METHOD OF PURIFYING MAGNESIUM

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This invention relates to magnesium and such alloys of magnesium in which the latter metal largely predominates and which, in the following, are considered to be included when the term "magnesium" is employed. This application is a continuation in part application of our copending application entitled "Method of purifying magnesium" and filed December 27, 1929. (S. N. 416,997).

An object of the invention is to provide a method which permits, by purification of the metal, to raise the resistance of magnesium to corrosion to a hitherto unattained degree.

Various methods for the purification of magnesium have been developed. The objects of these methods, however, was always restricted to the elimination, by the use of fluxes, of impurities consisting in salts or having acidic character. The resistance to corrosion of the apparently pure metal thus obtained does not, in every respect, answer all demands which result from the continually spreading industrial use of magnesium metals.

We have now ascertained that the comparatively low resistance to the action of corroding agents of magnesium and its alloys when purified in the aforesaid manner is only to a small extent an inherent property of the magnesium metal itself, but is largely due to the presence, in the metal, of very small quantities (fractions of one-tenth of one percent) of iron and, to a smaller degree, other impurities of a non-saline character which, although insoluble in the molten metal, are suspended therein in an extremely finely divided form and also remain present in the metal on solidification of the latter. In the following the invention is generally described with reference to iron only, but it is to be understood that where "iron" is referred to in the following the same equally applies to these other impurities of a non-saline character.

It has long been known that iron will not combine with magnesium to form an alloy. However, small quantities of this metal, generally in an extremely subdivided form, are frequently incorporated into the magnesium owing to the use of raw materials containing iron as an impurity or as a consequence of the introduction of alloying substances such as aluminium or zinc or silicon which contain certain quantities of iron, generally in the form of iron compounds, also as an impurity.

On solidification of the metal these iron particles, owing to their very minute size, remain suspended in the metal. When such metal comes into contact with water or aqueous solutions of salts, the iron particles probably behave as cathodes of local galvanic elements and the corrosive action of water is strongly stimulated.

Having recognized the deleterious effect caused by the presence of iron, we have endeavoured to find means by which to remove the contaminating iron from the metal and we have, in the course of extensive and laborious investigations, developed the method hereinafter described for this purpose.

It is well known that on cooling a melt composed of different constituents, solidification does, as a rule, not occur at a definite constant temperature, but over a temperature range in which primary crystals of one of the components (which shall be supposed as stable for the purpose of this description) are formed with falling temperature, while the ratio of the components remaining in the melt continuously changes, until finally, in most cases, the so-called eutectic concentration is reached in the latter, the remainder then solidifying at a definite "eutectic" temperature and as a whole. The nature and composition of the primary crystals formed substantially depends on the composition of the original melt, i.e. on the ratio of the constituents present therein.

We have now discovered that in the case of magnesium alloys any primary crystals first formed on solidification will envelop or chemically or mechanically combine with the iron impurities contained as solids in melts of this kind in a state of high dispersion thus freeing the melt from the latter. A natural explanation of this phenomenon would seem that the extremely minute particles of iron suspended in the melt act as nuclei or starting centres in the crystallization of the primary crystals, and thus become embedded in the latter; but we wish it to be understood that we do not limit ourselves to this explanation, which is a purely tentative and hypothetical one.

In order to make use of this phenomenon in the elimination of the said iron impurities from melts of magnesium and magnesium alloys it is of course necessary, not only to cause formation of such primary crystals, but also to remove the latter, in which the iron particles are supposed to be embedded, from the remaining melt. Further, in order to avoid as far as possible a substantial alteration in the composition of the metal or alloy to be treated, by the separation of such primary crystals from the molten metal as such, it is advisable to add to the bath of molten metal...
special constituents, hereinafter called purifying substances, of such a character and in such proportions, that they will form primary crystals on cooling after having been dissolved in the metal bath by the application of suitable temperatures... In order to avoid contamination of the bath proper by the participation of a considerable portion of the added constituents (which are only added for purposes of purification) in the formation of an eutectic, it is advantageous to employ, as additives which, together with magnesium, form an eutectic—if any—in which the ratio of the purifying substance to magnesium is as low as possible, as in this case all of the purifying substance added in excess of the eutectic ratio, on cooling of the melt, separates in the form of primary crystals and may be eliminated from the melt in any convenient manner. We have found that manganese and silicon are substances of this kind, which because of their low eutectic concentration, in their binary alloys with magnesium, of about 1.3 percent and 1.4 percent respectively, are particularly suited in this respect. In the case of magnesium alloys which contain, besides magnesium as the predominant constituent, also elements such as aluminium, zinc, cadmium, calcium, copper, lead and other metals, either singly or in combination, the effect of manganese and silicon is even still more pronounced, as the latter, for all practical purposes, do not enter the eutectic at all, substantially the whole amount of these elements present in the melt being separated from the melt as primary crystals on cooling.

