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ELECTROLYTIC METHOD FOR PRODUCING MAGNESIUM ALLOYS

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Fig. 1

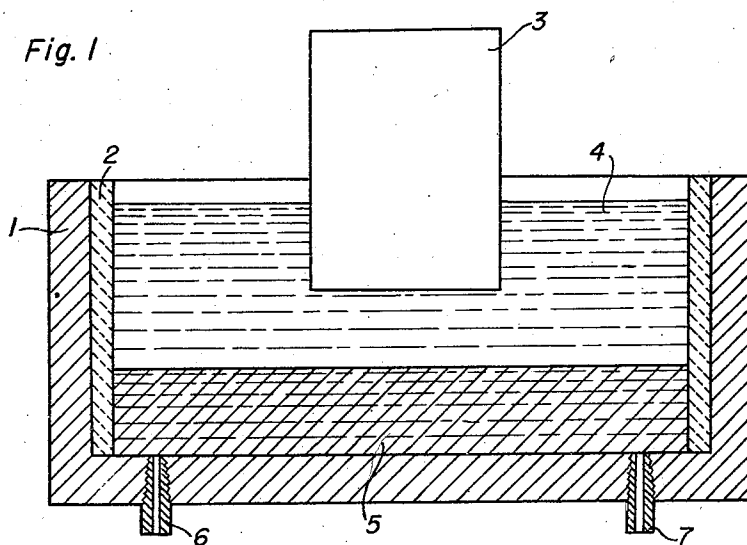


Fig. 2

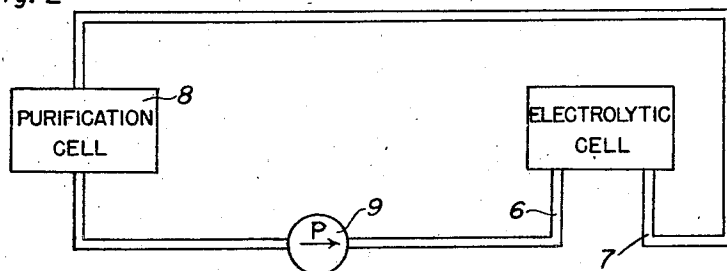
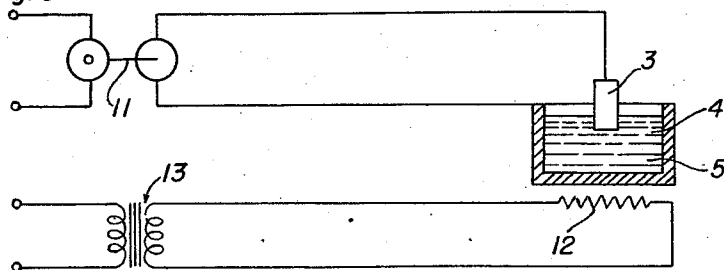


Fig. 3



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ELECTROLYTIC METHOD FOR PRODUCING
MAGNESIUM ALLOYS

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1

This invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to me of any royalty thereon.

This invention relates to electrolytic deposition of magnesium from a molten bath and more particularly to increasing the solubility of magnesia and the like in a molten bath containing magnesium halides.

Numerous attempts have been made to electrolyze magnesia in molten fluoride-oxide mixtures to obtain magnesium, e. g., U. S. 1,408,141; 1,408,142; 1,310,449; 1,584,689; and 1,533,911. These processes have not been fully successful, since magnesia has but low solubility in such baths (about 0.1% MgO; Thompson, M. de K. and Kaye, A. L. Trans. Electrochem. Soc. vol. 67, 22 pp., preprint 1935, The Decomposition Potentials and Conductivities of MgO, and Alkaline Earth Oxides in Fused Fluorides).

The principal object of my invention is the provision of an improved process for producing magnesium.

A further object is to increase the magnesium oxide content of a molten electrolytic bath, whereby to facilitate electrolysis and recoveries of magnesium.

While the invention may be practiced in various specific ways, and by the use of many types of apparatus, I show in the drawing one practical embodiment wherein

Fig. 1 is a sectional view through a suitable type of cell,

Fig. 2 is a diagrammatic view showing a cycle which may be used, and

Fig. 3 is an illustrative electrical installation.

