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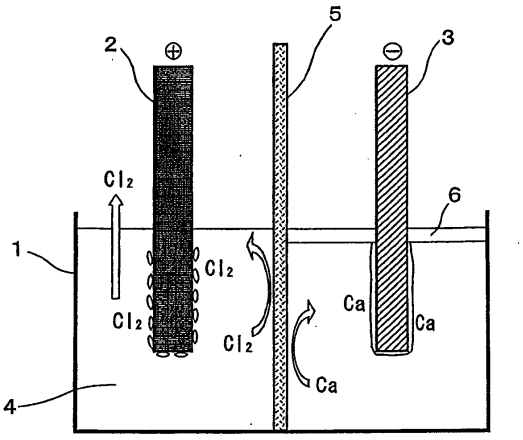
(54) METHOD FOR PRODUCING METAL

(57) A method for producing a metal by an electrolytic process using an yttria-containing porous ceramic body as a diaphragm is provided; the calcium formed by electrolysis cannot pass through the diaphragm, hence the back reaction can be effectively inhibited. Preferably, to be used is a diaphragm comprising a porous ceramic body having a purity of yttrium of 90 mass % or more (more preferably, 99% or more), a porosity of 1% or more and a pore diameter of 20 μm or less, and having a thickness of 0.05-50 mm and a metal halide is used as the electrolytic bath. The method can be utilized for producing metals such as calcium or rare earth elements, in particular. For example, when the method is applied to the production of calcium, metallic calcium can be produced with ease and at low cost without the need for enormous heat energy

Fig. 1



EP 1 835 049 A1

Description

Technical Field

[0001] The present invention relates to a method for producing a metal by an electrolytic process, in particular to a method of producing a metal which can be applied to the production of such a metal as calcium or a rare earth element.

Background Art

[0002] Metallic calcium is strong in reducing power and is a valuable metal usable as a reducing agent in producing other metals. Rare earth metals are used in various ways in a wide range of fields of industry, such as glasses (coloring agents), ceramics and, further, magnetic materials, nuclear materials, metallurgical additives, catalysts, etc.

[0003] Among those metals, rare earth metals are currently produced by the steps of: extracting specific rare earth metals (to be produced) from a refined ore containing them by a solvent extracting process; converting them to oxides by an alkali precipitation process, for instance; and then reducing the oxides by a fused or molten salt electrolysis or metallothermic reduction process, for instance.

[0004] On the other hand, calcium is currently produced mainly by the aluminum reduction process which comprises heating refined calcium carbonate with metallic aluminum and condensing the calcium vapor thus formed to yield metallic calcium. However, for increasing its purity, vacuum refining must be done and, for this and other reasons, the production cost becomes very high. Therefore, in spite of its being suitable as a reducing agent, calcium cannot be easily applied.

[0005] If metallic calcium can be produced by electrolysis of such a molten salt as molten calcium chloride, such a process will be very useful as a relatively inexpensive production process without requiring such a large quantity of thermal energy as required in the aluminum reduction process.

Such a molten salt electrolysis process can be applied to the production of rare earth metals as well. However, because of the excessively strong reducing power of calcium, the so-called back reaction readily occurs and the calcium formed on the cathode side immediately reacts with the chlorine formed on the anode (graphite) side to form calcium chloride again.

[0006] For preventing such a phenomenon, the application of a diaphragm process according to which a diaphragm is provided between the cathode and anode has been proposed. However, alkaline earth metals such as calcium and alkali metals are strong in reducing power and readily react with and reduce the ceramic material used as the diaphragm material. Therefore, such a diaphragm process has not yet been put to practical use.

[0007] In a related technical document (Waste Management, Vol. 17, No. 7, pp. 451-461, 1997. P. D. Ferro et al.: Application of Ceramic Membrane in Molten Salt Electrolysis of CaO-$CaCl_2$), it is described that magnesia (MgO) is best suited as a sheath material surrounding the anode for inhibiting the back reaction attributable to Ca at the time of electrolytic reduction in a CaO-$CaCl_2$ molten salt system.

