Patented May 31, 1949

2,472,025

UNITED STATES PATENT OFFICE

2,472,025

METHOD OF TREATMENT OF MAGNESIUM-BASE ALLOYS

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No Drawing. Application November 5, 1947, Serial No. 784,302

4 Claims. (Cl. 75—67)

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The invention relates to methods of treating molten magnesium-base alloys. It more particularly concerns an improved method of treating a molten magnesium-base alloy whereby castings made therefrom exhibit a finer grain structure than that of similar castings made conventionally. The invention has additional advantages as will appear as the description proceeds.

The term "magnesium-base alloy" is used herein and in the appended claims to mean an alloy of magnesium in which the magnesium content is at least about 85 per cent, the balance being one or more elements alloyable with magnesium. The usual alloying elements are aluminum, manganese and zinc, although small amounts of other elements such as calcium, cerium, and silicon are sometimes used. The most common of the structural magnesium-base alloys are the ternary alloys of magnesium, aluminum, and manganese, and the quaternary alloys of magnesium, aluminum, manganese, and zinc. Standard specifications of these ternary and quaternary magnesium-base alloys are found in the "Dowmetal Magnesium Alloys Data Book," published October 1, 1944, by The Dow Chemical Company, Midland, Michigan.

It is known in a general way that the finer the grain size of a cast magnesium-base alloy article the better the tensile strength and related concomitant properties. It is a desideratum in the art of producing a magnesium casting for its structure to be of fine grain. As regards obtaining a fine grain size, it is known that the thermal history of the magnesium-base alloy in the molten state is a factor. It has been found, for example, that by a prolonged superheating of the molten metal to at least 1472° F., i. e. 392 Fahrenheit degrees or more above the melting point (a temperature between 1600° and 1700° F. is usually employed), after the operation of purification by puddling the metal under a suitable saline flux, the grain size of castings made therefrom is markedly smaller than that of castings of non-superheated metal and the mechanical properties are improved.

This procedure of superheating before casting, as a method of reducing grain size and improving properties, has certain disadvantages which leave much to be desired. Some of these are that the relatively high temperature to which the molten

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metal must be subjected to produce a given degree of grain size reduction promotes oxidation of metal and consumption of flux, if used, and the life of the melting equipment is shortened due to the more rapid deterioration which occurs at the high temperatures used. In addition, there is an increased hazard attendant upon handling this metal as it is very active chemically at the higher temperatures involved. Another disadvantage is that the time required to produce the superheating effect is relatively long and this immobilizes melting equipment which otherwise could be used for the production of molten metal for castings. Still another disadvantage is that the superheated metal, being so much hotter than generally desirable for making castings, must be cooled to a suitable casting temperature before pouring into molds. This latter feature involves a further disadvantage in that the superheating effect rapidly disappears as the metal is cooled before casting so that the cooled superheat-treated metal must be poured into the molds soon after cooling if the grain refining effect of the superheating is to be retained. No method is now commercially available by which a body of a molten magnesium casting alloy may be maintained for long at casting temperature without grain coarsening occurring.

We have now discovered that by adding a carbide of an alkali earth metal to the conventional saline flux normally used for fluxing and protecting magnesium-base alloys in the molten state and maintaining an excess of the carbide in the flux while fluxing the molten metal, castings made from the so-fluxed molten metal exhibit a finer grain structure than that obtained when the metal is similarly treated with a saline flux but in the absence of the added carbide.

