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## GRAIN REFINEMENT OF ALUMINUM-CONTAINING MAGNESIUM-BASE ALLOYS

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6 Claims. (Cl. 75—67)

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This invention relates to methods for refining the grain structure of aluminum-containing magnesium-base alloys, which comprise treating such alloys with a suitable carbide.

It has long been recognized in the art of magnesium metallurgy that the refinement of grain structure of magnesium-base alloys was highly desirable, inasmuch as the reduction in grain size resulted in markedly improved physical or mechanical properties of the magnesium-base alloy castings. Several methods were devised early in the art for refining the grain structure of magnesium-base alloys, but most of these processes amounted merely to different methods for heating the molten metal prior to casting. The method which has met with the greatest success, and which is in general use today, comprises the superheating of the alloy above normal melt temperatures.

Superheating of magnesium-base alloys for grain refinement may be carried out by rapidly heating the metal to a temperature in the range of from about 1600° F. to about 1750° F. for a period of time up to about 15 minutes, after which the molten alloy is rapidly cooled. The rapid heating and cooling of the alloy in the superheating process of grain refinement is essential, since rapid heating of the metal is required to minimize drossing and the rapid cooling of the melt is necessary to retain the benefits of superheating on the refinement of the grain structure of the alloy. It was discovered that it was impracticable to effect rapid heating and cooling of the molten alloy in the large pot generally employed for melting the ingot magnesium. As a result, new procedures had to be developed in order to satisfactorily utilize the superheating methods of grain refinement.

It is thus customary, in present day processes for treating magnesium-base alloys, to melt the new ingots and returns in a large bulk melter of about 1700 to 2000 pounds capacity under a fluid flux cover. The metal is brought to a temperature considerably below the superheating temperature and is then poured from the bulk melter into a number of smaller steel crucibles ranging in capacity from 60 to about 500 pounds each. Each of these smaller crucibles with its metal is placed in one of a number of small furnaces for fluxing and superheating treatment. Fluxing is accomplished by stirring a layer of refining flux into the metal with an iron or steel fluxing tool, although in some instances the agitation necessary for fluxing is obtained by the use of a mechanical agitator. The fluxing operation is

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usually performed at temperatures of from about 1275° F. to 1375° F. After fluxing, the metal is covered again with a layer of flux, and the temperature increased to between about 1600° F. to about 1750° F. and held in this range for a period up to about 15 minutes, depending upon the temperature at which the metal is superheated. At the end of the holding time, the crucible and metal are removed from the furnace to cool as rapidly as possible to the pouring temperature which usually lies between about 1250° F. to 14.75° F.

The disadvantages connected with this superheating process of grain refinement arise principally from the fact that it is necessary to treat the metal in small batches. This small batch treatment requires considerable additional equipment as well as further handling of the metal. The smallness of the batch treated and the nonuniformity of the metal from one batch to another introduces factors which make large-scale production of superheated magnesium alloys difficult. Furthermore, the high temperatures to which the metal is superheated cause occasional burning of the melt as well as contamination by deleterious gases or by certain adventitious elements, such as iron, that adversely affect corrosion and other engineering qualities of the metal. Other disadvantages, such as criticalness of the time element and the poor working conditions resulting directly from the small batch treatment, which are not of serious proportions on laboratory or small-scale basis, become of prime importance when the operations assume the proportions of large-sale commercial production.

It has been suggested that carbon or carbonaceous material be used to treat molten magnesium and thus effect grain refinement. This method of producing grain refinement has proven highly successful, but, as in the development of most new processes, there are several disadvantages to which no solution has heretofore been offered. When carbon in the molecular form, such as graphite, coke, coal, etc., is employed, considerable difficulty is encountered in obtaining dissolution of the carbon in magnesium. These materials are very much lighter than the molten magnesium and therefore must be thoroughly puddled or mixed into the melt. When carbonaceous material is used in which the carbon is present as individual atoms, that portion of the carbonaceous material other than the carbon frequently has deleterious effects upon the magnesium melt.

It is an object of this invention, therefore, to provide a method of reducing the grain size in aluminum - containing magnesium-base alloys and, more particularly, to effect such reduction in grain size by treating such alloys with a suitable carbide.

Another object of this invention is to provide a method of refining the grain structure of aluminum-containing magnesium-base alloys which comprises treating such alloys with a carbon-containing material which contains no elements which adversely affect the magnesium melt.

Still another object of this invention is to provide a method for refining the grain structure of aluminum-containing magnesium-base alloys which may be carried out in large melting pots at a temperature so low as to obviate any danger of adverse high-temperature effects upon the melt.

