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METHOD OF GRAIN REFINEMENT OF
MAGNESIUM BASE ALLOYS

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This invention relates to an improved method of refining the grain structure of magnesium base alloys and more particularly relates to a method of refining the grain structure of aluminum-containing magnesium base alloys.

In the manufacture of high quality magnesium base alloy articles it is desirable to begin with a molten alloy which when cast and solidified possess a fine grained structure, is free of gas porosity and clear of non-metallic inclusions. A magnesium base alloy having a fine grained crystal structure is especially to be desired since such fine grained alloys are generally possessed of improved physical or mechanical properties. To obtain the above seemingly incompatible objectives in production practice has been a desideratum in the art for many years. While small batches of magnesium base alloy may be handled in a crucible in which the melt may be chlorinated for degassing and removal of non-metallic materials, heated to an elevated temperature for grain refinement and then cooled and poured, a large supply of metal which must be held for extended times at relatively low pouring temperatures, that is, below about 1400° F., especially for continuous casting or permanent mold operations, is quite subject to rapid grain coarsening of the melt.

Methods of grain refining proposed heretofore have been somewhat successfully used in refining particular magnesium base alloys but are subject to serious limitations hereinafter described.

One method that is in general use today is that of superheating the molten alloy above normal temperatures before casting. This is carried out by rapidly heating the metal to an elevated temperature in the range of 1600 to 1750° F., holding at this temperature for about 15 minutes, and rapidly cooling to the pouring temperature. This method is successfully applied only to magnesium base alloys containing more than about 4 to 5 percent of aluminum and requires the use of special equipment and an undesirable number of procedural steps. The so treated melt is subject to burning and to contamination by adventitious elements at the elevated temperature employed. The refined melt must be poured soon after cooling to pouring temperature to avoid grain growth thus limiting the method to the treatment of small batches. In addition the results are rather variable and uncertain, the exact elevated temperature required for grain refinement varying with alloy composition and sometimes even from melt to melt.

Another method of grain refining proposed heretofore is that of adding carbon or carbonaceous materials to the melt before pouring. Certain disadvantages inure to this method. Carbon in molecular form is difficult to introduce into the melt because of its lightness and therefore requires thorough puddling or mixing into the melt. The addition of carbon in most forms results in hydrogen gas pickup and increased porosity in the solidified metal. Non-metallics may also be introduced inadvertently with the carbon and removal by a flux refining operation is likely to cause still additional gas pickup. In an improved method of adding carbon in the form of carbides or hy-

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drocarbons a slight improvement in retention of the fine grain structure at pouring temperatures is obtained but the holding period at pouring temperatures is still limited to about 15 minutes and the so treated melt is still quite subject to gas pickup. Gas pickup is a problem in that if degassing by chlorination is carried out, subsequent to grain refining as above, grain coarsening takes place.

In addition it has been further demonstrated that grain refinement by carbon is difficult to achieve consistently at temperatures below about 1350° F.

It is an object of this invention to provide a method of grain refining molten aluminum-containing magnesium base alloys which is effective at temperatures below as well as above 1350° F.

Another object of the invention is to provide a method of refining the grain structure of magnesium base alloys whereby the so refined alloys retain their fine grained structure on holding at casting temperatures for extended periods of time.

Still another object of the invention is to provide a method of refining the grain structure of magnesium base alloys whereby the refined alloy has very little tendency to absorb hydrogen gas.

A further object of the invention is to provide a method of refining the grain structure of magnesium base alloys whereby non-metallic materials are not introduced and retained.

A still further object of the invention is to provide a method adapted to the refining of the grain structure of magnesium base alloys in large batches.

An additional object of the invention is to provide a method of refining the grain structure of magnesium base alloys which are not readily grain refined by superheating alone.

These and other objects and advantages of the invention will be more fully understood on becoming familiar with the following description and claims.

