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PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

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[54] Invention Title:
Process for Electrolysis of Melts Containing Neodymium Compounds

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Heraeus Elektrochemie GmbH, Moltech Invent SA

By:

Registered Patent Attorney

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Notice Of Entitlement

I, John Gordon Hinde, of 31 Market Street, Sydney, New South Wales, 2000, Australia, Patent Attorney for the Applicant/Nominated Person in respect of Application No. 30288/92 state the following:-

The Applicants/Nominated Persons have entitlement from the actual inventors as follows:-

The Applicants/Nominated Persons are the assignees of the actual inventors.

The Applicants/Nominated Persons are the applicants of the basic application listed on the Patent Request.

The basic application listed on the Patent Request is the first application made in a Convention Country in respect of the invention.

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John Gordon Hinde

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(54) Title
PROCESS FOR ELECTROLYSIS OF MELTS CONTAINING NEODYMIUM COMPOUNDS

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(56) Prior Art Documents
US 5143746
US 4964966
US 4828658

(57) Claim

1. A process for the electrolysis of a melt containing neodymium oxide, neodymium fluoride, alkali-metal fluoride, and, optionally, earth-alkali metal fluoride by means of one anode or a plurality of anodes immersed in the melt, wherein magnetite is used as the material of the anode.

14. The process according to any one of claims 1 to 13, wherein a melt composed of 2% to 5% by weight neodymium oxide, 35% to 92% by weight neodymium fluoride, 6% to 60% by weight lithium fluoride, 0% to 40% by weight barium fluoride, and 0% to 20% by weight calcium fluoride is subjected to electrolysis.

18. A purified neodymium-iron prealloy material for permanent magnets whenever prepared by the process according to any one of claims 1 to 17.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title: Process for Electrolysis of Melts Containing Neodymium Compounds

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

Technical Field

The invention relates to a process for the electrolysis of a melt containing neodymium oxide, neodymium fluoride, alkali-metal fluoride, and, optionally, earth-alkali metal fluoride by means of one anode or a plurality of anodes immersed in the melt.

Background Of The Invention

Both metallic neodymium and neodymium-iron prealloys, which are of growing importance as materials for the manufacture of permanent-magnet materials, eg., neodymium-iron-boron alloys (DE-A1 37 29 361), can be won by electrolytic reduction of salt melts containing neodymium compounds, wherein the neodymium-iron alloys can be obtained by using iron cathodes.

In "Direct Electrolysis of Rare Earth Oxides to Metals and Alloys in Fluoride Melts," Report of Investigations 7146, United States Department of the Interior, Bureau of Mines, 1968, E. Morrice *et al.* have suggested to produce neodymium and neodymium/iron alloys from molten electrolytes containing 50mole% lithium fluoride, 50mole% neodymium fluoride, and neodymium oxide dissolved therein by using graphite anodes and insoluble tungsten or molybdenum cathodes or sacrificial iron cathodes in an inert atmosphere.

JP 2-4994 A1 (Chemical Abstracts, vol. 112, 1990, 225539) describes the electrolysis of melts of 65.9% by weight (20mol %) neodymium fluoride and 34.1% by weight (80mole%) lithium fluoride or 2% by weight neodymium oxide, 64.6% by weight (20mole%) neodymium fluoride, and 33.4% by weight (80mole%) lithium fluoride with the aid of carbon anodes and carbon or iron cathodes. Electrolysis of the melt is effected in an oxygen-containing atmosphere in order to eliminate the carbon which accumulates on the surface of the melt during electrolysis.

EP 0 177 233 B1 likewise relates to producing neodymium-iron alloys by electrolytic smelting. A bath composed of 35% to 76% by weight neodymium fluoride, 20% to 60% by weight lithium fluoride, 0% to 40% by weight barium fluoride, and 0% to 20% by weight calcium fluoride is in a protective gas atmosphere subjected to electrolysis with at least one carbon anode and at least one iron cathode, wherein the neodymium precipitated at the iron cathode enters into reaction with the iron to form an alloy and the neodymium-iron alloy which is liquid at the temperature of the bath drips from the cathode into containers placed underneath. Electrolysis is effected at 770°C to 950°C by applying a dc. to the anode with a current density of 0.05 to 0.60A.cm^{-2} and to the iron cathode with a current density of 0.50 to 55A.cm^{-2}.