It is also an object of this invention to provide a method of refining the grain structure of magnesium-base alloys which comprises treating such alloys with a solid carbonaceous material of such a character as to provide carbon in the atomic form as well as other elements which act to beneficiate the magnesium melt.

Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description thereof.

It has been discovered that substantial reduction in the grain size of aluminum-containing magnesium-base alloys may be successfully achieved by treating such alloy melts with a suitable carbide. Although there are many carbides which will effect grain refinement, this invention relates essentially to those carbides which contain, in addition to the carbon, a metal or metals which do not adversely affect the magnesium melts. Some of the carbides which are particularly suitable in practicing the present invention are aluminum carbide and silicon carbide, and manganese carbide in the form of high-carbon, high-manganese ferromanganese.

The aluminum in the aluminum carbide has an especial affinity for the magnesium metal and, to a certain extent, imparts desirable physical characteristics to the resulting alloy. The manganese in the high-manganese high-carbon ferromanganese material is especially desirable in that it is soluble in the magnesium and readily dissolves, thus freeing carbon as individual atoms which are, therefore, in a form readily dissolved by the melt. The high specific gravity of the iron-manganese-carbon compound also makes it easy to introduce it as a fine powder into the melt. The manganese absorbed further helps to maintain the manganese above the minimum amount required in most commercial casting alloys.

In general, the method of treating magnesium melts with carbide comprises melting the magnesium, refining the molten magnesium, and adding a carbide in the powdered form to the melt, and stirring it in thoroughly. It is immaterial whether the magnesium alloy melt is refined before or after it is treated with the carbide. For example, highly satisfactory grain reduction has been accomplished by puddling the carbide into the magnesium metal while it is being melted and subsequently refining the melt that is produced. Another procedure which results in highly satisfactory grain-refinement is to treat the molten alloy with a suitable carbide after refinement with a flux in the usual manner. Several methods of refining magnesium melts have been devised and any one of these may be employed along with the carbide treatment. One method, however, which is especially satisfactory comprises treating the molten magnesium with chlorine in the gaseous form according to the procedure set forth in the copending application of James C. De Haven, Serial No. 619,887, filed October 2, 1945, and entitled Methods of reducing microporosity of magnesium-base alloy castings.



It is preferable to maintain the alloy at a temperature of approximately 1400° F. while it is being treated with the carbide; however, the treatment may be carried out from a temperature just above the melting point to the temperature at which the alloy burns, depending somewhat upon the form in which the carbide is added. In certain instances when the carbide is added in large pieces, it is necessary to maintain a higher temperature in order to assure dissolution of the carbide. The carbide may be added by sprinkling it in a powdered form over the top of the molten alloy, by mixing it in with the refining flux, or by enclosing it within a wire basket or a phosphorizing cup of a suitable material and placing the basket or cup at the bottom of the melting pot where the carbide is generally loosened from its container.

Although it is not known just exactly how much carbon must be dissolved in the alloy to effect grain size reduction, it has been determined empirically that approximately 0.005% carbon dissolved in the alloy is more than sufficient to effect a maximum degree of grain refinement. Wide variances in the amount of carbon added to the melt do not materially affect the refinement of the grain structure of the alloy, and, for this reason, from between about 0.1% to about 0.8% of the carbide may be added in order to insure the incorporation of an adequate amount of carbon.

The following specific example is given in order to illustrate the invention with such clarity as to enable anyone skilled in the art to readily practice it. A quantity of a magnesium alloy consisting essentially of 6% aluminum, 3% zinc, 0.2% manganese, and the balance magnesium was melted and heated to about 1300° F. The melt thus formed was then cleaned and degassed by passing chlorine therethrough for a period of between 10 to 20 minutes in the manner described in the copending application of James C. De Haven, above-cited. The temeprature was then raised to approximately 1400° F., and manganese carbide in the form of high-manganese high-carbon ferromanganese ground to a mesh size of approximately —35 was added in a phosphorizer cup and then stirred into the melt with a steel rod. After gently stirring in the manganese carbide for a period of about 3 minutes, the melt was poured at 1400° F. A ½-inch test bar thus produced showed an average grain size of 0.004 inch as compared with an average grain size of 0.012 inch in a similar test bar made of the same alloy run under the same conditions except for the omission of the grain refining treatment. The conventional superheating method produced a grain size of 0.004 inch in a similar test bar made of similar metal.

The above-outlined procedure was followed with the single exception that aluminum carbide having a mesh size of approximately —35 was used in place of the manganese carbide. The grain size of the resulting test bar averaged 0.005 inch.

