UNITED STATES PATENT OFFICE.

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ELECTRODEPOSITION OF MAGNESIUM.

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To all whom it may concern:

Be it known that I, GEORGE O. SEWARD, a citizen of the United States of America, residing in Jersey City, in the county of Hudson and State of New Jersey, have invented certain new and useful Improvements in the Electrodeposition of Magnesium, of which the following is a specification.

This invention relates to the electrodeposition of magnesium and the electrolytic production of magnesium alloyed with a molten base metal forming the cathode of an electrolytic cell. The electrolyte used is a molten bath of magnesium fluorid and one or more fluorids of metals more electro-positive than magnesium, magnesium oxid being introduced and maintained in suspension in, or floating upon, the bath. In the preferred practice the electrolyte is given such specific gravity as to support a layer of magnesium oxid floating on the bath.

A suitable method of practising the process is as follows:

Any suitable electrolytic cell is employed. A carbon lined pot of the same shape and dimensions as the modern aluminum furnace is suitable, with anodes of carbon or graphite (carbon being preferable) and with a cathode of copper, with which, as the process proceeds, the produced magnesium progressively alloys, so that the cathode becomes a copper-magnesium alloy of progressively increasing magnesium content.

A suitable electrolyte consists of fluorids of magnesium, sodium, and barium, the triple fluorid MgF_2: BaF_2:NaF, having a specific gravity of about 3.2, being an example. To this bath is added magnesium oxid, as will be explained.

In starting the process copper is placed at the bottom of the pot, and the electrolyte is melted, as by means of arcs from the carbon anodes to the copper. If alternating current is available for this melting operation no electrolysis occurs. During this melting, if performed with direct current, fluorin is given off at the anodes and magnesium at the cathode. The molten metallic cathode absorbs the magnesium as it is formed. Soon after starting the electrolysis (or even during the melting of the fluorids) magnesium oxid is added, which stops the noticeable production of fluorin, this gas acting strongly on the magnesium oxid present to form magnesium fluorid and oxygen, the oxygen mostly combining with the carbon of the anodes to form CO which to a large extent burns in the air to CO_2.

The magnesium oxid is added continuously and forms the raw material from which the magnesium is derived. Magnesium fluorid is constantly regenerated in the normal operation of the process, though it seems to be impossible to prevent a continual small loss of fluorin. This loss, however, is so small in regular operation that fluorin cannot be detected by the sense of smell.

Although magnesium oxid supplies the magnesium in this process, it is not, except to possibly a small degree, the compound which is directly dissociated by the electric current, since magnesium oxid dissolves in the fluorid bath to the extent of only 0.1 per cent. (differing therein from the Hall aluminum process wherein as much as 10 to 15 per cent. of aluminum oxid may be dissolved in the electrolyte).

The following series of reactions probably take place during the process:—

1. Magnesium fluorid is separated by the current into magnesium and fluorin.

2. The fluorin acts at once on the magnesium oxid present in the electrolyte to form magnesium fluorid and oxygen.

3. The oxygen attacks the carbon of the anodes, forming carbon monoxid, which to a large extent burns to carbon dioxid in the air.

The barium fluorid remains constant. The functions of this salt (which may be replaced by some other suitable heavy salt) are to keep the bath fluid, to reduce its melting point and to increase its specific gravity.

The barium or other heavy salt could be omitted, but in this case difficulty would be experienced in maintaining the desirable suspension of magnesium oxid in the bath. This oxid should be maintained in mechanical suspension, being as far as possible distributed throughout the bath. With a bath of low specific gravity such as the double salt MgF_2:2NaF (specific gravity about 2.07) it is necessary to resort to constant stirring in the effort to maintain the oxid in proper suspension; and this stirring is dif-

ficult and not wholly effective. It results that the oxid gradually sinks to the bottom and forms a hard crust overlying the cathode. The formation of this crust may be retarded by feeding the magnesium oxid to the bath slowly and at about the theoretical rate to quantitatively react with the fluorin evolved at the anodes, but this expedient is not practical, and as the anodes are not protected they waste or "neck in" badly just above the electrolyte.

