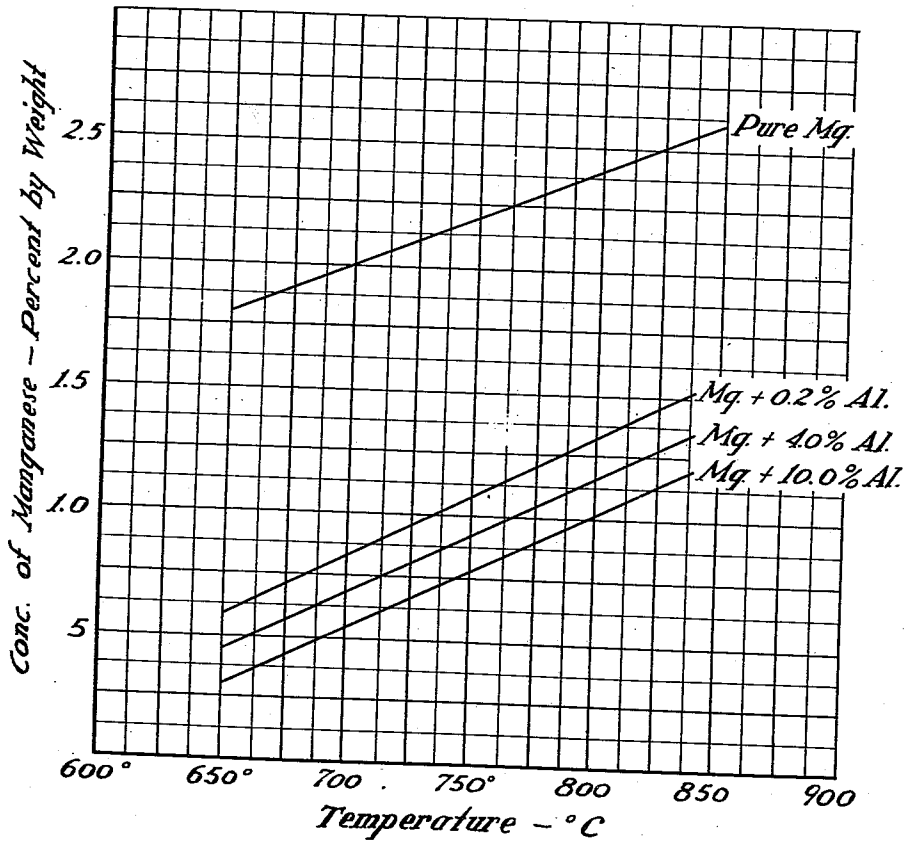
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REMOVAL OF IRON FROM MAGNESIUM-BASE ALLOYS

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REMOVAL OF IRON FROM MAGNESIUM-BASE ALLOYS

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This invention relates to the removal of iron impurities from magnesium and magnesium-base alloys.

For some time it has been appreciated that the tendency of uncoated articles of magnesium and magnesium-base alloys to corrode on exposure to moist air and to aqueous solutions is in some way dependent upon the presence of traces of iron in the metals. More recently it has been shown that there is a certain minute but critical proportion of iron, e. g. about 0.002 per cent in the case of magnesium-base alloys containing aluminum, below which these metals are highly corrosion resistant, but above which they are relatively corrosible. It is evident, then, that in order to render iron-contaminated magnesium and magnesium-base alloys resistant to attack the iron content thereof must be reduced to below the critical corrosion tolerance limit. Unfortunately, however, since at least part of the iron is in actual physical solution in the metal when molten, many of the removal processes described in the art are ineffective in reducing the iron concentration to a sufficiently low value. The remaining known processes, while more or less effective, are fraught with operating difficulties and are wasteful of expensive purifying agents. Moreover, the iron-free metal produced by such processes usually cannot be remelted and heated to casting temperatures in iron and steel containers without again becoming contaminated with iron.

It is accordingly an object of the present invention to provide a simple, convenient, and relatively inexpensive method of treating iron-contaminated magnesium and magnesium-base alloys to reduce the concentration of iron therein to a proportion well below the critical corrosion tolerance limit, i. e. to below 0.002 per cent for most alloys. Another object is to provide a method whereby magnesium and alloys thereof containing less than the critical corrosion limit of iron may be heated in contact with surfaces of metallic iron at temperatures up to 925° C. without dissolving iron. Other objects will be apparent from the description.

