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METHOD FOR THE RECOVERY OF RARE EARTH METAL ALLOYS

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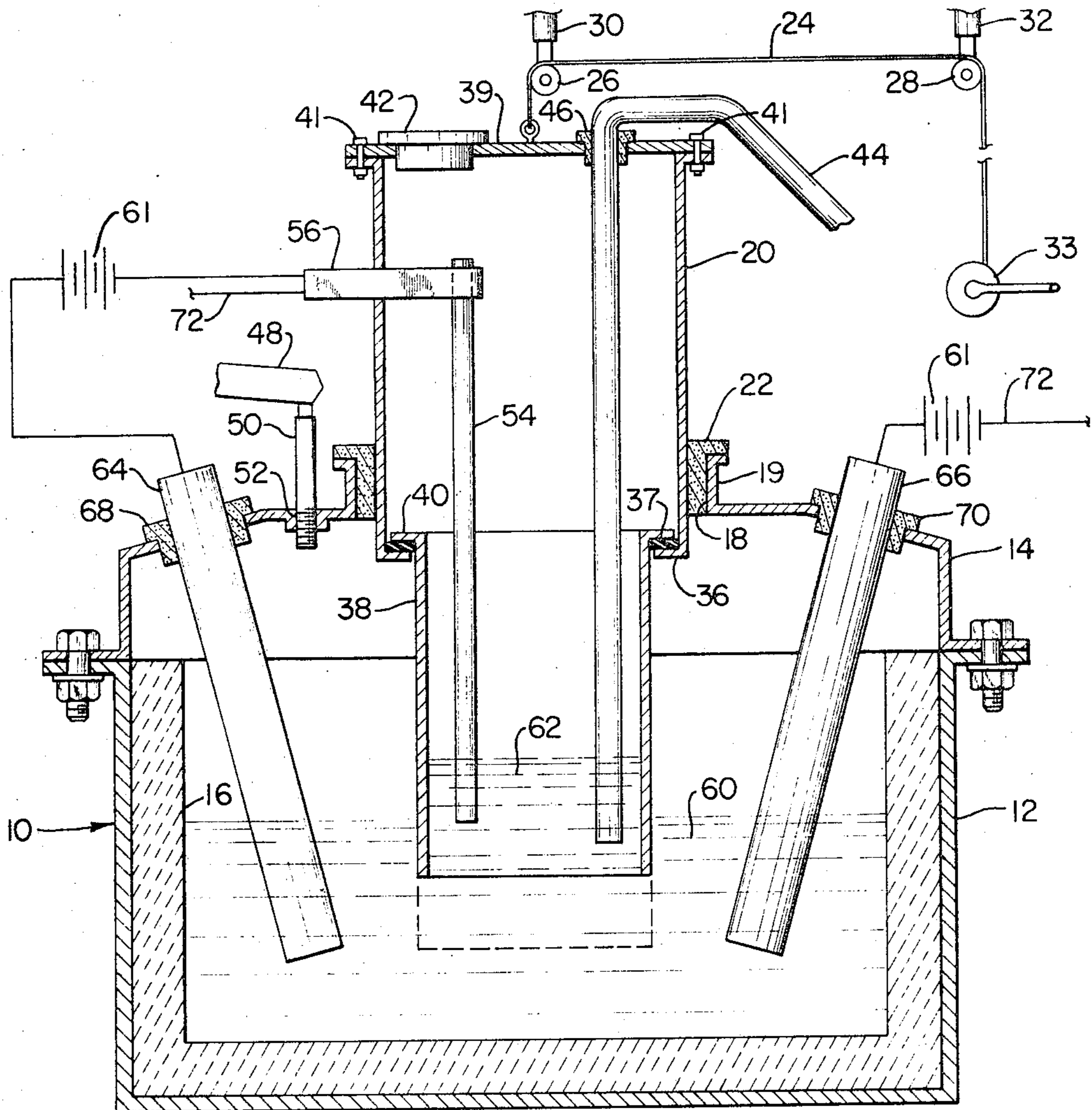


