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[54] **METHOD FOR PRODUCING RARE EARTH METAL-CONTAINING ALLOYS**

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[58] **Field of Search** 204/71

[56] **References Cited**

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[57] **ABSTRACT**

Rare earth metal-magnesium or rare earth metal-aluminum alloys are easily produced by subjecting a rare earth oxide and a magnesium or aluminum oxide to the simultaneous electrolytic reduction in a molten salts bath consisting of the fluorides of a corresponding rare earth metal and lithium and, optionally, of barium and/or magnesium or aluminum, by which to deposit out the reduced metals on a cathode. The alloys thus produced, having a relatively low melting point to be molten in the bath at the temperature of electrolysis, can be collected by means of a receptacle placed beneath the cathode, into which they fall.

16 Claims, No Drawings

METHOD FOR PRODUCING RARE EARTH METAL-CONTAINING ALLOYS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved method for the production of rare earth metal-containing alloys. More particularly, the invention relates to the production of alloys of rare earth and light metals.

2. The Prior Art

Alloys of rare earth and light metal such as yttrium-aluminum or of mixtures of light rare earths (mischmetall) and magnesium have found extensive use as a mother alloy for the manufacture of special ferrous and nonferrous alloys. On the other hand, these alloys have been used as intermediates for extraction of any pure rare-earth metals, contained therein. Demand for such alloys has been growing rapidly.

In the electrolytic production of rare earth metal-containing alloys, such as yttrium-cobalt and yttrium-maganese alloys, an oxide of yttrium is dissolved in a molten electrolyte salt bath and is electrolytically reduced by use of cobalt or manganese cathodes as consuming electrodes, to yield the alloys of yttrium and the electrode-constituting metals. The use of consuming electrodes is, however, not applicable to the production of rare earth metal-light metal alloys, such as yttrium-aluminum and mischmetall-magnesium alloys, because, if aluminum or magnesium rods are employed as the consuming electrodes, they would become molten and float on the surface of the molten electrolyte bath due to their low melting point and low density.

OBJECT OF THE INVENTION

The object of the present invention is to present an advantageous method for the production of rare earth metal-light alloys, or more specifically, of rare earth metal-magnesium and rare earth metal-aluminum alloys.

SUMMARY OF THE INVENTION

The present invention is directed to the simultaneous electrolytic reduction of a rare earth oxide and a magnesium or aluminum oxide dissolved in a molten electrolyte salt bath containing the fluorides of a corresponding rare earth metal and lithium, to produce alloys of the rare earth metal and magnesium or aluminum with great ease.

To explain further, the oxides of rare earth metals, in this case, yttrium, magnesium and aluminum are all very stable compounds. There is little difference among those oxides in energies required for the electrolytic reduction, since the free energies formed at 1,000°C are very close to each other as about −250, −220 and −200 Kcalories/mole O_2, respectively. With this theoretical consideration, the present invention has been completed by confirming experimentally that, according to the electrolytic method described above, the rare earth metal and magnesium or aluminum are deposited out simultaneously on the cathode at a temperature of from 800°C to 1,200°C, to form an alloy of the rare earth metal and magnesium or aluminum, having a relatively low melting point.

Further, it is an advantage of the present invention that an alloy of magnesium and a rare earth metal produced according to the method of the invention can be used as an intermediate material for obtaining magnesium metal by separating it from the rare earth metal ingredient by means of vacuum distillation.

The rare earth oxides employed in the method of the invention are exemplified by the oxides of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, prometheum, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and mixtures thereof. In some applications it is more advantageous to employ mixtures of the rare earth oxides because of their relatively low costs. For example, mixed oxides of light rare earth metals, derived from naturally occurring monazite or bastnasite and containing usually more than 40 percent by weight of cerium oxide, are advantageously employed for the production of mischmetal-magnesium or mischmetal-aluminum alloys. Mixed oxides of heavy rare earth metals, derived from naturally occurring xenotime and containing usually more than 40 percent by weight of yttrium oxide, known by the name of yttrium concentrate, are advantageously employed for the production of yttrium-magnesium or yttrium-aluminum alloys in the cases where the presence of small amounts of heavy rare earths other than yttrium has no adverse effects. When such mixed rare earth oxides are employed, the rare earth composition in the resulting alloys naturally differs from that in the starting mixed rare earth oxides.

Other oxides to be used together with the rare earth oxides are the oxides of magnesium and aluminum. They may be of commercial grade and, not necessarily of specially high purity.