The present invention depends upon the discovery that iron is virtually insoluble, i. e. soluble to an extent well below 0.002 per cent by weight, in molten magnesium and magnesium-base alloys when these metals contain manganese in a proportion substantially equal to its solubility limit. For instance, when manganese is dissolved in a molten iron-contaminated magnesium alloy in a quantity approximately sufficient to form a saturated solution, the dissolved iron is rendered insoluble and precipitates, until less than 0.002 per cent remains in solution. The resulting alloy, since it contains iron in a proportion below the critical corrosion limit, is highly corrosion resistant. Likewise, when a substantially iron-free magnesium-base alloy is heated in contact with iron surfaces, if the alloy is nearly saturated with manganese, there is little if any solution of iron from the surfaces into the metal, since the latter is already saturated with iron even though somewhat less than 0.002 per cent is present. The corrosion resistance of the alloy is not reduced.

In removing dissolved and suspended iron impurities from magnesium and magnesium-base alloys according to the invention, any of a variety of essentially similar procedures may be employed. In general, the metal to be purified is melted, ordinarily under a suitable protective saline flux, and manganese is dissolved therein in a proportion approximately equal to its solubility limit at a predetermined temperature below 925° C., such operation being carried out at a temperature at least as high as the predetermined temperature. After solution is complete, the temperature of the molten metal is then controlled at the predetermined temperature, whereby a substantially saturated solution of manganese is formed without appreciable precipitation of metallic manganese, and the dissolved iron is rendered insoluble and precipitates. This precipitate may then be separated from the molten metal, usually by maintaining the same without agitation, and preferably also without permitting the temperature to fall appreciably, for a time sufficient to permit the iron to settle out of solution. However, other separation methods, such as centrifuging, are entirely possible.

In the invention, the introduction of manganese into the magnesium or magnesium-base alloy may be accomplished by any suitable method. Thus, metallic manganese may be melted together with the magnesium, or stirred into the already molten metal. Alternatively, reducible manganese compounds, especially binary compounds such as manganous chloride, manganous fluoride, manganous oxide, manganese dioxide, etc., may be brought into contact with the molten magnesium, as by incorporating the compound in the protective melting flux, whereby the compound is reduced, forming manganese which dissolves in the magnesium. All these methods are comprehended by the term "dis-

solving" manganese in the metal, as herein employed.

The precise proportion of manganese required to form a substantially saturated solution with any given alloy and at any desired separation temperature may easily be determined by simple experiment. Typical solubility data are given in the accompanying drawing, which illustrates graphically the variation with temperature of the limiting solubility of manganese in molten magnesium, and in certain alloys of magnesium with aluminm. Inasmuch as alloying elements other than aluminum do not affect the manganese solubility markedly, the graph will also serve as a rough guide for adding manganese to almost all magnesium-base alloys encountered in commercial practice.

In a preferred form of the invention, the entire purification treatment is carried out at a substantially constant temperature below about 925° C., preferably in the range 650° C. to 850° C. The iron-contaminated magnesium or magnesium-alloy is melted and heated under a flux to the desired temperature. Manganese is then dissolved in the metal in a proportion sufficient to form a saturated solution at the operating temperature, the dissolved iron impurities being thus rendered insoluble and precipitating. The metal is then maintained without agitation for a time sufficient for the precipitated iron, and also any suspended iron particles initially present as such, to settle out of the metal, usually for 30 minutes or more to insure complete settling. After this, the purified metal is separated from the settled iron, as by decanting, and may be introduced into a casting mold wherein it is allowed to solidify. As stated, the dissolving, settling, and casting are all conducted while maintaining the metal at a substantially constant temperature, which is usually well above 700° C. to permit successful casting, although temperatures as low as 650° C. are operable. The resulting cast metal contains dissolved iron in an amount less than 0.002 per cent by weight. It may be remelted in iron containers and heated to temperatures as high as the original operating temperature without dissolving iron from the container.

In an alternative form of the invention, the settling and casting operations are carried out at a substantially constant temperature in the range 650° C. to 925° C., but the dissolving of manganese is carried out at any desired higher temperature. In this case, manganese is incorporated in the heated molten iron-contaminated metal in a proportion just sufficient to form a saturated solution at the subsequent lower settling temperature, the precise proportion being determined by the reference to a solubility diagram as explained. When the manganese is completely dissolved in the desired proportion, the melt is then cooled to the settling temperature, whereby a substantially saturated solution is formed, and the dissolved iron precipitates, and may be removed by means hereinbefore set forth.