In the practice of our invention we add the purifying substance in a quantity exceeding the eutectic concentration to a melt of the metal or alloy to be treated, preferably in finely divided form so as to promote its dissolution in the melt. On the other hand, in view of the subsequent separation, from the melt, of the primary crystals of the purifying substance, the quantity of the latter should not be excessive. As a rule, it will suffice to add a moderate percentage in excess of that corresponding to the eutectic concentration; in the case of manganese for instance about 4.5 percent of the total melt to be treated are quite sufficient. In some cases it is equally possible, or even preferable, to add the purifying substance to the melt as a chemical compound which is reduced by magnesium, such as for instance manganese chloride, since this manner of procedure particularly favours a rapid and thorough dissolution of the purifying substance within the melt, which may be otherwise also promoted by vigorous stirring. The temperature of the melt is then raised, until the purifying substance has entirely dissolved, this frequently requiring temperatures of 200° C. and more above the melting point of the metal or alloy to be treated. In order to avoid an excessive oxidation of the melt during this heating stage, it is necessary to protect the surface of the bath with a layer of one of the well-known saline fluxes generally employed in the purification of magnesium. When the purifying substance has dissolved, the temperature of the melt is then again lowered, which causes the purifying substance to separate from the melt in the form of primary crystals containing the iron impurities in combination. This cooling of the melt during this stage of our process is preferably carried down to the lowest temperature possible without the formation of crystals containing other constituents of the melt, in order to eliminate the purifying substance—and incidentally also the iron impurities—as efficiently as possible, without however otherwise altering the composition of the melt proper. Separation of the primary crystals from the remaining melt may subsequently be effected simply by settling (if possible) or preferably to perform the cooling stage of the process at a very slow rate, the overlying melt then being poured off, or by sieving, centrifuging or other appropriate means. In any case, the separated iron-containing primary crystals should be removed from the melt as completely as possible, because the former may also impair the resistance to corrosion of the metal to a certain extent, although in a much smaller degree than the free iron particles. The remaining melt is then ready for further handling (casting into ingots or moulds etc.).

In the treatment of alloys of magnesium with certain elements, particularly with aluminium and zinc, it has been observed that the presence of the major part of the iron impurities is due to the fact that the alloying elements introduced into the magnesium always contain larger or smaller quantities of iron as an alloyed contamination, and that this iron becomes incorporated with the magnesium bath by the formation of the magnesium alloy. A further difficulty arising in cases of this kind consists in that it is frequently impossible to ensure the dissolution of sufficient quantities of the purifying substance in the melt, even by the application of high temperatures, when alloying elements are already present in the melt; the reason being that the presence of some of the alloying elements of magnesium, particularly of aluminium, strongly reduces the solubility of the purifying substance, particularly of manganese and silicon in molten magnesium.

In order to overcome these difficulties it has proved advantageous, in the preparation of magnesium alloys free from iron impurities, to combine the purifying with the alloying process by incorporating the purifying substance, in an amount sufficient for attaining its purpose, in the molten unalloyed magnesium, and only after its dissolution in the latter, to add the element or elements to be alloyed with magnesium such as aluminium to the molten metal bath at the relatively high temperature prevailing. The addition of the alloying element immediately causes the greater part of the purifying substance, for instance manganese, to be precipitated as primary crystals together with the bulk of the iron impurities (included those contained in the alloying metal) even at these comparatively high temperatures because of the relatively reduced solubility of the manganese in the molten magnesium in the presence of other alloying elements, whereas the remainder of the manganese until any iron impurities still present, is precipitated in the shape of primary crystals by cooling the melt to a point not far above that of incipient solidification of the alloy proper thus formed.

