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3,298,935

**PREPARATION OF REACTIVE METAL SOLUTIONS
BY ELECTRODEPOSITION METHODS****Thomas A. Henrie, Donald G. Kesterke, and Edward
Morrice, all of Reno, Nev., assignors to the United
States of America as represented by the Secretary of
the Interior****No Drawing. Filed Apr. 13, 1965, Ser. No. 447,923****4 Claims. (Cl. 204-1.5)**

The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention relates to preparation of molten metal solutions suitable for use in preparation of alloys, as deoxidizers or nodularizers in ferroalloys, as intermediate products for preparation of pure reactive metals, etc.

The conventional technique for preparing alloys of this nature is that of melting the metals together. This technique, however, is complicated by the precautions necessary to avoid impurities such as oxygen, nitrogen, and carbon.

It is therefore an object of the present invention to provide a reliable, economical process for preparing molten metal solutions that are low in deleterious impurities.

It has now been found that this objective may be achieved by electrolytic reduction of metal oxides or other compounds in molten salt solution to form the desired molten metal solution on a nonconsumable metal cathode by simultaneous electrodeposition of the component metals.

The invention has been found to be particularly applicable to formation of molten solutions of one or more members of two groups of metals, i.e., (1) reactive metals such as thorium, uranium, titanium, yttrium, lanthanum and cerium and (2) conventional alloying metals such as nickel, copper and tin, as well as iron. The metals are simultaneously electrodeposited on a solid non-reactive cathode such as tungsten, where they form a liquid solution that drips off and collects at the bottom of the molten bath. The product is easily recovered, dense, slag free and in a form suitable for addition to ferro-alloys and for use as a source of reactive metal for an electro-refining cell.

Processes for electrodeposition from fused salt baths are conventional and a wide variety of materials have been used to form the molten bath in which the electrolysis is conducted. The molten salt electrolyte components used in the instant invention are conventional; however, particular compositions may be optimum for deposition of particular combinations of metals. Compositions comprising alkali metal or alkaline earth metal fluorides and fluorides of the metals to be deposited have been found to be particularly effective in the method of the invention. These compositions are, however, conventional and do not constitute the essence of the invention. Similar molten bath compositions are disclosed in U.S. Patent 2,033,172 to Andrieux—this patent discloses preparation of alloys of boron by deposition of the boron on a cathode of the metal to be alloyed. In some instances limited quantities of chlorides may be substituted for the fluorides in the instant invention.

The source (feed materials) of the metals to be co-deposited may be various compounds that are soluble in the molten bath. Most effective and convenient sources are usually the oxides. Other compounds that may be used are chlorides, nitrides, and fluorides.

Optimum proportions of the components of the molten bath and feed material will vary with the composition and amount of the particular alloy or molten metal mixture to

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be formed and are best determined experimentally. Generally, proportions of alkali or alkaline earth fluorides in the bath will range from about 15 to about 65 weight percent, with the fluorides of the metals to be deposited ranging from about 35 to about 85 percent.

The apparatus employed in the process of the invention is also conventional and consists of one or more anodes, usually carbon, and a non-consumable cathode, i.e., a cathode that does not react with the molten bath or the deposited metals at the operating temperature. The molten electrolyte bath is generally contained in a graphite crucible. Tungsten has been found to be a very satisfactory cathode material; other possible cathode materials are molybdenum, tantalum and graphite.

Temperature of the bath must be sufficient to maintain both the bath and deposited metals in a molten condition but not high enough to affect the cathode. Temperatures of from about 1050° C. to 1250° C. are usually satisfactory, although again optimum values may vary with different bath ingredients and feed materials. Cathode current density is also not critical; values will generally range from about 30 to 65 amperes per square inch. Use of an inert atmosphere, such as helium, is also usually desirable to prevent undesired contamination from the atmosphere.

Although the theoretical explanation for success of the process of the invention is not known with certainty, it is believed that codeposition of the metals, despite large differences in free energy of formation of their oxides, results from the limited solubility of the oxides or other feed materials in the molten bath. As a result, the two metals co-deposit in about the same proportion as their concentration in the electrolyte.

The invention will be more specifically illustrated by the following examples.

Example 1

In this example a thorium-nickel alloy was prepared. The experiment was conducted in a controlled atmosphere of helium. The electrode configuration consisted of two vertical 1/4 inch diameter carbon anodes and one vertical 1/10 inch diameter tungsten cathode, positioned in a 9 inch inside diameter graphite crucible. The electrolyte composition in weight-percent was 70 percent thorium fluoride, 2 percent nickel fluoride, 13 percent calcium fluoride, and 15 percent sodium fluoride. The electrolyte was melted by heat from a graphite resistor located immediately below the crucible. The electrolysis was begun at a bath temperature of 1150° C. and continued for about 2 hours at about 1170° C. During electrolysis an oxide mixture composed of 62 weight-percent thorium oxide and 38 weight-percent nickel oxide was fed to the cell in the vicinity of the anodes at a controlled rate. Electrodeposition of the two metals on the cathode formed a liquid alloy that dripped into a boron nitride-lined tungsten cup collection zone on the bottom of the cell. At the conclusion of the electrolysis the cell was heated to 1250° C. to insure a fluid alloy, then the cup was lifted from the cell and its contents poured into a mold. The resulting product contained 89 weight-percent thorium and 11 percent nickel.