[0008] However, when the present inventors happened to use magnesia as a material for the diaphragm to be disposed between the cathode and anode in electric reduction of a $CaCl_2$-based molten salt, the reduction attributable to Ca occurred. Further, it was also confirmed that alumina (Al_2O_3), silicon nitride (Si_3N_4) and zirconia (ZrO_2) are also reduced by reaction with Ca.

Dislcosure Of Invention

[0009] It is an object of the present invention to provide a method for producing a metal which can be applied to the production of such a metal as calcium and a rare earth element which is produced or producible by an electrolytic process.

[0010] To accomplish the above object, the present inventors made investigations on the application of the molten salt electrolysis method to be carried out with a diaphragm disposed between the anode and cathode (diaphragm method), in particular on the diaphragm material in terms of the resistance to the reducing action of calcium (calcium reduction resistance), the mechanical strength and the like, among others. As the results of these, they found that a porous ceramic body comprising yttria (Y_2O_3) as prepared by firing or sintering shows such a selective permeability that it allows the passage of calcium and chloride ions but does not allow the passage of metallic calcium.

[0011] Although yttria has a property such that it will not be reduced by even a metal having a strong reducing powder such as calcium, yttria has so far been regarded as being difficult to apply as a diaphragm from the viewpoint of strength and the like. However, as the results of investigations made by the present inventors, this strength problem also has been successfully overcome. Namely, it was revealed that an yttria-based porous ceramic body can be used on the occasion of molten salt electrolysis as a diaphragm which is highly resistant to reduction by calcium and has the above-mentioned selective permeability.

[0012] The gist of the present invention, which has been completed based on the above-mentioned findings and others, consists in an electrolytic method for producing metals wherein a porous ceramic article or body containing yttria

is used as a diaphragm.

The "diaphragm" so referred to herein has function of allowing the passage of calcium and chloride ions through itself but not allowing the passage of metallic calcium.

[0013] The method for producing metals according to the invention is characterized by the following first to tenth aspects or modes of embodiment.

In a first embodiment of the invention, the above-mentioned porous ceramic body is made of a material which is mainly constituted by yttria and can be highly and stably resistant to reduction by calcium. Further, in a second embodiment of the invention, a metal halide is used as an electrolytic bath.

[0014] In a third embodiment of the invention, the porous ceramic body has a porosity of 1% or more so that it may function as a diaphragm while securing the conductivity of the bath. In a fourth embodiment of the invention, the diaphragm desirably has a thickness of 0.05-50 mm. Further, in a fifth embodiment of the invention, the porous ceramic body has a pore diameter of 20 μm or less so that the passage of metallic calcium through it may effectively be inhibited.

[0015] In a sixth embodiment of the invention, the porous ceramic body has an yttria purity of 90 mass % or more so that a further improvement in resistance to calcium reduction may be produced. Further, in a seventh embodiment of the invention, a current density of 0.1-100 A/cm^2 is preferably employed in electrolysis.

[0016] In an eighth embodiment of the invention, a molten calcium salt or a mixed salt containing calcium salt in a molten state is used as an electrolytic bath to make it possible to obtain metallic calcium or a molten salt containing metallic calcium by applying the relevant method for producing a metal (inclusive of any of the above-mentioned embodiments).

In this case, the metallic calcium can be obtained as a solid in a ninth embodiment of the invention and, in a tenth embodiment of the invention, the metallic calcium can be obtained as a molten substance.

[0017] The method for producing a metal according to the invention is a method using an yttria-containing porous ceramic body as a diaphragm and can be utilized in the production of such a metal as calcium or a rare earth element and, in particular, is suited for the production of metallic calcium. When the method is applied to the production of calcium, for instance, metallic calcium can be produced with much ease and at low cost without consuming enormous heat energy to be needed in the prior art aluminum reduction method.

Brief Description Of The Drawing

[0018] Fig. 1 is a drawing schematically illustrating the configuration of an example of the apparatus in which the method for producing a metal according to the invention can be carried out.

