to control and the operation has safety problems. In addition, when hard scrap or soft scrap of cemented carbide tools is made to react with sodium nitrate molten salt, metals contained in the hard scrap or soft scrap of cemented carbide tools, such as vanadium and chromium, take the form of water-soluble metal oxide ions and enter the aqueous solution of sodium tungstate. As a result, because of the presence of such metals as impurities, high purity is difficult to achieve, which is problematic.

[0019] In the above-described method described in PTL 1, sodium sulfate molten salt serving as an oxidizing agent has a high melting point of 884° C. Accordingly, the temperature during reaction needs to be set to a high temperature of 884° C. or more. As a result, metal materials are corroded, which is problematic. In addition, the reaction proceeds slowly and hence the reaction is time-consuming and involves a large energy loss, which is problematic.

[0020] On the other hand, lithium is mainly extracted from lithium-containing ores (such as spodumene, amblygonite, petalite, and lepidolite), and salt lakes and underground brine

that have high lithium concentrations. However, Japan does not have lithium-containing ores or salt lakes. Accordingly, almost the whole amount of lithium is actually supplied by imports.

[0021] Thus, recently, studies were started regarding separation and recovery of lithium from, for example, lithium-containing waste generated in the production steps of lithium-containing products such as lithium batteries or waste of used lithium-containing products.

[0022] The following method for recovering lithium has been proposed: lithium cobalt oxide serving as the positive electrode material of lithium secondary batteries, together with metallic lithium, is subjected to a reduction reaction in lithium chloride molten salt, so that lithium oxide is generated and cobalt or cobalt oxide is separated by precipitation; after that, lithium oxide is electrolyzed in the lithium chloride molten salt, so that metallic lithium is deposited on the cathode and recovered (PTL 2: Japanese Unexamined Patent Application Publication No. 2005-011698).

[0023] However, in this method, in order to separate cobalt contained in the treatment object by reduction, addition of metallic lithium is required. The method employs the step of adding metallic lithium in order to recover metallic lithium and hence is inefficient, which is problematic.

[0024] A method for recovering lithium has been proposed in which a mixture of carbon and lithium manganese oxide serving as the positive electrode material of lithium secondary batteries is roasted in any one of the air atmosphere, an oxidizing atmosphere, an inert atmosphere, and a reducing atmosphere, to turn the lithium into lithium oxide; and this roasted substance is immersed in water so that lithium is leached in the form of lithium hydroxide and lithium carbonate (PTL 3).

[0025] However, in this method, since lithium hydroxide and lithium carbonate do not have high solubility, the recovery efficiency is low. In addition, a large amount of water is required to leach lithium hydroxide and lithium carbonate into water and, as a result of the treatment, a large amount of wastewater is generated, which is problematic.

[0026] Furthermore, tantalum (Ta) is mainly used in tantalum capacitors and can be recovered from tantalum capacitor scrap. Specifically, tantalum is recovered by processes of oxidation treatment, magnetic separation, screening, separation with running water, grinding, screening, leaching, oxidation treatment, reduction treatment, and leaching (refer to NPL 3, pages 319 to 326).

[0027] Vanadium (V) is used as an additive to steel or a desulfurization catalyst in oil refining. Vanadium used as an additive to steel is collected in the form of steel scrap and recycled as steel. Spent catalysts can be sequentially subjected to steps of classification, roasting, grinding, leaching, filtration, leaching solution, dehydration, thermal decomposition, and melting, so that vanadium pentoxide can be obtained (NPL 3, pages 391 to 396).

[0028] Molybdenum (Mo) is also used as an additive to steel, alloy, or a desulfurization catalyst in oil refining. Molybdenum used as an additive to steel or an alloy element is collected in the form of steel or alloy and used, without being extracted, in the form of steel or alloy. Spent catalysts can be sequentially subjected to steps of roasting, removal of oil, water, and sulfur, leaching in basic condition, and recovery, so that Mo can be obtained (NPL 3, pages 301 to 303).

[0029] Niobium (Nb) is mainly used as an additive to steel. Niobium used as an additive to steel is collected in the form of

steel scrap. However, the niobium content of high-tensile steel, stainless steel, and the like is very low and niobium itself is not recycled (NPL 3, page 339).

[0030] Manganese (Mn) is mostly used for steel and aluminum alloy and collected in the form of steel scrap and aluminum alloy scrap, respectively. In the case of recycling of steel, a high proportion of manganese is left in various slags and such manganese forming slags is not suitable for recycling. Manganese in slag is partially used in, for example, a manganese-calcium silicate fertilizer.

[0031] Aluminum cans containing such aluminum alloy are collected and then recycled (NPL 3, pages 343 to 344).

[0032] Chromium (Cr) used for steel (stainless steel) and superalloy is collected in the form of steel scrap and superalloy scrap, respectively, and then recycled; and extraction and recovery of elemental chromium is not performed (NPL 3, pages 219 to 221).

[0033] In the above-described recycling techniques, recovery involves a large number of processes such as roasting (heating), grinding, leaching, and reduction. And the processes are complicated and hence the treatment is time-consuming and costly, which is problematic.

[0034] In addition, the treatment requires roasting and, in the treatment, substances that are not the extraction target are also treated, resulting in unnecessary energy consumption. Furthermore, by subjecting substances that are not the treatment target to the roasting treatment, unnecessary oxides are generated, resulting in a large amount of waste. In addition, since acid treatment or base treatment is performed, the treatment produces acid or base wastewater, which exerts a load on the environment.

[0035] In summary, existing metal recycling techniques have problems as follows: for example, the treatment is costly, energy loss is large, the amount of waste is large, and the environmental load is heavy. In addition, because of problems in terms of cost or technique, some metals are not recycled as simple substances.

CITATION LIST

Non Patent Literature

[0036] PTL 1: Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. 11-505801

[0037] PTL 2: Japanese Unexamined Patent Application Publication No. 2005-011698

[0038] PTL 3: Japanese Unexamined Patent Application Publication No. 2011-094227

[0039] NPL 1: Courses of Contemporary Metallurgy, Smelting Part, Vol. 2, Nonferrous Metal Smelting, edited by The Japan Institute of Metals and Materials (1980), pages 46, 194, 199, 219, and 254

[0040] NPL 2: Rare-Metal High-Efficiency-Recovery-System Development Project "Recovery of tungsten etc. from waste cemented carbide tools", Metal Resource Report, Vol. 38, No. 4, November 2008, pp. 407-413

[0041] NPL 3: Compilation of Noble Metal and Rare Metal Recycling Techniques, published by NTS Inc., planned and edited by Bookers Ltd., the first impression of the first edition, Oct. 19, 2007

SUMMARY OF INVENTION

Technical Problem

[0042] In view of the above-described problems, an object of the present invention is to provide a method for producing a metal, the method being applicable to any ore and providing high purity metal at low cost; and an apparatus used for the production method. An object of the present invention is to provide a method for producing a metal, the method providing a particular metal at high purity, with safety, and at low cost, from a treatment object containing two or more metal elements; and an apparatus used for the production method.

Solution to Problem

[0043] An embodiment of the present invention is a method for producing a metal by molten salt electrolysis, the method including a step of dissolving, in a molten salt, a metal element contained in a treatment object containing two or more metal elements; and a step of depositing or alloying a particular metal present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing the dissolved metal element, by controlling a potential of the electrode members to a predetermined value.

[0044] In another embodiment of the present invention, the treatment object is an ore or a crude metal ingot obtained from the ore.

[0045] Another embodiment of the present invention is a method for producing tungsten, wherein a metal element contained in the treatment object is tungsten, in the step of dissolving, in a molten salt, a metal element from a treatment object, tungsten is dissolved from the treatment object, and in the step of depositing or alloying a particular metal, tungsten present in the molten salt is deposited on one of a pair of electrode members disposed in the molten salt containing dissolved tungsten, by controlling a potential of the electrode members to a predetermined value.

[0046] In another embodiment of the present invention, the treatment object is a metal material containing the tungsten.

[0047] In another embodiment of the present invention, the treatment object is a metal material containing tungsten and a transition metal.

[0048] In another embodiment of the present invention, the treatment object is a cemented carbide product.

[0049] Another embodiment of the present invention is a method for producing lithium, wherein a metal element contained in the treatment object is lithium, in the step of dissolving, in a molten salt, a metal element from a treatment object, lithium is dissolved from the treatment object, and in the step of depositing or alloying a particular metal, lithium present in the molten salt is deposited on one of a pair of electrode members disposed in the molten salt containing dissolved lithium, by controlling a potential of the electrode members to a predetermined value.

[0050] In another embodiment of the present invention, the treatment object is a material containing lithium and a transition metal.

[0051] In another embodiment of the present invention, the treatment object is a battery electrode material containing lithium.

[0052] In another embodiment of the present invention, the treatment object contains a transition metal or a rare earth metal.

[0053] In another embodiment of the present invention, the treatment object contains one or more metals selected from the group consisting of V, Nb, Mo, Ti, Ta, Zr, and Hf.

[0054] In another embodiment of the present invention, the treatment object contains Sr and/or Ba.

[0055] In another embodiment of the present invention, the treatment object contains one or more metals selected from the group consisting of Zn, Cd, Ga, In, Ge, Sn, Pb, Sb, and Bi.

[0056] In another embodiment of the present invention, the molten salt is selected such that, in the step of depositing or alloying a particular metal, a difference between a standard electrode potential of a simple substance or alloy of the particular metal and a standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

[0057] In another embodiment of the present invention, in the step of depositing or alloying a particular metal, the potential of the electrode members is controlled to the predetermined value so that the particular metal element in the molten salt is selectively deposited or alloyed.

[0058] In another embodiment of the present invention, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, the metal is dissolved in the molten salt by a chemical procedure.

[0059] In another embodiment of the present invention, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, a cathode and an anode that is formed of an anode material containing the treatment object are disposed in the molten salt, and a potential at the anode is controlled to a predetermined value so that a metal element corresponding to the controlled potential is dissolved in the molten salt from the treatment object.

[0060] In another embodiment of the present invention, the molten salt is selected such that, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, a difference between a standard electrode potential of a simple substance or alloy of the particular metal and a standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

[0061] In another embodiment of the present invention, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, the potential at the anode is controlled to a predetermined value so that the particular metal element is selectively dissolved in the molten salt.

[0062] In another embodiment of the present invention, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, one or more metals each serving as the particular metal are dissolved in the molten salt.

[0063] In another embodiment of the present invention, the particular metal deposited or alloyed is a transition metal.

[0064] In another embodiment of the present invention, the particular metal deposited or alloyed is a rare earth metal.

[0065] In another embodiment of the present invention, the particular metal deposited or alloyed is V, Nb, Mo, Ti, Ta, Zr, or Hf.

[0066] In another embodiment of the present invention, the particular metal deposited or alloyed is Sr or Ba.

[0067] In another embodiment of the present invention, the particular metal deposited or alloyed is Zn, Cd, Ga, In, Ge, Sn, Pb, Sb, or Bi.

[0068] In another embodiment of the present invention, the molten salt is a chloride or fluoride molten salt.

[0069] In another embodiment of the present invention, the molten salt is a molten salt mixture containing a chloride molten salt and a fluoride molten salt.

[0070] In another embodiment of the present invention, the treatment object has a form of particles or powder.

[0071] In another embodiment of the present invention, the treatment object having the form of particles or powder is compacted to form the anode.

[0072] Another embodiment of the present invention is a method for producing a metal by molten salt electrolysis, the method being a method for producing a particular metal by molten salt electrolysis from a treatment object containing two or more metal elements, wherein a cathode and an anode that is formed of an anode material containing the treatment object are disposed in a molten salt, and a potential at the anode is controlled to a predetermined value so that a metal element corresponding to the controlled potential is dissolved in the molten salt from the treatment object and a particular metal is left in the anode.

[0073] In another embodiment of the present invention, the treatment object is an ore or a crude metal ingot obtained from the ore.

[0074] Another embodiment of the present invention is a method for producing tungsten by molten salt electrolysis from a treatment object containing tungsten, wherein a cathode and an anode that is formed of an anode material containing the treatment object are disposed in a molten salt, and a potential at the anode is controlled to a predetermined value so that a metal element corresponding to the controlled potential is dissolved in the molten salt from the treatment object and tungsten is left in the anode.

[0075] In another embodiment of the present invention, the molten salt is selected such that, in the step of dissolving a metal element in the molten salt from the treatment object, a difference between a standard electrode potential of a simple substance or alloy of the particular metal and a standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

[0076] Another embodiment of the present invention is an apparatus used for a method for producing a metal by molten salt electrolysis, the apparatus including a container containing a molten salt; a cathode immersed in the molten salt contained within the container; and an anode that is immersed in the molten salt contained within the container and that contains a treatment object containing two or more metal elements, wherein the molten salt is movable into and out of the anode, the apparatus further includes a control unit configured to control a potential of the cathode and the anode to a predetermined value, and a value of the potential is changeable in the control unit.

[0077] Another embodiment of the present invention is an apparatus used for a method for producing a metal by molten salt electrolysis, the apparatus including a container containing a molten salt containing two or more dissolved metal elements; a cathode and an anode that are immersed in the molten salt contained within the container; and a control unit configured to control a potential of the cathode and the anode to a predetermined value, wherein a value of the potential is changeable in the control unit.

[0078] In another embodiment of the present invention, the two or more metal elements include at least one of tungsten and lithium.

Advantageous Effects of Invention

[0079] A method for producing a metal and an apparatus used for the production method according to the present invention are applicable to any ore. Use of a production method or an apparatus used for the production method according to the present invention can provide a particular metal at high purity, with safety, and at low cost, from a treatment object containing two or more metal elements.

BRIEF DESCRIPTION OF DRAWINGS

[0080] FIG. 1 is a flow chart for explaining an embodiment of the present invention.

[0081] FIG. 2 is a schematic view describing examples of deposition potentials of rare earth metals in a molten salt.

[0082] FIG. 3 is a graph illustrating examples of a relationship between treatment time and concentration of ions of a rare earth metal in a molten salt in an embodiment of the present invention.

[0083] FIG. 4 is a schematic sectional view for explaining the configuration of an apparatus according to an embodiment of the present invention.

[0084] FIG. 5 is a schematic sectional view for explaining the configuration of an apparatus according to an embodiment of the present invention.

[0085] FIG. 6 is a flow chart for explaining another embodiment of the present invention.

[0086] FIG. 7 is a schematic sectional view for explaining another embodiment of the present invention.

[0087] FIG. 8 is a schematic sectional view for explaining another embodiment of the present invention.

[0088] FIG. 9 is a schematic sectional view for explaining another embodiment of the present invention.

[0089] FIG. 10 is a schematic sectional view for explaining another embodiment of the present invention.

[0090] FIG. 11 is a schematic sectional view for explaining a modification of another embodiment of the present invention.

[0091] FIG. 12 is a schematic sectional view for explaining a modification of another embodiment of the present invention.

[0092] FIG. 13 is a schematic sectional view for explaining a modification of another embodiment of the present invention.

[0093] FIG. 14 is a photograph for explaining an anode electrode used in examples according to the present invention.

[0094] FIG. 15 is a graph illustrating the relationship between the value of anode current and time in an example according to the present invention.

[0095] FIG. 16 is a scanning electron micrograph of a surface portion of a cathode electrode used in an electrolysis step in an example according to the present invention. The scale in the lower right of the micrograph indicates a length of 8 μm .

[0096] FIG. 17 is a scanning electron micrograph illustrating Dy distribution status in the regions of the micrograph illustrated in FIG. 16.

[0097] FIG. 18 is a schematic sectional view for explaining an example of the configuration of an apparatus according to an embodiment of the present invention.

[0098] FIG. 19 is a schematic sectional view for explaining an example of the configuration of an apparatus according to an embodiment of the present invention.

DESCRIPTION OF EMBODIMENTS

[0099] An embodiment of the present invention is a method for producing a metal by molten salt electrolysis, the method including a step of dissolving, in a molten salt, a metal element contained in a treatment object containing two or more metal elements; and a step of depositing or alloying a particular metal present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing the dissolved metal element, by controlling a potential of the electrode members to a predetermined value.

