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PRODUCTION OF MAGNESIUM CASTINGS

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This invention relates to an improvement in the production of castings of magnesium and magnesium base alloys, especially those containing aluminum, and has as its chief object the provision of an economical treatment of the molten metal prior to casting to cleanse it of non-metallic impurities and produce a relatively fine grained structure in the cast article. Among the particular objects of the invention is the production of castings having high resistance to corrosion without sacrifice in strength. The term "casting" as herein employed refers to all types of cast products and includes those products that may be subsequently worked, such as ingots. In referring to "magnesium base alloys," it is to be understood that this term is applied to compositions containing at least 70 per cent magnesium by weight.

Castings constitute a large part of the total weight of the articles annually made from magnesium and magnesium base alloys, and special attention has therefore been given to methods of improving them and reducing their cost of manufacture. Nearly all of the castings are made from alloys which contain a substantial amount of aluminum. Many of the alloy castings are subjected to a solution heat treatment with or without subsequent precipitation hardening treatment to obtain a higher strength than that found in the as-cast articles. To obtain the maximum benefit from such thermal treatment, however, as well as to produce the highest strength in non-heat treated castings, attention must be given to grain size.

One of the problems faced in making castings is that of overcoming the natural tendency of magnesium and its common alloys to form a coarse grained structure. As is well recognized by those familiar with castings, a coarse grained article has lower strength and less ductility than a corresponding fine grained product, and hence to meet the minimum requirements for these two properties in a given casting an effort must be made generally to develop a fine grained structure therein. One way to accomplish this result, at least in some portions of a casting, is to chill the molten metal by contact with a relatively cold metal body. This may be done either by employing a metal mold or where a sand mold or core is used by embedding pieces of metal, known as chills, in the sand adjacent to the mold cavity. Both methods have obvious limitations in practice. Another method very generally used in making sand castings containing aluminum is to melt the alloy charge under protection of the

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usual type of fused salt flux cover and then raise the temperature of the charge to about 1650-1750° F. for a short period of time. Following this, the metal is poured into the mold. This method, referred to in the art as superheating, produces a relatively fine grained structure throughout the casting but in some sections, because of mold conditions, it may still be necessary to employ chills. Superheating has the obvious disadvantages of requiring additional heat and the use of melting equipment for a longer period of time than necessary for the melting operation alone. A third method of securing fine grained casting is to incorporate certain high melting point elements in the molten metal. This method is not used extensively because of difficulties in obtaining a uniform distribution of the element throughout the melt and subsequent castings.

Another requirement in high quality magnesium and magnesium alloy castings is substantial freedom from non-metallic impurities, such as oxide and flux particles, since their presence tends to reduce the soundness of the section or to promote corrosion if water or water vapor is also present. The removal of these impurities is usually accomplished by stirring a so-called refining salt flux into the molten metal after the initial melting period. Following the agitation, the melt is allowed to remain quiet so that the flux will settle to the bottom of the pot or crucible and carry the dross and other non-metallic impurities with it. The efficiency of this fluxing treatment is therefore of great importance in improving the resistance to corrosion of the castings. Another impurity which promotes corrosion is iron. Magnesium and magnesium base alloys are generally melted and held in iron or steel pots with the result that some of the iron may be dissolved, especially at temperatures above those normally used for melting and pouring. The superheating practice mentioned above thus tends to increase the iron content and thereby reduce the corrosion resistance of the castings involved.

A further difficulty encountered in making satisfactory castings of magnesium alloys is the absorption of hydrogen by the melt, especially during the melting and superheating operations or from the use of fluxes which yield hydrogen. This gas increases the amount of microporosity and enlarges the microshrinkage cavities. Most magnesium alloy castings, it is well known, are susceptible to both microshrinkage and microporosity and anything which accentuates these casting difficulties is to be avoided.