As already stated, the process of the invention depends upon maintaining the molten magnesium or magnesium-alloy substantially saturated with manganese at the temperature of settling. In the case of constant temperature operation, it is sometimes convenient to attain this result simply by adding an excess of manganese to the settling vessel. In general, however, it is highly preferable to avoid the presence of any substantial excess undissolved manganese. In this way, waste of expensive metal is eliminated and the heating problems resulting from the presence of metallic sludge are obviated, and in addition the corrosive attack by manganese on the iron and steel settling vessels ordinarily used is largely prevented. To avoid the presence of excess manganese, it is desirable to control quite carefully the quantity of manganese or reducible manganese compound added to the molten metal to be purified so as to approximate closely the saturation value at the settling temperature. In addition, it is preferable not to permit the manganese-saturated molten alloy to cool significantly during the iron-settling step, since such cooling would result in the formation of primary crystals of metallic manganese, which would settle out with the precipitated iron and give rise to the difficulties mentioned.

The invention is particularly applicable to making iron-free magnesium-base alloys containing aluminum and manganese in predetermined proportions between about 0.2 and about 12.0 per cent by weight of aluminum and between about 0.2 and about 2.0 per cent of manganese. In this instance, iron-contaminated magnesium is melted under a protective flux, and aluminum is alloyed therewith in the predetermined proportion. Minor quantities of other alloying elements, such as zinc, cadmium, silicon, or tin, may also be added if desired. When this operation is completed, manganese or a reducible manganese compound is added to the heated melt in a quantity sufficient to dissolve manganese in the alloy in the predetermined proportion. The temperature of the resulting alloy is then controlled to approximately that temperature in the range between about 650° C. and about 925° C. at which the solubility limit of manganese in the final alloy is equal to the proportion of manganese added. In this way, the alloy is rendered substantially saturated with manganese without appreciable precipitation thereof, and the dissolved iron impurities become insoluble and precipitate, and may be removed as hereinbefore explained. This method of operation, in which the aluminum is added to the magnesium prior to the introduction of the manganese, is advantageous in that the proportion of the aluminum can be carefully controlled, as by rapid hardness tests, without interference by the presence of manganese. It is within the invention, however, to add the alloying elements, including manganese, in any desired order, or together.

Thus far it has been assumed that in the process described the dissolving of manganese and the settling and casting steps are all carried out in direct sequence without allowing the metal to cool below its saturation temperature. However, there is another procedural sequence which also utilizes the principle of the invention. In this latter case, the iron-contaminated magnesium or magnesium-base alloy is melted and manganese is dissolved therein in a proportion substantially equivalent to its solubility limit at any desired predetermined temperature above 650° C., preferably in the range 725° C. to 850° C. The molten metal is then poured directly without a settling period into an ingot mold and allowed to solidify. The resulting ingot may then be stored or shipped, and remelted for casting at any later time. The melt so formed may then be heated without agitation to a casting temperature not appreciably above the predetermined manganese-saturation temperature. In this way, because the magnesium is saturated with manganese, the iron-impurities present in

the original alloy remain insoluble, and do not dissolve during the remelting operation, but settle out on the bottom of the remelting pot. The melt may then be separated from the settled iron as by decanting, and cast into molds to form finished products containing less than 0.002 per cent iron. This method of operation has the advantage that the metal may be heated at high temperatures, i. e. up to 925° C., prior to casting the ingot to effect a grain refinement, which persists even after the remelting and final casting operations.

In addition to all the foregoing, the principle of the invention may also be applied to those instances in which it is desired to melt purified magnesium or magnesium-base alloy already containing less than 0.002 per cent by weight of iron in an iron vessel at temperatures between about 700° C. and about 925° C., particularly above 725° C., without experiencing contamination of the purified metal. This result may be attained merely by dissolving and maintaining in the molten metal a proportion of manganese sufficient to form a saturated solution at the temperature of heating. Because of the manganese saturation, solution of iron from the vessel into the alloy is substantially prevented, and the high corrosion resistance of the purified alloy is not destroyed.

The following examples will serve further to illustrate the invention, but are not to be construed as limiting its scope.