Referring now generally to the invention, I have discovered that boron compounds, preferably when utilized within certain limits in the magnesium halides containing bath, will materially increase the solubility of magnesia therein, and that this increased solubility of magnesia makes more practical the electrolysis of this magnesia-containing bath to form magnesium metal. This increased solubility of the magnesia makes MgO more nearly the product reduced in practice, possibly since magnesia (according to Thompson and Kaye cited previously) has a lower decomposition voltage than has the magnesium halide $MgCl_2$. The amount of boron compound,

2

calculated as B_2O_3 , to give increased solubility of the magnesia may vary from traces to an upper limit of about 5% of the bath. At high concentrations of boron, the electrolytic production of magnesium boride obscures or prevents the reduction of magnesium metal. I have found that a satisfactory practical percentage is about 0.5%, although, as stated, up to about 5% may be used to advantage. Even 0.1% to 0.3% may be used to advantage.

The bath may contain any alkaline earth or alkali metal halide in addition to the magnesium halides. For example, a bath of $NaCl$, $MgCl_2$, B_2O_3 and MgO may be utilized. The use of salt and similar halides in the bath is usually for the purpose of rendering the bath more fluid or lowering its melting point.

Magnesium oxyhalides, such as magnesium oxychloride, magnesium chlorate, magnesium hypochlorite, magnesite, brucite, etc., may be substituted for magnesia. This bath may be used for electrolytic purposes, either to produce magnesium directly by usual practice or to plate into other metals, e. g. lead, either to form a useful alloy or one which can be subsequently refined to give magnesium metal.

The halide of magnesium preferably employed is magnesium chloride, as the basis of the bath. Into this is placed a boron compound, such as B_2O_3 , and such MgO as can be dissolved therein. The electrolytic production of magnesium is then carried out by methods old in the art.

The process employed is preferably a continuous one, although some of the features of my invention may be employed with equal advantage if the electrolysis is carried out on a batch basis. Using the continuous process, purified MgO is fed to the reduction cell along with such $MgCl_2$ and B_2O_3 (or other boron compound) as may be required, while electrolysis continues. Chlorine or oxygen or both are liberated at the surface and metallic magnesium is formed at the cathode. When a lead cathode is used, the magnesium mixes with the molten lead. The lead-magnesium mixture is circulated from the reduction cell to a separation furnace. The magnesium may be removed from the lead by electrolysis of the molten lead-magnesium alloy to yield metallic magnesium, as more fully described by Jessup in British Patent No. 268,737. The lead product re-

sulting from this separation, which still contains some magnesium, is returned to the reduction cell. Continued operation may result in building up impurities in the electrolyte or lead cathode in which event operations may be discontinued to renew or purify the constituents of the reduction cell.

Referring now to the drawings, I show in Fig. 1 the cell 1 with a refractory lining 2. An anode 3 projects into the electrolyte layer 4 which floats on top of the molten cathode 5, e. g. lead. A line 6 comprises an outlet for withdrawing the lead-magnesium mixture for separation, and the lead with reduced magnesium content is returned through the return line 7 comprising an inlet. A suitable purification or separation cell or furnace 8 receives the lead-magnesium mixture, reduces the magnesium content, and returns the lead to the reduction cell, a pump 9 of suitable design being employed to circulate the lead. The cell 9 and general arrangement of Fig. 2 are described by Jessup, in the patent referred to hereinabove.

Electrolysis of the magnesium oxide to magnesium requires direct current of controlled voltage. A motor generator set 11 may be employed, operating from commercial line voltage, and delivering power at suitable voltage to the cell through the anode 3 and cathode. The cell may be heated by resistance 12 through transformer 13, although other heating means may be employed. At times it may be necessary to cool the cell, in which case any suitable cooling means (not shown) may be used.

The following example may be taken as illustrative of the practice of my invention:

3000 grams of $MgCl_2$, 20 lbs. of lead, 10.2 grams of B_2O_3 and 300 grams of MgO were introduced into the cell and fused together at 800 degrees C. The anode was then placed in position and the power started. The cell was run for 21 hours, making frequent additions of MgO . The voltage averaged 4.5 with the current at 50 amperes during most of the period, but was later increased to 6.5 volts at 135 amperes. The current density was 20 amperes per square inch at 50 amperes and 35 amperes per square inch at 135 amperes. The gas given off at the anode was analyzed. The following table is illustrative of the results:

Amperes	Volts	O ₂ /Cl ₂ Ratio	Temp.	MgO In Cell
50.....	4.5	1.91	814	10%
50.....	4.5	5.05	816	Slightly greater than 10%
50.....	4.5	82.57	856	Excess MgO.
50.....	4.5	11.88	840	Excess—not all dissolved that would dissolve.
135.....	6.5	63.00	876	Excess.

