

## UNITED STATES PATENT OFFICE

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PRODUCTION OF REFINED MAGNESIUM  
AND MAGNESIUM ALLOYS

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This invention relates to improvements in purifying magnesium and its alloys.

The main object of the invention is to provide a simple and commercially practicable method which permits the obtainment of a substantially perfect refinement and minimum loss of the metallic material to be refined.

The refinement of magnesium and its alloys with carnallite (the double salt  $KCl \cdot MgCl_2$ ) or with magnesium chloride, which compounds were used as fluxes in the early period of the production of magnesium, did not answer the purpose: in this manner only metal interspersed with chloride inclusions was obtained, so that the purified metal had to be subjected to a special after-treatment for the purpose of removing the remnants of magnesium chloride still present. Therefore first attempts were made to give up the use of fluxes at all, and to perform the refinement with the aid of indifferent gases (hydrogen, helium, methane) caused to pass through the liquid metal. This method—not particularly inexpensive—actually yielded metal absolutely free from salts, but oxides and nitrides present in the metal were left behind. The practically satisfying solution of the problem was only brought about by using instead of pure magnesium chloride or carnallite, mixtures of these salts with additional substances acting as inspissating agents, to impart the flux such a viscosity that it sinks to the bottom after having adsorbed the impurities, and can then be separated from the purified metal by pouring off the latter. This process has become and remained the prevailing method of purification. When metal oxides (especially magnesium oxide) are used as inspissating agents the viscosity of the melt will rise about proportionally with the amount of oxide added. On the other hand, the effect of increasing additions of fluorides is first that the melting point of the flux is gradually lowering; only when the eutectic concentration had already been exceeded and the melting point curve is rising with further increase of the fluoride amounts added, thereupon the said additions will bring about a steadily increasing rise of the viscosity (Beck, Magnesium and its Alloys, Berlin, Julius Springer, 1939, 317). A typically composed flux of this kind consists of 70% carnallite, 20%  $CaF_2$ , and 10%  $MgO$ .

In contrast to the hydrogen process, this known process is capable of completely removing also oxidic and nitridic impurities and can, moreover, be used for the refinement of scrap. Refining processes, based on the principle that the sus-

5 pended matter collects, by agglutination, into a dross, specifically heavier than the melt, during stirring the bath, have, however, unavoidable disadvantages. Since the dross is sticky, it does not cleanly separate from the purified metal, so that losses arise resulting from removal of metal particles with the dross. At all events, however, a strongly contaminated residue of the liquid metal must be poured out separately. The fact that the sticky dross moves for the most part to the bottom and the walls of the crucible is attended with the fatal consequence that, on casting, particles of the dross may come loose and are then carried along by the purified metal; and it renders it necessary to give the crucible a complicated cleaning after casting. There is finally the drawback that an excess of expenditure is needed owing to a part of the magnesium chloride being consumed by the magnesium oxide added to act as inspissating agent.

All these difficulties have been overcome by a method of purification which fundamentally deviates from the known processes depending on the use of magnesium chloride or carnallite in so far as the flux contains as the main component chlorides which during stirring the bath dissociate and/or evaporate, that is to say, chlorides of iron or zinc or mixtures of these chlorides; besides the flux may still contain smaller quantities (about 30%) of magnesium halides. (Patent No. 2,066,579). By means of this process the removal of the foreign entrained matter is brought about by the decomposition of the fluxes giving rise to upward currents of gases in the metal causing suspended matter to rise to the top of the melt and join with surface scum to form a powdery dross, which separates readily and cleanly from the liquid metal. In case the flux contains, beside the volatile main purifier, as secondary ingredient non-volatile chlorides such as magnesium chloride, also these will be caused through the volatile chlorides to rise to the top without, however, making the separated dross sticky.

A later process of similar nature comprises intimately mixing the molten metallic material with a solid practically chlorine-free refining agent substantially consisting of fluorine compound which, at the melting or casting temperature, becomes vaporized or decomposed with the liberation of at least one fluorine-containing vaporous or gaseous constituent, while adding the said fluorine compound in an amount sufficient to effect the required purifying action as the refining agent proper. (Patent No. 2,124,957). A group of compounds particularly well suited for

the carrying out of that method are the metallic fluosilicates. The metal salts of hydrosilicofluoric acid ( $H_2SiF_6$ ) on being heated, give off gaseous silicon tetrafluoride ( $SiF_4$ ) which becomes uniformly finely distributed in the metallic melt while metallic fluoride remains behind in the non-fused state and becomes spread over the melt in the form of a coating. Magnesium fluosilicate ( $MgSiF_6$ ) has proved to be best suited for the purpose in view. Next in order of utility for the present purpose come the fluoborates. Furthermore, similar refining effects can also be obtained with neutral or acid ammonium fluoride or salts containing ammonium fluoride chemically combined in a complex form (such as for example ammonium silicofluoride), or with mixtures of ammonium fluorides. The gases generated by decomposition of the salts bubble through the molten matter and free it completely of non-metallic included matter such as oxides and nitrides, without leaving behind remnants of salts therein.