Example 1

Commercial metallic magnesium was melted under a protective flux having the following composition in per cent by weight: potassium chloride, 55; barium chloride, 9; magnesium chloride, 34; calcium fluoride, 2. The molten metal was heated to a temperature of 800° C., and metallic aluminum and metallic zinc were then stirred into the melt in quantities sufficient to form an alloy containing 9.0 per cent aluminum and 0.7 per cent zinc. The iron content of this alloy was found to be 0.037 per cent. Manganese was then dissolved in the melt in the proportion of 0.92 per cent, by stirring into the protective flux a sufficient quantity of a saline mixture consisting of manganese chloride, 72 per cent; potassium chloride, 23 per cent; barium chloride, 2.5 per cent; and calcium fluoride, 2.5 per cent. The resulting alloy, which was substantially saturated with manganese, was then maintained without agitation at 800° C. for two hours, during which time the iron impurities, rendered insoluble by the presence of manganese, settled out as a sludge. The purified alloy was then decanted from the sludge and poured into ingot molds to solidify. The resulting ingots contained only 0.0007 per cent iron, and were highly resistant to corrosion by moist air and by salt water. They could be remelted in iron containers at temperatures up to 800° C. or slightly higher without any observable increase in iron content.

Example 2

Commercial magnesium was melted under a protective flux as in Example 1, and heated at a temperature of 785° C. while sufficient finely-divided metallic manganese was stirred into the melt to form a solution containing 2.0 per cent by weight of manganese. The resulting alloy, which was found to contain 0.0126 per cent iron, was cooled to 700° C., at which temperature it became substantially saturated with manganese, and was held at that temperature without agitation for two hours, during which time the iron impurities settled out of the alloy. At the end of the period, less than 0.0007 per cent of iron remained dissolved in the metal.

Example 3

Commercial magnesium, metallic aluminum, and metallic manganese were melted together at 700° C. under a protective flux to form an alloy containing 10.0 per cent aluminum and 0.5 per cent manganese, which also contained 0.028 per cent iron as impurity. The molten alloy was then heated at 700° C. without agitation for two hours, the iron impurities settling out of the alloy, leaving a melt containing in solution slightly less than 0.002 per cent iron.

Example 4

Dowmetal R, a magnesium-base alloy containing 9.0 per cent aluminum, 0.7 per cent zinc, and 0.2 per cent manganese, the balance being magnesium, was melted under a protective flux and heated to 800° C. Sufficient metallic manganese to form a saturated solution at that temperature was stirred into the molten alloy, which was then immediately poured into ingot molds and allowed to solidify. The resulting ingots contained 0.004 per cent of iron as impurity. The ingots were later remelted under flux in a steel pot and heated slowly without agitation to a temperature of 800° C. During the remelting, the iron impurities present settled out of the alloy. The purified metal was then decanted from the settled iron and cast into billets, which were found to contain less than 0.001 per cent iron.

Example 5

Dowmetal H, a magnesium-base alloy containing 6.0 per cent aluminum, 3.0 per cent zinc, and 0.2 per cent manganese, the balance being magnesium, was melted under a protective flux, and metallic manganese was dissolved in the metal in a proportion corresponding to its solubility limit at 750° C. The resulting melt was heated with stirring at temperatures in the range 890° C. to 925° C. for a short period, and then immediately cast into ingots, which were found to contain 0.030 per cent iron as impurity. The ingots were later remelted and heated without agitation at 750° C. for a time sufficient to permit the iron impurities, which were insoluble at that temperature, to settle out. The settled alloy was then cast into billets. The latter contained 0.0015 iron, and exhibited the characteristic grain refinement resulting from the high temperature treatment given.

From the discussion, it will be evident that the invention provides a simple and successful method of removing iron impurities from magnesium and its alloys to values less than its critical corrosion limit. The method does not employ an excess of an expensive purifying ingredient, is not wasteful of heat, and substantially eliminates corrosion of iron and steel containers employed. Moreover, the purified alloy may be remelted at casting temperatures in iron pots without an observable increase in iron content. The method also provides a particularly convenient way of forming iron-free aluminum- and manganese-containing magnesium-base alloys.

It is to be understood that the foregoing description is illustrative rather than strictly limitative, and that the invention is co-extensive in scope with the following claims.