Best Modes For Carrying Out The Invention

[0019] In the following, the method for producing a metal according to the invention is described in detail, referring to the drawing.

Fig. 1 is a drawing schematically illustrating the configuration of an example of the apparatus in which the method for producing a metal according to the invention can be carried out. In Fig. 1, the electrolytic cell 1 comprises an anode 2 and a cathode 3 and retains molten calcium chloride ($CaCl_2$) as an electrolytic bath 4. A diaphragm 5 is disposed between the anode 2 and cathode 3, and the inside of the electrolytic cell 1 is divided thereby into an anode 2 side and a cathode 3 side.

[0020] When the molten calcium chloride is electrolyzed in the electrolytic cell 1, two electrode reactions occur according to the equation (1) and equation (2) given below and Cl_2 gas is generated in the vicinity of the surface of the anode 2 while Ca is formed in the vicinity of the surface of the cathode 3.

$$\text{Anode: } 2Cl^- \rightarrow 2e^- + Cl_2 \qquad (1)$$

$$\text{Cathode: } Ca^{2+} + 2e^- \rightarrow Ca \qquad (2)$$

[0021] The Cl_2 gas formed rises in the electrolytic bath 4 and then leaves the bath 4, while the Ca floats to the surface owing to the difference in specific gravity from the molten calcium chloride and forms a Ca layer 6 on the liquid surface of the molten calcium chloride. This Ca layer 6 is extracted and thereby metallic calcium can be obtained. The Cl_2 gas that has left the bath 4 is recovered and reused.

[0022] If there is provided no diaphragm 5, the so-called back reaction, namely the reaction between the Cl_2 gas formed and part of the Ca in the electrolytic bath 4 to return to $CaCl_2$, will occur, the current efficiency will then decrease and the production of Ca will be markedly obstructed. On the contrary, in the configuration example shown, neither of the Cl_2 gas nor Ca can pass through the diaphragm 5 and no back reaction will occur. The electrolysis sufficiently proceeds since $CaCl_2$ can pass through the diaphragm 5 in the form of ions (Ca^{2+}, Cl).

[0023] The method for producing a metal according to the invention is an "electrolytic method for producing a metal according to which an yttria-containing porous ceramic article or body is used as a diaphragm". That is, the method is characterized in that, in the apparatus configuration shown in Fig. 1, the diaphragm 5 comprises an yttria-containing porous ceramic body

[0024] The content of yttria is not particularly restricted since insofar as yttria is contained, the resistance to calcium reduction can be expected. However, a higher content of yttrium gives a greater resistance to calcium reduction, so that a porous ceramic body containing a considerable amount of yttria is used in practice.

[0025] The porosity and pore diameter, among others, of the porous ceramic body are not particularly restricted, either. The ceramic body is made of a material obtained via a process including the step of firing or sintering and, so long as it can be regarded as porous according to a generally accepted perception, the electrolytic bath can pass through the ceramic body to thereby enable electrolysis.

[0026] While, in the configuration example shown in Fig. 1, the diaphragm 5 is positioned approximately in the middle of the electrolytic cell 1 and divides the cell into the anode 2 side and cathode 3 side, the position of the diaphragm is not restricted to such position but may be much closer to the anode side or cathode side. Further, it may be disposed so as to surround the anode to prevent the calcium and chlorine from contacting with each other.

[0027] The first embodiment of the invention is directed to a production method which comprises using a porous ceramic article or body made of an yttria-based material as a diaphragm. The term "yttria-based" means that the yttria content is not less than 50 mass % .

[0028] There is no rigid reason why the yttria content should be not less than 50 mass %. When yttria accounts for at least half of the material constitution, however, the porous ceramic body obtained by firing the material exhibits the characteristics of yttria to a greater extent and the calcium reduction resistance thereof is insured to be good and stable.