First Embodiment

[0100] In the first embodiment, the treatment object is an ore containing two or more metal elements or a crude metal ingot obtained from the ore (hereafter sometimes simply referred to as a crude metal ingot).

[0101] That is, roughly speaking, this embodiment includes a process of dissolving, in a molten salt, a metal contained in an object (the ore or crude metal ingot), and a process of depositing a metal or an alloy of a separation-extraction target element on one of electrodes (cathode) from a molten salt containing the dissolved metal by molten salt electrolysis. A feature of this embodiment is that, by controlling the potential of the electrodes, a particular target element is selectively dissolved or deposited to achieve separation and smelting.

[0102] The process of dissolving, in a molten salt, a metal element contained in an object will be first described.

[0103] A procedure for dissolving, in a molten salt, a metal element contained in an ore or a crude metal ingot is, for example, a chemical procedure for dissolution. Specifically, an ore or a crude metal ingot is ground into particles or powder, mixed with a salt, and heated. As a result, two or more metal elements contained in the ore or the crude metal ingot can be dissolved in the molten salt. Alternatively, the treatment object may be placed in a molten salt and dissolved.

[0104] Another procedure is an electrochemical procedure. Specifically, an object is disposed as an anode in a molten salt and the value of the potential at the object is controlled to selectively dissolve an element contained in the object: molten salt electrolysis is characterized in that different elements are dissolved at different potentials; and such characteristics are utilized to selectively separate metals corresponding to potentials. In this way, by using an object as an anode and controlling the potential during dissolution, a metal element that is a smelting target can be selectively dissolved in a molten salt.

[0105] In the process of dissolving, in a molten salt, a metal element contained in an object, the potential is preferably controlled such that impurities contained in the object remain undissolved. As a result, entry of impurities in the subsequent deposition process can be reduced.

[0106] For this purpose, the molten salt is preferably selected such that, in the step of dissolving, in the molten salt, a metal element contained in an ore or a crude metal ingot, the difference between the standard potential of a simple substance or alloy of a particular metal (metal element to be dissolved) and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, the metal element that is dissolved in the molten salt can be sufficiently separated from the metal element that is left in the anode. The difference between the

standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0107] The value of the potential controlled at the anode can be calculated by Nernst equation described below.

[0108] In the case where a plurality of target particular metals are contained in an ore or a crude metal ingot used, the potential may be controlled such that respective metals are dissolved in a molten salt. Alternatively, after one of the particular metals is dissolved, the ore or crude metal ingot (anode) containing the remainder of the metals may be moved to another molten salt and the potential may be similarly controlled to a predetermined value so that the remainder of the particular metals is dissolved in the molten salt.

[0109] Some metals are more easily separated by deposition described below. In such cases, the entire treatment object may be dissolved or only a particular metal and some other metals may be dissolved.

[0110] From the standpoint of reduction of entry of impurities, in the step of dissolving, in a molten salt, a metal element contained in an ore or a crude metal ingot, the potential at the anode is preferably controlled to a predetermined value so that the particular metal element is selectively dissolved in the molten salt.

[0111] The molten salt can be selected from chlorides and fluorides. Examples of chloride molten salts include KCl, NaCl, CaCl₂, LiCl, RbCl, CsCl, SrCl₂, BaCl₂, and MgCl₂. Examples of fluoride molten salts include LiF, NaF, KF, RbF, CsF, MgF₂, CaF₂, SrF₂, and BaF₂. In the cases where rare earth elements are subjected to molten salt electrolysis, chloride molten salts are preferably used in view of efficiency; in particular, KCl, NaCl, and CaCl₂ are preferably used because they are inexpensive and easily available.

[0112] Among such molten salts, a plurality of molten salts can be combined and used as a molten salt having a desirable composition. For example, a molten salt having a composition such as KCl—CaCl₂, LiCl—KCl, or NaCl—KCl may be used.

[0113] The cathode is formed of carbon or a material that tends to form an alloy with an alkali metal such as Li or Na constituting cations in the molten salt. For example, aluminum (Al), zinc (Zn), gallium (Ga), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), lead (Pb), or bismuth (Bi) may be used.

[0114] When the ore or crude metal ingot is used as an anode, for example, the ore or crude metal ingot contained in a conductive basket formed of a metal or the like may be disposed in the molten salt. An opening may be formed in an upper portion of the basket so that the ore or crude metal ingot serving as the treatment object can be inserted through the opening into the basket; and a large number of holes may be formed in the side and bottom walls of the basket so that the molten salt can flow into the basket. The basket may be constituted by a desired material such as a mesh member knitted from metal wires or a sheet member that is a sheet-shaped metal plate having a large number of holes. In particular, it is effective that the material is formed of C, Pt, Mo, or the like.

[0115] In the cases where the object is an ore or the like and has a high electric resistance, the contact area between the object and the conductive material is preferably increased. The object is effectively used as an electrode by, for example, wrapping the object with a metal mesh member or filling the object into spaces within a metal porous member.

[0116] When the cathode and the basket containing an ore or crude metal ingot are disposed in the molten salt and the potential at the anode (basket) is controlled from the outside as described above, a target metal can be dissolved in the molten salt from the ore or crude metal ingot.

[0117] In the subsequent deposition process, molten salt electrolysis is performed with a pair of electrode members disposed in the molten salt so that a metal element dissolved in the molten salt is deposited on one of the electrode members (cathode). In this case, by controlling the potential value in the molten salt electrolysis, a particular metal element can be selectively deposited as metal or alloy on the cathode.

[0118] As in the dissolution process, in this deposition process, molten salt electrolysis is characterized in that different elements are deposited at different potentials as metal or alloy on the cathode; and such characteristics are utilized to separate the metals. Thus, even when a plurality of target particular metals are contained in the molten salt, by controlling the potential, the metals can be individually deposited on cathodes one by one.

[0119] The electrode members may be formed of, for example, nickel (Ni), molybdenum (Mo), or glassy carbon (C).

[0120] In this embodiment, the above-described two processes are used to separate and extract from an object a particular metal element that is a smelting target. In this embodiment, since a molten salt is used, the system needs to be heated such that the temperature of the system in the processes is equal to or more than the melting point of the molten salt.

[0121] A feature of the two processes is use of a molten salt. Thus, the fact that different molten salts have different dissolution-deposition potentials for elements is utilized and the processes can be designed by selecting a molten salt such that the dissolution-deposition potentials of a particular metal element that is a target element and the other impurity metal elements are values that allow easy performance of the processes. Specifically, the molten salt is preferably selected such that, in the step of depositing or alloying the particular metal, the difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. In the molten salt, the difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard electrode potential of a simple substance or alloy of another metal is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0122] In this way, in the step of depositing or alloying the particular metal, the potential of the electrode members is preferably controlled to a predetermined value so that the particular metal element in the molten salt is selectively deposited or alloyed.

[0123] The deposition potential of a simple substance or alloy of a metal to be deposited on the cathode can be determined by electrochemical calculation. Specifically, the calculation is performed with Nernst equation.

[0124] For example, the potential at which a simple substance of praseodymium (Pr) is deposited from trivalent Pr ions (hereafter represented by Pr(III)) can be determined with the following equation.

$$E_{Pr} = E_{Pr}^0 + RT/3F \cdot \ln(a_{Pr(III)}/a_{Pr(0)}) \quad \text{Equation (1)}$$

[0125] In Eq. (1), E_{Pr}^0 represents the standard potential, R represents the gas constant, T represents absolute temperature, F represents the Faraday constant, $a_{Pr(III)}$ represents the activity of Pr(III) ions, and $a_{Pr(0)}$ represents the activity of Pr simple substance.

[0126] When Eq. (1) is rewritten in view of activity coefficient $\gamma_{Pr(III)}$, since $a_{Pr(0)}=1$, the following equations are provided.

$$\begin{aligned} E_{Pr} &= E_{Pr}^0 + RT/3F \cdot \ln a_{Pr(III)} \\ &= E_{Pr}^0 + RT/3F \cdot \ln(\gamma_{Pr(III)} \cdot C_{Pr(III)}) \end{aligned} \quad \text{Equation (2)}$$

$$E_{Pr} = E_{Pr}^0 + RT/3F \cdot \ln C_{Pr(III)} \quad \text{Equation (3)}$$

[0127] In Eq. (3), $C_{Pr(III)}$ represents the concentration of trivalent Pr ions, and E_{Pr}^0 represents formal electrode potential (here, equal to $E_{Pr}^0 + RT/3F \cdot \ln \gamma_{Pr(III)}$).

[0128] Similarly, the potential at which PrNi alloy is deposited on the electrode surface (deposition potential: $E_{Pr.Ni}$) can be determined with the following equation.

$$E_{Pr.Ni} = E_{Pr.Ni}^0 + RT/3F \cdot \ln C_{Pr(III)} \quad \text{Equation (4)}$$

[0129] In Eq. (4), $E_{Pr.Ni}^0$ represents formal electrode potential (here, equal to $E_{Pr.Ni}^0 + RT/3F \cdot \ln \gamma_{Pr(III)}$).

[0130] Similarly, by using the above-described equations, deposition potentials of all deposits corresponding to different molten salts can be determined. In the process of depositing or alloying a particular metal on the cathode, in view of the deposition potential value of this particular metal or an alloy thereof, a deposit that provides a potential difference with respect to another metal or an alloy thereof is selected or the order of depositions is determined.

[0131] Voltage and current during operation vary depending on the size or positional relationship of electrodes. Accordingly, reference values of voltage and current are determined on the basis of conditions and subsequently voltage and current are determined in each step on the basis of the potential value and order determined by the above-described method.

[0132] As described above, in a method for producing a metal by molten salt electrolysis according to this embodiment, the potential value is controlled to thereby electrochemically dissolve and deposit a target metal. Accordingly, the steps can be simplified, compared with, for example, the existing wet treatment involving repeating of processes of dissolution and extraction using acid or the like; and a particular element can be selectively separated and recovered. In addition, adjustment of the specific gravity of the molten salt is not necessary; and, by selecting a low-temperature molten salt in which an object can be treated in the solid state, a simple apparatus configuration can be employed. Moreover, the operation pattern can also be simplified. As a result, the steps can be performed efficiently at low cost.

[0133] Alternatively, a particular metal can be smelted on the basis of an idea that is totally contrary to the above-described idea of depositing or alloying a particular metal on the cathode.

[0134] That is, a method for producing a metal according to this embodiment is a method for producing a particular metal by molten salt electrolysis from an ore containing two or more metal elements or a crude metal ingot obtained from the ore, wherein a cathode and an anode that is formed of an anode material containing the ore or crude metal ingot are disposed

in a molten salt, and the potential at the anode is controlled to a predetermined value so that a metal element corresponding to the potential is dissolved in the molten salt from the ore or crude metal ingot and a particular metal is left in the anode.

[0135] In this method, the object (the ore or crude metal ingot) is used as the anode and metal elements other than a particular metal element, that is, only metal elements serving as impurities are dissolved in the molten salt, so that the particular metal is left in the anode. In this case, by also controlling the potential at the anode, such a phenomenon is caused in which the metal element that is the smelting target is left in the anode and impurity elements are dissolved in the molten salt. As a result, a smelted metal material is obtained in the anode.

[0136] In this method, the molten salt is also preferably selected such that, in the step of dissolving, in the molten salt, a metal element from the ore or crude metal ingot, the difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, the particular metal can be sufficiently separated from the other metal and the particular metal alone can be left in the anode. The difference between the standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0137] The value of the potential controlled at the anode can be calculated by Nernst equation as described above.

[0138] Ores usable in the method for producing a metal by molten salt electrolysis according to this embodiment are ores containing target particular metals. Examples of the ores include gold ore, silver ore, copper ore, iron ore, aluminum ore, lead ore, zinc ore, tin ore, mercury ore, sulfur ore, phosphorus ore, nickel ore, cobalt ore, manganese ore, chromium ore, molybdenum ore, tungsten ore, antimony ore, arsenic ore, bismuth ore, strontium ore, beryllium ore, magnesium ore, barium ore, and calcium ore. For example, rare earth metals can be obtained from bastnaesite, monazite, loparite, apatite, xenotime, fergusonite, and eudialyte.

[0139] The crude metal ingot obtained from the ore denotes a metal containing a target particular metal at a low purity, such as a metal obtained by smelting the ore.

[0140] The method for producing a metal by molten salt electrolysis according to this embodiment is suitably applied to an ore or crude metal ingot obtained from the ore that is used as the anode and contains a transition metal or a rare earth metal.

[0141] The transition metal is not particularly limited and may be any element among from group 3 (group IIIA) to group 11 (group IB) of the periodic table. The rare earth metal is also not particularly limited and may be any element among scandium (Sc), yttrium (Y), and 15 lanthanoid elements in group 3 (group IIIA) of the periodic table.

[0142] The method for producing a metal by molten salt electrolysis according to this embodiment is also suitably applicable to the cases where particular metals deposited or alloyed on cathodes are rare earth metals. In this embodiment, appropriate selection of the composition of the molten salt allows even deposition of rare earth metals that cannot be deposited by aqueous solution electrolysis. Thus, rare earth metals that are difficult to mine as resources can be easily obtained.

[0143] In this embodiment, the ore or crude metal ingot obtained from the ore preferably has the form of particles or

powder. When the ore or crude metal ingot to be treated is prepared so as to have the form of particles or powder, the surface area is increased and the treatment efficiency can be increased. From this viewpoint, the maximum particle size of the ore or crude metal ingot is preferably 0.01 mm to 2 mm, more preferably 0.01 mm to 1 mm, still more preferably 0.01 mm to 0.2 mm.

[0144] In addition, the ore or crude metal ingot in the form of particles or powder is preferably compacted to form the anode. The ore or crude metal ingot in the form of powder can be compacted and, as a result, can be used as the anode. In this case, between the particles, there are desirably spaces that the molten salt can easily enter.

[0145] Hereinafter, this embodiment will be described with reference to drawings. In the drawings below, the same or corresponding parts are designated by the same reference signs and repetitive descriptions thereof are omitted.

First Embodiment-1

[0146] An example of this embodiment will be described that is a method for obtaining neodymium (Nd), dysprosium (Dy), and praseodymium (Pr) by molten salt electrolysis from an ore containing Nd, Dy, and Pr. Examples of the ore include monazite, apatite, xenotime, fergusonite, and eudialyte.

[0147] As illustrated in FIG. 1, a preparation step (S10) is first performed.

[0148] In this step, for example, an ore that is a treatment object, a molten salt to be used, and an apparatus including, for example, electrodes and a container for containing the molten salt are prepared. Optionally, in order to promote dissolution of the treatment object in the molten salt, the treatment object may be finely ground for the purpose of increasing the contact area between the treatment object and the molten salt.

[0149] The ore containing Nd, Dy, and Pr may be, for example, xenotime ore. For example, a xenotime ore has a composition of 3.0% Nd, 7.9% Dy, and 0.5% Pr.

[0150] Subsequently, a dissolution step in the molten salt (S20) is performed.

[0151] In this step (S20), the ore and (another) electrode member are immersed in the prepared molten salt; the ore and the electrode member are connected via a power supply so that the potential of the ore and the electrode member is controlled. By controlling the potential at the ore, rare earth elements (Nd, Dy, and Pr) in the ore are selectively dissolved in the molten salt. The molten salt used may be a molten salt having a desired composition.

[0152] For example, the molten salt may be LiF—NaF—KF; the other electrode member may be an electrode formed of glassy carbon; and the above-described ore may be used as the treatment object.

[0153] In this case, for example, while the molten salt is heated at 700° C., Nd, Dy, and Pr can be selectively dissolved in the molten salt from the ore. The potential is controlled to a value at which elements other than Nd, Dy, and Pr are scarcely dissolved in the molten salt but Nd, Dy, and Pr are dissolved in the molten salt.

[0154] Subsequently, as illustrated in FIG. 1, a separation extraction step (S30) is performed.