It has now been discovered that grain refinement of molten aluminum-containing magnesium-base alloys can be effected by the addition of inorganic carbon-nitrogen containing compounds selected from the group consisting of cyanides, cyanates, cyanamides, thiocyanates, ferrocyanides and ferricyanides, to the molten alloys at a temperature in the range of 1200 to 1700° F. The so-refined melts are capable of retaining the refined grain structure for extended periods of time on holding the melt at casting temperature. The method is applicable to non-superheatable as well as super heatable magnesium base alloys. Even alloys containing less than 1 percent of aluminum may be grain refined by the method provided the manganese content of the so-treated alloy does not exceed about 0.1 percent.

Because of the availability, low toxicity and low cost, cyanamides are the preferred carbon-nitrogen compounds employed in the method. If desired, the grain refining material employed may be first blended or admixed with a suitable flux such as one containing by weight 50 percent of $MgCl_2$, 25 percent of KCl , 20 percent of $BaCl_2$ and 5 percent of CaF_2 . Other materials such as inert inorganic chlorides, fluorides, carbonates and oxides may be employed to form an alkaline blend and reduce the hazard of using cyanides such as $NaCN$.

In carrying out the method of the invention upon a molten magnesium base alloy the melt is brought to a temperature in the range of 1200 to 1500° F., though higher temperatures may be employed, and the grain refining material in powdered or granular, plain or blended, form is added to the melt. Conveniently the grain refining material may be added to the molten alloy while the alloy is still at alloying temperatures ($>1350^\circ F.$) and the so-refined alloy may then be cooled to and held at pouring temperatures, such as 1200 to 1350° F., until

cast. A suitable proportion of grain refining material is that having a carbon content equivalent to from 0.01 to 1 percent of the weight of the melt. For example, suitable proportions, respectively, of sodium cyanide and calcium cyanamide based on the weight of the compound would be in the range of 0.04 to 4 percent and from 0.066 to 6.6 percent of the weight of the melt. In the preferred manner of carrying out the method of the invention there is employed a proportion of grain refining material containing a carbon content equivalent to 0.05 to 0.5 percent of the weight of the melt.

While grain refining material passing a 16 mesh sieve (U.S. Sieve Series) generally shows good grain refining action upon simple insertion into the melt, it is desirable to stir or otherwise agitate the melt during the addition to obtain intimate contact between the said grain refining material and the melt. Grain refinement at temperatures below about 1350° F. is enhanced by improving, and maintaining, intimate melt-carbon contact as by stirring or by repeated treatment with the grain refining material of the invention. Coarse particulate grain refining material not passing a 16 mesh sieve may be used quite satisfactorily if the melt is stirred more vigorously and/or a higher melt temperature is employed.

After the action of the grain refining material is completed the melt is in condition for casting unless flux refining is also necessary in which case flux refining is carried out in the usual manner and then the melt is ready for casting. The so-treated molten metal will generally stay in the grain refined condition for at least an hour at casting temperatures. Casting should be carried out before grain coarsening occurs.

In an alternative manner of adding the grain refining material the powdered or granular material, which may be conveniently wrapped first in aluminum foil, is placed in a phosphorizer cup formed of suitable material such as steel and the cup thrust into the melt and held there until the grain refining material enters or reacts with the melt. Stirring of the melt containing the so-added material enhances the grain refining action thereof.

In various tests to check the toxicity of the grain refining materials employed in the method of the invention, melts of magnesium base alloy were treated both by inserting and by stirring in, respectively, $K_3Fe(CN)_6$, NaCNO, $CaCN_2$ and a NaCN-MgO blend. In each case the hydrogen cyanide concentration over the melt was such as to be either not detectable or barely detectable using Mine Safety Appliance colorimetric detector tubes.

The following examples are illustrative of the practice of the invention. In each example the condition of the melt was ascertained by pouring a test specimen in the form of a 4 inch cube. The cube was sectioned and the average grain diameter of a center portion of the cube was determined metallographically.

