

Nov. 24, 1931.

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1,833,425

ELECTROLYTIC PROCESS FOR THE MANUFACTURE OF MAGNESIUM AND THE ALKALINE EARTH METALS, SUCH AS CALCIUM BY THE ELECTROLYSIS OF MOLTEN CHLORIDES, AND APPARATUS FOR CARRYING THE SAID PROCESS INTO EFFECT

Filed April 2, 1926

Fig. 1

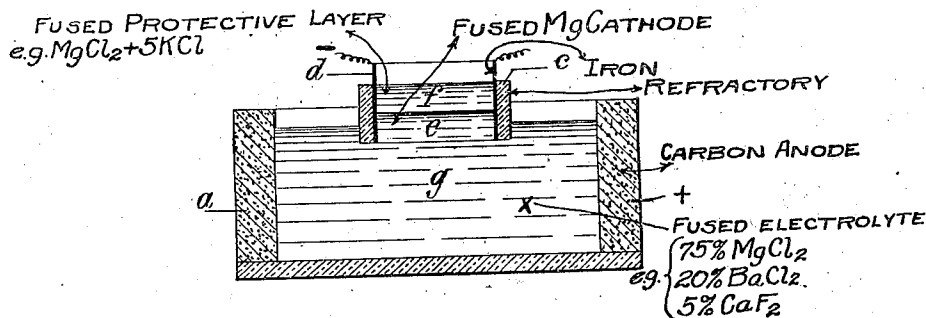


Fig. 2

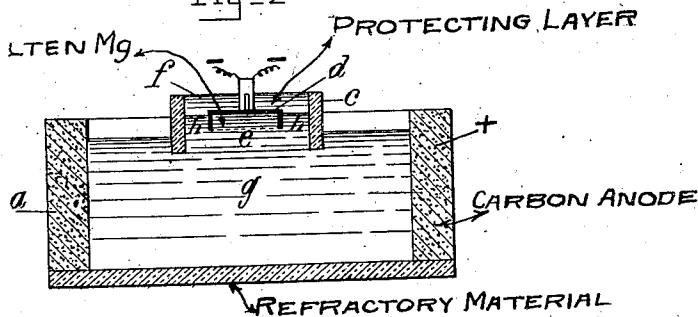
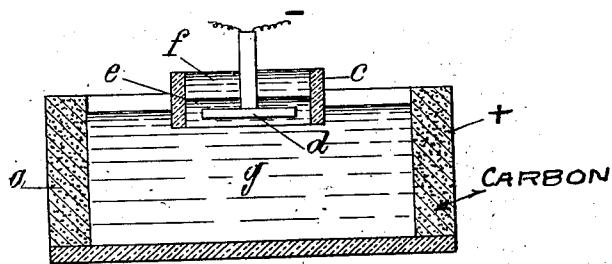


Fig. 3



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UNITED STATES PATENT OFFICE

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Application filed April 2, 1926, Serial No. 99,410, and in France August 5, 1925.

In the known methods for the manufacture of magnesium the electrolyte consists of salts which when molten form a bath whose density is greater than that of magnesium. The magnesium as it is produced floats upon the surface of the bath in the shape of molten globules which become oxidized with great ease and which move over the surface of the bath while burning, so that a part of the magnesium is necessarily lost by oxidation and chloridization, and it also becomes a difficult matter to collect the metal.

My invention relates to a process of manufacture wherein the electrolyte consists of a mixture of salts whose density exceeds that of the resulting metal at the working temperature, but wherein I obviate all formation of oxide or chloride, and am enabled to collect the metal with facility.

The said process consists essentially in collecting the said metal at the surface of the bath in the form of a liquid layer which itself serves as the active cathodic surface.

In order to form the said layer of molten metal serving as cathode at the surface of the bath, I may employ as the cathodic device a receptacle of refractory material of any suitable shape, disposed at the surface of the bath, and containing the requisite means for conducting the current, for instance a metal ring or cylinder.

The metal which is formed within the said receptacle will unite with the layer of liquid metal preliminarily placed therein and will float upon the surface of the electrolytic bath in the form of a liquid layer of a certain thickness which constitutes the active surface of the cathode.

By way of example and for the proper understanding of my said invention, I have set forth hereunder a particular method by which the same is carried into effect. The appended drawings show three constructional forms of the device employed for this purpose.

In the particular case of the manufacture of magnesium, the electrolyte consists preferably of magnesium chloride, optionally mixed with alkali metal chlorides or alkaline earth metal chlorides, and if necessary with fluorides, in such a manner that the density

of the molten bath is markedly higher than that of molten magnesium at the working temperature. I may for instance employ the following percentage composition:

	Per cent	
MgCl ₂ -----	75	55
BaCl ₂ -----	20	
CaF ₂ -----	5	

The anode may consist of the walls of the electrolytic vessel, or I may employ a ring of graphite or amorphous carbon. The bottom of the vessel consists of refractory material.

The cathode is disposed at the surface of the bath; and may be variously arranged; but in all cases the active part of the cathode consists of a layer of liquid magnesium. The cathodic device shown in Fig. 1 consists of a cylinder of sheet iron coated interiorly with a metal difficultly miscible with magnesium or with a very thin layer of a metal easily miscible with magnesium, and is coated on the external periphery with a refractory substance *c* or with a part of the chloride bath solidified by a cooling worm, the whole serving as a retainer for a continuous layer *e* of liquid magnesium which floats upon the surface of the bath *g*. This layer of metal is preserved on its upper surface from all contact with air, by a layer *f* of a melted mixture of chlorides which is so proportioned that it will be lighter than the liquid magnesium, for instance 5KCl, MgCl₂, or KCl.NaCl.