While the electrolysis proceeds, the carbon anodes used in this known process are consumed by oxidation so that they must be continuously readjusted and replaced frequently. Owing to the consumption of the anodes, both the melting baths and the developing neodymium-iron alloys are enriched with carbon and the impurities present in the anode material and enter as oxides and fluorides of carbon into the atmosphere around the electrolytic cell.

Summary Of The Invention

Therefore, the problem underlying the invention is to develop a process of the above-characterised type, making use of anodes which, compared with the anodes of carbon, are consumed less rapidly and have an improved chemical stability against the melting bath. The process is to provide neodymium and neodymium-iron alloys of high purity as required for the manufacture of permanently magnetic materials.

According to the invention, the process representing the solution to the problem is characterised in that magnetite is used as the anode material.

Detailed Description Of Preferred Embodiments

The anode material can be applied as a coating on an electrically conductive carrier material, eg., iron (EP 0 443 730 A1). Anodes completely composed of magnetite can be employed as well.

The anodes proper can be compact or hollow bodies. The latter is advantageous when a possible decomposition or conversion of the magnetite into iron oxides of lower conductivity is to be prevented. To this end, an inert gas may be pressed through the hollow body in the case of porous magnetite material or, in the case of dense magnetite material without pores, a negative pressure or excess pressure may be generated inside the hollow body. An inert gas is again used to generate the excess pressure.

The process proved to be particularly efficient when the electrolysis was carried out at a melt temperature ranging from about 750°C to about 1100°C and under an inert gas.

Used as inert gases are gases or gas mixtures which produce an inert, protective atmosphere and prevent in this way undesired reactions of the melt and the electrodes, particularly with the oxygen of the air. Helium, argon, and nitrogen are inert gases suitable for the process according to the invention.

Salt melts suitable for the process are composed particularly of about 2% to about 5% by weight neodymium oxide, about 35% to about 92% by weight neodymium fluoride, about 6% to about 60% by weight lithium fluoride, 0% to about 40% by weight barium fluoride, and 0% to about 20% by weight calcium fluoride.

Preferred are salt melts of about 2% to about 4% by weight neodymium oxide, about 78% to about 90% by weight neodymium fluoride, and about 8% to about 20% by weight lithium fluoride, and especially those of about 2% by weight neodymium oxide, about 80% by weight neodymium fluoride, and about 18% by weight lithium fluoride.

The process can be practised in electrolytic cells of the type known for salt melts containing neodymium compounds, eg., in the cells described by E. Morrice *et al.* or in EP 0 177 233 B1.

Insoluble cathodes of heat-resistant (refractory) metals, preferably of tungsten or molybdenum, or, for obtaining neodymium-iron alloys, sacrificial cathodes of iron are suitable for the process. There may be used one cathode or a plurality of cathodes which either are immersed in the melt or are arranged horizontally at the bottom of the electrolytic cell and are in this case completely covered by the melt.

The advantages of the process according to the invention, which is characterised by the use of magnetite in place of the self-consuming carbon as the anode material, are: simpler operation and longer service life, because the anodes need be readjusted less frequently and replaced less frequently. Moreover, the impurities resulting from carbon anodes in the melt and in the alloys produced as well as in the exhaust air are avoided. Owing to their purity, the neodymium-iron alloys produced with the process according to the invention are well suited for the manufacture of materials for permanent magnets.

The following examples serve to explain in detail the process according to the invention.

Example 1

A melt composed of 2% by weight neodymium oxide, 80% by weight neodymium fluoride, and 18% by weight lithium fluoride is prepared in the graphite crucible of a cell conforming to the cell described by E. Morrice *et al.* and is subjected to electrolysis at 1050°C at an anode of magnetite and a molybdenum cathode under argon. The current is 55A, the cell voltage 25V, the current density at the anode $0.8A.dm^{-2}$, the current density at the cathode $7A.dm^{-2}$, and the electrolysis lasts 3 hours. Liquid neodymium accumulates on the bottom of the cell.