FIG. 1

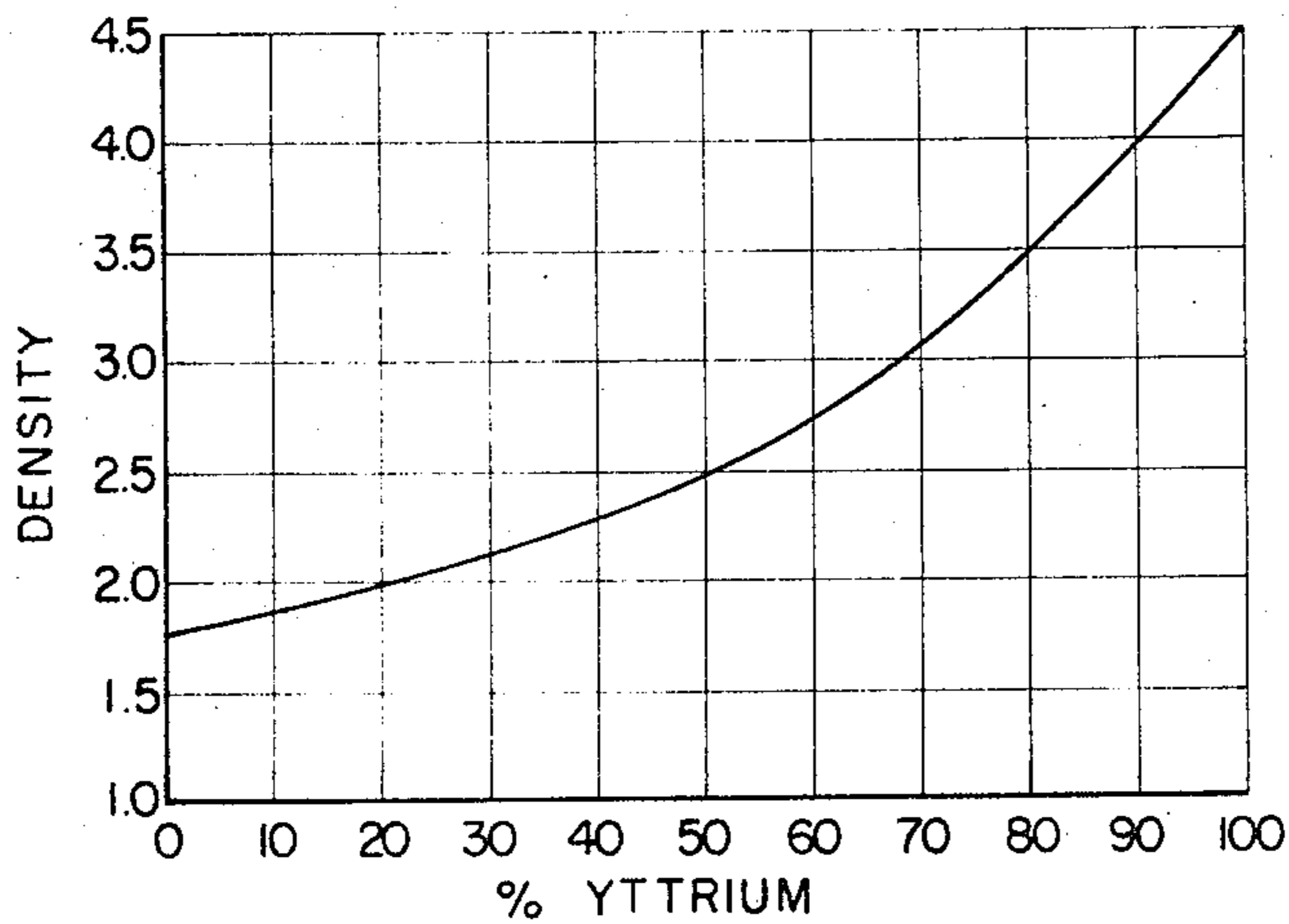


FIG. 2

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METHOD FOR THE RECOVERY OF RARE EARTH METAL ALLOYS

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24 Claims

ABSTRACT OF THE DISCLOSURE

A method for electrowinning of magnesium-rare earth metal alloys from fused salt baths having melting points and specific gravities above that of magnesium which comprises adding the rare earth metal oxide as feed material to a fused salt bath comprising the fluoride of the rare earth metal and an alkali metal fluoride with the optional inclusion of an alkaline earth metal fluoride, and electrolyzing the electrolyte mixture using carbon anodes and as a cathode, molten magnesium which floats on the electrolyte mixture and is confined near the anodes in a boron nitride sleeve and maintained as a cathode through a molybdenum connector extending into the molten magnesium but not into the molten electrolyte mixture.

BACKGROUND OF THE INVENTION

As used herein and in the claims "rare earth metals" includes the following metals as represented by their chemical symbols: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Reference herein to "fused bath," "fused salt bath" and "fused electrolyte bath" refers to the fused mixture of fluorides of alkali and alkaline earth metals and a rare earth metal used herein as a solvent for the rare earth metal oxide.

The invention is illustrated by application of the process and apparatus to the production of magnesium-yttrium alloy; however, it is not limited to this illustrative application as it can be used for the production of alloys of magnesium and other suitable metals with all of the rare earth metals and, in fact, is not limited to the production of rare earth metal alloys.

The electrolytic recovery of pure rare earth metals from their oxides dissolved in fused salt baths including fluorides of rare earth metal and alkali and alkaline earth metals using carbon anodes and a molybdenum cathode is well known. Likewise, the recovery of alloys of the rare earth metals by electrolysis from like electrolytic baths using high melting point metals with which the rare earth metals will alloy is well known. In the recovery of the pure metals the cathode used must be made of a material which does not alloy with the rare earth metal under the conditions of the electrolysis, has a much higher melting point than that of the fused bath, and is unreactive with the fused bath. Molybdenum is a suitable cathode. The cathode is, of course, not consumed in the process.