[0155] Specifically, in the molten salt in which Nd, Dy, and Pr are dissolved as described above, a pair of electrodes are inserted and the potential of the electrode members is controlled to a predetermined value. For example, in the case of using LiCl—KCl molten salt, as illustrated in FIG. 2, the

potential value is controlled to potentials corresponding to deposition potentials determined for respective rare earth metals. As a result, by controlling the potential, the rare earth metal deposited on the electrode can be selected. Thus, the rare earth metals can be selectively recovered element by element.

[0156] For example, as illustrated in FIG. 2, rare earth elements such as Nd, Dy, and Pr have different deposition potential values for respective elements. Specifically, as illustrated in FIG. 2, the deposition potential of Nd is about 0.40 V (vs. Li^+/Li); the deposition potentials of Pr and Dy are about 0.47 V (vs. Li^+/Li); and the deposition potential of DyNi_2 , which is a Dy compound, is about 0.77 V (vs. Li^+/Li).

[0157] The deposition potentials in FIG. 2 are described with reference to Li. In FIG. 2, the ordinate axis indicates deposition potential (unit: V). Such deposition potentials are values in the case where the molten salt is $\text{LiCl}-\text{KCl}$ and the temperature of the molten salt is set at 450° C.

[0158] As described above, elements and compounds have different deposition potentials. Accordingly, by immersing a pair of electrodes in a molten salt in which particular metals are dissolved and by controlling the potential at the cathode so as to correspond to the above-described deposition potentials, particular rare earth elements can be selectively deposited on the cathode. By changing the potential value at the cathode (for example, sequential potential changes), particular metals to be deposited can be selected.

[0159] For example, as illustrated in FIG. 3, different voltages are sequentially applied across a pair of electrodes immersed in the molten salt in which Nd, Dy, and Pr are dissolved. The concentrations (ion concentrations) of Nd, Dy, and Pr in the molten salt are each 0.5 mol %.

[0160] When data described in FIG. 2 are used as deposition potential values, for example, $\text{LiCl}-\text{KCl}$ is used as the molten salt and the temperature of the molten salt is set at 450° C. In FIG. 3, the abscissa axis indicates treatment time and the ordinate axis indicates the ion concentrations of rare earth elements in the molten salt. The unit in the ordinate axis is mol %.

[0161] In STEP 1, when Ni is first used as a cathode material and the potential at the cathode is set to a value that is less noble than 0.77 V (vs. Li^+/Li) and slightly more noble than 0.63 V (vs. Li^+/Li) (for example, the potential difference is set to 0.631 V (vs. Li^+/Li)), Dy ions are alloyed with the cathode material Ni so that DyNi_2 is deposited on the cathode surface. As a result, as illustrated in FIG. 3, the Dy ion concentration in the molten salt is sharply decreased. Dy can be recovered until the Dy ion concentration in the molten salt becomes about 3.6×10^{-4} mol %.

[0162] Subsequently, in STEP 2, when another electrode (for example, a Mo electrode) is used as a cathode and the potential at the cathode is set to a value that is slightly more noble than 0.40 V (vs. Li^+/Li) (for example, the potential difference is set to 0.401 V (vs. Li^+/Li)), Pr is deposited on one of the electrodes (cathode). As a result, as illustrated in FIG. 3, the Pr ion concentration in the molten salt is sharply decreased. Pr can be recovered until the Pr ion concentration in the molten salt becomes about 0.017 mol %.

[0163] The electrode used in STEP 2 is different from the electrode on which DyNi_2 has been deposited in STEP 1. For example, the electrode on which DyNi_2 has been deposited in STEP 1 may be removed from the molten salt before STEP 2 is started, and another electrode may be immersed in the molten salt; alternatively, the electrode on which DyNi_2 has

been deposited may be left unremoved and, in STEP 2, the potential at another electrode may be controlled.

[0164] Subsequently, in STEP 3, when the potential at still another electrode (for example, a Mo electrode) is set to 0.10 V (vs. Li^+/Li), Nd is deposited on this electrode (cathode). As a result, as illustrated in FIG. 3, the Nd ion concentration in the molten salt is sharply decreased. Nd can be recovered until the Nd ion concentration in the molten salt becomes, for example, about 2.7×10^{-7} mol %.

[0165] The electrode on which Pr has been deposited in STEP 2 may be removed from the molten salt before STEP 3 is started, and another electrode may be immersed in the molten salt; alternatively, the electrode on which Pr has been deposited in STEP 2 may be left immersed in the molten salt and, in STEP 3, another electrode may be used.

[0166] DyNi_2 recovered in STEP 1 is treated in STEP 4: the electrode on the surface of which DyNi_2 has been deposited and another electrode (for example, a Mo electrode) are immersed in a molten salt; and the potential at the DyNi_2 electrode is set to be in a potential range in which Dy is dissolved but Ni is not dissolved (0.77 or more and 2.6 or less V (vs. Li^+/Li)), so that Dy can be dissolved in the molten salt and Dy alone can be deposited on the surface of the other electrode.

[0167] As has been described above, the target particular metals can be individually recovered from the molten salt.

Apparatus Used for Method of this Embodiment

[0168] Hereinafter, an apparatus used for the method of this embodiment in FIG. 1 will be described with reference to FIGS. 4 and 5. A recovery apparatus illustrated in FIG. 4 includes a container 1 containing a molten salt, a molten salt 2 contained within the container 1, a basket 4 containing a treatment object (the ore or crude metal ingot) 3, electrodes 6 to 8, a heater 10 for heating the molten salt 2, and a control unit 9 electrically connected to the basket 4 and the electrodes 6 to 8 via conductive wires 5. The control unit 9 is configured to control the potential (change the potential) of one electrode that is the basket 4 and the other electrode that is one of the electrodes 6 to 8. In the control unit 9, the value to which the potential is controlled is changeable. The heater 10 is disposed so as to circularly surround the container 1. The electrodes 6 to 8 may be formed of desired materials. For example, the electrode 6 may be formed of nickel (Ni). For example, the electrodes 7 and 8 may be formed of carbon (C). The container 1 may have a bottom surface that has a circular shape or a polygonal shape. The basket 4 may be the above-described basket.

[0169] The basket 4 and the electrodes 6 to 8 are controlled by the control unit 9 to predetermined potential values. By controlling the electrodes 6 to 8 to different potentials, different particular metals corresponding to the controlled potential values are deposited on the surfaces of the electrodes 6 to 8 as described below. For example, as described below, the potential value set for the electrode 6 can be adjusted so that a DyNi_2 film 11 is deposited on the surface of the electrode 6. By adjusting the potential set for the electrode 7, a Pr film 12 can be deposited on the surface of the electrode 7. By adjusting the potential set for the electrode 8, a Nd film 13 can be deposited on the surface of the electrode 8.

[0170] The electrode 6 on which the DyNi_2 film 11 is deposited is then placed in a container 1 containing a molten salt 2 as illustrated in FIG. 5. Furthermore, another electrode is placed in the molten salt 2 so as to face the electrode 6 on the

surface of which the DyNi_2 film 11 is deposited. The electrodes 6 and 15 are connected to a control unit 9 via conductive wires 5. While the molten salt 2 is heated with a heater 10 disposed so as to surround the container 1, the control unit 9 is used to control the potential of the electrodes 6 and 15 to a predetermined value. At this time, the potential is controlled such that the potential at the cathode (electrode 15) is the deposition potential of Dy.

[0171] As a result, from the DyNi_2 film 11 deposited on the surface of the electrode 6, Dy is dissolved in the molten salt 2 and a Dy film 16 is deposited on the surface of the electrode 15. The heating temperature for the molten salt 2 with the heater 10 may be, for example, 800°C . in both of the treatments using the apparatuses illustrated in FIGS. 4 and 5. In this way, particular metals can be deposited as simple substances on the surfaces of the electrodes 7, 8, and 15.

[0172] In the case where the method of this embodiment is performed with the apparatuses illustrated in FIGS. 4 and 5, for example, the method may be performed in the following manner.

[0173] The ore (9 kg) is first prepared as the treatment object 3 and LiF—NaF—KF is prepared as the molten salt 2. For example, the ore may contain 3.0 wt % of Nd, 0.5 wt % of Pr, and 7.9 wt % of Dy. The ore is ground and placed within the basket 4. From the viewpoint of enhancement of the treatment efficiency, the size of the ore serving as the treatment object 3 is preferably minimized by grinding. For example, the ore is ground into particles having a maximum particle size of 2 mm or less, preferably 1 mm or less, more preferably 0.2 mm or less. The amount of the molten salt 2 is about 16 liters (mass: 25 kg).

[0174] The treatment object 3 contained in the basket 4 and one of the electrodes 6 to 8 are used as a pair of electrodes and STEP 1 to STEP 3 of the method of this embodiment described with reference to FIGS. 2 and 3 are performed. Specifically, in the above-described STEP 1, the treatment object 3 contained in the basket 4 and the electrode 6 are used as a pair of electrodes and the potential of the electrodes is controlled to a predetermined value. As a result, DyNi_2 is deposited on the surface of the electrode 6. In the above-described STEP 2, the treatment object 3 contained in the basket 4 and the electrode 7 are used as a pair of electrodes and the potential of the electrodes is controlled to a predetermined value. As a result, Pr is deposited on the surface of the electrode 7. The mass of a Pr film deposited on the surface of the electrode 7 in FIG. 4 is, for example, about 30 g to about 50 g.

[0175] In the above-described STEP 3, the treatment object 3 contained in the basket 4 and the electrode 8 are used as a pair of electrodes and the potential of the electrodes is controlled to a predetermined value. As a result, Nd is deposited on the surface of the electrode 8. The mass of a Nd film deposited on the surface of the electrode 8 is, for example, about 200 g to about 300 g.

[0176] In the above-described STEP 4, the electrode 6 and the electrode 15 are placed in the apparatus illustrated in FIG. 5 and the potential of the electrodes in the molten salt is controlled to a predetermined value. As a result, Dy is deposited on the surface of the electrode 15. The mass of a Dy film 16 deposited on the surface of the electrode 15 is, for example, 600 g to 800 g.

[0177] As described with reference to FIG. 4, the step of dissolving target metals in the molten salt 2 and the step of depositing particular metals as simple substances on the sur-

faces of the electrodes 7, 8, and the like can be performed within the same apparatus (with the same molten salt 2). On the other hand, the step of separating and extracting Dy from DyNi_2 described above in STEP 4 is preferably performed in an apparatus (apparatus illustrated in FIG. 5) other than the apparatus (apparatus illustrated in FIG. 4) used for the step of dissolving metals in the molten salt 2 described with reference to FIG. 4.

[0178] As has been described above, particular metals (for example, Dy, Pr, and Nd) can be recovered from an ore or crude metal ingot serving as the treatment object 3.

First Embodiment-2

[0179] An example of this embodiment will be described that is a method for obtaining neodymium (Nd), dysprosium (Dy), and praseodymium (Pr) by molten salt electrolysis from a crude metal ingot obtained by smelting an ore containing Nd, Dy, and Pr.

[0180] The crude metal ingot containing Nd, Dy, and Pr may be, for example, mixed rare earth metal (didymium). A smelting method for obtaining the mixed rare earth metal is not particularly limited and may be selected from publicly known methods.

[0181] As illustrated in FIG. 6, a step (S11) of preparing a crude metal ingot serving as a treatment object is first performed. Specifically, as illustrated in FIG. 7, a crude metal ingot serving as a treatment object 3 is immersed in a molten salt 2 contained within a container 1; and a conductive wire 5 is connected to the treatment object 3, the conductive wire 5 being used for connection to a power supply in a control unit 9. The salt used was LiCl—KCl .

[0182] In the molten salt 2, an electrode material 25 contained within a basket 24 and serving as the other electrode is immersed together with the basket 24. The electrode material 25 is a material that tends to form an alloy with an alkali metal such as Li and Na constituting cations in the molten salt. Examples of the electrode material 25 include aluminum (Al), zinc (Zn), gallium (Ga), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), lead (Pb), and bismuth (Bi).

[0183] Subsequently, as illustrated in FIG. 6, a step (S21) of dissolving Nd, Dy, and Pr in a molten salt is performed.

[0184] Specifically, as illustrated in FIG. 7, the potential of the treatment object 3 and the electrode material 25 contained within the basket 24 is controlled with the control unit 9, so that the potential at the treatment object 3 is adjusted to a predetermined value. As a result, rare earth elements such as Nd, Dy, and Pr are dissolved in the molten salt 2 from the crude metal ingot serving as the treatment object 3.

[0185] Subsequently, as illustrated in FIG. 6, a step (S31) of depositing DyNi_2 by electrolysis is performed. Specifically, instead of the electrode material 25 contained in the basket 24 in FIG. 7, as illustrated in FIG. 8, an electrode 6 formed of nickel is immersed in the molten salt 2. This electrode 6 is connected to the control unit 9 via a conductive wire 5. In this state, the control unit 9 is used to control the potential of the treatment object 3 serving as one electrode and the electrode 6 serving as the other electrode, to a predetermined value.

[0186] As a result, rare earth elements such as Dy are dissolved in the molten salt 2 from the treatment object 3 and DyNi_2 is deposited on the surface of the electrode 6 from the molten salt 2.

[0187] Subsequently, as illustrated in FIG. 6, a step (S32) of recovering Pr by electrolysis is performed. Specifically, as illustrated in FIG. 9, instead of the treatment object 3, an

electrode 27 formed of carbon is immersed as one electrode in the molten salt 2. In addition, instead of the electrode 6 in FIG. 8, an electrode 7 formed of carbon is placed at a position so as to face the electrode 27 and be immersed in the molten salt 2. The electrode 27 and the electrode 7 are electrically connected to the control unit 9 via conductive wires 5. In this state, the potential of one electrode 27 and the other electrode 7 is controlled to a predetermined value.

[0188] As a result, Pr dissolved in the molten salt 2 is deposited on the surface of the electrode 7. When a chloride is used as the molten salt 2, chlorine gas (Cl_2) is released from the region around the electrode 27.

[0189] Subsequently, as illustrated in FIG. 6, a step (S33) of recovering Nd by electrolysis is performed. Specifically, instead of the electrode 7, as illustrated in FIG. 10, an electrode 8 formed of carbon is placed so as to face the electrode 27 and be immersed in the molten salt 2. This electrode 8 is electrically connected to the control unit 9 via a conductive wire 5. The control unit 9 is used to control the potential of the electrode 8 and the electrode 27 to a predetermined value. As a result, Nd is deposited on the surface of the electrode 8. At this time, chlorine gas is released from the region around the electrode 27.

[0190] Subsequently, a step (S34) of recovering Dy by electrolysis from DyNi_2 recovered in the step (S31) is performed. Specifically, as illustrated in FIG. 5, the electrode 6 on the surface of which DyNi_2 is deposited (refer to FIG. 8) is immersed in the molten salt 2; the other electrode 15 is disposed so as to be immersed in the molten salt 2; and the control unit 9 is used to control the potential of the electrodes 6 and 15 to a predetermined value. As a result, Dy is temporarily dissolved in the molten salt 2 from DyNi_2 deposited on the surface of the electrode 6 and then a Dy film 16 is deposited on the surface of the electrode 15. Thus, Nd, Dy, and Pr, which are rare earth metals, can be individually recovered.

[0191] The above-described steps (S21 to S32) may be performed with the following apparatus configurations. For example, the above-described step (S31) may be performed with an apparatus configuration illustrated in FIG. 11.

[0192] Specifically, instead of the treatment object 3 in the apparatus configuration in FIG. 8, the basket 24 containing a material 26 alloyed by the step illustrated in FIG. 7 is immersed in the molten salt 2. As illustrated in FIG. 11, this basket 24 is electrically connected to the control unit 9 via a conductive wire 5. The potential of the electrode 6 and the material 26 contained within the basket 24 and alloyed by the step illustrated in FIG. 7 is controlled to a predetermined value. As a result, Dy dissolved in the molten salt 2 is deposited as DyNi_2 on the surface of the electrode 6. Dy can be recovered as a simple substance from DyNi_2 deposited on the surface of the electrode 6, by the same step as the step (S34) in FIG. 6.