Another procedure for treating magnesium alloys with carbides which is very satisfactory, and which in certain respects is superior to the pro-

cedure outlined immediately above, consists of puddling the grain refining carbide into the magnesium melt as the solid charge is melted. The temperature is then raised to about 1300 F., at which temperature the melt would be cleaned and degassed, preferably by bubbling chlorine therethrough as above described. The melt is then raised to the pouring temperature of between 1350° and 1450° F. and poured into the molds.

Other variations and modifications of the present invention as above described will become apparent to those skilled in the art and it is not intended to limit the scope of the present invention except as defined in the appended claims when read in view of the specification.

It is apparent from the above description that the present invention relates to methods for refining the grain structure of aluminum-containing magnesium-base alloys and comprises treating such alloys with a suitable carbide. By the words "suitable carbide," as used in the specification and the appended claims, is meant any carbide which contains no elements of such a nature as to adversely effect aluminum-containing magnesium-base alloys. Calcium carbide, for example, is excluded by this definition from the category of "suitable carbide," because the calcium increases the grain size and thus negatives the effect of the carbon. By the utilization of the present invention magnesium-base alloys may be produced having grain sizes comparable to those obtained by means of superheating without the accompanying disadvantages of high temperatures and small batch treatment. The present invention further provides a method for introducing carbon into the molten magnesium alloy in the atomic form without simultaneously introducing therein elements which adversely affect the physical characteristics of the alloy.

Having thus described the present invention, what is claimed is:

1. A method of refining the grain structure of aluminum-containing magnesium-base alloys, which comprises bringing such an alloy into contact with a carbide of the group consisting of silicon carbide, aluminum carbide, and manganese carbide while said alloy is in the molten condition.

2. In a method of treating aluminum-containing magnesium-base alloys which includes melting such an alloy, fluxing the molten alloy, and casting the fluxed alloy, the step which comprises bringing the molten alloy into intimate contact with a carbide of the group consisting of silicon carbide, aluminum carbide, and manganese carbide prior to the casting thereof.



3. In a method of treating aluminum-containing magnesium-base alloys which includes melting such an alloy, fluxing the molten alloy, and casting the fluxed alloy, the step which comprises adding between about 0.1% to about 0.8% by weight of a granular carbide of the group consisting of silicon carbide, aluminum carbide, and magnesium carbide to such an alloy while it is heated to approximately 1400° F.

4. In a method of treating aluminum-containing magnesium-base alloys comprising melting such an alloy, fluxing the melt, and casting the fluxed melt, the step which includes bringing the melt into contact with a granular carbide of the group consisting of silicon carbide, aluminum carbide, and manganese carbide having a particle size of about −35 +200 mesh prior to casting said melt for a sufficient period to effect dissolution of at least about 0.005% of the carbon in the metal.

5. In a method of treating aluminum-containing magnesium-base alloys comprising melting such an alloy and fluxing the melt, the step which comprises bringing the melt into intimate contact with a carbide of the group consisting of silicon carbide, aluminum carbide, and manganese carbide in a divided form and agitating the molten alloy until sufficient carbon contained in the carbide has dissolved in the metal to effect grain refinement of the alloy.

6. A method of refining the grain structure of aluminum-containing magnesium-base alloys, which comprises bringing the molten alloy into contact with a carbide of the group consisting of silicon carbide, aluminum carbide, and manganese carbide for a time sufficient for the carbon contained in the carbide to dissolve in the metal and thus to effect grain refinement of the alloy.

JAMES A. DAVIS.

## REFERENCES CITED

The following references are of record in the file of this patent:

Mahoney et al., Metals Technology, vol. 12, T. P. 1892, "A Study of Factors Influencing Grain Size in Magnesium Alloys and a Carbon Inoculation Method for Grain Refinement," pub. June 1945, by the American Institute of Mining and Metallurgical Engineers, Inc., York, Pa., pages 16 and 17.

Eastwood et al., Project Report Number 4 on Research Project Contract, W. P. B. 135, "An Investigation of Cast Magnesium Alloys and of the Existing Foundry Techniques and Practices," published April 1, 1945, pp. 222 to 229.

## Certificate of Correction

Patent No. 2,429,221. October 21, 1947.

JAMES A. DAVIS

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 12, for "14.75° F." read *1475° F.*; line 35, for "large-sale" read *large-scale*; column 4, line 51, for "temepra-ture" read *temperature*; column 6, line 8, for "magnesium" read *manganese*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of December, A. D. 1947.

[SEAL]

THOMAS F. MURPHY,
*Assistant Commissioner of Patents.*