In the usual fluxing procedures for magnesium and its alloys, the fluxes are generally composed of mixtures of chlorides of alkali and alkaline earth metals and may include a small amount of a fluoride. The common chlorides, e. g. sodium chloride, potassium chloride, lithium chloride, magnesium chloride, and calcium chloride are usually used in various combinations and proportions. These fluxes are usually quite thin but, for some purposes, are inspissated by the addition of magnesium oxide or calcium fluoride, or both may be used. The most commonly used

mixture generally contain magnesium chloride and either sodium chloride or potassium chloride and a small amount of calcium fluoride. Similar fluxes are used for autogenous welding of magnesium alloys. In some instances, for foundry flux, barium chloride may be present to increase the specific gravity so as to cause the flux to float the molten metal. In the conventional use of such fluxes the molten metal is covered or sprinkled with the flux which melts forming a film or crust over the metal and a considerable quantity of flux may underlie the metal and float the metal. The molten metal is usually stirred with the flux so as to bring all the molten metal into contact with the flux, the amount of flux being from about 5 per cent to 30 per cent of the weight of the metal, although other proportions are sometimes used. The flux has a purifying action in that non-metallic impurities such as oxide or dross are taken up by the flux. After fluxing, as by agitating the metal and flux, additional flux may be added to ensure coverage of the surface of the molten metal with flux and thereby prevent excessive atmospheric attack on the molten metal.

In carrying out the invention, the carbide added to the flux may be in granular form. It is preferable to employ the carbide in the form of pellets or lumps, such as pieces having an average diameter in the order of ½ to ¾ of an inch. We prefer to use commercial calcium carbide, such as that used for the manufacture of acetylene, which contains about 80 per cent by weight of CaC_2. The carbide is added to the molten flux preferably while in the usual melting equipment, such as the ordinary open top melting pot. The carbide usually settles to the bottom of the melt if not agitated. As soon as the carbide is added, a prompt and vigorous evolution of gas usually occurs indicating carbide decomposition, the reaction subsiding generally in less than one minute. Stirring the flux with the carbide sometimes tends to promote further gas evolution. Sufficient carbide is used so that carbide will be present in the flux after gas evolution has substantially subsided. This addition of the carbide to the flux may be made while the flux is in the presence of the molten magnesium alloy or before the alloy is melted under the flux or afterward.

We have found that a relatively small amount of the carbide is usually sufficient, such as about 0.1 per cent of the weight of the metal to be fluxed and as much as 5 per cent, or more, may be used. Ordinarily, we prefer to use an amount of commercial calcium carbide equal to about 1 per cent by weight of the alloy to be fluxed, the carbide being in the form of pellets having an average diameter of about ¾ of an inch. As moisture of the atmosphere in contact with the melt of flux and metal decomposes the carbide, it is advisable from time to time to either add additional amounts of carbide to the flux, or if there be an excess of carbide present, to occasionally stir the flux so as to bring it into contact with the excess of settled carbide.

On being fluxed with carbide-containing flux, the molten magnesium alloy undergoes a change such that when separated from the flux and solidified by cooling, as in the usual casting operation, the solidified metal exhibits a fine grain structure, the fineness of the grain depending upon the duration of contact between the molten metal and the carbide treated flux until a maximum grain size reduction is obtained. We have found, for example, that by merely maintaining a molten magnesium-base alloy in contact with carbide-containing molten saline flux for one or two minutes, or more, the grain size is markedly reduced. Continuance of the contact of the molten metal and carbide-containing flux does not usually significantly further reduce the grain size of the treated metal. In addition, we have found that once the grain size has been reduced, the molten metal may be left in contact with the molten carbide-containing saline flux for a long time without loss of grain size reduction effect. This is an important advantage because the treated metal need not be heated beyond ordinary pouring temperatures and may be maintained in the molten state for long periods in readiness for pouring into molds to give castings having a fine grain structure. Furthermore, no added equipment is required in the foundry to produce fine grain structure castings over that needed for conventional melting and fluxing.