[0193] Subsequently, the above-described step (S32) may be performed by a treatment with an apparatus configuration illustrated in FIG. 12. Specifically, instead of the electrode 6 in FIG. 11, as illustrated in FIG. 12, an electrode 7 formed of carbon is placed at a position so as to face the basket 24 and be immersed in the molten salt 2. This electrode 7 is electrically connected to the control unit 9 via a conductive wire 5. The control unit is used to control the potential of the electrode 7 and the alloy 26 contained within the basket 24, to a predetermined value. As a result, Pr dissolved in the molten salt 2 is deposited on the surface of the electrode 7.

[0194] Subsequently, the above-described step (S33) may be performed by a treatment with an apparatus configuration illustrated in FIG. 13. Specifically, as illustrated in FIG. 13, instead of the electrode 7 in FIG. 12, an electrode 8 formed of carbon is placed at a position so as to face the basket 24 and be immersed in the molten salt 2. The electrode 8 is electrically connected to the control unit 9 via a conductive wire 5. The control unit 9 is used to control the potential of the electrode 8 and the alloy 26 disposed within the basket 24, to a predetermined value. As a result, Nd is deposited on the surface of the electrode 8.

[0195] By using the method having been described, particular metals contained in a crude metal ingot can be sequentially individually recovered. According to the method of this embodiment, the apparatus configuration can be simplified and the treatment time can also be decreased, compared with the existing wet separation method and the like. Thus, the cost incurred for obtaining elements such as rare earth elements can be reduced. In addition, by appropriately setting a potential at an electrode, a particular metal can be deposited as a simple substance on the electrode surface and hence high purity metal can be obtained. The potentials for depositing individual metals and alloys can be determined by the above-described calculation.

Second Embodiment

[0196] A method for producing tungsten by molten salt electrolysis according to this embodiment is a method for producing tungsten by molten salt electrolysis from a treatment object containing tungsten, the method including a step of dissolving, in a molten salt, tungsten from the treatment object, and a step of depositing tungsten present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing dissolved tungsten, by controlling a potential of the electrode members to a predetermined value.

[0197] That is, roughly speaking, this embodiment includes a process of dissolving, in a molten salt, tungsten contained in the treatment object, and a process of depositing tungsten on one of electrodes (cathode) from the molten salt containing dissolved tungsten by molten salt electrolysis. A feature of this embodiment is that, by controlling the potential of the electrodes, tungsten is selectively deposited from a treatment object to provide high purity tungsten.

[0198] The process of dissolving, in a molten salt, tungsten contained in a treatment object will be first described.

[0199] A procedure for dissolving, in a molten salt, tungsten contained in a treatment object is, for example, a chemical procedure for dissolution. Specifically, a treatment object is ground into particles or powder, mixed with a salt, and heated. As a result, tungsten contained in the treatment object can be dissolved in the molten salt. Alternatively, a treatment object may be placed in a molten salt and dissolved.

[0200] Another procedure is an electrochemical procedure. Specifically, an anode formed of an anode material containing a treatment object is placed in a molten salt and the value of the potential at the treatment object placed as the anode is controlled to selectively dissolve tungsten contained in the treatment object. Molten salt electrolysis is characterized in that different elements are dissolved at different potentials. Such characteristics can be utilized to separate tungsten from other metals. In this way, by using a treatment object as an anode and controlling the potential during dissolution, tungsten can be selectively dissolved in a molten salt.

[0201] In this step, the entire treatment object may be dissolved, or a tungsten-containing portion of the treatment object or tungsten alone may be dissolved. Conditions under which non-tungsten metals contained in the treatment object are dissolved may be employed; however, if possible, the potential is preferably controlled so that tungsten alone is dissolved. That is, in the step of dissolving tungsten in a molten salt, the potential of the anode and the cathode is preferably controlled to a predetermined value so that tungsten is selectively dissolved in the molten salt. As a result, entry of impurities in the subsequent deposition step can be reduced.

[0202] For this purpose, the molten salt is preferably selected such that, in the step of dissolving, in the molten salt, tungsten from the treatment object, the difference between the standard electrode potential of a simple substance or alloy of tungsten and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, tungsten that is dissolved in the molten salt can be sufficiently separated from the metal element that is left in the anode. The difference between the standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0203] The value of the potential controlled at the anode can be calculated by Nernst equation described below.

[0204] The cathode used in the dissolution step is formed of carbon or a material that tends to form an alloy with an alkali metal such as Li or Na constituting cations in the molten salt. For example, aluminum (Al), zinc (Zn), gallium (Ga), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), lead (Pb), or bismuth (Bi) may be used.

[0205] When the treatment object containing tungsten is used as an anode, for example, the treatment object contained within a conductive basket (anode material) formed of metal or the like may be disposed in the molten salt. An opening may be formed in an upper portion of the basket so that the treatment object can be inserted through the opening into the basket; and a large number of holes may be formed in the side and bottom walls of the basket so that the molten salt can flow into the basket. The basket may be constituted by a desired material such as a mesh member knitted from metal wires or a sheet member that is a sheet-shaped metal plate having a large number of holes. In particular, it is effective that the material is formed of C, Pt, Mo, or the like.

[0206] In the cases where the object is an oxide or the like and has a high electric resistance, the contact area between the object and the conductive material is preferably increased. The object is effectively used as an electrode by, for example, wrapping the object with a metal mesh member or filling the object into spaces within a metal porous member.

[0207] The cathode and an anode formed of an anode material containing the treatment object (for example, a metal basket containing the treatment object) are disposed in the molten salt; a control unit configured to control the potential of the electrodes from the outside is connected; and the potential is controlled as described above. As a result, tungsten can be dissolved in the molten salt from the treatment object.

[0208] In the subsequent deposition process, molten salt electrolysis is performed with a pair of electrode members disposed in the molten salt containing dissolved tungsten so that tungsten is deposited on one of the electrode members (cathode). In this case, by controlling the potential value in the molten salt electrolysis, tungsten can be selectively deposited as metal or alloy on the cathode.

[0209] As in the dissolution process, in this deposition process, tungsten is separated from other metals by utilizing the following characteristics: in molten salt electrolysis, different elements are deposited at different potentials as metal or alloy on the cathode. Thus, even when metals other than tungsten are contained in the molten salt, by controlling the potential, tungsten alone can be deposited on the cathode. As a result, high purity tungsten can be obtained.

[0210] In deposition of tungsten, when the difference between the dissolution-deposition potential of tungsten and the dissolution-deposition potential of another metal contained in the molten salt is so small that tungsten is difficult to separate from the metal, the cathode material may be selected and the potential may be controlled such that an alloy of the cathode material and tungsten is deposited. As a result, tungsten in the molten salt can be separated as a tungsten alloy from the other impurity metal; and, after that, for example, a dissolution step and a deposition step in another molten salt can be performed with the cathode material alloyed with tungsten to thereby provide high purity tungsten.

[0211] The electrode members used in the deposition step may be formed of, for example, nickel (Ni), molybdenum (Mo), or glassy carbon (C).

[0212] In this embodiment, the above-described two processes are used to separate and extract tungsten from a treatment object. In this embodiment, since a molten salt is used, the system needs to be heated such that the temperature of the system in the processes is equal to or more than the melting point of the molten salt.

[0213] Alternatively, smelting in the processes can be performed on the basis of a totally contrary idea. That is, a treatment object is used as the anode and only metal elements serving as impurities are dissolved in a molten salt. In this case, by also controlling the potential at the anode to a predetermined value, such a phenomenon is caused in which tungsten is left in the anode and impurity elements are dissolved. As a result, tungsten is provided in the anode.

[0214] A feature of the two processes is use of a molten salt. Thus, the characteristics of molten salt electrolysis in which different molten salts have different dissolution-deposition potentials for elements are utilized; and the processes can be designed by selecting a molten salt such that the dissolution-deposition potential of tungsten and the dissolution-deposition potential of a non-tungsten impurity metal are sufficiently different values that allow easy performance of the processes.

[0215] Specifically, the molten salt is preferably selected such that, in the step of depositing or alloying tungsten, the difference between the standard electrode potential of a simple substance or alloy of tungsten and the standard electrode potential of a simple substance or alloy of another impurity metal in the molten salt is 0.05 V or more. The difference between the standard electrode potential of a simple substance or alloy of tungsten and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0216] In this way, in the step of depositing or alloying tungsten, the potential of the electrode members is preferably controlled to a predetermined value so that the tungsten in the molten salt is selectively deposited or alloyed.

[0217] The deposition potential of tungsten to be deposited on the cathode can be determined by electrochemical calculation. Specifically, the calculation is performed with Nernst equation.

[0218] For example, the potential at which a simple substance of tungsten (W) is deposited from divalent W ions (hereafter represented by W(II)) can be determined with the following equation.

$$E_W = E_W^0 + RT/3F \cdot \ln(a_{W(II)}/a_{W(O)}) \quad \text{Equation (1)}$$

[0219] In Eq. (1), E_W^0 represents the standard potential, R represents the gas constant, T represents absolute temperature, F represents the Faraday constant, $a_{W(II)}$ represents the activity of W(II) ions, and $a_{W(O)}$ represents the activity of W simple substance.

[0220] When Eq. (1) is rewritten in view of activity coefficient $\gamma_{W(II)}$, since $a_{W(O)}=1$, the following equations are provided.

$$\begin{aligned} E_{Wr} &= E_W^0 + RT/3F \cdot \ln a_{W(II)} \\ &= E_W^0 + RT/3F \cdot \ln(\gamma_{W(II)} \cdot C_{W(II)}) \end{aligned} \quad \text{Equation (2)}$$

$$E_W = E_W^0 + RT/3F \cdot \ln C_{W(II)} \quad \text{Equation (3)}$$

[0221] In Eq. (3), $C_{W(II)}$ represents the concentration of divalent W ions, and E_W^0 represents formal electrode potential (here, equal to $E_W^0 + RT/3F \cdot \ln \gamma_{W(II)}$).

[0222] Similarly, by using the above-described equations, deposition potentials of all deposits corresponding to different molten salts can be determined. Similar calculations can also be performed in the case of depositing tungsten as an alloy. In the process of depositing or alloying tungsten on the cathode, in view of the deposition potential values of tungsten simple substance and tungsten alloy, the molten salt and the cathode material are selected such that a sufficiently high potential difference is achieved with respect to the deposition potential of a simple substance or alloy of another metal, and whether tungsten is deposited or a tungsten alloy is deposited is decided.

[0223] Voltage and current during operation vary depending on the size or positional relationship of electrodes. Accordingly, reference values of voltage and current are determined on the basis of conditions and subsequently voltage and current are determined in each step on the basis of the potential value and order determined by the above-described method.

[0224] As described above, in a method for producing tungsten by molten salt electrolysis according to this embodiment, the potential value is controlled to thereby electrochemically dissolve and deposit tungsten. Accordingly, the steps can be simplified, compared with, for example, the existing wet treatment involving repeating of processes of dissolution and extraction using acid or the like; and the particular element can be selectively separated and recovered. In addition, adjustment of the specific gravity of molten salt is not necessary; and, by selecting a low-temperature molten salt in which tungsten can be treated in the solid state, a simple apparatus configuration can be employed. Moreover, the operation pattern can also be simplified. As a result, the steps can be performed efficiently at low cost.

[0225] Alternatively, as described above, tungsten can be smelted on the basis of an idea that is totally contrary to the idea of depositing or alloying tungsten on the cathode.

[0226] That is, a method for producing a metal according to this embodiment is a method for producing tungsten by molten salt electrolysis from a treatment object containing tungsten, wherein a cathode and an anode that is formed of an anode material containing the treatment object are disposed in a molten salt, and the potential at the anode is controlled so that a metal element corresponding to the potential value is dissolved in the molten salt from the treatment object and tungsten is left in the anode.

[0227] In this method, the anode material containing the treatment object is used as the anode and metal elements other than tungsten, that is, only metal elements serving as impurities are dissolved in the molten salt, so that tungsten is left in the anode. In this case, by also controlling the potential at the anode, such a phenomenon can be caused in which tungsten as the smelting target is left in the anode and impurity elements are dissolved in the molten salt. As a result, smelted tungsten is provided in the anode.

[0228] In this method, the molten salt is also preferably selected such that, in the step of dissolving, in the molten salt, a metal element from the treatment object, the difference between the standard electrode potential of a simple substance or alloy of tungsten and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, tungsten can be sufficiently separated from the other metal and tungsten alone can be left in the anode. The difference between the standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0229] The value of the potential controlled at the anode can be calculated by Nernst equation as described above.

[0230] In a method for producing tungsten by molten salt electrolysis according to this embodiment, the treatment object containing tungsten is preferably, for example, a metal material containing tungsten. Examples of the metal material containing tungsten include tungsten heaters.

[0231] This embodiment is also suitably applicable to cases where the treatment object is a metal material containing tungsten and a transition metal. Such a transition metal is not particularly limited and may be any element among from group 3 (group IIIA) to group 11 (group IB) of the periodic table. Examples of the metal material containing tungsten and a transition metal include cemented carbide.

[0232] The treatment object may be, for example, cemented carbide products. Herein, cemented carbide products collectively denote products including cemented carbide materials, such as cutting tools, jigs, dies, and molds including cemented carbide materials.

[0233] The molten salt can be selected from chloride molten salts and fluoride molten salts. A molten salt mixture containing a chloride molten salt and a fluoride molten salt may be used.

[0234] Examples of chloride molten salts include KCl, NaCl, CaCl₂, LiCl, RbCl, CsCl, SrCl₂, BaCl₂, and MgCl₂. Examples of fluoride molten salts include LiF, NaF, KF, RbF, CsF, MgF₂, CaF₂, SrF₂, and BaF₂. Chloride molten salts are preferably used in view of efficiency; in particular, KCl, NaCl, and CaCl₂ are preferably used because they are inexpensive and easily available.

[0235] Among such molten salts, a plurality of molten salts can be combined and used as a molten salt having a desirable composition. For example, a molten salt having a composition such as KCl—CaCl₂, LiCl—KCl, or NaCl—KCl may be used.

[0236] In a method for producing tungsten by molten salt electrolysis according to this embodiment, the following apparatuses can be preferably used. That is, an apparatus used for a method for producing tungsten by molten salt electrolysis according to this embodiment includes a container containing a molten salt; a cathode immersed in the molten salt contained within the container; and an anode that is immersed in the molten salt contained within the container and that contains a conductive treatment object containing tungsten, wherein the molten salt is movable into and out of the anode, the apparatus further includes a control unit configured to control the potential of the cathode and the anode to a predetermined value, and the value of the potential is changeable in the control unit. An apparatus used for a method for producing tungsten by molten salt electrolysis according to this embodiment includes a container containing a molten salt containing dissolved tungsten; and a cathode and an anode that are immersed in the molten salt contained within the container, wherein the apparatus includes a control unit configured to control the potential of the cathode and the anode to a predetermined value, and the value of the potential is changeable in the control unit.

[0237] The apparatuses for this embodiment will be described with reference to FIGS. 18 and 19. An apparatus illustrated in FIG. 18 includes a container 1 containing a molten salt, a molten salt 2 contained within the container 1, a basket 4 containing a treatment object 3 containing tungsten, an electrode 6, a heater 10 for heating the molten salt 2, and a control unit 9 electrically connected to the basket 4 and the electrode 6 via conductive wires 5.

[0238] The control unit 9 is configured to control the potential of one electrode (anode) that is the basket 4 and the other electrode (cathode) that is the electrode 6, to a predetermined value. In the control unit 9, the value to which the potential is controlled is changeable. The heater 10 is disposed so as to circularly surround the container 1. The electrode 6 may be formed of a desired material, for example, carbon. The container 1 may have a bottom surface that has a circular shape or a polygonal shape. The basket 4 may be the above-described basket.

[0239] The potential of the basket 4 and the electrode 6 is controlled by the control unit 9 to a predetermined potential value. As a result, tungsten is dissolved in the molten salt 2 from the treatment object 3.

[0240] After tungsten is sufficiently dissolved from the treatment object 3, the basket 4 and the electrode 6 are removed and another electrode 7 (cathode) and another electrode 8 (anode) are placed in the molten salt 2. These electrodes 7 and 8 are connected to the control unit 9 via conductive wires 5. The control unit 9 is used to control the potential of the electrodes 7 and 8 to a predetermined value. At this time, the potential is controlled such that the potential at the electrode 7 is the deposition potential of tungsten. As a result, tungsten dissolved in the molten salt 2 is deposited on the surface of the electrode 7 (cathode). The electrodes 7 and 8 may be formed of a material such as glassy carbon (C).