The rare earth oxides and magnesium or aluminum oxide are dissolved in the electrolyte bath separately or as a mixture. They are preferred to be in powdery form in order to facilitate their dissolution into the molten salts bath at the temperature of electrolysis. In some cases, pelletized form is preferred, since it entertains easy handling.

The molten electrolyte salt bath employed in the method of the present invention comprises essentially the fluoride or fluorides of certain rare earth metal or metals and the fluoride of an alkali metal such as lithium, and optionally the fluoride of an alkaline earth metal such as barium and the fluoride of magnesium or aluminum. The formulation of the mixed fluoride bath is in the range shown below, percentages being all by weight.

- Rare earth fluoride: 20 to 80 percent, preferably, 40 to 70 percent
- Lithium fluoride: 80 to 20 percent, preferably, 50 to 20 percent
- Barium fluoride: 0 to 20 percent, preferably, 5 to 15 percent
- Magnesium or aluminum fluoride: 0 to 5 percent

The rare earth metals contained in the above-mentioned rare earth fluorides should correspond to the rare earth metals used in the preparation of the oxides. For example, when the rare earth metal to be alloyed with magnesium or aluminum is yttrium, cerium, lanthanum or erbium, the fluorides are of yttrium, cerium, lanthanum and erbium, respectively. When the mixed rare earth oxides are employed, the rare earth composition of the rare earth oxides and that of the mixed rare earth fluorides should be the same.

The oxides of rare earth metal and magnesium and aluminum are easily dissolved in the electrolyte bath of the above-mentioned formulation at the temperature of

electrolysis. Too great an amount of the rare earth fluoride, however, in the composition of the electrolyte bath makes the density of the bath higher than that of the resulting alloy and, consequently, the alloy will float on the surface of the bath to disturb the smooth performance of the electrolysis. On the other hand, too great an amount of the lithium fluoride results to lower the solubility of the oxides in the electrolyte bath.

The oxides of barium, magnesium and aluminum may be added in order to improve the current efficiency and, at the same time, to prevent the unfavorable reactions between the fluoride bath and the alloys once formed. One of the important conditions in the formulation of the mixed fluoride bath pertains to the density of the molten bath which should be less than that of the rare earth metal-magnesium or rare earth metal-aluminum alloys to be produced.

In a preferred embodiment of the invention, electrolysis is carried out in a stainless steel cell having graphite linings, wherein the mixed fluorides which are charged are made molten by heating by suitable means. The oxides of the rare earth metal and magnesium or aluminum are put into the molten fluoride bath either separately or as a mixture, to be readily dissolved. In the electrolysis, the graphite-lined electrolyte cell serves an an anode, while a refractory rod of molybdenum, tungsten or tantalum is provided to serve as a cathode. In some instances, it is required to keep the ambient atmosphere inert by use of an inert gas, such as nitrogen, argon or helium. When a graphite rod is employed as the anode, it is preferred to have its surface corrugated to thereby increase the surface area.

Now, speaking of the proportional use of the oxides of the rare earth metal and magnesium or aluminum, it is ovserved observed too much of magnesium or aluminum oxide leads to the accumulation of large amount of undissolved residue on the bottom of the electrolytic cell in the course of electrolysis, thus rendering the continuation of electrolysis reactions very difficult. In addition, too much of magnesium or aluminum oxide results in a smaller content of the rare earth metal in the resulting alloy. On the other hand, too much of the rare earth oxide results in rendering the melting point of the resulting alloy higher than the electrolysis temperature and, consequently, the resulting alloy deposited on the cathode will be in a solid state and not in a molten state and does not fall downward into a receptacle placed beneath the cathode for recovery, thus disturbing the desired, smooth performance of electrolysis. Usually, the content of the rare earth oxide in the mixed oxides is selected in the range of between 30 and 90 percent by weight and the content of magnesium or aluminum oxide is selected in the range between 70 and 10 percent by weight.

The electrolytic voltage is preferably kept at below 15 volts from the standpoints of power efficiency and safety. Any lower voltages, e.g. as low as 3 volts may be employed, though undesirable because of low productivity. The electric current of the electrolysis depends largely on the dimensions and constuction of the electrolytic cell and the electrodes. For example, a current of from 50 to 150 amperes is employed for a cell as large as 100 mm in diameter; a current of 500 amperes for a cell, 20 mm in diameter.

The temperature at which the electrolysis is carried out is selected in the range between 800°C and 1,200°C, depending on the composition of the alloys to be produced and the composition of the electrolyte salt bath employed. With such a temperature, the resulting alloy deposited on the cathode is in the molten state and readily falls down into a receptable positioned beneath the cathode in the salt bath. The receptable is made of a refractory metal, such as molybdenum, which does not react with the fluoride bath or the alloys produced in the electrolyte bath.