[0029] The second embodiment of the invention is directed to a production method comprising using a metal halide as the electrolytic bath. In the production of metallic calcium, calcium chloride ($CaCl_2$) and calcium fluoride (CaF_2) are suitable as the "metal halide". In the production of rare earth metals, the respective metal chlorides or fluorides are preferably used.

[0030] The third embodiment of the invention is directed to a production method according to which the porous ceramic body to be used as the diaphragm has a porosity of 1% or more. The "porosity" so referred to herein is the porosity measured by mercury porosimetry. When this porosity is less than 1%, the electrolytic bath will fail to pass through the diaphragm to a sufficient extent, so that the resistance on the occasion of electrolysis will increase, possibly rendering the operation difficult.

[0031] The upper limit to the porosity is fixed of its own accord under the restrictions as to the constitution (strength in particular) of the diaphragm. For efficient and smooth progress of the electrolysis, however, the porosity of the ceramic body is desirably 10-40%, more desirably 20-30%.

[0032] The fourth embodiment of the invention is directed to a production method according to which the diaphragm to be used has a thickness of 0.05-50 mm. The "diaphragm thickness" defined herein is the thickness of the diaphragm when a single diaphragm is disposed as shown in Fig. 1 and, when two or more diaphragms are disposed, it corresponds to the sum of the respective thicknesses of the diaphragms.

[0033] When the diaphragm thickness is less than 0.05 mm, the diaphragm is so thin that the strength thereof cannot be secured and the selective permeation function which is inherently held by the diaphragm cannot be fully performed. On the other hand, when the thickness exceeds 50 mm, the passage of the electrolytic bath becomes difficult and the resistance on the occasion of electrolysis is great, leading to a failure in smooth operation. The diaphragm thickness is desirably 2-10 mm.

[0034] The fifth embodiment of the invention is directed to a production method according to which a porous ceramic body having a pore diameter of 20 μm or less is used as the diaphragm. The "pore diameter of porous ceramic body" so referred to herein is the pore diameter measured by mercury porosimetry. When this pore diameter is 20 μm or less, the Ca formed in the vicinity of the cathode surface is effectively prevented from passing through the diaphragm. The lower limit to the pore diameter is not particularly set since an excessively small pore diameter results in an increase in electric resistance, which in turn makes the operation difficult, and, in this manner, the lower limit is fixed of its own accord. For efficiently performing the electrolysis while inhibiting the passage of Ca through the diaphragm, it is desirable that the ceramic body have a pore diameter of 0.1-10 μm.

[0035] The sixth embodiment of the invention is directed to a production method which comprises using a porous ceramic body made of a material comprising yttria at a purity of 90 mass % or more as the diaphragm. The diaphragm used in this mode of embodiment is constituted of a ceramic body mostly made of yttria and therefore is highly resistant to calcium reduction. The yttria purity is desirably 99% or more.

[0036] The seventh embodiment of the invention is directed to a production method wherein the current density on the occasion of electrolysis is 0.1-100 A/cm^2.

[0037] The eighth embodiment of the invention is directed to a method for producing a metal wherein a calcium salt or a mixed salt containing calcium salt in the molten state is used as the electrolytic bath and metallic calcium or a

metallic calcium-containing molten salt is obtained by applying the method for producing a metal according to the invention (including the above-mentioned first to seventh embodiment).

[0038] Suited for use as the above-mentioned calcium salt are calcium chloride and calcium fluoride (CaF_2). The mixed salt containing calcium salt is a mixture resulting from addition, to a calcium salt, of such a chloride as potassium chloride (KCl), lithium chloride (LiCl) or barium chloride ($BaCl_2$) or another salt (but only the salt being higher in decomposition voltage than the calcium salt) for the purpose of lowering the melting point and/or adjusting the viscosity.

[0039] The configuration example shown in Fig. 1 corresponds to a case where calcium chloride is used as the electrolytic bath. The calcium formed by electrolysis may be separated as a solid or a molten substance; either mode of practice can be employed. The calcium formed, either in the form of a solid or in the form of a molten substance, is lower in specific gravity than molten calcium chloride and forms a Ca layer 6 on the liquid surface of the electrolytic bath 4.