[0241] The heating temperature for the molten salt 2 with the heater 10 may be, for example, 800° C. in both of the treatments using the apparatuses illustrated in FIGS. 18 and 19. In this way, tungsten can be deposited as a simple substance on the surface of the electrode 7.

[0242] The potential of the electrodes 7 and 8 may be controlled such that an alloy of tungsten and the cathode material is deposited on the surface of the electrode 7 (cathode). In this

case, the above-described dissolution step and deposition step may be performed with the alloyed electrode 7. That is, the apparatus illustrated in FIG. 18 is newly prepared and the electrode 7 alloyed with tungsten is used instead of the above-described treatment object 3.

[0243] In the case where the method for producing tungsten of this embodiment is performed with the apparatuses illustrated in FIGS. 18 and 19, for example, the method may be performed in the following manner.

[0244] Cemented carbide cutting tools (9 kg) are first prepared as the treatment object 3 and KCl—NaCl is prepared as the molten salt 2. For example, the cemented carbide cutting tools may contain 90 wt % of tungsten carbide (WC) and 10 wt % of cobalt (Co). The cemented carbide cutting tools are ground and placed within the basket 4. From the viewpoint of enhancement of the treatment efficiency, the size of the cemented carbide cutting tools serving as the treatment object 3 is preferably minimized by grinding. For example, the cemented carbide cutting tools are ground into particles having a maximum particle size of 5 mm or less, preferably 3 mm or less, more preferably 1 mm or less. The amount of the molten salt 2 is about 16 liters (mass: 25 kg).

[0245] The above-described dissolution step may be performed with a carbon electrode serving as the electrode 6. Subsequently, the deposition step may be performed with electrodes formed of glassy carbon and serving as the electrodes 7 and 8.

[0246] As has been described, tungsten can be recovered from cemented carbide cutting tools serving as the treatment object 3. According to the method for producing tungsten by molten salt electrolysis of this embodiment, the apparatus configuration can be simplified and the treatment time can also be decreased, compared with the existing wet separation method and the like. Thus, the cost incurred can be reduced. In addition, by appropriately setting a potential at an electrode, tungsten can be deposited as a simple substance on the electrode surface and hence high purity tungsten can be obtained. The potentials for depositing tungsten and a tungsten alloy can be determined by the above-described calculation.

Third Embodiment

[0247] A method for producing lithium by molten salt electrolysis according to this embodiment is a method for producing lithium by molten salt electrolysis from a treatment object containing lithium, the method including a step of dissolving, in a molten salt, lithium from the treatment object, and a step of depositing lithium present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing dissolved lithium, by controlling a potential of the electrode members to a predetermined value.

[0248] That is, the lithium production method of this embodiment includes a process of dissolving, in a molten salt, lithium contained in the treatment object, and a step of depositing lithium on one of electrodes (cathode) from the molten salt containing dissolved lithium by molten salt electrolysis. A feature of this embodiment is that, by controlling the potential of the electrodes in the step of dissolving lithium, lithium is selectively dissolved from the treatment object; and, by controlling the potential of the electrodes to a predetermined value in the step of depositing lithium, lithium is selectively deposited on the cathode from the molten salt to thereby provide high purity lithium.

[0249] The step of dissolving, in a molten salt, lithium contained in a treatment object will be first described.

[0250] A procedure for dissolving, in a molten salt, lithium contained in a treatment object is, for example, a chemical procedure for dissolution. Specifically, a treatment object is ground into particles or powder, mixed with a salt, and heated. As a result, lithium contained in the treatment object can be dissolved in the molten salt. Alternatively, a treatment object may be placed in a molten salt and dissolved.

[0251] Another procedure is an electrochemical procedure. Specifically, an anode formed of an anode material containing a treatment object is placed in a molten salt and the value of the potential at the treatment object placed as the anode is controlled to selectively dissolve lithium contained in the treatment object. Molten salt electrolysis is characterized in that different elements are dissolved at different potentials. Accordingly, in this way, by using a treatment object as an anode and controlling the potential during dissolution, lithium can be selectively dissolved in a molten salt to separate lithium from the other metals.

[0252] In this step, the entire treatment object may be dissolved, or a lithium-containing portion of the treatment object or lithium alone may be dissolved. Non-lithium metals contained in the treatment object may also be dissolved; however, if possible, the potential value is preferably controlled so that lithium alone is dissolved. That is, in the step of dissolving lithium in a molten salt, the potential of the anode and the cathode is preferably controlled to a predetermined value so that lithium is selectively dissolved in the molten salt. As a result, entry of impurities in the subsequent deposition step can be reduced.

[0253] For this purpose, the molten salt is preferably selected such that, in the step of dissolving, in the molten salt, lithium from the treatment object, the difference between the standard electrode potential of a simple substance or alloy of lithium and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, lithium that is dissolved in the molten salt can be sufficiently separated from the metal element that is left in the anode. The difference between the standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0254] The value of the potential controlled at the anode can be calculated by Nernst equation described below.

[0255] The cathode used in the dissolution step is formed of carbon or a material that tends to form an alloy with an alkali metal such as Li or Na constituting cations in the molten salt. For example, aluminum (Al), zinc (Zn), gallium (Ga), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), lead (Pb), or bismuth (Bi) may be used.

[0256] When the treatment object containing lithium is used as an anode, for example, the treatment object contained within a conductive basket (anode material) formed of metal or the like may be disposed in the molten salt. An opening may be formed in an upper portion of the basket so that the treatment object can be inserted through the opening into the basket; and a large number of holes may be formed in the side and bottom walls of the basket so that the molten salt can flow into the basket. The basket may be constituted by a desired material such as a mesh member knitted from metal wires or a sheet member that is a sheet-shaped metal plate having a large number of holes. In particular, it is effective that the material is formed of C, Pt, Mo, or the like.

[0257] In the cases where the object is an oxide or the like and has a high electric resistance, the contact area between the object and the conductive material is preferably increased. The object is effectively used as an electrode by, for example, wrapping the object with a metal mesh member or filling the object into spaces within a metal porous member.

[0258] The cathode and an anode formed of an anode material containing the treatment object (for example, a metal basket containing the treatment object) are disposed in the molten salt; a control unit configured to control the potential of the electrodes from the outside to a predetermined value is connected; and the potential is controlled as described above. As a result, lithium can be dissolved in the molten salt from the treatment object.

[0259] In the subsequent deposition step, molten salt electrolysis is performed with a pair of electrode members disposed in the molten salt containing dissolved lithium so that lithium is deposited on one of the electrode members (cathode). In this case, by controlling the potential value in the molten salt electrolysis, lithium can be selectively deposited as metal or alloy on the cathode.

[0260] As in the dissolution step, in this deposition step, lithium is separated from other metals by utilizing the following characteristics: in molten salt electrolysis, different elements are deposited at different potentials as metal or alloy on the cathode. Thus, even when metals other than lithium are contained in the molten salt, by controlling the potential, lithium alone can be deposited on the cathode. As a result, high purity lithium can be obtained.

[0261] In deposition of lithium, when the difference between the dissolution-deposition potential of lithium and the dissolution-deposition potential of another metal contained in the molten salt is so small that lithium is difficult to separate from the metal, the cathode material may be selected and the potential may be controlled such that an alloy of the cathode material and lithium is deposited. As a result, lithium in the molten salt can be separated as a lithium alloy from the other impurity metal; and, after that, a dissolution step and a deposition step in another molten salt are performed with the cathode material alloyed with lithium to thereby provide high purity lithium.

[0262] The electrode members used in the deposition step may be formed of, for example, nickel (Ni), molybdenum (Mo), or glassy carbon (C).

[0263] In this embodiment, the above-described two steps are used to separate and recover lithium from a treatment object.

[0264] In this embodiment, since a molten salt is used, the system needs to be heated such that the temperature of the system in the steps is equal to or more than the melting point of the molten salt.

[0265] A feature of the two steps is use of a molten salt as the electrolytic solution. Thus, the characteristics of molten salt electrolysis in which different molten salts have different dissolution-deposition potentials for elements are utilized; and the steps can be designed by selecting a molten salt such that the dissolution-deposition potential of lithium and the dissolution-deposition potential of a non-lithium impurity metal are sufficiently different values that allow easy performance of the steps.

[0266] Specifically, the molten salt is preferably selected such that, in the step of depositing or alloying lithium, the difference between the standard electrode potential of a simple substance or alloy of lithium and the standard elec-

trode potential of a simple substance or alloy of another impurity metal in the molten salt is 0.05 V or more. The difference between the standard electrode potential of a simple substance or alloy of lithium and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0267] In this way, in the step of depositing or alloying lithium, the potential of the electrode members is preferably controlled to a predetermined value so that the lithium in the molten salt is selectively deposited or alloyed.

[0268] The deposition potential of lithium to be deposited on the cathode can be determined by electrochemical calculation. Specifically, the calculation is performed with Nernst equation.

[0269] For example, the potential at which a simple substance of Li is deposited from lithium ions (Li^+) can be determined with the following equation.

$$E_{\text{Li}} = E_{\text{Li}}^0 + RT/3F \cdot \ln(a_{\text{Li}(T)}/a_{\text{Li}(O)}) \quad \text{Equation (1)}$$

[0270] In Eq. (1), E_{Li}^0 represents the standard potential, R represents the gas constant, T represents absolute temperature, F represents the Faraday constant, $a_{\text{Li}(T)}$ represents the activity of Li ions, and $a_{\text{Li}(O)}$ represents the activity of Li simple substance.

[0271] When Eq. (1) is rewritten in view of activity coefficient $\gamma_{\text{Li}(T)}$, since $a_{\text{Li}(O)}=1$, the following equations are provided.

$$\begin{aligned} E_{\text{Li}} &= E_{\text{Li}}^0 + RT/3F \cdot \ln a_{\text{Li}(T)} \\ &= E_{\text{Li}}^0 + RT/3F \cdot \ln(\gamma_{\text{Li}(T)} \cdot C_{\text{Li}(T)}) \end{aligned} \quad \text{Equation (2)}$$

$$E_{\text{Li}} = E_{\text{Li}}^{\circ'} + RT/3F \cdot \ln C_{\text{Li}(T)} \quad \text{Equation (3)}$$

[0272] In Eq. (3), $C_{\text{Li}(T)}$ represents the concentration of Li ions, and $E_{\text{Li}}^{\circ'}$ represents formal electrode potential (here, equal to $E_{\text{Li}}^0 + RT/3F \cdot \ln \gamma_{\text{Li}(T)}$).

[0273] Similarly, in the case where LiM alloy (M represents an alloyed metal) is deposited on the electrode surface, the potential (deposition potential: E_{LiM}) can be determined with the following equation.

$$E_{\text{LiM}} = E_{\text{LiM}}^{\circ'} + RT/3F \cdot \ln C_{\text{Li}(T)} \quad \text{Equation (4)}$$

[0274] In Eq. (4), $E_{\text{LiM}}^{\circ'}$ represents formal electrode potential (here, equal to $E_{\text{LiM}}^0 + RT/3F \cdot \ln \gamma_{\text{Li}(T)}$).

[0275] Similarly, by using the above-described equations, deposition potentials of all deposits corresponding to different molten salts can be determined. In the step of depositing or alloying lithium on the cathode, in view of the deposition potential values of lithium simple substance and lithium alloy, the molten salt and the cathode material are selected such that a sufficiently high potential difference is achieved with respect to the deposition potential of a simple substance or alloy of another metal, and whether lithium is deposited or a lithium alloy is deposited is decided.

[0276] Voltage and current during operation vary depending on the size or positional relationship of electrodes. Accordingly, reference values of voltage and current are determined on the basis of conditions and subsequently voltage and current are determined in each step on the basis of the potential value and order determined by the above-described method.

[0277] As described above, in a method for producing lithium by molten salt electrolysis according to this embodiment, the potential value is controlled to thereby electrochemically dissolve and deposit lithium. Accordingly, the steps can be simplified, compared with, for example, the existing wet treatment involving repeating of steps of dissolution and extraction using acid or the like; and the particular element can be selectively separated and recovered. In addition, adjustment of the specific gravity of molten salt is not necessary; and, by selecting a low-temperature molten salt in which lithium can be treated in the solid state, a simple apparatus configuration can be employed. Moreover, the operation pattern can also be simplified. As a result, the steps can be performed efficiently at low cost.

[0278] In a method for producing lithium by molten salt electrolysis according to this embodiment, the treatment object is not limited as long as it is a material containing lithium. Preferred examples of the treatment object include negative electrode materials of lithium primary batteries and positive electrode materials of lithium-ion secondary batteries.

[0279] Examples of positive electrode active materials of positive electrode materials of lithium-ion secondary batteries include lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2), lithium nickel cobalt oxide ($\text{LiCo}_{0.3}\text{Ni}_{0.7}\text{O}_2$), lithium manganese oxide (LiMn_2O_4), lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), lithium manganese oxide compounds ($\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$); M=Cr, Co, Ni), and lithium acid.

[0280] The molten salt can be selected from chloride molten salts and fluoride molten salts. A molten salt mixture containing a chloride molten salt and a fluoride molten salt may be used.

[0281] Examples of chloride molten salts include KCl, NaCl, CaCl_2 , LiCl, RbCl, CsCl, SrCl_2 , BaCl_2 , and MgCl_2 . Examples of fluoride molten salts include LiF, NaF, KF, RbF, CsF, MgF_2 , CaF_2 , SrF_2 , and BaF_2 . Chloride molten salts are preferably used in view of efficiency; in particular, KCl, NaCl, and CaCl_2 are preferably used because they are inexpensive and easily available.

[0282] Among such molten salts, a plurality of molten salts can be combined and used as a molten salt having a desirable composition. For example, a molten salt having a composition such as KCl— CaCl_2 , LiCl—KCl, or NaCl—KCl may be used.

[0283] In a method for producing lithium by molten salt electrolysis according to this embodiment, the following apparatuses can be preferably used. That is, an apparatus used for a method for producing lithium by molten salt electrolysis according to this embodiment includes a container containing a molten salt; a cathode immersed in the molten salt contained within the container; and an anode that is immersed in the molten salt contained within the container and that contains a conductive treatment object containing lithium, wherein the molten salt is movable into and out of the anode, the apparatus further includes a control unit configured to control the potential of the cathode and the anode to a predetermined value, and the value of the potential is changeable in the control unit.

[0284] An apparatus used for a method for producing lithium by molten salt electrolysis according to this embodiment includes a container containing a molten salt containing dissolved lithium; and a cathode and an anode that are immersed in the molten salt contained within the container, wherein the apparatus includes a control unit configured to

control the potential of the cathode and the anode to a predetermined value, and the value of the potential is changeable in the control unit.

[0285] The apparatuses for this embodiment will be described with reference to FIGS. 18 and 19. An apparatus illustrated in FIG. 18 includes a container 1 containing a molten salt, a molten salt 2 contained within the container 1, a basket 4 containing a treatment object 3 containing lithium, an electrode 6, a heater 10 for heating the molten salt 2, and a control unit 9 electrically connected to the basket 4 and the electrode 6 via conductive wires 5.

[0286] The control unit 9 is configured to control the potential of one electrode (anode) that is the basket 4 and the other electrode (cathode) that is the electrode 6, to a predetermined value. In the control unit 9, the value to which the potential is controlled is changeable. The heater 10 is disposed so as to circularly surround the container 1. The electrode 6 may be formed of a desired material, for example, aluminum. The container 1 may have a bottom surface that has a circular shape or a polygonal shape. The basket 4 may be the above-described basket.

[0287] The potential of the basket 4 and the electrode 6 is controlled by the control unit 9 to a predetermined potential value. As a result, lithium is dissolved in the molten salt 2 from the treatment object 3.