For these reasons it is highly desirable to use a bath of such specific gravity that the magnesium oxid fed onto the electrolyte will form a floating layer thereon, which more perfectly intercepts and combines with the fluorin, and protects the anodes to a large extent from oxidation or necking in above the bath. The specific gravity of the triple fluorid preferred (about 3.22) so nearly approaches that of magnesium oxid (about 3.60) that the latter will neither sink readily in the bath nor remain wholly in flotation thereon, but tends to remain in suspension around the anodes and in the most perfect condition for reacting with the evolving fluorin.

A desirable working temperature is about 950° C. An electrolyte of MgF_2:2NaF melts at about 825° C. The triple fluorid MgF_2:BaF_2:NaF melts at about 835° C. If a lower melting point is desired for the electrolyte a mixture of 50% MgF_2, 12.5% NaF, 25% BaF_2 and 12.5% LiF may be employed, which melts at 678° C.; but the high cost of lithium salts makes their use uneconomical.

The constituents of the bath may be considerably varied without affecting the process. The sodium salt may be replaced by a potassium salt. A strontium salt may be used instead of the barium salt; certain rare earth salts may be used, for example lanthanum fluorid or thorium fluorid or yttrium fluorid. It is practically essential that the magnesium fluorid be present in such concentration that all of the electric current finds magnesium fluorid in proper quantity in immediate contact with the cathode; a bath too weak in magnesium fluorid will not be reduced perfectly by the current, and sodium may appear at the surface of the bath and there burn to oxid.

Instead of feeding magnesium oxid as the raw material the same result may be accomplished by using magnesium carbonate, which, being distributed over the bath, floats thereon and quietly calcines to the oxid, and in some respects improves the behavior of the process.

The new process herein described is based upon the discovery that it is possible in the electrolysis of molten fluorids to add magnesium oxid in great excess beyond what the fluorid bath will dissolve, and to utilize practically all the fluorin resulting from electrolysis to react upon the excess magnesium oxid thus added to the bath, so that the magnesium oxid thus introduced supplies the entire magnesium resulting from the decomposition.

As a cathode metal to absorb the produced magnesium, copper is excellent. It alloys with magnesium in all proportions to form fusible alloys; it is heavy; it has practically no alloying effect with sodium; and the diffusion of magnesium through copper is rapid. I have found no metal so satisfactory as copper in these respects.

The correct current density to employ in operating this process should keep the electrolyte molten, but will not overheat it. I have operated successfully at 400 amperes per square foot of cathode surface. The process should be conducted at as low a temperature as is consistent with a sufficiently fluid electrolyte. It is of considerable advantage to cool the alloy by a current of air blown continuously against the furnace bottom, or by a water-cooled plate, in contact with the furnace bottom. The latter expedient gives very good results and permits of a greater saturation of the copper by the magnesium than can be obtained where cooling is neglected.

The alloy may be removed from the furnace by tapping or otherwise transferring into a closed vessel, exposure to the air being avoided, since at the high temperature of the furnace the alloy oxidizes very readily in contact with air.

The presence of compounds of metals not desired in the alloy should be avoided in the raw materials used. Silica, iron-oxid, etc., would be completely reduced to metal during the process and enter the copper with the magnesium. But a copper-magnesium-silicon alloy is readily made, if desired, by the deliberate addition of silica to the bath, and other complex alloys with metals more easily reducible than magnesium are easily made in a similar manner.

I have stated above the series of reactions which probably take place during the process; nevertheless, it is to be understood that the supposition as to the nature of these reactions may be in error, and it is not improbable that other or intermediate reactions may occur. It is quite possible that the current acts to decompose sodium fluorid into sodium and fluorin, and that the nascent sodium reduces magnesium fluorid, setting free the magnesium which alloys with the cathode, and regenerating sodium fluorid while freeing nascent fluorin, which in turn acts on the suspended magnesium oxid to form magnesium fluorid, the oxygen freed by this reaction combining with carbon from the anodes to form carbon monoxid. Whatever may be the nature of the reaction,

the process, as practically demonstrated, decomposes magnesium oxid, alloys magnesium with the cathode metal, and sets free oxygen which combines with the carbon from the anodes.

It is found in the practice of this process that it is desirable to agitate the molten cathode or alloy at the bottom in some way, as by rocking the pot or stirring by hand with an iron instrument, as such agitation assists in the diffusion of the magnesium through the copper and the current efficiency is thereby improved.