I have already pointed out that certain features of cell construction and operation heretofore suggested by others may be employed in the practice of my invention. Instead of a lead cathode, other molten metals may be used such as tin, zinc and bismuth, from which magnesium may be suitably separated. Other types of cells may be used. With the particular design of cell shown in the drawing, it is desirable that a carbonaceous anode be used, such as a graphite anode, as the gases evolved are particularly corrosive to metal anodes if directly exposed to them. Since a graphite anode is burned by the gases evolved, to CO and CO₂, it is desirable also that it be readily replaceable.

In the practice of my invention, many compounds of boron may be used to secure the ad-

vantageous results described. Examples other than B_2O_3 , are borax, borax glass, ulexite, boracite, colemanite, kernite, boric acid and the like. Boron oxide, B_2O_3 , however, is the preferred boron compound to use, so far as I have observed from results heretofore obtained. This compound increases markedly the solubility of MgO in a $MgCl_2$ bath, and the rate of solution is such that MgO can be continuously added. Other magnesium compounds are more readily introduced into the solution as well, such as magnesium oxyhalides, which by heat are reduced to oxides and chlorides, and subsequently electrolyzed in the same manner as is MgO .

It should be understood that my invention is not limited by the specific details of construction and operation of a cell discussed above. Any suitable electrolyte may be used, such as $MgCl_2$ to which other electrolyte salts have been added. By my invention MgO may be made, at least for the most part, the ultimate material reduced. The ratio of oxygen to chlorine in the table shows that much more oxide is reduced than chloride, and I believe that it is merely a question of determining optimum conditions to substantially reduce only MgO and practically no $MgCl_2$.

I wish to point out also, that instead of employing a molten metal, such as lead for the cathode, molten magnesium itself may be used as the cathode providing a suitable cell construction is used so that MgO may be added and the evolved gas, O_2 and Cl_2 , can be kept out of contact with the metallic magnesium.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A process which consists of subjecting to electrolysis a fused mixture of magnesium oxide, magnesium chloride and from 0.1 to 5.0% calculated as B_2O_3 of at least one boron compound, as a solubility promoter for MgO , selected from the group consisting of boron trioxide, boric acid, borax, borax glass, ulexite, boracite, colemanite and kernite, said electrolysis being carried out while employing as a molten metallic cathode at least one metal capable of alloying with magnesium, said metal being selected from the group consisting of lead, tin, zinc and bismuth, to produce an alloy of magnesium with said molten cathode metal.

2. A process which consists of subjecting to electrolysis a fused mixture of magnesium oxide, magnesium chloride and from 0.1 to 5.0% of boron trioxide, as a solubility promoter for MgO , said electrolysis being carried out while employing molten lead as a cathode to produce an alloy of magnesium with lead.

3. A process which consists of subjecting to electrolysis a fused mixture of magnesium oxide, magnesium chloride and about 0.5% boron trioxide, as a solubility promoter for MgO , said electrolysis being carried out while employing as a molten metallic cathode at least one metal capable of alloying with magnesium, said metal being selected from the group consisting of lead, tin, zinc, and bismuth, to produce an alloy of magnesium with said molten cathode metal.

4. A process which consists of subjecting to electrolysis a fused mixture of magnesium oxide, magnesium chloride and about 0.5% calculated as B_2O_3 of at least one boron compound, as a solubility promoter for MgO , selected from the group consisting of boron trioxide, boric acid, borax, borax glass, ulexite, boracite, colemanite and kernite, said electrolysis being carried out

while employing molten lead as a cathode to produce an alloy of magnesium with lead.

5. A process which consists in fusing together 3000 grams of $MgCl_2$, 20 pounds of lead, 10.2 grams of B_2O_3 and 300 grams of MgO , heating the mixture to $800^\circ C$. then subjecting said mixture to electrolysis while employing the molten lead as a cathode at a voltage of 4.5 to 6.5 and a current density of 20 to 35 amperes per square inch, and recovering a molten alloy of lead and magnesium.

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15

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