[0288] After lithium is sufficiently dissolved from the treatment object 3, the basket 4 and the electrode 6 are removed and, as illustrated in FIG. 19, another electrode 7 (cathode) and another electrode 8 (anode) are placed in the molten salt 2. These electrodes 7 and 8 are connected to the control unit 9 via conductive wires 5. The control unit 9 is used to control the potential of the electrodes 7 and 8 to a predetermined value. At this time, the potential is controlled such that the potential at the electrode 7 is the deposition potential of lithium. As a result, lithium dissolved in the molten salt 2 is deposited on the surface of the electrode 7 (cathode). The electrodes 7 and 8 may be formed of a material such as glassy carbon (C).

[0289] The heating temperature for the molten salt 2 with the heater 10 may be, for example, 800° C. in both of the treatments using the apparatuses illustrated in FIGS. 18 and 19. In this way, lithium can be deposited as a simple substance on the surface of the electrode 7.

[0290] The potential of the electrodes 7 and 8 may be controlled to a value such that an alloy of lithium and the cathode material is deposited on the surface of the electrode 7 (cathode). In this case, the above-described dissolution step and deposition step may be performed with the alloyed electrode 7. That is, the apparatus illustrated in FIG. 18 is newly prepared and the electrode 7 alloyed with lithium is used instead of the above-described treatment object 3.

[0291] In the case where the method for producing lithium of this embodiment is performed with the apparatuses illustrated in FIGS. 18 and 19, for example, the method may be performed in the following manner.

[0292] A lithium-containing positive electrode material of lithium-ion batteries is first prepared as the treatment object 3 and KCl—NaCl is prepared as the molten salt 2. For example, the positive electrode material is a powder containing lithium cobalt oxide (LiCoO₂) or lithium manganese oxide. The positive electrode material is ground and placed within the basket 4. From the viewpoint of enhancement of the treatment efficiency, the size of the positive electrode material serving as the treatment object 3 is preferably minimized by grinding.

For example, the positive electrode material is ground into particles having a maximum particle size of 5 mm or less, preferably 3 mm or less, more preferably 1 mm or less. The above-described dissolution step may be performed with a carbon electrode serving as the electrode 6. Subsequently, the deposition step may be performed with electrodes formed of glassy carbon and serving as the electrodes 7 and 8.

[0293] As has been described, lithium can be recovered from the positive electrode material serving as the treatment object 3.

[0294] According to the method for producing lithium by molten salt electrolysis of this embodiment, the apparatus configuration can be simplified and the treatment time can also be decreased, compared with the existing wet separation method and the like. Thus, the cost incurred can be reduced. In addition, by appropriately setting a potential value at an electrode, lithium can be deposited as a simple substance on the electrode surface and hence high purity lithium can be obtained.

Fourth Embodiment

[0295] This embodiment is a method for producing a metal by molten salt electrolysis, the method including a step of dissolving, in a molten salt, a metal element contained in a treatment object containing two or more metal elements; and a step of depositing or alloying a particular metal present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing the dissolved metal element, by controlling a potential of the electrode members to a predetermined value.

[0296] Roughly speaking, this embodiment includes a process of dissolving, in a molten salt, a particular metal contained in the treatment object, and a process of depositing the particular metal on one of electrodes (cathode) from the molten salt containing the dissolved particular metal by molten salt electrolysis. A feature of this embodiment is that, by controlling the potential of the electrodes to a predetermined value, the particular metal is selectively deposited from the treatment object to provide the particular metal at high purity.

[0297] The process of dissolving, in a molten salt, a particular metal contained in a treatment object will be first described.

[0298] A procedure for dissolving, in a molten salt, a particular metal contained in a treatment object is, for example, a chemical procedure for dissolution. Specifically, a treatment object is ground into particles or powder, mixed with a salt, and heated. As a result, the particular metal contained in the treatment object can be dissolved in the molten salt. Alternatively, the treatment object may be placed in a molten salt and dissolved.

[0299] Another procedure is an electrochemical procedure. Specifically, a cathode and an anode that is formed of an anode material containing the treatment object are disposed in the molten salt; and the potential at the anode is controlled to a predetermined value so that a metal element corresponding to the controlled potential value is dissolved in the molten salt from the treatment object. Molten salt electrolysis is characterized in that different elements are dissolved at different potentials; and such characteristics are utilized to thereby separate a particular metal from other metals. In this way, by using a treatment object as an anode and controlling the potential during dissolution, a particular metal can be selectively dissolved in a molten salt.

[0300] In this step, all the metals contained in the treatment object may be dissolved. Alternatively, a particular metal and another metal contained in the treatment object may be dissolved. Preferably, only a particular metal contained in the treatment object is dissolved. Conditions under which a particular metal and another metal contained in the treatment object are dissolved may be employed; however, if possible, the potential is preferably controlled so that the particular metal alone is dissolved. That is, in the step of dissolving a particular metal in a molten salt, the potential at the anode is preferably controlled to a predetermined value so that the particular metal element is selectively dissolved in the molten salt. As a result, entry of impurities in the subsequent deposition step can be reduced.

[0301] For this purpose, the molten salt is preferably selected such that, in the step of dissolving, in the molten salt, a particular metal from the treatment object, the difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, the particular metal that is dissolved in the molten salt can be sufficiently separated from the other metal element that is left in the anode. The difference between the standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0302] The value of the potential controlled at the anode can be calculated by Nernst equation described below.

[0303] When one or more target particular metals are contained in the treatment object, in the dissolution step, one or more particular metals are dissolved in the molten salt.

[0304] When the treatment object contains only one particular metal, as described above, this particular metal is dissolved and then the deposition step is performed to provide the target metal. When the treatment object contains two or more target particular metals, only one of the metals may be dissolved in a molten salt; a deposition step may be subsequently performed; and, after that, another dissolution step may be performed so that the remainder of the particular metals is dissolved in the molten salt. In this case, the treatment object having been used in the initial dissolution step may be moved from the molten salt used in this dissolution step to another molten salt and subjected to a dissolution step to thereby dissolve the remainder of the particular metals.

[0305] When two or more particular metals contained in the treatment object are dissolved in a molten salt, the subsequent deposition step may be performed such that the particular metals present in the molten salt are deposited or alloyed one by one on electrode materials, so that desired particular metals can be produced. In this case, after one particular metal is deposited or alloyed on an electrode material, this electrode material may be replaced by another electrode material and another particular metal dissolved in the molten salt may be deposited or alloyed on this electrode material.

[0306] The cathode used in the dissolution step is formed of carbon or a material that tends to form an alloy with an alkali metal such as Li or Na constituting cations in the molten salt. For example, aluminum (Al), zinc (Zn), gallium (Ga), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), lead (Pb), or bismuth (Bi) may be used.

[0307] When the treatment object containing a particular metal is used as an anode, for example, the treatment object contained within a conductive basket (anode material) formed of metal or the like may be disposed in the molten salt.

An opening may be formed in an upper portion of the basket so that the treatment object can be inserted through the opening into the basket; and a large number of holes may be formed in the side and bottom walls of the basket so that the molten salt can flow into the basket. The basket may be constituted by a desired material such as a mesh member knitted from metal wires or a sheet member that is a sheet-shaped metal plate having a large number of holes. In particular, it is effective that the material is formed of C, Pt, Mo, or the like.

[0308] In the cases where the object is an oxide or the like and has a high electric resistance, the contact area between the object and the conductive material is preferably increased. The object is effectively used as an electrode by, for example, wrapping the object with a metal mesh member or filling the object into spaces within a metal porous member.

[0309] The cathode and an anode formed of an anode material containing the treatment object (for example, a metal basket containing the treatment object) are disposed in the molten salt; and the potential at the anode is controlled to a predetermined value. As a result, a particular metal can be dissolved in the molten salt from the treatment object.

[0310] In the subsequent deposition process, molten salt electrolysis is performed with a pair of electrode members disposed in the molten salt containing the dissolved particular metal so that the particular metal is deposited on one of the electrode members (cathode). In this case, by controlling the potential value in the molten salt electrolysis, the particular metal can be selectively deposited as metal or alloy on the cathode.

[0311] As in the dissolution process, in this deposition process, the particular metal is separated from other metals by utilizing the following characteristics: in molten salt electrolysis, different elements are deposited at different potentials as metal or alloy on the cathode. Thus, even when metals other than the particular metal are contained in the molten salt, by controlling the potential of the electrode members to a predetermined value, the particular metal element can be selectively deposited or alloyed on the cathode. That is, the particular metal at high purity can be obtained.

[0312] In deposition of a particular metal, when the difference between the dissolution-deposition potential of the particular metal and the dissolution-deposition potential of another metal contained in the molten salt is so small that the particular metal is difficult to separate from the other metal, the cathode material may be selected and the potential may be controlled such that an alloy of the cathode material and the particular metal is deposited. As a result, the particular metal in the molten salt can be deposited as an alloy and separated from the other impurity metal; and, after that, for example, a dissolution step and a deposition step in another molten salt can be performed with the cathode material alloyed with the particular metal to thereby provide the particular metal at high purity.

[0313] The electrode members used in the deposition step may be formed of, for example, nickel (Ni), molybdenum (Mo), or glassy carbon (C).

[0314] In this embodiment, the above-described two processes are used to separate and extract a particular metal from a treatment object. In this embodiment, since a molten salt is used, the system needs to be heated such that the temperature of the system in the processes is equal to or more than the melting point of the molten salt.

[0315] Alternatively, as described below, smelting can be performed on the basis of an idea that is totally contrary to that of the processes. That is, a treatment object is used as the anode and only metal elements serving as impurities are dissolved in a molten salt. In this case, by also controlling the potential at the anode, such a phenomenon is caused in which a particular metal is left in the anode and impurity elements are dissolved. As a result, the particular metal is provided in the anode.

[0316] A feature of the two processes is use of a molten salt. Thus, the characteristics of molten salt electrolysis in which different molten salts have different dissolution-deposition potentials for elements are utilized; and the processes can be designed by selecting a molten salt such that the dissolution-deposition potential of a particular metal and the dissolution-deposition potential of an impurity metal other than the particular metal are sufficiently different values that allow easy performance of the processes.

[0317] Specifically, the molten salt is preferably selected such that, in the step of depositing or alloying a particular metal, the difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

[0318] The difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard electrode potential of a simple substance or alloy of another metal in the molten salt is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0319] In this way, in the step of depositing or alloying a particular metal, the potential of the electrode members is preferably controlled to a predetermined value so that the particular metal element in the molten salt is selectively deposited or alloyed.

[0320] The deposition potential of a particular metal to be deposited on the cathode can be determined by electrochemical calculation. Specifically, the calculation is performed with Nernst equation.

[0321] For example, the potential at which a simple substance of molybdenum (Mo) serving as the particular metal is deposited from a molten salt in which molybdenum is dissolved into tetravalent Mo ions (hereafter represented by Mo(IV)) can be determined with the following equation.

$$E_{Mo} = E_{Mo}^0 + RT/3F \cdot \ln(a_{Mo(IV)}/a_{Mo(0)}) \quad \text{Equation (1)}$$

[0322] In Eq. (1), E_{Mo}^0 represents the standard potential, R represents the gas constant, T represents absolute temperature, F represents the Faraday constant, $a_{Mo(IV)}$ represents the activity of Mo(IV) ions, and $a_{Mo(0)}$ represents the activity of Mo simple substance.

[0323] When Eq. (1) is rewritten in view of activity coefficient $\gamma_{Mo(IV)}$, since $a_{Mo(0)}=1$, the following equations are provided.

$$\begin{aligned} E_{Mo} &= E_{Mo}^0 + RT/3F \cdot \ln a_{Mo(IV)} \\ &= E_{Mo}^0 + RT/3F \cdot \ln(\gamma_{Mo(IV)} \cdot C_{Mo(IV)}) \end{aligned} \quad \text{Equation (2)}$$

$$E_{Mo} = E_{Mo}^0 + RT/3F \cdot \ln C_{Mo(IV)} \quad \text{Equation (3)}$$

[0324] In Eq. (3), $C_{Mo(IV)}$ represents the concentration of tetravalent Mo ions, and E_{Mo}^0 represents formal electrode potential (here, equal to $E_{Mo}^0 + RT/3F \cdot \ln \gamma_{Mo(IV)}$).

[0325] Similarly, by using the above-described equations, deposition potentials of all deposits corresponding to different molten salts can be determined.

[0326] Similar calculations can also be performed in the case of depositing molybdenum as an alloy.

[0327] In the process of depositing or alloying molybdenum on the cathode, in view of the deposition potential values of molybdenum simple substance and molybdenum alloy, the molten salt and the cathode material are selected such that a sufficiently high potential difference is achieved with respect to the deposition potential of a simple substance or alloy of another metal, and whether molybdenum simple substance is deposited or a molybdenum alloy is deposited is decided.

[0328] Voltage and current during operation vary depending on the size or positional relationship of electrodes. Accordingly, reference values of voltage and current are determined on the basis of conditions and subsequently voltage and current are determined in each step on the basis of the potential value and order determined by the above-described method.

[0329] As described above, in a method for producing a particular metal by molten salt electrolysis according to this embodiment, the potential value is controlled to thereby electrochemically dissolve and deposit the particular metal. Accordingly, the steps can be simplified, compared with, for example, the existing wet treatment involving repeating of processes of dissolution and extraction using acid or the like; and a particular metal can be selectively separated and recovered. In addition, adjustment of the specific gravity of molten salt is not necessary; and, by selecting a low-temperature molten salt in which the particular metal can be treated in the solid state, a simple apparatus configuration can be employed. Moreover, the operation pattern can also be simplified. As a result, the steps can be performed efficiently at low cost.

[0330] Alternatively, as described above, a particular metal can be smelted on the basis of an idea that is totally contrary to the idea of depositing or alloying a particular metal on the cathode.

[0331] That is, a method for producing a metal by molten salt electrolysis according to this embodiment is a method for producing a particular metal by molten salt electrolysis from a treatment object containing two or more metal elements, wherein a cathode and an anode that is formed of an anode material containing the treatment object are disposed in a molten salt, and the potential at the anode is controlled to a predetermined value so that a metal element corresponding to the potential is dissolved in the molten salt from the treatment object and the particular metal is left in the anode.

[0332] In this production method, the anode material containing the treatment object is used as the anode and metal elements other than the particular metal, that is, only metal elements serving as impurities are dissolved in the molten salt, so that the particular metal is left in the anode. In this case, by also controlling the potential at the anode, such a phenomenon can be caused in which the particular metal as the smelting target is left in the anode and impurity elements are dissolved in the molten salt. As a result, the smelted particular metal is provided in the anode.

[0333] In this method, the molten salt is also preferably selected such that, in the step of dissolving, in the molten salt, a metal element from the treatment object, the difference between the standard electrode potential of a simple substance or alloy of the particular metal and the standard elec-

trode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more. As a result, the particular metal can be sufficiently separated from the other metal and the particular metal alone can be left in the anode. The difference between the standard electrode potentials is more preferably 0.1 V or more, still more preferably 0.25 V or more.

[0334] The value of the potential controlled at the anode can be calculated by Nernst equation as described above.

[0335] In a method for producing a metal by molten salt electrolysis according to this embodiment, the treatment object containing two or more metal elements is not limited at all as long as it is a metal material containing a target particular metal. For example, Mn, Co, Sb, and the like can be obtained from collected battery materials; Nb and the like can be obtained from metal superconducting materials; Bi, Sr, and the like can be obtained from oxide superconducting materials; V can be obtained from ferrovanadium; Mo and the like can be obtained from Mo—Cu heat spreaders; and Ge and the like can be obtained from optical fiber materials.

[0336] This embodiment is also suitably applicable to cases where the treatment object is a metal material containing a transition metal or a rare earth metal. Such a transition metal is not particularly limited and may be any element among from group 3 (group IIIA) to group 11 (group IB) of the periodic table. This embodiment is also suitably applicable to cases where the treatment object contains, as a transition metal, one or more metals selected from the group consisting of V, Nb, Mo, Ti, Ta, Zr, and Hf.

[0337] In addition, this embodiment is also suitably applicable to cases where the treatment object contains a metal that is one or both of Sr and Ba. Furthermore, this embodiment is also suitably applicable to cases where the treatment object contains one or more metals selected from the group consisting of Zn, Cd, Ga, In, Ge, Sn, Pb, Sb, and Bi.