We claim:

1. The method of removing dissolved iron impurities from iron-contaminated molten magnesium and magnesium-base alloys which comprises: adding to the molten metal a sufficient quantity of a substance selected from the class consisting of manganese and reducible manganese compounds to form in the molten metal a solution containing manganese in a proportion approximately equal to its solubility limit in the metal at a predetermined temperature between about 650° C. and about 925° C., while maintaining the metal at a temperature at least as high as the predetermined temperature; then controlling the temperature of the metal at approximately the predetermined temperature, whereby a substantially saturated solution of manganese in the metal is formed without appreciable precipitation of metallic manganese, and the dissolved iron is rendered insoluble and precipitates; and separating the molten metal from the precipitated iron while still maintaining approximately the predetermined temperature.

2. The method of removing dissolved iron impurities from iron-contaminated molten magnesium and magnesium-base alloys which comprises: adding to the molten metal a substance selected from the class consisting of manganese and reducible manganese compounds in a proportion at least sufficient to form in the metal a solution substantially saturated with manganese, while maintaining the metal at a substantially constant operating temperature below about 925° C., whereby the dissolved iron is rendered insoluble and precipitates; and thereafter separating the precipitated iron from the molten metal while it is still at the said operating temperature.

3. The method of removing dissolved iron impurities from molten magnesium and magnesium-base alloys which comprises: stirring the molten metal and adding thereto a substance selected from the class consisting of manganese and reducible manganese compounds in a quantity sufficient to form a solution containing manganese in a proportion approximately equal to its solubility limit in the metal at a predetermined temperature between about 650° C. and about 925° C. while maintaining the metal at a temperature at least as high as the predetermined temperature; discontinuing stirring and maintaining the metal without agitation at about the predetermined temperature, whereby there is formed a substantially saturated solution of manganese in the metal, and the dissolved iron is rendered insoluble and settles out of the molten metal; and separating the purified molten metal from the settled iron while still maintaining approximately the predetermined temperature.

4. In a method of forming castings comprising less than 0.002 per cent by weight of iron from molten magnesium and magnesium-base alloys containing dissolved iron as an impurity, the steps which include: adding to the molten metal a substance selected from the class consisting of manganese and reducible manganese compounds in a proportion approximately equal to but not in excess of that required to form in the metal a solution substantially saturated with manganese, whereby the dissolved iron is rendered insoluble and precipitates without appreciable precipitation of metallic manganese; separating the precipitate from the molten metal; and introducing the metal thus purified into a casting mold wherein it is allowed to solidify, said dissolving, separating, and casting operations all being carried out at a substantially constant temperature in the range between about 650° C. and about 925° C.

5. In a method of preparing a substantially iron-free manganese- and aluminum-containing magnesium-base alloy from a molten iron-contaminated aluminum-containing magnesium-base alloy, the steps which comprise: adding to the molten alloy manganese supplied in a proportion approximately equal to its solubility limit in the alloy at a predetermined temperature between about 650° C. and about 925° C., said proportion being between about 0.2 and about 2.0 per cent by weight; controlling the temperature of the alloy to about said predetermined temperature, whereby a substantially saturated solution of manganese in the alloy is formed without appreciable precipitation of metallic manganese, and the dissolved iron is rendered insoluble and precipitates; and separating the molten alloy from the precipitated iron while still maintaining approximately the predetermined temperature.

6. In a method of preparing a magnesium-base alloy containing less than 0.002 per cent by weight of iron and comprising aluminum and manganese in predetermined proportions between about 0.2 and about 12 per cent of aluminum and between about 0.2 and about 2.0 per cent of manganese, the steps which comprise: forming a molten magnesium-base alloy containing manganese and aluminum in the aforesaid proportions; controlling the temperature of the alloy thus formed to approximately that temperature in the range between about 650° C. and about 925° C. at which the solubility limit of manganese in the alloy is equal to the added proportion of manganese, whereby there is formed a molten alloy substantially saturated with manganese in the desired proportion, and the dissolved iron is rendered insoluble and precipitates without appreciable precipitation of metallic manganese; and separating the molten alloy from the precipitate while still maintaining approximately the said temperature.

7. In a method of preparing a magnesium-base alloy containing less than 0.002 per cent by weight of iron and comprising aluminum and manganese in predetermined proportions between about 0.2 and about 12 per cent of aluminum and between about 0.2 and about 2.0 per cent of manganese, the steps which comprise: providing a body of molten magnesium and alloying aluminum therewith in the predetermined proportion; adding to the resulting alloy a substance selected from the class consisting of manganese and reducible manganese compounds in a quantity sufficient to dissolve manganese in the alloy in the predetermined proportion; controlling the temperature of the alloy thus formed to approximately that temperature in the range between about 650° C. and about 925° C. at which the solubility limit of manganese in the alloy is equal to the predetermined desired proportion of manganese, whereby there is formed a molten alloy substantially saturated with manganese in the desired proportion, and the dissolved iron is rendered insoluble and precipitates; and separating the molten alloy from the precipitate while still maintaining approximately the said temperature.

