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GRAIN REFINING MAGNESIUM ALLOYS

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1

This invention relates to magnesium alloys and more particularly to magnesium alloys containing aluminum, and has for its object the provision of an improved method of producing such alloys of fine grain structure, and the provision, as a new article of commerce, of an agglomerate containing carbon for the treatment of magnesium base alloys.

Magnesium alloys, particularly those containing aluminum with or without zinc, when made by customary methods of alloying and refining, inherently solidify in a coarse grain structure. It is now a matter of common knowledge that such magnesium alloys when of fine grain structure possess superior mechanical properties, enhanced amenability to solution treatment, shorter heat-treating requirements, and improved machineability. It is also now a matter of common knowledge that this desirable fine grain structure can be obtained by superheating the molten alloy to temperatures far above the melting temperature of the alloy, as, for example, by superheating at a temperature between 900 and 950° C. The alloy is heated to the superheating temperature, and then cooled to pouring or casting temperature, generally in the neighborhood of 650 to 800° C. This "superheating," as it is called, imparts to the solidified alloy a relatively fine grain structure with the attendant superior properties hereinbefore mentioned. The fine grain structure tends to persist through subsequent remeltings of the alloy, so that castings subsequently produced from superheated alloy possess a fine grain structure.

Superheating of the magnesium alloy is expensive, both on account of the labor and equipment required, and is moreover characterized by uncertainty of duplication and difficulty of control. The temperature required for superheating may vary with alloy composition and conditions, and sometimes a superheating temperature giving satisfactory grain refinement with a particular melt may actually give unsatisfactory results when applied to another melt of a similar composition.

We have discovered that carbon when introduced into a molten magnesium base alloy at a temperature above its melting temperature imparts to the solidified or subsequently cast alloy a fine grain structure. Based on that discovery, the present invention involves treating a magnesium base alloy with carbon in a finely divided or granular form. The treatment temperature may be only sufficient to maintain the alloy in a molten state, but in practice is preferably some-

2

what higher, although no advantage has been observed with treatment temperatures in excess of about 800° C. The reaction of the carbon with the molten alloy takes place promptly, and treatment periods of a few minutes to an hour, for example 10 to 60 minutes, are usually satisfactory.

Carbon in the form of graphite, carbon black, petroleum coke, pitch coke and the like may be satisfactorily used in the practice of the invention. The carbon preferably should be in a finely divided or granular state to insure its wide dissemination throughout the body of molten alloy undergoing treatment. Usually about 0.5 gram of carbon per pound of alloy being treated (0.1% by weight) gives satisfactory results, or more generally from 0.05 to 0.5% by weight based on the weight of alloy undergoing treatment. While carbon in excess of that required to give satisfactory grain refinement is not harmful, we prefer to use not more than about 2 grams of carbon per pound of alloy being treated.

The carbon may be introduced into the molten alloy in any appropriate manner. Thus, the carbon may be placed in the bottom of a crucible and the molten alloy poured into the crucible, or the carbon may be placed on top of the molten alloy in a crucible or the like and disseminated by stirring or plunging the molten alloy. Again, the carbon may be injected or sprayed into a stream of the molten alloy. Ingots of the alloy, prior to melting, may be coated, as by spraying or the like, with carbon, and upon subsequent melting the carbon coating acts to impart to the alloy the contemplated grain refinement of the invention. Water or oil dispersions of carbon may be used for spraying such ingots. The carbon may be introduced in the manufacture or compounding of the magnesium base alloy itself to become effective on subsequent remelting.

The grain refining treatment of the invention may be carried out when the magnesium base alloy is first made or compounded and cast into ingots or the like for subsequent remelting and use in foundries and the like. Or ingots of the magnesium base alloy may be remelted and grain-refined in accordance with the invention at the plant of their production or of their use, or at both plants. It is usually preferable to add or introduce the carbon in two or more lots, as for example during melting down of the melt, the final carbon addition being made before refining. Thus, the carbon additions may advantageously be distributed over the melt down, the first addition of one-third when melting has commenced, another one-third when melting is well under

way, and the final one-third when melting is complete. Following the final carbon addition, the molten alloy is agitated by stirring or plunging before refining. The introduction of carbon and its action upon the molten magnesium base alloy does not interfere with the usual refining practices, and hence the refining of the alloy may be advantageously carried out in accordance with customary practices after the final carbon addition has been made.