The positive charge of the rare earth metal ion is released at the molybdenum cathode and molten rare earth metal is formed which rolls down the cathode's surface into a collector at the bottom of the electrolytic cell. The anodes used are always some form of carbon, such as graphite, as this material is unreactive with the fused salt bath and the carbon enters into the chemical reaction and supplies the carbon for the carbon monoxide generated. Depending upon conditions during electrolysis there can be both carbon monoxide and carbon dioxide generated. In these applications, the temperature of the reaction and salt bath is necessarily high because of the

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melting points of the rare earth metals (over 795° C.). If the molten rare earth metal collected at the cathode is to be removed intermittently by tapping, it is necessary to maintain the temperature of the bath well above the melting point of the particular rare earth metal being recovered.

In making alloys of the rare earth metals with high melting point metals, such as cobalt, iron, nickel, etc. (melting points of 1355° C. and above) by the same electrolytic process, these metals can be used as the cathode. The rare earth metal formed at the cathode is immediately alloyed with the metal of the cathode. The degree of alloying of the two metals is controlled by the temperature of the cathode and the salt bath.

Magnesium-rare earth metal alloys are now feasible, and particularly magnesium-yttrium alloys, so that a need for a master alloy exists. The electrowinning process of this invention provides a low cost method for making these alloys utilizing the fused salt bath referred to above.

The fact that magnesium melts at 650° C. while the lowest feasible fused bath temperature is around 700° C. prohibits the use of solid magnesium as a cathode in making alloys of it with rare earth metals as in the case of iron and nickel. Furthermore, the specific gravity of magnesium is 1.74 while that of the fused salt bath is approximately 3.0. As a result, the magnesium is molten at the operating bath temperature, as compared to iron, cobalt or nickel which are solid at this temperature, and the molten magnesium, having a lower specific gravity than the fused salt bath, will float on the surface of the bath.

Accordingly, it is a principal object of this invention to provide a method and apparatus for the electrolytic recovery from a fused salt bath comprised of fluorides of a rare earth metal and alkali and alkaline earth metals, of an alloy of the rare earth metal and a metal having a melting point and a specific gravity below that of the fused salt bath.