Example 2

In this example a thorium-iron alloy was prepared. Experimental conditions were similar to those of Example 1 except that the electrolyte was composed of 35 weight-percent ThF₄, 60 weight-percent BaF₂, and 5 weight-percent LiF. The oxide feed mixture consisted of 77 weight-percent thorium oxide and 23 weight-percent ferric oxide. The resulting product contained 88 weight-percent thorium and 12 weight-percent iron.

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Example 3

In this example an iron-yttrium alloy was prepared. The electrode arrangement consisted of two vertical 0.75 inch diameter carbon anodes and one vertical 0.20 inch diameter tungsten cathode. The electrolyte mixture, 85 weight-percent YF_3 and 15 percent LiF , was packed into a 5-inch diameter graphite crucible. The electrolyte was melted by passing alternating current through a graphite resistor submerged between the anodes in the powdered electrolyte. When the electrolyte reached a temperature of 1050°C ., the anodes were raised off the resistor and direct current turned on. During electrolysis alternating current was passed between the anodes as supplementary power. Approximately 170 grams of a mixture of 72 weight-percent Y_2O_3 , 14 percent F_2O_3 and 14 percent FeF_3 was fed to the bath. The electrolysis was conducted at a bath temperature of approximately 1100°C . for $1\frac{1}{2}$ hours. The bath was allowed to solidify, the electrolyte was crushed, and the iron-yttrium nodules recovered. Analyses showed the nodules to contain from 28 to 34 percent iron with 0.02 percent carbon as the major impurity. Typical operating conditions of this example, as well as examples 1 and 2, are given in the following table:

TABLE 1.—OPERATIONAL DATA FOR THE PREPARATION OF VARIOUS METAL SOLUTIONS BY ELECTRODEPOSITION METHODS

Operational Parameter	Metal Solution		
	Th-Ni	Th-Fe	Y-Fe
Avg. electrolysis current, amp.	75	150	75
Avg. electrolysis voltage, volts.	4.5	7.5	25
Avg. alternating current, amp.	(1)	(1)	135
Avg. alternating current voltage, volts.	(1)	(1)	52
Duration of electrolysis, hrs.	2	3	1.5
Bath temperature, $^\circ\text{C}$	1,170	1,160	1,100
Oxide feed rate, g./min.	2.8	3.8	2

¹ Not used.

What is claimed is:

1. A process for the electrolytic preparation of a molten solution of at least two metals comprising:

- (a) dissolving metal oxides of said at least two metals in a molten salt electrolyte, one of said at least two metals selected from the group consisting of thorium, uranium, titanium, yttrium, lanthanum and cerium, and another of said at least two metals selected from the group consisting of nickel, copper, tin and iron,

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said molten salt electrolyte comprising a fluoride of at least one of said at least two metals and a fluoride selected from the group consisting of alkali metal fluoride and alkaline earth metal fluorides;

- (b) electrolytically reducing said metal oxides dissolved in said electrolyte;
- (c) electro-codepositing said reduced metal oxides as a molten solution of said at least two metals on a non-reactive cathode in contact with said molten salt electrolyte, said electrolyte being maintained at a temperature sufficiently high enough to maintain said deposited metals in a molten condition;
- (d) passing said molten metal solution which deposits on said cathode to a collection zone.

2. A process for the preparation of a molten solution of thorium and nickel from a source material of oxides of said thorium and nickel comprising electro-codepositing said thorium and nickel on a tungsten electrode from a molten salt electrolyte bath containing said oxides dissolved therein, said bath comprising thorium fluoride, nickel fluoride, calcium fluoride and sodium fluoride.

3. A process for the preparation of a molten solution of thorium and iron from a source material of oxides of said thorium and iron comprising electro-codepositing said thorium and iron on a tungsten electrode from a molten salt electrolyte bath containing said oxides dissolved therein, said bath comprising thorium fluoride, barium fluoride and lithium fluoride.

4. A process for the preparation of a molten solution of yttrium and iron from a source material of oxides of said yttrium and iron comprising electro-codepositing said yttrium and a iron on a tungsten electrode from a molten salt electrolyte bath containing said oxides dissolved therein, said bath comprising yttrium fluoride and lithium fluoride.

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