I have discovered that the foregoing difficul-

ties associated with superheating and flux refining can be greatly minimized, if not eliminated, by introducing halogenated hydrocarbons into the molten magnesium or magnesium base alloy shortly before pouring the metal into the molds. These compounds are unique in that they bring about both grain refinement and removal of non-metallic impurities when used in sufficient quantity. For convenience in handling, it is preferred that these substances be in solid or liquid form at room temperature and at ordinary atmospheric pressure. However, when acting upon the molten metal, they or their decomposition products are in vaporous or gaseous form by virtue of the heat derived from the hot metal. In practice, a solid compound may be thrust into the melt and held near the bottom of the pot or crucible until it vaporizes. If the quantity used is not excessive, the vaporization will not yield a sufficient volume of gas to produce any dangerous spattering of the metal and indeed when some compounds are used, I have observed that there is very little or no disturbance at all of the surface of the molten metal charge because of the apparent rapid reaction of the compounds with the metal. Another method of introducing a solid or liquid halogenated hydrocarbon compound is to place it in a heated container having a tube or conduit leading therefrom which can be thrust into the body of molten metal whereby the gas or vapor generated in the container is released below the surface of the metal charge. Alternatively, a compressed gas can be employed and fed to the molten metal charge in the same manner. Following the treatment with the halogenated hydrocarbon, the solid impurities rise to the surface of the melt or sink to the bottom of the crucible depending upon their apparent density, or they may be carried to the bottom of the crucible if the usual refining flux is employed.

The halogenated hydrocarbons, in general, are effective both in removing impurities and producing a fine grained structure in magnesium and magnesium base alloys, especially those that contain aluminum. Those compounds which are solid or liquid at ordinary temperature and pressure are preferred as mentioned above, but in any case the halogenated substance should vaporize or decompose into a vaporous product at the temperature of the molten metal. Both aliphatic and aromatic hydrocarbons, their derivatives, and substituted compounds, that have been halogenated are useful, but again I prefer to use those compounds of the aromatic series, and in any case the chlorinated compounds are considered to be the best. In referring to halogenated hydrocarbons, it is to be understood that one or more halogen atoms are present in the hydrocarbon molecule. Also, there may be more than one kind of halogen atom present, for example, both fluorine and chlorine may be in the compound. The hydrocarbon may or may not be completely halogenated, but I have found that better results are obtained where all of the hydrogen atoms have been replaced by a halogen, particularly chlorine; thus, carbon tetrachloride (CCl_4), hexachloroethane (C_2Cl_6), and hexachlorobenzene (C_6Cl_6) are preferred, especially the last named compound. I have found that it is especially advantageous to use hexachlorobenzene (C_6Cl_6) because it not only is solid at room temperature, refines the grain size, and effectively removes non-metallic impurities, but it yields virtually no fumes, thus

eliminating provision for any special ventilation. Those compounds, such as paradichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$), which contain both hydrogen and a halogen are still useful, but in general their efficiency for my purpose increases as the proportion of the hydrogen replaced by a halogen increases. Elements other than carbon and hydrogen may be present in the molecule and, in some cases, may even be beneficial. However, if the additional elements interfere with the functioning of the halogen as far as treatment of the molten metal is concerned, or if there is an adverse effect upon the metal, such compounds are obviously not suitable. In some cases it may be desirable or even unavoidable to introduce two or more kinds of halogenated hydrocarbons. My invention contemplates the use of at least one such hydrocarbon whether by itself or as a component of a mixture.

Where solid or liquid halogenated compounds are used I have found that, for the best results, they should be employed in an amount equivalent to between 0.01 and 0.30 per cent of the weight of metal being treated. If a gaseous compound is used, then the weight of the gas in liquid form may be taken within the same percentage range as an approximation of the correct amount to be employed. In any event, an appreciable or measurable amount of the hydrocarbon is to be employed, the least amount to be used being that which will effect some refinement of the grain size. This quantity will also reduce the non-metallic impurity content of the treated metal. The precise amount required in any given case can be readily determined from the effectiveness with which the grain size is refined and the impurities removed from the melt.

The temperature of the metal into which the halogenated hydrocarbon is introduced will vary with the alloy and pouring temperature desired. In general, the temperature should lie between about 1300 and 1550° F., the usual melting and pouring temperature range, but this is dictated by economic and metallurgical considerations apart from the behavior of the hydrocarbon compounds.