[0338] In a method for producing a metal by molten salt electrolysis of this embodiment, by selecting a transition metal or a rare earth metal as the particular metal to be deposited or alloyed, the transition metal or the rare earth metal can be obtained. Such a transition metal is not particularly limited and may be any element among from group 3 (group IIIA) to group 11 (group IB) of the periodic table.

[0339] Similarly, by selecting the particular metal to be deposited or alloyed from V, Nb, Mo, Ti, Ta, Zr and Hf, or Sr and Ba, or Zn, Cd, Ga, In, Ge, Sn, Pb, Sb, and Bi, such metals can be obtained.

[0340] As described above, in the dissolution step, one or more of these metals contained in the treatment object can be dissolved in a molten salt and particular metals can be sequentially deposited or alloyed on electrode members from the molten salt.

[0341] The treatment object preferably has the form of particles or powder. When the treatment object is prepared so as to have the form of particles or powder, the surface area is increased and the treatment efficiency can be increased.

[0342] In addition, the treatment object prepared in the form of particles or powder can be compacted and used as the anode. In this case, between the particles, there are desirably spaces that the molten salt can easily enter.

[0343] The molten salt can be selected from chloride molten salts and fluoride molten salts. A molten salt mixture containing a chloride molten salt and a fluoride molten salt may be used.

[0344] Examples of chloride molten salts include KCl, NaCl, CaCl_2 , LiCl, RbCl, CsCl, SrCl_2 , BaCl_2 , and MgCl_2 . Examples of fluoride molten salts include LiF, NaF, KF, RbF, CsF, MgF_2 , CaF_2 , SrF_2 , and BaF_2 . Chloride molten salts are preferably used in view of efficiency; in particular, KCl, NaCl, and CaCl_2 are preferably used because they are inexpensive and easily available.

[0345] Among such molten salts, a plurality of molten salts can be combined and used as a molten salt having a desirable composition. For example, a molten salt having a composition such as KCl— CaCl_2 , LiCl—KCl, or NaCl—KCl may be used.

[0346] In a method for producing a metal by molten salt electrolysis according to this embodiment, the following apparatuses can be preferably used. That is, preferably, the apparatus includes a container containing a molten salt; a cathode immersed in the molten salt contained within the container; and an anode that is immersed in the molten salt contained within the container and that contains a conductive treatment object containing two or more metal elements, wherein the molten salt is movable into and out of the anode, the apparatus further includes a control unit configured to control the potential of the cathode and the anode to a predetermined value, and the value of the potential is changeable in the control unit. An apparatus used for a method for producing a metal by molten salt electrolysis according to this embodiment is preferably an apparatus that includes a container containing a molten salt containing a dissolved particular metal; and a cathode and an anode that are immersed in the molten salt contained within the container, wherein the apparatus includes a control unit configured to control the potential of the cathode and the anode to a predetermined value, and the value of the potential is changeable in the control unit.

[0347] The apparatuses will be described with reference to FIGS. 18 and 19. An apparatus illustrated in FIG. 18 includes a container 1 containing a molten salt, a molten salt 2 contained within the container 1, a basket 4 containing a treatment object 3 containing two or more metal elements, an electrode 6, a heater 10 for heating the molten salt 2, and a control unit 9 electrically connected to the basket 4 and the electrode 6 via conductive wires 5.

[0348] The control unit 9 is configured to control the potential of one electrode (anode) that is the basket 4 and the other electrode (cathode) that is the electrode 6, to a predetermined value. In the control unit 9, the value to which the potential is controlled is changeable. The heater 10 is disposed so as to circularly surround the container 1. The electrode 6 may be formed of a desired material, for example, carbon. The container 1 may have a bottom surface that has a circular shape or a polygonal shape. The basket 4 may be the above-described basket.

[0349] The potential of the basket 4 and the electrode 6 is controlled by the control unit 9 to a predetermined potential value. As a result, a particular metal is dissolved in the molten salt 2 from the treatment object 3.

[0350] After the particular metal is sufficiently dissolved from the treatment object 3, the basket 4 and the electrode 6 are removed and another electrode 7 (cathode) and another electrode 8 (anode) are placed in the molten salt 2. These electrodes 7 and 8 are connected to the control unit 9 via conductive wires 5. The control unit 9 is used to control the potential of the electrodes 7 and 8 to a predetermined value. At this time, the potential is controlled such that the potential at the electrode 7 is the deposition potential of the particular

metal. As a result, the particular metal dissolved in the molten salt **2** is deposited on the surface of the electrode **7** (cathode). The electrodes **7** and **8** may be formed of a material such as glassy carbon (C).

[0351] The heating temperature for the molten salt **2** with the heater **10** may be, for example, 800° C. in both of the treatments using the apparatuses illustrated in FIGS. **18** and **19**. In this way, the particular metal can be deposited as a simple substance on the surface of the electrode **7**.

[0352] The potential of the electrodes **7** and **8** may be controlled such that an alloy of the particular metal and the cathode material is deposited on the surface of the electrode **7** (cathode). In this case, the above-described dissolution step and deposition step may be performed with the alloyed electrode **7**. That is, the apparatus illustrated in FIG. **18** is newly prepared and the electrode **7** alloyed with the particular metal is used instead of the above-described treatment object **3**.

[0353] In the cases where the method for producing a metal of this embodiment is performed with the apparatuses illustrated in FIGS. **18** and **19**, for example, the method may be performed in the following manner. Hereinafter, examples relating to vanadium, molybdenum, strontium, and germanium will be described.

(Vanadium)

[0354] For example, the method for producing a metal of this embodiment is used to obtain vanadium. Ferrovandium (1 kg) is first prepared as the treatment object **3** and NaCl—KCl is prepared as the molten salt **2**. For example, the ferrovanadium contains 75 wt % of vanadium (V) and 25 wt % of iron (Fe). The ferrovanadium is ground and placed within the basket **4**. The amount of the molten salt **2** is about 15 liters.

[0355] The above-described dissolution step may be performed with a carbon electrode serving as the electrode **6**. Subsequently, the deposition step may be performed with electrodes formed of glassy carbon and serving as the electrodes **7** and **8**.

(Molybdenum)

[0356] The method for producing a metal of this embodiment is used to obtain molybdenum. Mo—Cu heat spreaders (1 kg) are first prepared as the treatment object **3** and LiCl—KCl is prepared as the molten salt **2**. For example, the Mo—Cu heat spreaders contain 50 wt % of molybdenum (Mo) and 50 wt % of copper (Cu). The heat spreaders are ground and placed within the basket **4**. The amount of the molten salt **2** is about 5 liters.

[0357] The above-described dissolution step may be performed with a carbon electrode serving as the electrode **6**. Subsequently, the deposition step may be performed with electrodes formed of glassy carbon and serving as the electrodes **7** and **8**.

(Strontium)

[0358] The method for producing a metal of this embodiment is used to obtain molybdenum. An oxide superconducting material (1 kg) is first prepared as the treatment object **3** and LiF—CaF₂ is prepared as the molten salt **2**. For example, the oxide superconducting material contains 17 wt % of strontium (Sr) and 8 wt % of calcium (Ca). The oxide superconducting material is ground and placed within the basket **4**. The amount of the molten salt **2** is about 4 liters.

[0359] The above-described dissolution step may be performed with a carbon electrode serving as the electrode **6**. Subsequently, the deposition step may be performed with electrodes formed of glassy carbon and serving as the electrodes **7** and **8**.

(Germanium)

[0360] The method for producing a metal of this embodiment is used to obtain germanium. An optical fiber material (1 kg) is first prepared as the treatment object **3** and LiF—CaF₂ is prepared as the molten salt **2**. For example, the optical fiber material contains 3 wt % of germanium (Ge). The optical fiber material is ground and placed within the basket **4**. The amount of the molten salt **2** is about 4 liters.

[0361] The above-described dissolution step may be performed with a carbon electrode serving as the electrode **6**. Subsequently, the deposition step may be performed with electrodes formed of glassy carbon and serving as the electrodes **7** and **8**.

[0362] As has been described, by using ferrovanadium, Mo—Cu heat spreaders, oxide superconducting material, and optical fiber material as the treatment object **3**, vanadium, molybdenum, strontium, and germanium can be obtained, respectively. From the viewpoint of enhancement of the treatment efficiency, the size of ferrovanadium, Mo—Cu heat spreaders, oxide superconducting material, and optical fiber material serving as the treatment object **3** is preferably minimized by grinding: for example, the treatment object **3** is preferably ground into particles having a maximum particle size of 5 mm or less, more preferably 3 mm or less, still more preferably 1 mm or less.

[0363] According to the method for producing a metal by molten salt electrolysis of this embodiment, the apparatus configuration can be simplified and the treatment time can also be decreased, compared with the existing recovery methods and the like. Thus, the cost incurred can be reduced. In addition, by appropriately setting a potential at an electrode, a particular metal can be deposited as a simple substance on the electrode surface and hence high purity metal can be obtained.

[0364] The potentials for depositing vanadium, a vanadium alloy, molybdenum, a molybdenum alloy, strontium, a strontium alloy, germanium, and a germanium alloy can be determined by the above-described calculation.

[0365] First to Fourth embodiments have been individually described so far. However, for example, in order to obtain tungsten, lithium, transition metals, and rare earth metals in Second to Fourth embodiments, methods in other embodiments may be entirely or partially employed.

EXAMPLES

First Embodiment

Example

[0366] Nd, Dy, and Pr were produced by molten salt electrolysis from an ore containing rare earth metals.

(Sample)

[0367] The ore serving as a treatment object was xenotime ore. The xenotime ore was ground with a crusher or a ball mill

so as to have a particle size of about 2 mm. The ground sample (xenotime ore) was wrapped with a molybdenum (Mo) mesh (50 mesh).

[0368] As illustrated in FIG. 14, the sample powder contained within the mesh was used as an anode (anode electrode).

(Details of Experiment)

[0369] A molten LiF—NaF—KF eutectic salt was employed as the molten salt. This salt was completely melted by heating at 700° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode electrode was formed of glassy carbon.

Dissolution Step:

[0370] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode was maintained at a predetermined potential. After about 4 hours lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Electrolysis Step:

[0371] After the dissolution step, a cathode electrode formed of Ni and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that Dy—Ni alloy was formed in the LiF—NaF—KF molten salt. After a predetermined time lapsed, the surface status of the cathode electrode was observed.

(Result)

Regarding Dissolution Step:

[0372] The anode current observed in the dissolution step varied with time as illustrated in FIG. 15.

[0373] In FIG. 15, the abscissa axis indicates time (unit: min), and the ordinate axis indicates the value of anode current (unit: mA). As illustrated in FIG. 15, the current value decreased with time. The change rate of current value with respect to time had the following tendency: the change rate was the highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0374] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of Nd and Dy in the molten salt was confirmed.

Regarding Electrolysis Step:

[0375] FIGS. 16 and 17 illustrate results of observation of a section of the surface layer of the cathode electrode with a scanning electron microscope (SEM). As illustrated in FIGS. 16 and 17, Dy—Ni alloy 32 was deposited on the surface of an electrode body part 31 constituting the cathode electrode and formed of Ni. This Dy—Ni alloy 32 was probably formed by the reaction between Dy present in the molten salt and Ni constituting the cathode electrode, and deposited on the surface of the cathode electrode. In this way, Dy contained in the xenotime ore can be separated and extracted as Dy—Ni alloy from the ore.

[0376] FIG. 16 illustrates a back-scattered electron image observed with the SEM. FIG. 17 illustrates the distribution of Dy atoms in the regions illustrated in FIG. 16 and subjected to X-ray analysis. As illustrated in FIG. 17, Dy was scarcely detected in a region 33 corresponding to the electrode body part 31; however, Dy was detected in a region 34 corresponding to the Dy—Ni alloy 32.

Second Embodiment

Example

[0377] Cemented carbide tools were used as the metal material containing tungsten and tungsten was produced by molten salt electrolysis.

(Sample)

[0378] The cemented carbide tools serving as a treatment object were cutting tools containing 90 wt % of tungsten carbide and 10 wt % of cobalt serving as a binder. The cutting tools were ground with a bead mill or an attritor so as to have a particle size of about 2 mm. The ground sample (cutting tools) was wrapped with a molybdenum (Mo) mesh (50 mesh). As illustrated in FIG. 14, the sample powder (treatment object) contained within the Mo mesh was used as an anode (anode electrode).

(Details of Experiment)

[0379] A molten NaCl—KCl eutectic salt was employed as the molten salt. This salt was completely melted by heating at 700° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode electrode was formed of glassy carbon.

Dissolution Step:

[0380] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode was maintained at a predetermined potential. After a predetermined time lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by ICP-AES.

Electrolysis Step:

[0381] After the dissolution step, a cathode electrode formed of glassy carbon and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that tungsten was deposited in the NaCl—KCl molten salt. After a predetermined time lapsed, the surface status of the cathode electrode was observed.

(Result)

Regarding Dissolution Step:

[0382] The anode current observed in the dissolution step varied with time as in First embodiment (example) (FIG. 15). In FIG. 15, the abscissa axis indicates time (unit: min), and the ordinate axis indicates the value of anode current (unit: mA). As illustrated in FIG. 15, the current value decreased with time. The change rate of current value with respect to time had the following tendency: the change rate was the

highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0383] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of tungsten in the molten salt was confirmed.

Regarding Electrolysis (Deposition) Step:

[0384] Observation of a section of the surface layer of the cathode electrode with a scanning electron microscope (SEM) revealed deposition of tungsten on the surface of an electrode body part constituting the cathode electrode and formed of glassy carbon.

[0385] In this way, high purity tungsten was obtained from the cemented carbide cutting tools containing tungsten.

Third Embodiment

Example

[0386] Commercially available lithium-ion secondary batteries were used as the treatment object containing lithium and lithium was produced by molten salt electrolysis.

(Sample)

[0387] Commercially available lithium-ion secondary batteries (the positive electrode was formed of lithium cobalt oxide and the negative electrode was formed of graphite, lithium cobalt oxide content: mass %)

(Separation of Lithium Battery Positive Electrode Material)

[0388] The lithium-ion secondary batteries were immersed in an electrolytic solution (5% NaCl) and discharged until the voltage became 0.1 mV. After that, the positive electrode material was taken out by manual disassembly, and ground with a cutter mill to provide a positive electrode material powder having an average particle size of 0.1 mm. The composition of the powder is described in Table I. As a result of analysis, it was confirmed that the powder obtained by the separation was lithium cobalt oxide.

TABLE I

Composition (mass %)	
Li	7
Co	60

[0389] The powder was wrapped with a molybdenum (Mo) mesh (200 mesh). As illustrated in FIG. 14, the sample powder contained within the Mo mesh was used as an anode (anode electrode).

(Preparation of Electrolysis Apparatus)

[0390] A molten NaCl—KCl eutectic salt was employed as the molten salt. This salt was completely melted by heating at 700° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode (cathode electrode) was formed of carbon.

(Electrolysis Dissolution Step)

[0391] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode

was maintained at a predetermined potential. After a predetermined time lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by ICP-AES.

[0392] The anode current observed in the dissolution step varied with time as in First embodiment (example) (FIG. 15). In FIG. 15, the abscissa axis indicates time (unit: min), and the ordinate axis indicates the value of anode current (unit: mA). As illustrated in FIG. 15, the current value decreased with time. The change rate of current value with respect to time had the following tendency: the change rate was the highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0393] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of lithium in the molten salt was confirmed.

(Electrolysis Deposition Step)

[0394] After the dissolution step, a cathode electrode formed of glassy carbon and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that lithium was deposited in the NaCl—KCl molten salt. After a predetermined time lapsed, a section of the surface layer of the cathode electrode was observed with a scanning electron microscope (SEM).

[0395] The observation revealed deposition of lithium on the surface of an electrode body part constituting the cathode electrode and formed of glassy carbon.

[0396] In this way, lithium was recovered from the positive electrode material containing lithium.

Fourth Embodiment (Example)-1

[0397] Ferrovandium was used as the metal material containing vanadium and vanadium was produced by molten salt electrolysis.