The magnesium produced by the electrolysis will collect below (and of course quickly mix with, the layer of liquid magnesium which must preliminarily be present in order to start the electrolysis, and the equilibrium of the densities is so balanced that the metal will not escape from the ring serving as cathodic support. The magnesium as collected is taken out through the top layer *f* of molten chlorides.

In another modification as shown in Fig. 2, I employ a cathode device of sheet iron having the shape of an inverted basin of large diameter and small height; the said device is placed face downwards and touches the surface of the bath. The device in ques-

tion is preliminarily filled with liquid magnesium, and during the electrolysis the magnesium, which deposits on the layer of liquid magnesium overflows the lower edge of the device, and collects in the annular space *h* between the latter and a suitable external cylinder *c* consisting of refractory material used alone or covered with sheet metal on its internal surface, or in place of the refractory cylinder *c* I may use a cylinder of sheet metal surrounded by a coating of chloride which is solidified by a cooling worm immersed in the bath in proximity to said cylinder, or simply of solidified chloride.

The magnesium which collects in the said annular space may be withdrawn from the bath as it is formed, or it may be united in a single layer and covered with a light mixture of molten chlorides in order to avoid oxidation, as in the preceding case.

The apparatus according to my invention may further comprise either a ring of refractory material optionally covered with a suitable metal on its internal surface, or a ring of sheet metal having a coating of chloride which is solidified by a cooling worm, or simply a ring of solidified chloride within which is disposed the conducting part of the cathode; the latter may consist of a grid or a perforated plate, or of an inverted basin, and is made of a metal which is infusible and only slightly miscible with magnesium, such as chromium, molybdenum, tungsten, manganese, vanadium, titanium, silicon and their alloys, or of an infusible non-miscible metal employed either alone or covered with one of the above mentioned metals or with a fusible metal which is difficultly miscible with magnesium such as antimony, bismuth or tin, or with a thin layer of a miscible metal such as copper, zinc or aluminum.

By the use of the aforesaid metals, I am enabled to form upon their surface a layer of alloys saturated with magnesium or a layer of adherent magnesium upon which the molten magnesium is deposited, which will then act as cathode. In certain cases, I may dispense with the preliminary use of the layer of molten magnesium. It should be noted that in this latter case the protecting layer of light chlorides is added only after the formation of a layer of molten magnesium covering the whole surface and thus obviating all mixture of the light chlorides with the electrolyte.

In the second example of the invention, I may again replace the usual sheet metal cathode device of Fig. 2 by one consisting of a metal as above mentioned in connection with the third example. When the said metal or alloy is infusible at the working temperature, said device can be made of one of the aforesaid metals. But when the selected metal is fusible at the working temperature, I prefer to construct the said receptacle of iron

which is covered with one of the aforesaid metals.

Obviously, my said invention is not limited to the special constructions shown in the drawings. In particular, the cathode may consist of any suitable combinations of parts forming the aforesaid cathodes, thus comprising rings, inverted basins, plates, grids, or the like. In this case, the term "ring" is not intended to restrict the same to a cylindrical or round body, but the ring may be of any desired shape.

One can also use this cell as a secondary instead of primary, by substituting as anode an alloy of magnesium heavier than the electrolyte for the anodes of graphite or hard carbon.

I claim:

1. In a process for the electrolytic preparation of light metals such as fused magnesium and fused calcium, starting with a fused electrolyte heavier than the fused metal forming at the cathode, the step of applying a protective layer of fused salts inert to said fused metal, above the said layer of fused metal in order to isolate the metal from contact with the atmosphere, such layer of fused salts being of lower specific gravity than the fused light metal formed.

2. A process of obtaining magnesium and calcium, which comprises the step of forming three superposed layers arranged in the order of the relative densities; first—at the bottom, a relatively heavy layer containing the chloride of the metal which is to be obtained which layer constitutes the electrolyte, second—above the electrolyte, a layer of the metal to be obtained, serving as the cathode, and third—upon said metal, a layer of molten salts having a composition different from the first mentioned layer and which is free from action on the obtained metal, and which third layer isolates the said metal from contact with the ambient atmosphere, such third layer being of lower specific gravity than the second layer, every part of the cathode being out of vertical alignment with the anode.

3. A cell for the electrolytic preparation of light metals such as magnesium and calcium, comprising at the upper part of the cell, at near and partly below the normal liquid level, a ring of electrically insulating material, in the interior of this ring a piece formed of a conducting material and capable of being wetted by the molten metal to be obtained which latter forms the cathode element, whereby the metal produced at the cathode during the normal operation is confined by said ring of insulating refractory material, and means for preventing overflow of material from said cell during normal operation thereof.

4. A cell according to claim 3 in which the piece in the interior on which the metal to be obtained collects, is a metallic piece which is

only slightly alloyable with the metal to be
obtained, such metallic piece being wholly
submerged in the fused contents of the cell,
and an electrical connection to said metallic
5 piece, from above.

In testimony whereof I have affixed my
signature.

ALFRED JESSUP.

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