Example I

Suitable proportions of aluminum, manganese and magnesium were melted together at about 1400° F. to produce a magnesium base alloy containing 2 percent of aluminum, 0.2 percent of manganese, the balance magnesium. The so-prepared alloy was allowed to cool to 1250° F. and a test specimen was cast in the form of a 4 inch cube. The solidified test specimen was found to have an average grain diameter (referred to hereinafter as AGD) of 0.100 inch at its center. The molten alloy was then treated at 1,250° F. with about 2.2 percent by weight of a blend consisting of, by weight, 14 percent of NaCN, 18 percent of brucite, 18 percent of NaCl, 47.5 percent of $BaCl_2$ and 2.5 percent of CaF_2 . The blend was added to the melt by means of a phosphorizer cup and the melt was then stirred for about 1 minute. After about 5 minutes a second test specimen was cast in the form of a 4 inch cube. The solidified casting showed an AGD in the center of the cube of 0.020 inch. The melt was then heated to 1400° F. and held at that tem-

perature for 30 minutes and another test specimen was cast. The solidified casting was examined and found to have an AGD of 0.20 inch at its center. The melt was further heated to 1550° F. and maintained at that temperature for 30 minutes after which still an additional test specimen was cast. The center of the solidified casting was examined and was found to have an AGD of 0.020 inch showing that the melt had retained the grain refined condition.

Example II

Suitable proportions of aluminum, manganese and magnesium were melted together at about 1400° F. to produce a magnesium base alloy containing 9 percent of aluminum, 0.2 percent of manganese, the balance magnesium. The so-prepared alloy was allowed to cool to 1250° F. and a test specimen was cast in the form of a 4 inch cube. Metallographic examination of the solidified test specimen indicated an AGD of 0.060 inch at the center of the cube. The molten alloy was then treated at 1250° F. with 1 percent by weight of a blend consisting of, by weight, 10 percent of NaCN, 12 percent NaCl, 25 percent Na_2CO_3 and 53 percent $BaCl_2$. The blend was stirred into the melt and after about 5 minutes a second test specimen in the form of a 4 inch cube was cast. The solidified casting showed an AGD of 0.009 inch at its center. The melt was then held at 1250° F. for an additional 90 minutes after which a third test specimen was cast. The solidified casting was examined and found to have an AGD of 0.009 inch at its center showing that the melt had retained the grain refined condition.

Example III

Suitable proportions of aluminum, zinc, manganese and magnesium were melted together at about 1400° F. to produce a magnesium base alloy containing 9 percent of aluminum, 2 percent of zinc, 0.2 percent of manganese, the balance magnesium. The so-prepared alloy was allowed to cool to 1250° F. and a test specimen was cast in the form of a 4 inch cube. Metallographic examination of the solidified test specimen indicated an AGD of 0.060 inch at the center of the cube. The molten alloy was then treated at about 1250° F. by stirring in 0.9 percent by weight of potassium ferricyanide. After about 5 minutes a second test specimen was cast in the form of a 4 inch cube. The solidified casting showed an AGD of 0.012 inch at the center of the cube. Upon holding the melt for 1 hour at 1250° F. and casting an additional test specimen the AGD was found to be 0.012 inch. The temperature of the melt was then increased to 1400° F. and held at that temperature for 15 minutes whereupon still an additional test specimen was cast. The AGD of the solidified casting was found to be 0.007 inch. A supplemental addition of 0.9 percent potassium ferricyanide did not alter the grain size.

Example IV

A magnesium base alloy having the same composition and prepared as described in Example III was allowed to cool to about 1250° F. A test specimen was cast and the AGD of the test specimen was found to be 0.030 inch. 0.45 percent by weight of NaCNO was stirred into the melt and another test specimen was cast. The AGD of the solidified test specimen was found to be 0.006 inch. After holding the melt for 75 minutes at temperatures up to 1400° F. an additional test specimen was cast. Examination of the solidified casting showed the AGD had increased only to 0.008 inch.

Example V

A magnesium base alloy having the composition and prepared as described in Example III was allowed to cool to about 1250° F. A test specimen was cast and the AGD of the test specimen was found to be 0.080 inch. 0.45 percent by weight of $CaCN_2$ was stirred into

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the melt and another test specimen was cast. The AGD of the solidified test specimen was found to be 0.006 inch. After holding the melt for 75 minutes at temperatures up to 1400° F. an additional test specimen was cast. Examination of the solidified casting showed the AGD had increased only to 0.010 inch.