[0040] The ninth embodiment of the invention is directed to a method for producing a metal wherein metallic calcium is obtained as a solid in the above-mentioned eighth mode of embodiment. When, for example, the electrolytic bath temperature is maintained at a temperature higher than the melting point of the calcium salt or the mixed salt containing calcium salt, which constitutes the bath, but lower than the melting point of calcium, the metallic calcium formed by electrolysis is obtained as a solid matter.

Therefore, the metallic calcium that has floated to the surface can be extracted from the electrolytic cell in the form of solid metallic calcium or together with the molten salt in the form of a molten salt containing solid metallic calcium.

[0041] The tenth embodiment of the invention is directed to a method for producing a metal wherein metallic calcium is obtained as a molten substance in the above-mentioned eighth mode of embodiment. In this case, the electrolytic bath temperature is maintained at a temperature higher than the melting point of calcium. The metallic calcium formed by electrolysis floats, as a molten substance, to the surface of the electrolytic bath 4, so that it can be extracted from the electrolytic cell either as a molten substance of metallic calcium or together with the molten salt.

[0042] As mentioned above, the method for producing a metal according to the invention is characterized in that the diaphragm used on the occasion of electrolysis is constituted of an yttria-containing porous ceramic article or body For producing this porous ceramic body that constitutes the diaphram, it is desirable that an yttria powder having a predetermined purity be pressure-molded and the molded body be sintered by burning at a temperature of 1600°C or higher for 0.5-10 hours.

[0043] The yttria powder desirably has a particle diameter within the range of 0.1-500 μm. When the content of particles having a diameter exceeding this range is high, it will become difficult for the body after molding to maintain the shape thereof, or the ceramic body after sintering will be low in strength and the use thereof as a diaphragm will be sometimes hindered. When the content of particles having a diameter smaller than the above range is high, the desired porosity cannot be obtained in some instances.

[0044] For the pressure-molding, an appropriate amount of water is added to the above-mentioned yttria powder, and the mixture is placed in a mold and molded by applying a pressure of about 0.2-20 MPa. At a pressure lower than 0.2 MPa, it is difficult to maintain the shape of the molded body after removal from the mold while application of a pressure exceeding 20 MPa will result only in a slight increase in strength after molding, hence it is not necessary to further increase the pressure to be applied.

[0045] The sintering or firing is carried out in a fairly high temperature range, namely 1600°C or above, because yttria is sintered without adding any sintering auxiliary. At a temperature lower than 1600°C, the sintering will not be effected to a sufficient extent. The upper limit to the firing temperature is fixed of its own accord from the viewpoint of plant capacity and of reduction in energy required for sintering, hence it is not particularly specified, but it is considered to be about 1800°C. The firing time may be properly adjusted within the range mentioned above according to the firing temperature, taking into consideration the thickness of the ceramic body and the desired porosity, among others.

[0046] The porosity and pore diameter of the sintering product (ceramic body) can be controlled by properly combining the firing conditions (firing temperature and time) with the particle diameter of the yttria powder.

[0047] The thus-obtained porous ceramic body contains no added sintering auxiliary, is made of a material based on yttria highly resistant to calcium reduction, has a necessary level of mechanical strength, and can be satisfactorily used as the diaphragm in the method (electrolytic method) for producing a metal according to the invention.

[0048] The cathode to be used on the occasion of electrolysis is desirably made of a material which will not form an alloy with the metal to be produced. In the case of production of Ca, metallic titanium or pure iron, for instance, is preferably used. As the anode, graphite is generally used.

Examples

[0049] An electrolytic cell was prepared applying metallic titanium as the cathode and graphite as the anode, calcium chloride mixed with 25 mole percent of potassium chloride was used as the electrolytic bath, and the bath temperature was adjusted to 700-750°C (in certain tests, 850°C).

[0050] A diaphragm was disposed between the cathode and anode, and electrolysis was carried out for 300 minutes.