Separation of the primary crystals is effected in the manner hereinbefore described. In this case, a reducible compound of the purifying substance, such as manganese chloride may be added to the bath instead of the purifying substance as such.

In the stage of dissolving the required amount of purifying substance in magnesium and immediately adding the alloying elements such as aluminium, it is of course equally possible to
proceed in the following manner. Technically pure magnesium is first treated with the purifying substance alone as described above, and the primary crystals of the purifying substance which form a large proportion of the iron impurities originally present in the magnesium are separated from the melt which is then allowed to solidify, for instance cast into ingots. The latter, which still contain an amount of the purifying substance approximately corresponding to its eutectic concentration in magnesium, and the impurities, which are present in larger proportions than in the primary crystals, are removed, for instance aluminium, is added, whereupon, owing to the reduced solubility of the purifying substance in magnesium in the presence of such alloying elements, the purifying substance together with the iron impurities as yet unre moved—including those originally contained in the alloying element recently added—is precipitated from the melt and may be separated therefrom in the manner already described.

While the primary crystals formed and separated from the melt according to the present invention mainly consist of impurities, their exact composition varies according to circumstances, and is moreover generally most difficult to ascertain. When for example silicon is employed as the purifying substance, primary crystals of MgSi are precipitated, or when calcium is also present in sufficient amount, CaSi. Manganese is probably precipitated as such; it may however also contain a certain percentage of magnesium in solid solution. As a result of the present process, by far the greater part of the iron impurities is removed from the metal or alloy treated, particularly when magnesium is used as the purifying substance. Such quantities of iron as may be left in the metal after the treatment is completed, these being in any case but a small fraction of the original content, are moreover combined with manganese, the total of both these metals being often less than 0.2 percent. When in this form, the unfavourable influence of these exceedingly small amounts of iron upon the resistance to corrosion of the metal is no longer perceivable. This appears from the fact that the metal or alloys treated in accordance with the present process with manganese, when brought into contact with sea water develop at least 20 percent less hydrogen in a given time than the corresponding untreated alloys containing the same percentage of manganese.

Example 1

1000 kg. of pure magnesium are melted and the temperature of the melt is raised to about 900° C. When this temperature is reached, 45 kg. of finely ground manganese metal are added to the melt and thoroughly stirred therewith for about 15 minutes. The temperature of the melt is then lowered to about 700° C. and the metal is allowed to settle for about two hours, a temperature of 700° C. being maintained. During this settling period the greater part of the manganese and iron contained in the melt settles down and gathers on the bottom of the melting pot. The molten metal is then poured off from these impurities. The iron content of the alloy, which originally amounted to 0.06 percent, is now found to be reduced to 0.02 percent and the manganese content does not exceed 2 percent. The alloy thus obtained is particularly useful for sheet-rolling, and, owing to the practical absence of iron, offers an exceedingly high resistance to corrosion.

Example 2

In order to produce a magnesium alloy containing 10 percent of aluminium, 4.5 kg. of manganese chloride MnCl2 (anhydrous) are added to 100 kg. of molten metal and thoroughly stirred therewith at about 750 to 800° C. An alloy containing about 1 percent of manganese, balance magnesium, is thus formed, the MgCl2 produced by the reaction collecting at the surface of the bath and forming a protective layer on the latter. To this still molten alloy, 11 kg. of aluminium metal are added at the same temperature while stirring. Part of the manganese is thereby immediately precipitated from the alloy together with the bulk of the iron impurities present, particularly including the iron incorporated in the melt owing to contamination of the aluminium employed. The surface of the melt is then covered with a protective layer of one of the usual fluxes for magnesium and subsequently slowly cooled to 650° C. and maintained at this temperature for about two hours. During this period, the manganese content of the alloy is, owing to the separation and settling of further quantities of primary crystals, reduced to about 0.2 percent, and the iron impurities, which are enveloped or chemically or mechanically combined with the manganese crystals, are removed to such an extent, that only a quantity of the order of 0.001 percent remains in the molten metal. The latter is then poured off from the residue and represents an alloy containing 10 percent of aluminium, balance substantially magnesium, in which less than 0.2 percent of manganese are present and which offers a high resistance to the action of corroding agents such as water, or even sea water.