8. In a method of preparing a magnesium-base alloy containing less than 0.002 per cent by weight of iron and comprising aluminum and manganese in predetermined proportions between about 0.2 and about 12 per cent of

aluminum and between about 0.2 and about 2.0 per cent of manganese, the steps which comprise: providing a body of molten magnesium and alloying aluminum therewith in the predetermined proportion; adding to the resulting alloy a substance selected from the class consisting of manganese and reducible manganese compounds in a quantity approximately equal to but not in excess of that required to dissolve manganese in the alloy in the predetermined proportion; controlling the temperature of the alloy thus formed to approximately that temperature in the range between about 650° C. and about 925° C. at which the solubility limit of manganese in the alloy is equal to the added proportion of manganese, whereby there is formed a molten alloy substantially saturated with manganese in the desired proportion, and the dissolved iron is rendered insoluble and precipitates without appreciable precipitation of metallic manganese; and separating the molten alloy from the precipitate while still maintaining approximately the said temperature.

9. In a method of preparing, from a molten iron-contaminated magnesium-base alloy, an ingot capable of being remelted in an iron container at a predetermined temperature between about 650° C. and about 925° C. to form a molten alloy containing less than 0.002 per cent by weight of iron, the steps which comprise; adding to the molten iron-contaminated alloy a sufficient quantity of a substance selected from the class consisting of manganese and reducible manganese compounds to form in the metal a solution containing manganese in a proportion approximately equal to its solubility limit at the predetermined remelting temperature, and thereafter without settling introducing the resulting alloy into a mold wherein it is allowed to solidify.

10. A process according to claim 9 wherein the molten metal is heated to a temperature sufficiently high to effect grain refinement prior to introducing it into the mold.

11. In a method of preparing, from a molten iron-contaminated magnesium-base alloy, an ingot capable of being remelted and settled in an iron container at a predetermined temperature between about 650° C. and about 925° C. to form a molten alloy containing less than 0.002 per cent by weight of iron, the steps which comprise: adding to the molten iron-contaminated alloy a substance selected from the class consisting of manganese and reducible manganese compounds in a proportion sufficient to but not in excess of that required to form in the metal a solution containing manganese in a proportion approximately equal to its solubility limit at the predetermined remelting temperature, and thereafter without settling introducing the resulting alloy into a mold wherein it is allowed to solidify.

12. In a method of preparing a magnesium-base alloy casting containing less than 0.002 per cent by weight of iron from an ingot of an iron-contaminated magnesium-base alloy containing manganese in a proportion substantially equal to its solubility limit in the alloy at a predetermined temperature above 700° C.; the steps which comprise melting the ingot and heating the same without agitation to a casting temperature not substantially above the predetermined temperature, whereby a substantially saturated solution of manganese in the alloy is formed and the iron-impurities remain insoluble and settle out of the molten alloy; separating the alloy from the settled iron without allowing the metal to cool appreciably; and introducing the purified alloy into a mold wherein it is allowed to solidify.

13. In a method of preparing a magnesium-base alloy casting containing less than 0.002 per cent by weight of iron from an ingot of an iron-contaminated magnesium-base alloy containing manganese in a proportion substantially equal to its solubility limit in the alloy at a predetermined temperature above 700° C.; the steps which comprise melting the ingot and heating the same without agitation to a casting temperature substantially equal to the predetermined temperature, whereby a substantially saturated solution of manganese in the alloy is formed and the iron-impurities remain insoluble and settle out of the molten alloy without appreciable precipitation of metallic manganese; separating the alloy from the settled iron without allowing the metal to cool appreciably; and introducing the purified alloy into a mold wherein it is allowed to solidify.

14. In a process wherein a magnesium-base alloy initially containing less than 0.002 per cent by weight of iron is heated at a temperature between about 700° C. and about 925° C. in contact with metallic iron, the method of preventing solution of iron in the molten metal which comprises maintaining therein a proportion of manganese sufficient to form a substantially saturated solution at the temperature of heating.

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