By further improving these two purifying methods depending on volatile purifying agents, the aim has now been attained to return to the fluxes containing magnesium chloride or carnallite as the main component, without giving up the advantages of the purification with the aid of upward currents of gases. By systematically increasing the proportion of the magnesium chloride additions, it has been found out, that in the presence of magnesium chloride, even if the proportion considerably exceeds one-half of the total mass, volatile fluxes of the kind of chlorides or iron or zinc or mixtures of both these chlorides, and also of the fluorine compounds, which serve as the only purifiers in the case of the process of Patent No. 2,124,957, are capable of transporting, practically speaking, the total amount of impurities to the top of the melt in the state of a dry dross, which is readily skimmed. It has, furthermore, come to light, that in such salt mixtures also carnallite may be used instead of magnesium chloride without bringing the slightest traces of alkali chloride into the refined metal. Since carnallite is the cheapest material and possesses a very good capacity for dissolving magnesium oxide and -nitride and a fair fluxing efficacy and seeing that its melting point lies far below that of magnesium chloride, by this possibility alone a considerable progress in the art would have been brought about.

The proportion of the non-volatile purifier which is (practically speaking) entirely carried along by the gaseous vehicle, can be increased by introducing additions into the composition which are capable of lowering the melting point and the viscosity of the non-volatile component or components of the flux. Therefore, by using these additions for the present process, the very opposite is aimed at of what is the object of the inspissating agents taken for the commonly used purifying method. Additions particularly well suited for carrying out the present process are the alkali chlorides and calcium chloride, that is to say compounds which when used with the known process serve a purpose diametrically different to their object in the present method. The explanation of this apparent contradiction is found in the fact that the amounts of the additions to be used in the present process are not allowed to essentially exceed the eutectic concentrations. Thus for instance potassium chloride melts at  $776^\circ C.$ , magnesium chloride at  $711^\circ C.$ , whereas

the melting point of carnallite lies at  $490^\circ C.$  By decreasing the proportion of magnesium chloride from 50 mol-per cent to 33 mol-percent a mixture of salts is obtained the melting point of which is as low as  $426^\circ C.$ , and parallelly therewith runs the decrease of viscosity. There is the possibility of approaching the concentration to conditions most favorable for the present process by adjusting the non-volatile component of the flux in such a manner as to contain magnesium chloride and potassium chloride, in reciprocal proportions approaching to one of the eutectic concentrations in the system  $KCl.MgCl_2$ .

The above embodiment of the invention is thus based on the principle that instead of increasing the viscosity of magnesium chloride or carnallite by the addition of inspissating agents, the viscosity (and the melting point) of the magnesium chloride component of the flux is diminished with a view to make the most of the sweeping force of the gases or vapors evolved from the volatile component of the flux.

Since the dross does not stick to the walls and the bottom of the crucible, there is no danger of dirt being carried along by the refined metal or being left behind in the crucible in pouring the casting. The skimmed dross is absolutely free of metal. Consequently the losses by burning are reduced to the least amount attainable. On the other hand, also the refined metal is recovered in a completely salt-free condition. In comparison with the above discussed previous proposals concerning the use of volatile fluxes, the present process offers the advantages of being more economical.

The following salt mixtures are given as examples, all percentages mentioned being percentages by weight:

40%  $KCl.MgCl_2$  + 20%  $MgCl_2$  - 40%  $FeCl_3$   
 40%  $KCl.MgCl_2$  + 20%  $MgCl_2$  - 40%  $ZnCl_2$   
 40%  $KCl.MgCl_2$  + 20%  $MgCl_2$  - 30%  $FeCl_3$ , 10%  $ZnCl_2$   
 40%  $KCl.MgCl_2$  + 20%  $MgCl_2$  - 40%  $MgSiF_6$   
 40%  $KCl.MgCl_2$  + 20%  $MgCl_2$  - 35%  $MgSiF_6$ , 5%  $(NH_4)_2 SiF_6$   
 40%  $KCl.MgCl_2$  + 20%  $MgCl_2$  - 30%  $FeCl_3$ , 10%  $MgSiF_6$

A flux containing calcium chloride consists by way of example of 55%  $MgCl_2$ , 35%  $FeCl_3$  and 10%  $CaCl_2$ .

The magnesium containing material is molten down while sprinkling the flux little by little over it, the total quantity of the flux amounting preferably to from 1 to 3 per cent by weight. While vigorously stirring the flux into the molten metal, the bath is maintained between  $720$  and  $750^\circ C.$  Celsius. The setting free of gases and/or by decomposition of the volatile portion of the flux, gives rise to upward currents in the molten metal, which cause non-metallic inclusions and suspended matter to rise to the top of the melt and join with the surface scum. The covering flux separates effectively, together with the entrained impurities, from the molten metal beneath. When making use of the process subject of the Patent No. 2,126,786, there are applied to the bath practically anhydrous solid organic substances which burn with the formation of a froth inert to magnesium, and which yield, on carbonization, a hard crust of a nature not to become wetted by molten magnesium, such as for instance asphalt, casein, horn meal, and sugar. Before pouring, the coating is detached from the rim of the crucible and the pure metal poured from beneath the coating.