The composition of the alloys produced by the present method is determined by (a) the ratio of the rare earth oxide to magnesium or aluminum oxide, (b) the composition of the mixed fluoride bath and (c) the electrolytic conditions with respect to temperature, voltage and current density. Satisfactory results can be obtained by choosing these parameters in the ranges mentioned above.

Illustrative of the efficacy of the present invention are the following specific examples wherein all percentages specified are on a weight basis.

EXAMPLE 1

Into a graphite crucible (100 mm in diameter and 150 mm deep) having a cathode of a molybdenum rod at its center and a receptable made of molybdenum positioned beneath the cathode on its bottom, about 3 kg of mixed fluorides composed of 50 percent of yttrium fluoride, 45 percent of lithium fluoride and 5 percent of barium fluoride were charged and kept in molten state at 950°C. Mixed powder of the oxides composed of 60 percent of yttrium oxide and 40 percent of magnesium oxide was supplied into the molten bath at a rate of 2 g/minute. Then, electrolytic reduction was carried out for 2 hours with the average voltage of 5.5 volts and the average current of 110 amperes. 80 g of yttrium-magnesium alloy having a yttrium content of 73 percent were collected into the receptable.

EXAMPLE 2

In a graphite crucible similar to that used in Example 1, a mixed fluoride bath composed of 50 percent of yttrium fluoride, 45 percent of lithium fluoride and 5 percent of barium fluoride was formed. While the bath was kept in molten state at 1,150°C and the mixed powder of oxides composed of 40 percent of yttrium oxide and 60 percent of aluminum oxide, was supplied into the molten bath at a rate of 1.0 g/minute. Electrolysis was carried out for 2 hours with the average voltage of 5.2 volts and the average current of 120 amperes. 35 g of yttrium-aluminum alloy containing 30 percent of yttrium was obtained.

EXAMPLE 3

In a graphite crucible similar to that employed in Example 1, a mixed fluoride bath composed of 60 percent of cerium fluoride, 20 percent of lithium fluoride, 15 percent of barium fluoride and 5 percent of magnesium fluoride was formed. The bath was kept in the molten state at 850°C and the mixed powder of oxides, composed of 60 percent of cerium oxide and 40 percent of magnesium oxide, was supplied into the molten bath at a rate of 1.5 g/minute. Electrolysis was carried out for 1.5 hours with the average voltage of 5.8 volts and the average current of 150 amperes. 83 g of cerium-magnesium alloy containing 78 percent of cerium was obtained.

EXAMPLE 4

In a graphite crucible similar to that employed in Example 1, a mixed fluoride bath composed of 50 percent of lanthanum fluoride, 40 percent of lithium fluoride and 10 percent of barium fluoride was formed. The bath was kept in the molten state at 1,100°C and the mixed powder of oxides, composed of 30 percent of lanthanum oxide and 70 percent of aluminum oxide, was supplied into the molten bath at a rate of 1.0 g/minute. Electrolysis was carried out for 1.5 hours with the average voltage of 5.3 volts and the average current of 125 amperes. 40 g of lanthanum-aluminum alloy containing 37 percent of lanthanum was obtained.

EXAMPLE 5

In a graphite crucible similar to that used in Example 1 was formed about 3 kg of a fluoride bath composed of 63 percent of mixed fluorides of rare earth metals (consisting of about 60 percent of yttrium, about 10 percent of dysprosium, about 8 percent of erbium and ytterbium and about 22 percent of other rare earth elements), 21 percent of lithum fluoride, 14 percent of barium fluoride and 2 percent of magnesium fluoride, which was then kept in molten state at 1,000°C. Then, a mixture of oxide powders composed of 65 percent of mixed oxides of rare earth metals (consisting of about 60 percent of yttrium, about 10 percent of dysprosium, about 8 percent of erbium and ytterbium and about 22 percent of other rare earth elements) and 35 percent of magnesium oxide was introduced into the fluoride bath at a rate of 1.0 g/minute. Electrolysis was carried out for 2 hours with an average voltage of 5.6 volts and an average current of 160 amperes. 82 g of rare earth metals-magnesium alloy containing 66 percent of the mixed rare earth metals were obtained.