Example 3

To 300 kg. of technically pure magnesium in the molten state are added 9 kg. of silicon in finely divided form while thoroughly stirring the melt and heating it to about 900° C. At this temperature, the silicon has become entirely dissolved in the melt whereupon the latter is allowed to cool slowly and to stand at a temperature of 675° C. for four hours. After such standing, most of the silicon exceeding the eutectic concentration of 1.4 percent has settled in the form of primary crystals containing the iron impurities to the bottom of the melting pot, so that the supernatant melt may be separated therefrom by pouring off. The iron impurities contained in the melt which originally amounted to about 0.2 percent are now reduced to about 0.08 percent and the silicon content of the magnesium amounts to 1.8 percent.

We claim:—

1. The method of removing iron impurities from magnesium comprising dissolving in the molten metal, by the application of temperatures above about 700° C., a purifying substance selected from manganese, silicon and manganese chloride, in a quantity sufficient to form primary crystals on cooling of the melt while simultaneously combining with the said impurities, cooling the melt to a temperature not exceeding about 700° C., and separating the crystals containing the purifying substance and the impurities from the melt.

2. The method of removing iron impurities from magnesium comprising adding manganese to the molten metal in such a manner as to ensure...
its solution in the melt, cooling the melt to a temperature below the point of formation of manganese-containing crystals, and separating the crystals from the melt.

3. The method of removing iron impurities from magnesium comprising dissolving in the molten metal, by the application of temperatures above about 700°C, a finely divided purifying substance selected from manganese, silicon and manganese chloride, in a quantity sufficient to form primary crystals on cooling of the melt while simultaneously combining with the said impurities, stirring the mixture until the substance added has been dissolved, cooling the melt to a temperature not exceeding about 700°C, allowing the melt to settle for at least two hours and pouring off the melt from the residue.

4. The method of removing iron impurities from magnesium comprising dissolving manganese in finely divided form in the molten metal, by the application of temperatures above about 700°C, cooling the melt to a temperature not exceeding about 700°C, and separating the crystals containing the manganese and the impurities from the melt.

5. The method of removing iron impurities from magnesium comprising dissolving silicon in finely divided form in the molten metal, by the application of temperatures above about 700°C, cooling the melt to a temperature not exceeding about 700°C, and separating the crystals containing the silicon and the impurities from the melt.

6. The method of removing iron impurities from magnesium comprising dissolving manganese in the molten metal in an amount slightly in excess of the eutectic concentration of said manganese, cooling the melt to a temperature below the point of formation of manganese-containing crystals, and separating the crystals from the melt.

7. The method of removing iron impurities from magnesium comprising dissolving silicon in the molten metal in an amount slightly in excess of the eutectic concentration of said silicon, cooling the melt to a temperature below the point of formation of silicon-containing crystals, and separating the crystals from the melt.

8. The method of removing iron impurities from magnesium comprising dissolving in the molten metal between about 1.0 and about 4.5 percent of manganese, adding an alloying metal to the melt, cooling the melt to a temperature not far above the point of crystallization of the melt proper, and separating the precipitated primary crystals containing manganese and a substantial portion of the impurities from the melt.

9. A method of producing substantially iron-free magnesium base alloys which comprises dissolving in the molten magnesium a purifying substance in quantities sufficient to form primary crystals on cooling of the melt while simultaneously combining with any iron impurities present in the magnesium, adding to the melt an additional alloying substance which causes precipitation of said purifying substance with its associated impurities, separating the said precipitated purifying substance and associated impurities from the melt, and subsequently further cooling the molten residue of partially purified magnesium base alloy to a temperature not far above the point of crystallization of the melt proper so as to induce further precipitation of a substantial portion of the remaining purifying substance and associated impurities.

10. The method of producing a substantially iron-free magnesium base alloy with aluminum which comprises dissolving in the molten magnesium a quantity of manganese sufficient to form primary crystals on cooling of the melt while simultaneously combining with the said iron impurities, adding to the melt aluminum in the amount required for forming the desired alloy, said added aluminum causing precipitation from the melt of a substantial portion of manganese with its associated iron impurities, separating the said precipitated manganese and associated impurities from the melt, and subsequently further cooling the molten residue of partially purified magnesium-aluminum alloy to a temperature not far above the point of crystallization of the melt proper so as to induce further precipitation of a substantial portion of the remaining manganese and associated impurities.

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