Instead of using copper as the molten cathode other heavy metals can be used, which function in a manner analogous to copper in the operation of the process.

I claim as my invention:—

1. The process of electrodepositing magnesium, which consists in passing an electric current through a molten bath including magnesium fluorid, said bath carrying magnesia in substantial excess of the proportion soluble therein.

2. The process of electrodepositing magnesium, which consists in passing an electric current through a molten bath including magnesium fluorid, said bath carrying magnesia in substantial excess of the proportion soluble therein, and containing sufficient of a heavier ingredient to raise the specific gravity of the bath to approximately three or more.

3. The process of electrodepositing magnesium, which consists in passing an electric current through a molten bath including magnesium fluorid to a cathode of a molten metal capable of alloying with magnesium, said bath carrying magnesia in substantial excess of the proportion soluble therein.

4. The process of electrodepositing magnesium, which consists in passing an electric current through a molten bath including magnesium fluorid to a cathode of a molten metal capable of alloying with magnesium, said bath carrying magnesia in substantial excess of the proportion soluble therein, and containing sufficient of a heavier ingredient to raise the specific gravity of the bath to approximately three or more.

5. Electrolyzing molten fluorids including magnesium fluorid, with magnesium oxid held in suspension, in presence of a cathode of copper with which the separated magnesium progressively alloys.

6. Electrolyzing with a cathode of molten metal, molten fluorids including magnesium fluorid, with sufficient of a heavier ingredient to raise the specific gravity of the bath to approximately 3 or more, and with magnesium oxid held in suspension in the bath.

7. Electrolyzing with a cathode of molten metal molten fluorids including magnesium fluorid, with sufficient of a heavier ingredient to raise the specific gravity of the bath to approximately 3 or more, and with magnesium oxid held in suspension in the bath, while maintaining a layer of magnesium oxid floating on the bath.

8. Electrolyzing with a cathode of molten metal molten fluorids of magnesium and sodium with sufficient of a heavier molten compound to raise the specific gravity of the bath to approximately 3 or more, and with magnesium oxid held in suspension in the bath, while maintaining a layer of magnesium oxid floating on the bath.

9. Electrolyzing with a cathode of molten metal molten fluorids of magnesium, sodium and barium forming a bath having a specific gravity approximating 3 or more, and maintaining magnesium oxid in suspension in the bath.

10. Electrolyzing with a cathode of molten metal molten fluorids including magnesium fluorid, with sufficient of a heavier ingredient to raise the specific gravity of the bath to approximately 3 or more, and with magnesium oxid held in suspension in the bath, and progressively feeding magnesium oxid as a layer floating on the bath.

11. Electrolyzing against a cathode of molten metal a mixture of magnesium-fluorid, one or more alkali fluorids, and one or more earth alkali fluorids to from a bath of a specific gravity of approximately 3 or more, maintaining magnesium oxid in suspension in the bath, and progressively feeding magnesium-oxid as a layer floating on the bath.

12. Electrolyzing against a cathode of molten metal a mixture of magnesium-fluorid, sodium-fluorid, and barium-fluorid to form a bath of a specific gravity of approximately 3 or more, maintaining magnesium-oxid in suspension in or floating upon the bath, and feeding magnesium-oxid to maintain a layer floating upon the bath.

13. A process comprising electrolyzing a molten fluorid bath, including magnesium-fluorid, at a temperature maintained above the calcining point of magnesium carbonate, and supplying magnesium carbonate to the surface of said bath and calcining it thereon.

14. A process comprising electrolyzing a molten fluorid bath, including magnesium-fluorid, at a temperature maintained above the calcining point of magnesium carbonate, and supplying magnesium carbonate to the surface of said bath and calcining it thereon, said bath having a specific gravity of approximately three or more, whereby the magnesium oxid resulting from the calcination may become suspended in the bath.

15. In a process of preparing magnesium alloys by the electrolysis of a molten fluorid bath, the step which consists in cooling the

cathode alloy during the deposition of magnesium therein.

16. In a process of preparing magnesium alloys by the electrolysis of a molten fluorid bath, the step which consists in agitating the cathode alloy during the deposition of magnesium therein.

In witness whereof, I have hereunto signed my name in the presence of two subscribing witnesses.

GEORGE O. SEWARD.

Witnesses:

CHARLES WOODWARD,

E. ELMORE WICKER.