The following example is illustrative of a mode of carrying out the invention. A quantity of a magnesium foundry flux weighting about 100 pounds composed of approximately 34 per cent of magnesium chloride, 55 per cent of potassium chloride, 2 per cent of calcium fluoride, and about 9 per cent of barium chloride was melted in a conventional open cast steel pot, the temperature being maintained at approximately 1350° F. To the molten flux was added approximately 900 pounds of a magnesium-base alloy having a nominal composition of 10 per cent aluminum, 0.1 per cent manganese, 0.3 per cent zinc, the balance being magnesium, and the heating continued until the metal was melted and its temperature raised to about 1400° F. Approximately 5 pounds of commercial calcium carbide was thrown into the pot and mixed with the flux by agitating the flux in the presence of the metal whereupon a prompt and vigorous evolution of gas occurred. After the cessation of the vigorous evolution of gas, the molten metal was sampled from time to time by withdrawing a portion and forming a test casting. This was sectioned, polished, etched, and the etched metal examined for grain size. In the as-melted condition, i. e. before adding the carbide to the flux, the metal gave test castings having grain sizes averaging about 0.010 inch in diameter. Fifteen minutes after the carbide treatment, the average grain size was 0.002 inch.

Similar tests were made using 40 pound melts of a magnesium-base alloy having a nominal composition of about 9 per cent aluminum, 0.1 per cent manganese, 2 per cent zinc, the balance being magnesium. In each of these tests, about 10 pounds of flux of the same composition, as in the foregoing example, was used to which was added, while melted and maintained at about 1400° F., 0.5 pound of commercial calcium carbide. After the initial vigorous evolution of gas subsided, the batch of treated flux and melt of magnesium alloy was maintained at about 1400° F. and periodically examined to determine the grain size of test castings made therefrom.

The results obtained are tabulated in the following table showing the average grain size of the cast metal at different times after the commencement of the treatment of the molten metal with the flux in contact with the carbide. For comparison, the average grain size of the cast metal before the treatment of the metal commenced, that is, in the "as-melted" state, is also given. In the table, data are given for runs of

the same alloy composition treated in similar manner.

Table

Time Held at 1400° F. with Calcium Carbide-Containing Flux in Minutes	Average Grain Size Diameter in Thousandths of an Inch	
	Run No. 1	Run No. 2
0 (as-melted)	8	7
1	6	4
2	6	3
3	5	4
4	5	3
5	5	4
6	5	4
7	5	4
8	4	5
9	4	4
10	4	4
15	5	5
20	4	5
25	5	5
30	5	5
45	4	5

The data in the table show that by treating the molten metal with the molten flux containing calcium carbide, the grain size of the metal cast after such treatment progressively decreases until a few minutes have elapsed, thereafter the grain size does not materially change.

The temperature at which the beneficial effect is obtained may vary over a considerable range, the lowest effective temperature being approximately 1350° F. It does not appear to be necessary to operate the method at temperatures above 1400° F., although higher temperatures may be used. The process may be carried out advantageously at casting temperature.

In addition to reducing the grain size, the fluxing with the carbide-containing flux has the advantage of preventing loss of metallic calcium from magnesium-base alloys containing metallic calcium as an alloying constituent. This result is in sharp contrast to that obtained with flux not containing the carbide as in the latter case, the metallic calcium content, if any, of the alloy

declines during conventional fluxing as by holding the metal in a molten state in contact with a conventional flux.

This application is a continuation-in-part of our copending application, Serial No. 587,222, filed April 7, 1945, now abandoned.

We claim:

1. The method of treating an aluminum-containing magnesium-base alloy which comprises maintaining the same in the molten state at a casting temperature in contact with a saline flux therefor, the flux having about 0.1 to 5 per cent of a carbide of an alkaline earth metal in admixture therewith, separating the so-treated metal from the flux, and casting the separated metal.

2. The method according to claim 1 in which the carbide is calcium carbide.

3. The method according to claim 1 in which the flux comprises a mixture of a chloride of an alkali metal and a chloride of an alkaline earth metal and the carbide is calcium carbide.

4. The method according to claim 1 in which the flux comprises a mixture of magnesium chloride and potassium chloride and the carbide is calcium carbide.

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