UNITED STATES PATENT OFFICE.

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ELECTROLYSIS OF FUSED SALTS.

No. 865,648. Specification of Letters Patent. Patented Sept. 10, 1907.

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To all whom it may concern:

Be it known that we, FRANZ VON KÜGELGEN, a subject of the German Emperor, and GEORGE O. SEWARD, a citizen of the United States, both residing at Holcombs Rock, in the county of Bedford and State of Virginia, have jointly invented certain new and useful Improvements in the Electrolysis of Fused Salts, of which the following is a specification.

The prevailing theory in regard to the electrolysis of a mixture of fused metallic salts is that the less electro-positive metal is separated before the more electro-positive metal. This has proved to be true for salt mixtures having the same anion. Thus, zinc is deposited from an electrolyte of zinc chlorid and sodium chlorid; and magnesium is separated from an electrolyte of $MgCl_2$ and KCl, etc.

With salt mixtures where the metals are combined with different anions, the situation is different. If we have the less electro-positive metal in combination with a stronger anion than the anion of the more electro-positive metal, and of such a position in the table of relative potentials that the decomposition voltage of its compound is higher than the decomposition voltage of the compound of the more electro-positive metal, the latter will be decomposed first, because the current has a tendency to do the easier work first. While the anion of the more electro-positive metal is separated at the anode, the cation will react in a secondary reaction with the anion of the less electro-positive metal. Thus the result of the electrolysis would be also the separation of the less electro-positive metal from the salt mixture, if the secondary reaction was complete. This is, however, the case only under certain conditions, which are difficult to maintain, while, in most cases, an alloy of both metals is obtained.

When a fused mixture of $MgCl_2$, NaCl, and KCl, containing about 13 per cent. Mg, is subjected to electrolysis, we get pure magnesium. When, however, we replace most of the $MgCl_2$ by MgF_2, keeping all other conditions the same, we get an alloy of magnesium with alkali metals instead of pure magnesium. Electrolyzing a mixture of MgF_2 and $CaCl_2$ results in an alloy of magnesium and calcium with constant separation of chlorin at the anode. The results in these cases are explained if we look at the decomposition voltages of the different compounds and the figures for the heat of combination. According to Richards (*Aluminum*, 3rd ed. pp. 234 and 237) NaCl requires for its decomposition 4.3 volts; MgF_2 requires 4.6 volts, and NaF requires 4.7 volts. The reactions are,—

$$2NaCl \text{ (electrolyzed)} = 2Na + 2Cl;$$
$$MgF_2 + 2Na = Mg + 2NaF.$$
(210,000 calories) (219,400 calories.)

Sodium chlorid is decomposed first, its decomposition voltage being lower than that of the MgF_2, and the MgF_2 is in turn reduced by the sodium, though this secondary reaction is not complete because the heat of combination of 2NaF is only a little higher than that of MgF_2. The result of electrolyzing a mixture of MgF_2 and $CaCl_2$ is similarly explained, the $CaCl_2$ being decomposed before the MgF_2 and the MgF_2 being reduced in a secondary reaction by the nascent calcium. The secondary reaction is not complete because the heat of combination of CaF_2 is only slightly higher than that of MgF_2. An alloy of Mg and calcium therefore is obtained. These cases illustrate sufficiently the difficulty of separating the less electro-positive metal from a mixed electrolyte of compounds having different anions, if the metal sought is in combination with a stronger anion than that of the more electro-positive metal. The present invention takes advantage of this fact in the production of alloys from a molten mixture of salts by selecting a compound of the less electro-positive metal having a higher decomposition voltage than the compound of the more electro-positive metal, and so regulating the electrolytic conditions that the secondary reaction between the more electro-positive metal (which is set free first) and the compound of the less electro-positive metal is not complete, but takes place only to the extent necessary for the formation of the desired alloy.

The electrolyte chosen is such that what we call the more electro-positive metal is not only stronger as respects its own anion, but also as respects the anion of the less electro-positive metal than the less electro-positive metal, so that it can reduce the compound of the less electro-positive metal in a secondary reaction. Both cations are obtained at the cathode, but only the anion of the more electro-positive metal is obtained at the anode.

We claim as our invention:—

1. The production of alloys by electrolysis of a mixture of fused metallic salts having such combination of anions and cations that the decomposition voltage of the compound containing the more electro-positive metal is lower than the decomposition voltage of the compound containing the less electro-positive metal, and regulating the conditions of the electrolysis so that the secondary reaction between the more electro-positive metal and the compound containing the less electro-positive metal is only partially complete, so that the desired alloy is obtained.

2. The production of alloys of earth alkali metals and less electro-positive metals by the electrolysis of a mixture of their fused salts in which the compound containing the less electro-positive metal has a higher decomposition voltage than the compound containing the earth-alkali metal, and regulating the electrolysis so that the secondary reaction between the earth-alkali metal and the compound of the less electro-positive metal is only partially complete, so that the desired alloy is obtained.

3. The production of alloys of earth-alkali metals and less electro-positive metals by the electrolysis of a mixture of fused earth-alkali chlorid and a fluorid of a less electro-positive metal of higher decomposition voltage than the earth-alkali chlorid, and regulating the electrolysis so that

the secondary reaction between the earth-alkali metal and the fluorid is only partially complete, so that the desired alloy is obtained.

4. The production of alloys of earth-alkali metals and magnesium by electrolysis of a mixture of fused earth-alkali chlorid and megnesium fluorid, regulating the electrolysis so that the secondary reaction between the earth-alkali metal and magnesium fluorid is only partially complete, so that the desired alloy is obtained.

5. The production of magnesium-calcium alloy by the electrolysis of a fused mixture of $CaCl_2$ and MgF_2, and regulating the electrolysis so that the secondary reaction between calcium and MgF_2 takes place only to a limited degree.

In witness whereof, we have hereunto signed our names in the presence of two subscribing witnesses.

FRANZ VON KÜGELGEN.
GEORGE O. SEWARD.

Witnesses:
FR. VON BIDDER,
J. H. WEBB.