According to a present preferred practice, the finely divided or granular carbon is agglomerated, by briquetting or the like, into pellets weighing from a few ounces to a pound, usually 4 to 10 ounces, and the pellets are introduced into the molten alloy in any appropriate manner. While the pellets may be made up solely of carbon, with a minimum amount of a suitable binder or bonding agent such as pitch, we prefer to mix the carbon with small or fine pieces of magnesium base metal and agglomerate or briquet the mixture into pellets of the desired size. The magnesium base metal may be commercial magnesium metal, but preferably is a magnesium base alloy of about the composition of the alloy to be treated. Metal turnings and sawings of magnesium base alloys may advantageously be thus mixed with carbon and formed into pellets. We have made very satisfactory pellets with from 3 to 8 ounces of magnesium base metal and 1 to 2 ounces of carbon. Generally speaking the carbon content of the pellet should be from about 10% to about 50% of its weight. Pellets composed solely of carbon float on the molten alloy, while pellets containing a large proportion, say 50 to 90%, of magnesium base metal tend to sink below the surface of the molten alloy.

Satisfactory pellets may also be made of petroleum coke of high carbon content (e. g. 95% carbon). Such coke is mixed with pitch of high carbon content and formed into agglomerates or pellets by briquetting or extrusion. The agglomerates may be heated in a kiln to drive off volatile compounds, in amount usually less than 5%. The agglomerates are then ready for use in the practice of the invention, being used in the proportion of about 0.5 gram per pound of alloy treated. It has been found that pitch coke can be satisfactorily substituted for all or part of the petroleum coke in the agglomerates.

The agglomerates or pellets, whether of carbon, or mixtures of carbon with magnesium base metal, may contain a predetermined, and preferably standardized, amount of carbon say for example 25 grams. Thus, one pellet will introduce sufficient carbon to refine the grain structure of 50 pounds of magnesium base alloy, where the ratio of carbon to melt is 0.5 gram per pound of melt. As many pellets will be used as needed for the treatment of the entire batch of molten alloy. The pellets are of particular advantage in treating alloys in the foundry or on the remelt floor, either initially or as retreatments of previously grain-refined ingots or the like. The pellets may be used with complete satisfaction and success by ordinary foundry labor.

Another preferred practice of the invention utilizes a dry mixture of carbon and a commercial magnesium refining flux, say in the weight proportion of from 50 to 95% of refining flux and from 50 to 5% of carbon. The customary commercial refining fluxes consist generally of a chloride base salt, for example, a mixture of alkali-metal chlorides and alkali-earth metal chlorides, and contain 20 to 40% of inspissating or

thickening agents, such as magnesia and calcium fluoride (e. g. fluorite). The carbon and flux, in finely divided or granular form, are thoroughly mixed together and are incorporated into the molten magnesium base alloy at the temperatures hereinbefore described. This carbon-flux mixture is spread on the surface of the melt and is stirred into the metal in accordance with the usual practice of stirring refining flux into molten magnesium. Like the aforementioned pellets, the carbon-flux mixture may be used with complete satisfaction and success by ordinary foundry labor.

Practice of the invention consistently produces exceptionally fine-grained magnesium alloys which are characterized by initially good mechanical properties which are noticeably carried over on subsequent remelting cycles, even though neither re-treatment in accordance with the invention nor superheating is resorted to in such subsequent remelting cycles. However, fine-grained magnesium alloys produced in accordance with the invention can be superheated or re-treated in accordance with the invention on the remelt floor without injury. In fact, brief re-treatment in accordance with the invention on the remelt floor tends to quickly establish an optimum fine grain structure so that the quantity of recycled scrap metal on the melting floor becomes unimportant whereas in present practice it is generally considered desirable to add at least 30% of risers, runners and similar scrap to each heat.