(Sample)

[0398] The ferrovanadium serving as a treatment object contained 75 wt % of vanadium and 25 wt % of iron. The ferrovanadium was ground with a bead mill or an attritor so as to have a particle size of about 2 mm. The ground sample (ferrovanadium) was wrapped with a molybdenum (Mo) mesh (50 mesh). As illustrated in FIG. 14, the sample powder (treatment object) contained within the Mo mesh was used as an anode (anode electrode).

(Details of Experiment)

[0399] A molten NaCl—KCl eutectic salt was employed as the molten salt. This salt was completely melted by heating at 700° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode electrode was formed of glassy carbon.

Dissolution Step:

[0400] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode was maintained at a predetermined potential. At this time, the potential was set such that iron was not dissolved but vanadium alone was selectively dissolved. After a predetermined

time lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by ICP-AES.

Electrolysis Step:

[0401] After the dissolution step, a cathode electrode formed of glassy carbon and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that vanadium was deposited in the NaCl—KCl molten salt. After a predetermined time lapsed, the surface status of the cathode electrode was observed.

(Result)

Regarding Dissolution Step:

[0402] The anode current observed in the dissolution step varied with time as in First embodiment (example) (FIG. 15). In FIG. 15, the abscissa axis indicates time (unit: min), and the ordinate axis indicates the value of anode current. As illustrated in FIG. 15, the current value decreased with time. The change rate of current value with respect to time had the following tendency: the change rate was the highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0403] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of vanadium in the molten salt was confirmed.

Regarding Electrolysis (Deposition) Step:

[0404] Observation of a section of the surface layer of the cathode electrode with a scanning electron microscope (SEM) revealed deposition of vanadium on the surface of an electrode body part constituting the cathode electrode and formed of glassy carbon.

[0405] In this way, high purity vanadium was obtained from the ferrovanadium containing vanadium.

Fourth Embodiment (Example)-2

[0406] Mo—Cu heat spreaders were used as the metal material containing molybdenum and molybdenum was produced by molten salt electrolysis.

(Sample)

[0407] The Mo—Cu heat spreaders serving as a treatment object contained 50 wt % of molybdenum and 50 wt % of copper. The heat spreaders were ground with a bead mill or an attritor so as to have a particle size of about 2 mm. The ground sample (heat spreaders) was wrapped with a platinum (Pt) mesh (50 mesh). The sample powder (treatment object) contained within the Pt mesh was used as an anode (anode electrode).

(Details of Experiment)

[0408] A molten LiCl—KCl eutectic salt was employed as the molten salt. This salt was completely melted by heating at 450° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode electrode was formed of glassy carbon.

Dissolution Step:

[0409] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode was maintained at a predetermined potential. At this time, the potential was set such that copper was not dissolved but molybdenum alone was selectively dissolved. After a predetermined time lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by ICP-AES.

Electrolysis Step:

[0410] After the dissolution step, a cathode electrode formed of glassy carbon and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that molybdenum was deposited in the LiCl—KCl molten salt. After a predetermined time lapsed, the surface status of the cathode electrode was observed.

(Result)

Regarding Dissolution Step:

[0411] The value of anode current observed in the dissolution step decreased with time as in the above-described case relating to vanadium. The change rate of current value with respect to time had the following tendency: the change rate was the highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0412] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of molybdenum in the molten salt was confirmed.

Regarding Electrolysis (Deposition) Step:

[0413] Observation of a section of the surface layer of the cathode electrode with a scanning electron microscope (SEM) revealed deposition of molybdenum on the surface of an electrode body part constituting the cathode electrode and formed of glassy carbon.

[0414] In this way, high purity molybdenum was obtained from the heat spreaders containing molybdenum.

Fourth Embodiment (Example)-3

[0415] An oxide superconducting material was used as the metal material containing strontium and strontium was produced by molten salt electrolysis.

(Sample)

[0416] The oxide superconducting material serving as a treatment object contained 17 wt % of strontium and 8 wt % of calcium. The oxide superconducting material was ground with a bead mill or an attritor so as to have a particle size of about 2 mm. The ground sample (oxide superconducting material) was wrapped with a platinum (Pt) mesh (50 mesh). The sample powder (treatment object) contained within the Pt mesh was used as an anode (anode electrode).

(Details of Experiment)

[0417] A molten LiF—CaF₂ eutectic salt was employed as the molten salt. This salt was completely melted by heating at

850° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode electrode was formed of glassy carbon.

Dissolution Step:

[0418] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode was maintained at a predetermined potential. At this time, the potential was set such that strontium and calcium alone were selectively dissolved and the other elements contained were not dissolved. After a predetermined time lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by ICP-AES.

Electrolysis Step:

[0419] After the dissolution step, a cathode electrode formed of glassy carbon and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that strontium was deposited in the LiF—CaF₂ molten salt. After a predetermined time lapsed, the surface status of the cathode electrode was observed.

(Result)

Regarding Dissolution Step:

[0420] The value of anode current observed in the dissolution step decreased with time as in the above-described case relating to vanadium. The change rate of current value with respect to time had the following tendency: the change rate was the highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0421] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of strontium in the molten salt was confirmed.

Regarding Electrolysis (Deposition) Step:

[0422] Observation of a section of the surface layer of the cathode electrode with a scanning electron microscope (SEM) revealed adhesion of strontium to the surface of an electrode body part constituting the cathode electrode and formed of glassy carbon. Since strontium has a melting point of 768° C., strontium was in the liquid state. When the amount of strontium adhering to the electrode body becomes large, the strontium rises to the surface due to the specific gravity difference relative to the molten salt. Accordingly, a jig for collecting strontium rising to the surface was disposed on the upper side of the electrode.

[0423] In this way, high purity strontium was obtained from the oxide superconducting material containing strontium.

Fourth Embodiment (Example)-4

[0424] An optical fiber material was used as the metal material containing germanium and germanium was produced by molten salt electrolysis.

(Sample)

[0425] The optical fiber material serving as a treatment object contained 3 wt % of germanium. The optical fiber material was ground with a bead mill or an attritor so as to

have a particle size of about 2 mm. The ground sample (optical fiber material) was wrapped with a platinum (Pt) mesh (50 mesh). The sample powder (treatment object) contained within the Pt mesh was used as an anode (anode electrode).

(Details of Experiment)

[0426] A molten LiF—CaF₂ eutectic salt was employed as the molten salt. This salt was completely melted by heating at 850° C. In this molten salt, the above-described anode electrode and a cathode electrode were wired and immersed. The cathode electrode was formed of glassy carbon.

Dissolution Step:

[0427] While the anode electrode and the cathode electrode were thus immersed in the molten salt, the anode electrode was maintained at a predetermined potential. At this time, the potential was set such that germanium alone was selectively dissolved and the other elements contained were not dissolved. After a predetermined time lapsed, a sample was taken from the molten salt and the sample was subjected to composition analysis by ICP-AES.

Electrolysis Step:

[0428] After the dissolution step, a cathode electrode formed of glassy carbon and an anode electrode formed of glassy carbon were immersed in the molten salt. The potential at the cathode electrode was maintained at a predetermined potential. Specifically, the potential was maintained such that germanium was deposited in the LiF—CaF₂ molten salt. After a predetermined time lapsed, the surface status of the cathode electrode was observed.

(Result)

Regarding Dissolution Step:

[0429] The anode current observed in the dissolution step decreased with time as in the above-described case relating to vanadium. The change rate of current value with respect to time had the following tendency: the change rate was the highest at the beginning of the measurement (at the beginning of application of current) and, after that, the change rate gradually decreased.

[0430] The sample taken from the molten salt was subjected to composition analysis by ICP-AES. As a result, dissolution of germanium in the molten salt was confirmed.

Regarding Electrolysis (Deposition) Step:

[0431] Observation of a section of the surface layer of the cathode electrode with a scanning electron microscope (SEM) revealed deposition of germanium on the surface of an electrode body part constituting the cathode electrode and formed of glassy carbon.

[0432] In this way, high purity germanium was obtained from the optical fiber material containing germanium.

[0433] The embodiments and examples disclosed above are given by way of illustration in all respects and should be considered as non-limitative. The scope of the present invention is indicated not by the above descriptions but by Claims and is intended to embrace all the modifications within the meaning and range of equivalency of the Claims.

INDUSTRIAL APPLICABILITY

[0434] The present invention is suitably applicable to a method for obtaining a particular metal at high purity from a treatment object containing two or more metal elements. The present invention is also suitably applicable to a method for obtaining a desirable metal from an ore or a crude metal ingot. The present invention is also suitably applicable to a method for obtaining tungsten at high purity from a treatment object containing at least one of tungsten and lithium.

REFERENCE SIGNS LIST

[0435] 1 container; 2 molten salt; 3 treatment object; 4, 24 basket; 5 conductive wire; 6 to 8, 15, 27 electrode; 9 control unit; 10 heater; 11 DyNi₂ film; 12 Pr film; 13 Nd film; 16 Dy film; 25 electrode material; 26 alloy; 31 electrode body part; 32 Dy—Ni alloy; 33, 34 region

1. A method for producing a metal by molten salt electrolysis, the method comprising:

a step of dissolving, in a molten salt, a metal element contained in a treatment object containing two or more metal elements; and

a step of depositing or alloying a particular metal present in the molten salt, on one of a pair of electrode members disposed in the molten salt containing the dissolved metal element, by controlling a potential of the electrode members to a predetermined value.

2. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the treatment object is an ore or a crude metal ingot obtained from the ore.

3. The method for producing a metal by molten salt electrolysis according to claim 1,

wherein the method is a method for producing tungsten, a metal element contained in the treatment object is tungsten,

in the step of dissolving, in a molten salt, a metal element from a treatment object, tungsten is dissolved from the treatment object, and

in the step of depositing or alloying a particular metal, tungsten present in the molten salt is deposited on one of a pair of electrode members disposed in the molten salt containing dissolved tungsten, by controlling a potential of the electrode members to a predetermined value.

4. The method for producing a metal by molten salt electrolysis according to claim 3, wherein the treatment object is a metal material containing the tungsten.

5. The method for producing tungsten a metal by molten salt electrolysis according to claim 3, wherein the treatment object is a metal material containing tungsten and a transition metal.

6. The method for producing a metal by molten salt electrolysis according to claim 3, wherein the treatment object is a cemented carbide product.

7. The method for producing a metal by molten salt electrolysis according to claim 1,

wherein the method is a method for producing lithium, a metal element contained in the treatment object is lithium,

in the step of dissolving, in a molten salt, a metal element from a treatment object, lithium is dissolved from the treatment object, and

in the step of depositing or alloying a particular metal, lithium present in the molten salt is deposited on one of a pair of electrode members disposed in the molten salt

containing dissolved lithium, by controlling a potential of the electrode members to a predetermined value.

8. The method for producing a metal by molten salt electrolysis according to claim 7, wherein the treatment object is a material containing lithium and a transition metal.

9. The method for producing a metal by molten salt electrolysis according to claim 7, wherein the treatment object is a battery electrode material containing lithium.

10. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the treatment object contains a transition metal or a rare earth metal.

11. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the treatment object contains one or more metals selected from the group consisting of V, Nb, Mo, Ti, Ta, Zr, and Hf.

12. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the treatment object contains Sr and/or Ba.

13. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the treatment object contains one or more metals selected from the group consisting of Zn, Cd, Ga, In, Ge, Sn, Pb, Sb, and Bi.

14. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the molten salt is selected such that, in the step of depositing or alloying a particular metal, a difference between a standard electrode potential of a simple substance or alloy of the particular metal and a standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

15. The method for producing a metal by molten salt electrolysis according to claim 1, wherein, in the step of depositing or alloying a particular metal, the potential of the electrode members is controlled to the predetermined value so that the particular metal in the molten salt is selectively deposited or alloyed.

16. The method for producing a metal by molten salt electrolysis according to claim 1, wherein, in the step of dissolving, in a molten salt, a metal element contained in a treatment object,

the metal element is dissolved in the molten salt by a chemical procedure.

17. The method for producing a metal by molten salt electrolysis according to claim 1, wherein, in the step of dissolving, in a molten salt, a metal element contained in a treatment object,

a cathode and an anode that is formed of an anode material containing the treatment object are disposed in the molten salt, and a potential at the anode is controlled to a predetermined value so that a metal element corresponding to the controlled potential is dissolved in the molten salt from the treatment object.

18. The method for producing a metal by molten salt electrolysis according to claim 17, wherein the molten salt is selected such that, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, a difference between a standard electrode potential of a simple substance or alloy of the particular metal and a standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

19. The method for producing a metal by molten salt electrolysis according to claim 17, wherein, in the step of dissolving, in a molten salt, a metal element contained in a treatment

object, the potential at the anode is controlled to a predetermined value so that the particular metal element is selectively dissolved in the molten salt.

20. The method for producing a metal by molten salt electrolysis according to claim 1, wherein, in the step of dissolving, in a molten salt, a metal element contained in a treatment object, one or more metals each serving as the particular metal are dissolved in the molten salt.

21. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the particular metal deposited or alloyed is a transition metal.

22. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the particular metal deposited or alloyed is a rare earth metal.

23. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the particular metal deposited or alloyed is V, Nb, Mo, Ti, Ta, Zr, or Hf.

24. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the particular metal deposited or alloyed is Sr or Ba.

25. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the particular metal deposited or alloyed is Zn, Cd, Ga, In, Ge, Sn, Pb, Sb, or Bi.

26. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the molten salt is a chloride or fluoride molten salt.

27. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the molten salt is a molten salt mixture containing a chloride molten salt and a fluoride molten salt.

28. The method for producing a metal by molten salt electrolysis according to claim 1, wherein the treatment object has a form of particles or powder.

29. The method for producing a metal by molten salt electrolysis according to claim 28, wherein the treatment object having the form of particles or powder is compacted to form the anode.

30. A method for producing a metal by molten salt electrolysis, the method being a method for producing a particular metal by molten salt electrolysis from a treatment object containing two or more metal elements,

wherein a cathode and an anode that is formed of an anode material containing the treatment object are disposed in a molten salt, and a potential at the anode is controlled to a predetermined value so that a particular metal is left in the anode by performing a step of dissolving a metal element corresponding to the controlled potential in the molten salt from the treatment object.

31. The method for producing a metal by molten salt electrolysis according to claim 30, wherein the treatment object is an ore or a crude metal ingot obtained from the ore.

32. The method for producing a metal by molten salt electrolysis according to claim 30, wherein the method is a

method for producing tungsten by molten salt electrolysis from a treatment object containing tungsten,

a cathode and an anode that is formed of an anode material containing the treatment object are disposed in a molten salt, and a potential at the anode is controlled to a predetermined value so that a metal element corresponding to the controlled potential is dissolved in the molten salt from the treatment object and tungsten is left in the anode.

33. The method for producing a metal by molten salt electrolysis according to claim 30, wherein the molten salt is selected such that, in the step of dissolving a metal element in the molten salt from the treatment object, a difference between a standard electrode potential of a simple substance or alloy of the particular metal and a standard electrode potential of a simple substance or alloy of another metal in the molten salt is 0.05 V or more.

34. An apparatus used for a method for producing a metal by molten salt electrolysis, the apparatus comprising:

a container containing a molten salt;

a cathode immersed in the molten salt contained within the container; and

an anode that is immersed in the molten salt contained within the container and that contains a treatment object containing two or more metal elements,

wherein the molten salt is movable into and out of the anode,

the apparatus further comprises a control unit configured to control a potential of the cathode and the anode to a predetermined value, and

a value of the potential is changeable in the control unit.

35. An apparatus used for a method for producing a metal by molten salt electrolysis, the apparatus comprising:

a container containing a molten salt containing two or more dissolved metal elements; a cathode and an anode that are immersed in the molten salt contained within the container; and a control unit configured to control a potential of the cathode and the anode to a predetermined value,

wherein a value of the potential is changeable in the control unit.

36. The apparatus according to claim 34, wherein the two or more metal elements include at least one of tungsten and lithium.

37. The apparatus according to claim 35, wherein the two or more metal elements include at least one of tungsten and lithium.

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