Example 2

A melt composed of 2% by weight neodymium oxide, 80% by weight neodymium fluoride, and 18% by weight lithium fluoride is prepared in the graphite crucible of a cell conforming to the cell described by E. Morrice *et al.* and is subjected to electrolysis at 980°C at an anode of magnetite and an iron cathode under argon. The current is 55A, the cell voltage 29V, the current density at the anode $0.8A.dm^{-2}$, the current density at the cathode $7A.dm^{-2}$, and the electrolysis lasts 2 hours. The alloy which drips from the iron cathode into a vessel underneath consists of 72% by weight neodymium and 28% by weight iron.

The claims defining the invention are as follows:-

1. A process for the electrolysis of a melt containing neodymium oxide, neodymium fluoride, alkali-metal fluoride, and, optionally, earth-alkali metal fluoride by means of one anode or a plurality of anodes immersed in the melt, wherein magnetite is used as the material of the anode.

2. The process according to claim 1, wherein said electrolysis is carried out at a temperature of the melt ranging from 750°C to 1100°C.

3. The process according to claim 1 or claim 2, wherein said electrolysis is carried out in an inert gas.

4. The process according to any one of claims 1 to 3, wherein the magnetite forms a coating on an electrically conductive carrier material.

5. The process according to any one of claims 1 to 3, wherein one anode, or a plurality of anodes, composed completely of magnetite are used.

6. The process according to claim 5, wherein the magnetite anodes are configured as hollow pieces.

7. The process according to claim 6, wherein hollow bodies of porous magnetite are used.

8. The process according to claim 7, wherein an inert gas is forced through the hollow bodies.

9. The process according to claim 6, wherein hollow bodies of pore free dense magnetite are used.

10. The process according to claim 9, wherein a negative pressure is generated within the hollow bodies.

11. The process according to claim 9, wherein an excess pressure of inert gas is generated within the hollow bodies.

12. The process according to any one of claims 1 to 11, wherein one cathode, or a plurality of cathodes, of tungsten or molybdenum are used.

13. The process according to any one of claims 1 to 11, wherein one iron cathode, or a plurality of iron cathodes, immersed in the melt are used.

14. The process according to any one of claims 1 to 13, wherein a melt composed of 2% to 5% by weight neodymium oxide, 35% to 92% by weight neodymium fluoride, 6% to 60% by weight lithium fluoride, 0% to 40% by weight barium fluoride, and 0% to 20% by weight calcium fluoride is subjected to electrolysis.

15. The process according to claim 14, wherein a melt composed of 2% to 4% by weight neodymium oxide, 78% to 90% by weight neodymium fluoride, and 8% to 20% by weight lithium fluoride is subjected to electroylsis.

16. The process according to claim 15, wherein a melt composed of about 2% by weight neodymium oxide, about 80% by weight neodymium fluoride, and about 18% by weight lithium fluoride is subjected to electrolysis.

17. A process for the electrolysis of a melt containing neodymium oxide, neodymium fluoride, alkali-metal fluoride, and, optionally, earth-alkali metal fluoride by means of one anode or a plurality of anodes immersed in the melt, said process being substantially as hereinbefore described with reference to any one of the examples.

18. A purified neodymium-iron prealloy material for permanent magnets whenever prepared by the process according to any one of claims 1 to 17.

Dated 2 September, 1994
Heraeus Electrochemie GmbH

Patent Attorneys for the Applicant/Nominated Person
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Process for Electrolysis of Melts Containing Neodymium Compounds

Abstract

When neodymium and neodymium-iron prealloys of materials for permanent magnets are produced by electrolysis of fluoride melts containing neodymium, impurities are eliminated by using magnetite anodes in place of sacrificial anodes of carbon. The electrolysis is carried out preferably in an inert gas.