The invention provides a simple and rapid method of grain refinement permitting the production of fine-grained magnesium alloy structures possessing the properties and characteristics of the fine-grained structures produced by the heretofore customary superheating practices. The grain refinement effected by the invention can be consistently duplicated in successive heats of the same alloy with high regularity in grain size. Thus, the invention enables the consistent production of cast alloys possessing grain sizes smaller than 0.005 inch average intercept value, and, with careful practice, of cast alloys having grain sizes as small as 0.001 inch average intercept value. Like grain refinement by superheating, the invention is particularly applicable to magnesium base alloys containing aluminum, say 2.5 to 12% aluminum, with or without zinc, say 0.2 to 3.5% zinc. The invention is, however, generally applicable to all magnesium base alloys capable of responding to present superheating practices to bring about grain refinement, and the invention creates or sets up in the molten alloy a condition that results in the production in the subsequently cast alloy of a very fine-grained structure possessing the properties and characteristics of the fine-grained structure heretofore produced by superheating. Hence, for the purposes of the invention, the term magnesium base alloy is defined as a magnesium base alloy, and more particularly an aluminum-bearing magnesium base alloy, capable of responding to the commonly known art of superheating or raising the molten alloy to an elevated temperature, for instance 900° C., in order to induce grain refinement in the alloy.

The following examples illustrate practices of the invention:

Example 1.—Ingots totaling 150 pounds in weight of a magnesium base alloy containing 10% aluminum were melted down in a crucible. As soon as some molten metal was present in the

5

crucible one pellet (mixed magnesium base alloy and carbon) containing 25 grams of carbon was added, and the surface of the melt was sprinkled with just sufficient melting flux to prevent burning of the metal. When approximately half of the melt was molten, another pellet was added. When the entire melt was molten, the third and final pellet was added. After an interval of about 5 minutes, the melt was thoroughly stirred. The melt was then refined with the customary refining flux in accordance with the usual practice at a temperature of about 730° C. While standing for approximately 15 minutes under a protective refining flux cover, the melt reached a temperature of 780° C. The temperature of the melt was then allowed to drop to the desired casting temperature, when it was poured off and cast. The grain size of the resulting cast alloy was of the order of 0.0018 inch average intercept value.

Example II.—This was a 2 ton alloying heat. The alloying metals in ingot form (5% aluminum and 0.4% zinc) together with 300 to 400 pounds of previously alloyed magnesium metal (broken magnesium alloy ingots and the like) were melted down in a crucible. During melting, the surface of the melt was covered with 8 pounds of powdered graphite (in another example carbon black was found to be equally satisfactory). When this initial charge was melted, sufficient molten magnesium metal was poured into the crucible to bring the melt up to 4000 pounds. The melt was then stirred, manganous chloride was added to introduce about 0.15% manganese into the finished alloy, the melt was covered with a substantial layer of refining flux, and refining was carried out in accordance with the usual practice. After refining, the melt was allowed to reach a temperature of approximately 790° C., and the crucible was removed from the furnace. When the melt had cooled to the casting temperature it was poured off into ingots. The grain size of the resulting cast alloy was of the order of 0.005 inch average intercept value.

We claim:

1. The method of producing magnesium base alloys of fine grain structure which comprises melting a magnesium base alloy and subjecting the molten alloy to the action of finely divided carbon.

2. The method of producing magnesium base alloys of fine grain structure which comprises melting a magnesium base alloy and subjecting the molten alloy to the action of finely divided carbon in amount of from 0.05 to 0.5% by weight based on the weight of alloy treated.

3. The method of producing magnesium base alloys of fine grain structure which comprises melting a magnesium base alloy and subjecting the molten alloy at a temperature not exceeding about 800° C. to the action of finely divided graphite.

6

4. The method of producing magnesium base alloys of fine grain structure which comprises melting a magnesium base alloy and subjecting the molten alloy at a temperature not exceeding about 800° C. to the action of finely divided carbon in amount of from 0.1 to 0.5% by weight based on the weight of alloy treated.

5. The method of producing magnesium base alloys of fine grain structure which comprises melting a magnesium base alloy and subjecting the molten alloy to the action of about 0.5 gram of finely divided graphite per pound of alloy treated.

6. The method of producing magnesium base alloys of fine grain structure which comprises melting down a magnesium base alloy containing aluminum in the presence of finely divided carbon, the carbon being added to the melt, agitating the melt when completely molten and after all of the carbon has been added, and then subjecting the melt to the action of a magnesium refining flux.

7. The method of producing magnesium base alloys of fine grain structure which comprises melting down a magnesium base alloy containing aluminum, adding a mixture of carbon and magnesium refining flux to the molten metal, and effecting an intimate mixture of the molten metal and the carbon-flux mixture.

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