It is another object of this invention to provide a method and apparatus for the electrolytic recovery of alloys of magnesium and rare earth metals from the oxide of the rare earth metal contained in a fused salt bath comprising the fluoride of the rare earth metal and alkali metal fluorides with the optional inclusion of alkaline earth metal fluorides.

It is another object of this invention to provide a method and apparatus for recovering pure rare earth metals from electrolytic baths including fluorides of the rare earth metal and alkali metals with the optional inclusion of alkaline earth metal fluorides, the baths having the oxide of the metal dissolved therein, by first electrolytically recovering an alloy of the rare earth metal with magnesium and finally recovering the pure rare earth metal from the magnesium-rare earth metal alloy.

SUMMARY OF THE INVENTION

The process of the invention comprises the electrolytic recovery from the oxide of the rare earth metal dissolved in a fused salt bath including the fluorides of the rare earth metal, an alkali metal fluoride and, optionally, an alkaline earth metal fluoride, of the metal as an alloy with a metal which has a melting point and a specific gravity below that of the bath, by electrolyzing the electrolyte mixture using graphite anodes and a cathode of the low melting point metal in molten form floating on the electrolyte mixture and confined near the anodes in a boron nitride sleeve, the molten metal being maintained as a cathode through a conducting metal connector which has a higher melting point than that of the electrolyte mixture and is not attacked by the molten metal cathode. After the alloy is formed, it can be mechanically removed by various procedures, such as ladling, tapping, etc. The

density of the alloy is ordinarily controlled by the time of electrolysis to keep it floating on the bath; however, electrolysis can be allowed to proceed to the point where the density of the alloy exceeds that of the bath to cause it to sink to the bottom where it can be recovered. The pure rare earth metal can be recovered from the collected alloy by distilling off the low melting point metal, selective solution, or selective chemical treatment.

In the illustrative modification presented herein, the rare earth metal is yttrium and the low melting point metal with which it is alloyed is magnesium. Correspondingly, yttrium oxide is used as the feed material and yttrium fluoride is used as the rare earth metal fluoride in the electrolyte mixture.

The electrolytic cell comprises a container lined with carbon or other inert material, graphite anodes, and as a cathode a molten metal floating on the bath and confined near the anodes in a vertically adjustable boron nitride sleeve and maintained as a cathode through a molybdenum connector connecting the molten metal with direct current, the connector extending into the molten metal but not into the bath.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a partial schematic cross-section of the electrolytic cell of the invention, and

FIG. 2 is a graph in which the theoretical density of yttrium-magnesium alloy is plotted against percent yttrium in the alloy.

Referring to FIG. 1, the electrolytic cell is represented generally by the numeral 10. The outer container 12 has a body made of steel or other suitable material with a cover or cap 14 of semi-hemispherical construction also made of steel. The outer container may be surrounded by thermal insulation if required. A graphite liner or crucible 16 for containing the fused salt bath is seated inside the outer container 12. The cover 14 is provided with a central opening 18 having a neck or collar 19 in which a cylindrical steel sleeve 20 is movably mounted in an asbestos rope packing 22 seated in the collar. The packing 22 provides a gas tight seal between collar 19 and steel sleeve 20. The sleeve 20 is supported in collar 19 by means of cable 24 which in turn is mounted on pulleys 26 and 28 supported by supports 30 and 32, respectively. Cable 24 extends to a crank and ratchet device, shown schematically at 33, for raising and lowering the sleeve 20 by means of the cable.

The vertically movable steel sleeve 20 is constructed with an internal annular flange 36 at its bottom. For confining molten metal near the anodes, an open-ended cylindrical boron nitride sleeve 38 is seated on flange 36 by means of external annular flange 40 made integral with the boron nitride sleeve 38. An insulating washer 37 is seated between the flanges. The flanges 36 and 40 may be secured together by non-conductive attachment means. The steel sleeve 20 is closed at the top with cover 39 attached by bolts 41. The sleeve may be made open at the top. If it is closed at the top as shown an opening with a closure 42 is provided for the purpose of inspection of the interior of the cell, ladling alloy out of the boron nitride sleeve 38, etc. For removing alloy from the sleeve 38, a syphon tube 44 may be mounted in the sleeve 20 in gas tight relationship by means of asbestos rope packing 46. For introduction of feed material into the cell by means of a conventional feeder schematically represented at 48, spout 50 of the feeder is mounted in cover 14 at 52 in an airtight manner by mutually cooperating threads as shown or otherwise.