To attain a more intimate mixture, it is advantageous to previously melt the salt mixture

to be used according to the present invention, and to crush the hardened flux before use.

What we claim is:

1. The method of purifying magnesium and alloys thereof which comprises treating the impure metallic material with a flux containing a mixture of carnallite and magnesium chloride with a content of from 25 to 40 mol-per cent potassium chloride, and besides a compound which, at the melting or casting temperature, becomes vaporized or decomposed with the liberation of gases, the amount of the said volatile component of the flux being at least sufficient to transport, by means of upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

2. The method of purifying magnesium and alloys thereof, which comprises treating the impure metallic material with a flux composed of a major portion of non-volatile body comprising magnesium chloride and potassium chloride in a non-inspissated condition, and of a minor portion of volatile body comprising at least one compound which, at the melting or casting temperature of the metallic material under treatment becomes vaporized or decomposed with the liberation of gases, the non-volatile body having a melting point not above that of carnallite, and the volatile portion being present at least in an amount sufficient to transport, by means of the upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

3. The method of purifying magnesium and alloys thereof, which comprises treating the impure metallic material with a flux composed of a major portion of non-volatile body comprising magnesium chloride and potassium chloride in a non-inspissated condition, and of a minor portion of volatile body comprising at least one compound selected from the group consisting of chlorides of iron and zinc, metallic fluosilicate, metallic fluoborate, and ammonium fluoride, the melting point of said non-volatile component of the flux being not above that of carnallite, and the amount of the said volatile component of the flux being at least sufficient to transport, by means of the upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

4. The method of purifying magnesium and alloys thereof, which comprises treating the impure metallic material with a flux containing as a major component carnallite in a non-inspissated condition and as a minor component a material which, at the melting or casting temperature, becomes vaporized or decomposed with the liberation of gases, the amount of the said volatile constituent of the flux being at least sufficient to transport, by means of upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

5. The method of purifying magnesium and alloys thereof, which comprises treating the impure metallic material with a flux composed of a major portion of non-volatile body comprising magnesium chloride and potassium chloride in a non-inspissated condition, but, on the contrary, incorporated with additions capable of lowering the melting point and the viscosity of the said body, and of a minor portion of a material which, at the temperature of the metallic material under treatment, becomes vaporized or decomposed

with the liberation of gases, the amount of the said volatile component of the flux being at least sufficient to transport, by means of upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

6. A process as defined in claim 2, in which the non-volatile component of the flux consists of magnesium chloride and potassium chloride in reciprocal proportions approaching to one of the eutectic concentrations in the system KCL-MgCl<sub>2</sub>.

7. A process as defined in claim 5, in which to a non-volatile basis of carnallite there is added magnesium chloride in an amount approaching to the eutectic concentration.

8. A fluxing material suitable for use in melting and refining metallic magnesium and its alloys, which consists of an intimate mixture containing a minor proportion of material which, at the melting or casting temperature, becomes vaporized or decomposed with the liberation of gases, and a major proportion of a non-volatile basis comprising magnesium chloride and potassium chloride, the said non-volatile basis of the flux having a melting point not above that of carnallite, and the amount of the said volatile component of the flux being at least sufficient to transport, by means of upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

9. The method of purifying magnesium and alloys thereof which comprises mixing the metal in molten form with a non-volatile fluxing agent consisting of a non-inspissated mixture of magnesium chloride and potassium chloride, which mixture has a melting point not above that of carnallite, and including with said fluxing agent a lesser quantity of a mineral salt which assumes a gaseous character in contact with the molten metal, whereby the gases produced by said mineral salt carry the generated dross upwardly to the surface of the melt.

10. A fluxing material suitable for use in melting and refining metallic magnesium and its alloys, which comprises an intimate mixture containing a minor proportion of a compound selected from the group consisting of chlorides of iron and zinc, metallic fluosilicate, metallic fluoborate, and ammonium fluoride, and a major proportion of non-inspissated carnallite, the amount of the volatile component of the flux being at least sufficient to transport, by means of upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

11. A fluxing material suitable for use in melting and refining metallic magnesium and its alloys, which comprises an intimate mixture containing a minor proportion of a compound which, at the melting or casting temperature, assumes a gaseous character, and a major proportion of a base of a non-volatile character, the non-volatile base comprising carnallite in admixture with additions capable of lowering the viscosity and the melting point of said non-volatile base, the amount of the volatile component of the flux being at least sufficient to transport, by means of upward currents produced, substantially the whole bulk of the generated dross to the top of the melt.

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