The diaphragm was constituted with a porous ceramic body obtained by firing an yttria-containing material under varied conditions. The purity of yttria, the porosity, pore diameter and thickness of the ceramic body obtained, and the current density on the occasion of electrolysis are shown in Table 1.

[0051] As the yttria-containing material, employed was high-purity yttria (≥ 99.9 mass %) whose content of impurities (Fe_2O_3, SiO_2, etc.) resulting from the production process was less than 0.1 mass %. For investigating the influence of the yttria purity, materials being low in yttria purity were used in some test runs.

[0052] The porosity and pore diameter of each porous ceramic body were measured by mercury porosimetry using a Micromeritics model AutoPore III 9400 mercury porosimeter. The pore diameter and porosity measured by this method are respectively represented by the average pore diameter and porosity defined as follows:

Average pore diameter (D):
The value ($D = 4V/A$) obtained by dividing the total pore volume ($V = \pi D^2 L/4$) by the total pore surface area ($A = nDL$) on the assumption that each pore is cylindrical. Here, V is the total volume of all pores, and L is the average pore depth.

Porosity:
The ratio of the total volume of open/through-wall pores (the pores stretching from one side of the ceramic body to the opposite side) to the volume of the ceramic body. The volume of closed pores is not included.

[0053] For comparison, electrolysis was carried out in the same manner for the cases where a ceramic body obtained by firing alumina, magnesia, silicon nitride or zirconia (each being a high-purity material) was used as the diaphragm.

(Table 1)

[0054]

Table 1

Test No.	Diaphragm				Current density (A/cm^2)	Current efficiency (%)	Remarks
	Purity of Y_2O_3 (mass%)	Porosity (%)	Pore diameter (μm)	Thickness (mm)			
1	25	19	5	5	1.0	61	
2	50	20	6	5	1.0	77	
3	90	20	6	5	1.0	83	
4	≧99.9	18	5	5	1.0	100	
5	≧99.9	3	4	5	1.0	80	
6	≧99.9	8	5	5	1.0	85	
7	≧99.9	13	5	5	1.0	97	
8	≧99.9	21	6	5	1.0	100	
9	≧99.9	42	7	5	1.0	96	
10	≧99.9	55	8	5	1.0	91	
11	≧99.9	17	0.5	5	1.0	100	Increase in electrolytic resistance
12	≧99.9	18	5	5	1.0	100	
13	≧99.9	20	11	5	1.0	98	
14	≧99.9	19	18	5	1.0	97	
15	≧99.9	20	24	5	1.0	96	
16	≧99.9	20	5	0.3	1.0	87	
17	≧99.9	18	4	1.5	1.0	92	

(continued)

Test No.	Diaphragm				Current density (A/cm^2)	Current efficiency (%)	Remarks
	Purity of Y_2O_3 (mass%)	Porosity (%)	Pore diameter (μm)	Thickness (mm)			
18	≧99.9	20	5	5	1.0	100	
19	≧99.9	19	5	20	1.0	100	Increase in electrolytic resistance
20	≧99.9	20	5	5	0.2	100	
21	≧99.9	20	6	5	1.0	100	
22	≧99.9	18	7	5	10	100	
23	≧99.9	20	5	5	20	98	
24	≧99.9	19	5	5	0.2	100	
25	≧99.9	20	6	5	1.0	100	
26	≧99.9	19	6	5	10	100	
27	≧99.9	20	5	5	20	100	
28	Al_2O_3	20	6	5	1.0		Unusable as a diaphragm because of being reduced by Ca
29	MgO	19	5	5	1.0		Ditto
30	Si_3N_4	20	5	5	1.0		Ditto
31	ZrO_2	20	5	5	1.0		Ditto

[0055] The current efficiency data obtained in the electrolysis tests are also shown in Table 1. Each current efficiency value was calculated from the yield of calcium (theoretical precipitate amount) calculated from the quantity of electricity as supplied and the sum of the amount of calcium actually formed in the vicinity of the cathode and found adhering to the cathode and the amount of calcium actually formed and retained by the electrolytic bath (on the bath surface and within the bath). The above-mentioned total amount of calcium was determined by causing the portion of calcium adhering to the cathode and the portion of calcium retained by the electrolytic bath to react with H_2O, determining the amount of H_2 thus produced and converting this amount to the amount of Ca.