A conducting connector 54 of suitable metal is supported by an insulating conduit 56 for electrical terminals in steel sleeve 20. The connector 54 is preferably made of molybdenum.

In operation, the cell is supplied with a fused salt bath 60 to be described later. The sleeve 38 contains molten metal 62, such as magnesium, in its bottom section. When

the cell is operated the connector 54 is connected to the negative terminal of a source of direct current 61 and the bottom of the connector 54 extends into the molten metal 62 but not into the bath 60 so that the molten metal 62 becomes the cathode of the cell. Graphite anodes 64 and 66 are mounted in the cover 14 by means of asbestos rope packings 68 and 70, respectively, to seal the chamber at this point and to electrically insulate the anodes from the chamber walls. They are connected at their upper ends to the positive terminal of the direct current source 61. The anodes 64 and 66 are so constructed and mounted that their lower ends extend into the bath 60 in close proximity to the cathodized molten metal 62.

The molybdenum cathode 54 serves as a cathode for the entire cell. The cell contained four anodes spaced 90° apart, the molybdenum connector 54 connected to the cathode making the entire molten magnesium bath 62 cathodic. The number of anodes used depends on the amperage used in electrolysis as well as the diameter of the anodes. It is desirable to use sufficient anode area to obtain as low an anode current density as possible.

The composition of the fused salt bath 60 in weight percentages is approximately about 33 to 66 percent rare earth metal fluoride, about 10 to 35 percent alkali metal fluoride, and 10 to 33 percent alkaline earth metal fluoride. The composition of the bath can vary within the percentage limits stated but it preferably contains a major percent of the rare earth fluoride. The alkaline earth metal fluoride can be omitted and replaced by alkali metal fluoride in substantially the same amount. One purpose of the fluorides is for controlling the operating temperature of the bath or electrolyte 60. Lithium, sodium or potassium fluorides can be used as the alkali metal fluorides and barium, calcium and strontium fluorides can be used as the alkaline earth metal fluorides. The feed material or electrolyte is preferably the oxide of the rare earth metal being recovered and, accordingly, the fluoride of this metal will preferably be used in the fused salt bath. Other feed materials, such as the carbonates and fluorides, can be used to provide a rare earth metal cation in the fused salt bath, the oxide being preferred because of its comparatively low cost. Mixed alloys can be produced by using mixtures of rare earth metal oxides as feed material. Mixtures of rare earth metal fluorides can be used in the fused salt bath and the fluoride used in the bath need not have a cation corresponding to that of the oxide used.

The fused salt bath 60 serves as a solvent for the rare earth metal oxide. Also, it does not react chemically with the rare earth metal oxide or the rare earth metal alloy formed at the cathode. It is well known that the rare earth metals have very similar chemical properties, and that their oxides can be successfully reduced by electrolytic action in the molten salt bath which has been described.

The material of the sleeve 38 is quite critical to the operation of the invention. The material must have a high temperature resistance with a melting point above that of the fused salt bath, must be electrically nonconductive, and be inert to the molten low melting point metal and the molten fluoride salts of the bath.

As most high temperature refractories are oxides of zirconium, aluminum, magnesium or calcium, these cannot be used as the material for the sleeve 38 as the highly reactive fluorides of the bath would quickly dissolve them.

While other materials can be used, boron nitride was found to be the most suitable of the materials tested. This material has a specific gravity of 2.25, a melting point in excess of 2730° C., will not conduct electricity, and is inert to the fluoride salts of the bath and most molten metals.