EXAMPLE 6

In a graphite crucible similar to that used in Example 1 was formed about 3 kg of a fluoride bath composed of 70 percent of mixed fluorides of rare earth metals (consisting of about 50 percent of cerium, about 20 percent of lanthanum, about 10 percent of neodymium and about 20 percent of other rare earth elements), 24 percent of lithium fluoride, 5 percent of barium fluoride and 1 percent of aluminum fluoride, which was then kept in the molten state at 950°C. Then, a mixture of oxide powders composed of 85 percent of mixed oxides of rare earth metals (consisting of about 50 percent of cerium, about 20 percent of lanthanum, about 10 percent of neodymium and about 20 percent of other rare earth elements) and 15 percent of aluminum oxide was introduced into the fluoride bath at a rate of 1.3 g/minute. Electrolysis was carried out for 1.5 hours with the average voltage of 5.5 volts and the average current of 130 amperes. 75 g of rare earth metals-aluminum alloy containing 94 percent of the mixed rare earth metals were obtained.

EXAMPLE 7

In a graphite crucible similar to that used in Example 1, about 3 kg of mixed fluoride bath composed of 60 percent of erbium fluoride, 35 percent of lithium fluoride and 5 percent of barium fluoride was formed and kept in molten state at 1,000°C. Then, a mixture of oxide powders composed of 60 percent of erbium oxide and 40 percent of magnesium oxide was supplied into the molten fluoride bath at a rate of 1.0 g/minute. Electrolysis was carried out for 1.5 hours with the average voltage of 5.7 volts and the average current of 120 amperes. 73 g of erbium-magnesium alloy containing 70 percent of erbium was obtained.

What is claimed is:

1. Method of producing an alloy compound of a rare earth metal and a light metal selected from the group consisting of magnesium and aluminum, which comprises formulating a salt bath by melting in molten state a composition of fluorides of a rare earth metal and lithium, introducing into said composition an oxide of the same light metal in said alloy and an oxide of the same rare earth metal in said alloy, and thereafter contacting with a cathode and subjecting the oxides of said light metal and the said rare earth metal to simultaneous electrolytic reduction, whereby the said alloy is deposited on the cathode in contact with said salt bath.

2. The method as claimed in claim **1**, wherein said oxide of rare earth metal comprises yttrium oxide.

3. The method as claimed in claim **1**, wherein said oxide of rare earth metal comprises an oxide of cerium.

4. The method as claimed in claim **1**, wherein said oxide of rare earth metal comprises an oxide of lanthanum.

5. The method as claimed in claim **1**, wherein said oxide of rare earth metal comprises an oxide of erbium.

6. The method as claimed in claim **1**, wherein said oxide of rare earth metal comprises a mixture of oxides of light rare earth metals containing more than 40 percent by weight of a cerium oxide.

7. The method as claimed in claim **1**, wherein said oxide of rare earth metal comprises a mixture of oxides of heavy rare earth metals containing more than 50 percent by weight of yttrium oxide.

8. The method as claimed in claim **1**, wherein said oxide of rare earth metal is selected from the group consisting of the oxides of scandium, praseodymium, neodymium, prometheum, samarium, europium, gadolinium, terbium, dysprosium, holminum, thulium, ytterbium, lutetium and mixtures thereof.

9. The method as claimed in claim **1**, wherein said salt bath is composed of from about 20 to about 80 percent by weight of the fluoride of said rare earth metal and from about 80 to about 20 percent by weight of the fluoride of lithium.

10. The method as claimed in claim **1**, wherein said salt bath additionally contains from 0 to about 20 percent by weight of the fluoride of barium.

11. The method as claimed in claim **1**, wherein said salt bath additionally contains from 0 to about 5 percent by weight of the fluoride of said light metal.

12. The method as claimed in claim **1**, wherein said salt bath additionally contains from 0 to about 20 percent by weight of the fluoride of barium and from 0 to about 5 percent by weight of the fluoride of said light metal.

13. The method as claimed in claim **1**, wherein an admixture of said oxides of the rare earth metal and the light metal are introduced into said salt bath.

14. The method as claimed in claim **1**, wherein said simultaneous electrolytic reduction is carried out at a temperature in the range of from about 800°C to about

1,200°C and at a voltage in the range of from about 3 V to about 15 V.

15. The method as claimed in claim **13,** wherein said form of admixture is composed of from about 30 to about 90 percent by weight of said oxide of rare earth metal and from about 70 to about 10 percent by weight of said light metal.

16. The method as claimed in claim **1,** wherein said alloy is deposited on said cathode and collected by allowing same to fall into a receptacle made of a refractory non-reactive metal placed beneath said cathode.

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