[0056] In Table 1, Test Nos. 1-4 each is the case where the yttria purity was varied (the porosity, pore diameter, thickness and current density were retained at almost constant levels). A higher current efficiency was obtained at a higher purity and, at a purity of 99.9 mass % or more, the current efficiency was 100%.

The decrease in current efficiency with the decrease in yttria purity is the result of reduction of alumina by the metallic calcium formed and the passage of calcium through the diaphragm to cause the back reaction.

[0057] Test Nos. 5-10 each is the case where the porosity of the ceramic body was varied while the other conditions were maintained almost constant. In Test Nos. 7 and 8, where the porosity was in the above-mentioned desirable range (10-40%), the current efficient was 100% or close thereto.

[0058] Test Nos. 11-15 each is the case where the pore diameter of the ceramic body was varied. There was found a tendency for the current efficiency to increase with the decrease in pore diameter. When the pore diameter was 0.5 μm, however, the resistance on the occasion of electrolysis increased to some extent.

[0059] Test Nos. 16-19 each is the case where the diaphragm thickness was varied. The current efficiency increased with the increase in diaphragm thickness. When the thickness was 20 mm, however, the resistance in electrolysis increased. When the thickness was 0.3 mm (Test No. 16), the current efficiency decreased to some extent and this was presumably due to occurrence of the back reaction as a result of the passage of a very small proportion of the formed calcium through the diaphragm.

[0060] Test Nos. 20-23 each is the case where the electrolytic bath temperature was raised (to 850°C) and the metallic calcium was obtained as a molten substance. The current efficiency was good, namely 100% or close thereto. Among the tests, in Test No. 23 in which the current density was 20 A/cm^2, the current efficiency decreased, although to a slight extent. Since the metallic calcium was in a molten state, it was easy for the same to pass through the diaphragm accompanying the passage of large quantities of the electrolytic bath (Ca^{2+}, Cl^-) through the diaphragm and the decrease in current density was presumably due to the actual passage of a very slight portion of the molten calcium through the diaphragm to cause the back reaction.

[0061] Test Nos. 24-27 each is the case where the electrolytic bath temperature was maintained at 700-750°C to obtain the metallic calcium as a solid matter, and the current efficiency was 100% in all the cases. In these cases, the metallic calcium was a solid and presumably no passage of metallic calcium through the diaphragm occurred even at increased current density levels.

[0062] Test Nos. 28-31 are comparative examples in which the diaphragm to be used was constituted of a sintered alumina (Al_2O_3), magnesia (MgO), silicon nitride (Si_3N_4) or zirconia (ZrO_3). In each case, the diaphragm suffered reduction by the calcium formed by electrolysis and allowed the passage of calcium through the same, so that the back reaction occurred and the current efficiency fell too far and, thus being impossible to be employed as the diaphragm.

[0063] As is evident from the results shown above, the method for producing a metal according to the invention which comprises using an yttria-containing porous ceramic body as the diaphragm makes it possible to produce metallic calcium with a high current efficiency not less than 80%.

Industrial Applicability

[0064] The method for producing a metal according to the invention is the one which uses an yttria-containing porous ceramic body as the diaphragm and can be utilized in producing such a metal as calcium or a rare earth element, in particular. When it is applied to the production of calcium, for instance, it is possible to produce metallic calcium in an easy and simple manner and at low cost without the need for enormous heat energy, and the method can be expected to contribute greatly to promoted utilization of calcium, in particular, as a reducing agent.

Claims

1. A method for producing a metal by an electrolytic process, **characterized in that** an yttria-containing porous ceramic body is used as a diaphragm.