The connector 54 must be made of a metal which can withstand the temperatures at which the electrolysis in the cell proceeds, is electrically conductive, and is not attacked by the molten metal 62. Suitable metals are molybdenum and tungsten which have high melting

batch operation, it can be operated as a continuous operation by removing the rare earth metal alloy as it is formed with continuous replenishment of magnesium and rare earth metal oxide feed material.

The invention is not limited to the use of the disclosed low melting point metals alloyed with the disclosed rare earth metals. The process of the invention can be used to form alloys of a first metal contained as ions in an electrolyte fused salt bath and a second metal having a lower melting point and specific gravity than that of the electrolyte fused bath. As the melting point of the bath can be adjusted by the content of the alkali and alkaline earth fluorides therein, the bath can be operated at higher temperatures so that any suitable second metal having a melting point and specific gravity below that of the bath can be used as the cathode, and the oxides of suitable first metals which alloy with the second metal used as feed materials.

In other words, the invention is not limited to any particular metals but finds application where it is desirable to recover by electrolysis from a fused salt bath an alloy of a metal which has a lower melting point and specific gravity than the bath with a higher melting point metal. For example, where it is practicable, an alloy of magnesium with second metals other than the rare earth metals can be recovered from the fused salt bath electrolyte incorporating the oxide of the second metal. Other higher melting point metals than magnesium can be used as a cathode if they have lower melting points and specific gravities than the fused salt bath. In the use of higher melting point metals than magnesium for the cathode, the electrolysis is operated at higher temperatures of the electrolyte mixture, and the requirements for the materials of the connector 54 and the sleeve 38 are the same on a relative basis.

It is an advantage of the invention that it provides a means for electrowinning alloys of magnesium and rare earth metals directly by electrolysis of the rare earth metal oxides, thus avoiding the difficulty of making alloys of magnesium with yttrium recovered by other methods. Another advantage of the process is that it provides an effective method for the recovery of pure rare earth metals by first electrowinning the alloy and recovering the pure rare earth metal from the alloy. A further advantage of the process is that it provides a method for controlling the percentage composition of magnesium rare earth metal alloys.

What is claimed is:

1. A method for producing an alloy of a first and second metal by electrolysis of a fused salt bath in which an oxide of said first metal is dissolved, said second metal having a melting point and specific gravity below that of said fused salt bath, which method comprises: floating said second metal in molten form on said bath confined on a portion of the surface of said bath in a hollow enclosure or sleeve of an electrically non-conductive material having a melting point higher than that of said bath and being inert to said bath and said molten metals, cathodizing said second metal so confined, electrolyzing said oxide or bath whereby said first metal is deposited on said second metal cathode and alloyed therewith, and mechanically recovering said alloy from the bath.

2. The method of claim 1 in which oxides of more than one metal are dissolved in the fused salt bath and a mixed alloy of said second metal is formed.

3. The method of claim 1 in which said molten second metal is cathodized by connecting it to a direct current source with an electrically conducting metal connector which is inert to the molten metals and has a melting point above that of the bath.

4. The method of claim 3 in which the material confining said second molten metal is boron nitride.

5. The method of claim 4 in which said fused salt bath comprises a major percent of the fluoride of said first

metal and fluorides of at least one alkali metal or at least one alkaline earth metal.

6. The method of claim 1 including the final step of recovering the pure first metal from said alloy.

7. A method for electrodeposition of at least one rare earth metal as an alloy with magnesium by electrolytic decomposition of the oxide of the rare earth metal in a fused salt bath comprising a fluoride of the rare earth metal and at least one fluoride selected from the group consisting of alkali metal and alkaline earth metal fluorides which method comprises: confining said molten magnesium floating on said bath in a hollow enclosure or sleeve of an electrically non-conductive material having a melting point above that of the bath and inert to the bath and the molten metals; cathodizing said confined molten metal by connecting it to a direct current source with an electrically conducting metal connector which is inert to said molten metals and has a melting point above that of the bath; electrolyzing said oxide or bath to deposit said rare earth metal on said molten magnesium cathode to form an alloy therewith; and mechanically recovering said alloy.

8. The method of claim 7 in which said connector is made of a material from the class consisting of molybdenum and tungsten.