Example VI

Suitable proportions of aluminum, zinc and magnesium were melted together at about 1400° F. to produce a magnesium base alloy containing 1 percent of aluminum, 6 percent of zinc, the balance magnesium. The so-prepared alloy was allowed to cool to 1250° F. and a test specimen was cast. The AGD of the test specimen was found to be 0.200 inch. The molten alloy was grain refined by a 0.45 percent addition of CaCN_2 which was stirred into the melt at a temperature of 1250° F. after which an additional test specimen was cast. The AGD of the solidified test specimen was found to be 0.010 inch.

Two additional blank tests were made for the purpose of comparing the use of the inorganic carbon-nitrogen compounds of the method of the invention with the use of calcium carbide which is known in the art.

In the first blank test a magnesium base alloy having the same composition and prepared as described in Example III was allowed to cool to 1250° F. and a test specimen was cast. The AGD of the solidified test specimen was found to be 0.060 inch. The melt was then grain refined by a 0.45 percent addition of calcium carbide at a temperature of 1250° F. and an additional test specimen was cast. The AGD of the test specimen was found to be 0.030 inch. Upon holding the melt for 1 hour at 1250° F. and casting still an additional test specimen the AGD of the melt was found to have reverted back to its original value of 0.060 inch.

In the second blank test aluminum, zinc and magnesium were melted together at about 1400° F. to produce a magnesium base alloy containing 2 percent of aluminum, 3 percent of zinc, the balance magnesium. A test specimen was cast and the AGD of the solidified specimen was found to be 0.060 inch. The melt was grain refined by the addition of 3.7 percent of calcium carbide based on the weight of the melt whereafter a test specimen was cast and the AGD of the solidified specimen was found to be 0.050 inch. Upon holding the refined melt for 15 minutes at 1400° F. and casting still

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an additional test specimen the AGD of the specimen was found to be 0.080 inch.

A comparison of the blank tests with the examples of the invention shows the very marked improvement in retention of the fine grained condition by melts treated according to the method of the invention.

What is claimed is:

1. The method of treating an aluminum-containing magnesium base alloy so as to insure a grain refined structure being obtained on casting a melt thereof which comprises adding to the melt at a temperature in the range of 1200 to 1700° F. a proportion of an inorganic carbon-nitrogen compound selected from the group consisting of cyanides, cyanates, cyanamides, ferrocyanides, ferricyanides and thiocyanates, said proportion of inorganic carbon-nitrogen compound having a carbon content by weight equivalent to 0.01 to 1 percent of the weight of the melt.

2. The method as in claim 1 in which the inorganic carbon-nitrogen compound is admixed with material selected from the group consisting of inert inorganic chlorides, fluorides, carbonates and oxides.

3. The method as in claim 1 in which the said proportion of inorganic carbon-nitrogen compound is added to the melt while the melt is at a temperature in the range of 1250 to 1350° F.

4. The method as in claim 1 in which the inorganic carbon-nitrogen compound is calcium cyanamide.

5. The method as in claim 1 in which the said proportion of inorganic carbon-nitrogen compound contains a carbon content by weight equivalent to 0.05 to 0.5 percent of the weight of the melt.

6. The method as in claim 2 in which the inorganic carbon-nitrogen compound sodium cyanide is admixed with magnesium oxide.

7. The method as in claim 1 in which the said proportion of inorganic carbon-nitrogen compound is added to the melt while the melt is at a temperature in the range of 1350 to 1500° F., and the melt is subsequently cooled to a pouring temperature in the range of 1200 to 1350° F.

References Cited in the file of this patent

FOREIGN PATENTS

548,673 Canada Nov. 12, 1957

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,976,143

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 3, for "0.20" read -- 0.020 --.

Signed and sealed this 5th day of December 1961.

(SEAL)

Attest:

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