2. The method for producing a metal as set forth in Claim 1, **characterized in that** the porous ceramic body is made of a material which is mainly constituted by yttria.

3. The method for producing a metal as set forth in Claim 1, **characterized in that** a metal halide is used as an electrolytic bath.

4. The method for producing a metal as set forth in Claim 1, **characterized in that** the porous ceramic body has a porosity of not less than 1%.

5. The method for producing a metal as set forth in Claim 1, **characterized in that** the diaphragm has a thickness of 0.05-50 mm.

6. The method for producing a metal as set forth in Claim 1, **characterized in that** the porous ceramic body has a pore diameter of not more than 20 μm.

7. The method for producing a metal as set forth in Claim 1, **characterized in that** the porous ceramic body has an yttria purity of not less than 90 mass %.

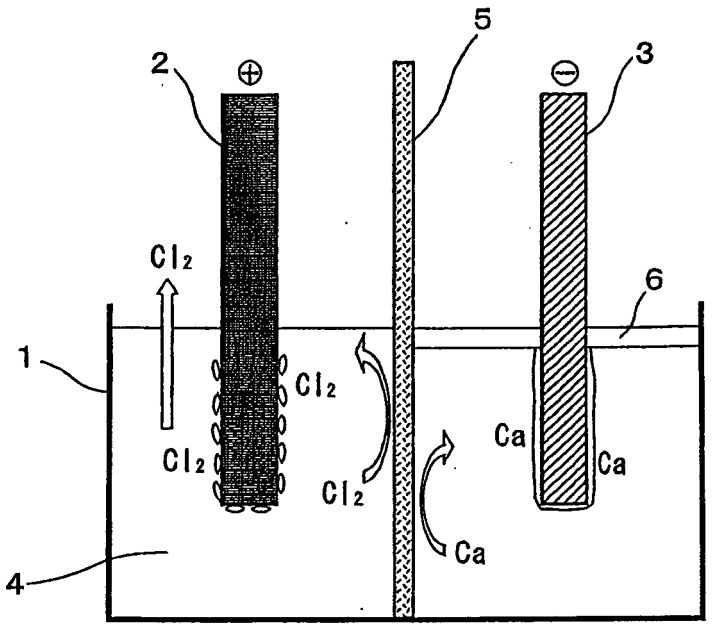
8. The method for producing a metal as set forth in Claim 1, **characterized in that** a current density in electrolysis is 0.1-100 A/cm^2.

9. A method for producing a metal, **characterized in that** a calcium salt or a mixed salt containing calcium salt in a molten state is used as an electrolytic bath and the method for producing a metal as defined in any of Claims 1-8 is applied to obtain metallic calcium or a molten salt containing metallic calcium.

10. The method for producing a metal as set forth in Claim 9, **characterized in that** the metallic calcium is obtained in the form of a solid.

11. A method for producing a metal as set forth in Claim 9, **characterized in that** the metallic calcium is obtained in the form of a molten substance.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/022651

A. CLASSIFICATION OF SUBJECT MATTER
C25C7/04(2006.01), ***C25C3/02***(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25C7/04(2006.01), ***C25C3/02***(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2002-075410 A (Mitsui Engineering & Shipbuilding Co., Ltd.), 15 March, 2002 (15.03.02), Par. No. [0009] (Family: none)	1-8 9-11
Y A	JP 11-350972 A (Nippon Steel Corp.), 21 December, 1999 (21.12.99), Par. No. [0024] (Family: none)	1-8 9-11
Y A	JP 05-312768 A (Fujikura Ltd.), 22 November, 1993 (22.11.93), Par. No. [0011] (Family: none)	1-8 9-11

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 March, 2006 (10.03.06)	20 March, 2006 (20.03.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/022651

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2003-105580 A (National Institute of Advanced Industrial Science and Technology), 09 April, 2003 (09.04.03), Par. No. [0014] & US 2003/0057104 A1	1-8 9-11

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REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- **P. D. FERRO.** *Waste Management,* 1997, vol. 17 (7), 451-461 **[0007]**