9. The method of claim 8 in which the connector is constructed of molybdenum and said sleeve is constructed of boron nitride.

10. The method of claim 7 in which said rare earth metal is yttrium.

11. The method of claim 7 in which said fused salt bath comprises from about 33 to about 66 percent of yttrium fluoride, from about 10 to about 33 percent of barium fluoride, and from about 10 to about 35 percent of lithium fluoride.

12. The method of claim 7 in which the oxide of more than one rare earth metal is contained in the fused salt bath, and a mixed alloy of magnesium is formed.

13. The method of claim 7 in which the percentage composition and density of said alloy is controlled by controlling the electrolysis.

14. The method for electrodeposition of a rare earth metal as a magnesium-rare earth metal alloy by electrolytic decomposition of the oxide of the rare earth metal in a fused salt bath comprising a rare earth metal fluoride and at least one fluoride selected from the group consisting of alkali metal and alkaline earth metal fluorides, utilizing a molten magnesium cathode, which method comprises: confining molten magnesium in a boron nitride sleeve on top of the fused salt bath in proximity to the anode; maintaining the molten magnesium as a cathode by connecting it to a direct current source with a molybdenum connector; adding rare earth metal oxide to the fused bath; electrolyzing the rare earth metal oxide to deposit rare earth metal on the molten magnesium cathode to alloy it therewith; and mechanically recovering the formed alloy.

15. The method of claim 14 in which the rare earth metal is yttrium.

16. The method of claim 14 in which the alloy is continuously produced by adding the rare earth oxide at approximately the same rate at which it is consumed in the electrolysis.

17. A method for the continuous production of magnesium-yttrium alloy by the electrolytic decomposition of yttrium oxide dissolved in a fused salt bath comprising a major percentage of yttrium fluoride and the remainder at least one fluoride selected from the group consisting of alkali metal and alkaline earth metal fluorides, using at least one anode which is inert to the bath and a molten magnesium cathode, which method comprises: confining molten magnesium in a boron nitride sleeve on top of the bath in proximity to said anode; maintaining said molten magnesium as a cathode by connecting it to a direct current source with a molybdenum connector; electrolyzing said bath while feeding yttrium oxide to it

at the approximate rate at which it is decomposed by electrolysis; and continuously removing formed and collected magnesium-yttrium alloy from the cell.

18. A method for producing magnesium-rare earth alloys by electrodeposition which comprises: electrolyzing an electrolyte containing cations of the rare earth metal in a fused fluoride salt bath including the fluoride of the rare earth metal and using molten magnesium as a cathode, whereby the rare earth metal is deposited on the magnesium cathode and alloyed therewith.

19. The method of claim 18 wherein the fused fluoride salt bath includes at least one fluoride of an alkali metal.

20. The method of claim 19 wherein the molten magnesium is confined in a boron nitride sleeve in proximity to the anode and is maintained as a cathode by connection to a direct current source with a molybdenum connector.

21. A method for producing an alloy of a first and second metal by electrolysis of a fused salt bath containing ions of said first metal, said second metal having a melting point and specific gravity below that of said fused bath, which method comprises: floating said second metal in molten form on said bath confined on a portion of the surface of the bath in a hollow enclosure or sleeve of an electrically non-conductive material having a melting point higher than that of said bath and being inert to said bath and said molten metals, cathodizing said second metal so confined, electrolyzing said bath containing said metal ions whereby said first metal is deposited on said second metal cathode and alloyed therewith, and mechanically recovering said alloy from the bath.

22. The method of claim 21 in which ions of more than one first metal are present in said fused salt bath and a mixed alloy of said second alloy is formed.

23. The method of claim 21 in which the percentage composition and density of said alloy is controlled by controlling the duration of said electrolysis.

24. The method for producing an alloy of magnesium and a rare earth metal from molten magnesium and a molten electrolyte containing ions of the rare earth metal which comprises: maintaining molten magnesium floating on the molten bath in a hollow enclosure or sleeve as a cathode and electrolyzing the bath to deposit rare earth metal on the molten magnesium cathode to alloy it therewith.

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