Although the halogenated hydrocarbons are effective, at least in some degree, in producing a small grain size and eliminating dross and non-metallic impurities from commercially pure magnesium, the most important field of use is in the treatment of magnesium base alloys, and in particular, magnesium base alloys containing from about 3 to 12 per cent aluminum. In such aluminum-containing alloys other common alloying elements such as zinc, silicon, manganese, tin, or lead may also be present, but they are generally employed in smaller proportions than aluminum. It has been found that the treatment with the halogenated hydrocarbon compounds reduces, if it does not entirely neutralize, the grain coarsening effect of certain alloying elements.

Through the above described treatment of molten magnesium alloys which normally would be superheated to refine their grain size, I have been able to produce at least as fine a grain size as by superheating, if not finer, without superheating. This is accomplished without raising the temperature of the metal above that required for pouring castings and without stirring the molten metal in the manner required when a salt flux is employed, thus saving expense, time, and use of equipment in handling a given amount

of metal. I have observed moreover that the iron content of the treated metal is lower than that in metal which has been superheated and thus it possesses a higher resistance to corrosion.

The treatment with halogenated hydrocarbons serves to remove non-metallic impurities, such as oxide, dross, and flux particles, and thus may eliminate the need for the refining salt flux treatment which is normally employed, especially on melts that would be superheated. If the refining salt flux is omitted, it may still be necessary to protect the melt against oxidation by use of a fused salt cover or protective atmosphere. Where the treatment is used in conjunction with a refining salt flux, much better elimination of non-metallic impurities is obtained than with the salt flux alone. Furthermore, the treatment with halogenated hydrocarbons removes a portion of hydrogen or other gas which contributes to microshrinkage and microporosity that a salt flux does not eliminate. This improvement is particularly noticeable in production castings that are subjected to the standard air pressure tests. Castings from metal which has been treated with a halogenated hydrocarbon show less leakage than castings from the metal handled in the usual manner. For the purpose of this invention, hydrogen and similar gases are regarded as being non-metallic impurities.

An example may be cited to illustrate the benefits gained from treating a magnesium base alloy with hexachlorobenzene (C_6Cl_6), as compared to superheating the alloy. The alloy tested had a nominal composition of 9 per cent aluminum, 2 per cent zinc, 0.2 per cent manganese, and balance magnesium. Two 400-pound heats were made of this alloy using the ordinary melting practice which included keeping the surface of the molten charge covered with a salt flux. One heat was treated with the usual refining flux, stirred and brought to a temperature of about 1750° F. It was cooled to 1520° F. and poured into a production mold and a test bar mold. The second heat was treated with the usual refining flux and then treated with 100 grams of hexachlorobenzene (C_6Cl_6) at 1430° F., heated to a pouring temperature of 1520° F., and poured into the same kind of mold as the first heat. The test bars from the superheated metal in the as-cast condition had an average tensile strength of 23,890 p. s. i. and an elongation of 1.6 per cent. The test bars from the other heat had a tensile strength of 25,105 p. s. i. and an elongation of 1.9 per cent. This difference is attributed to a difference in grain size since all conditions were the same except for the treatment with the chlorinated hydrocarbon. Other test bars from these two heats were subjected to 100-hour exposure to a standard alternate immersion test in an aqueous sodium chloride solution. The superheated alloy lost 74.1 per cent in tensile strength and 37.2 per cent in elongation as compared to the properties of the uncorroded test bars. The test bars from the melt treated with hexachlorobenzene (C_6Cl_6) lost only 53.3 per cent in tensile strength and 15.8 per cent in elongation. The better resistance to corrosion is indicative of reduced amounts of impurities in the latter bars.

In another test on the same alloy, actual grain size measurements were made and it was observed that the superheated casting had an average grain diameter of 0.0045 inch, while the casting made from hexachlorobenzene-treated metal had an average grain diameter of only 0.003 inch.

In referring to refining the grain size of magnesium and magnesium base alloys, it is to be understood that this means that the average grain size in the casting is substantially smaller or finer than in the same casting which has received no treatment to change the grain size. Also, the comparison is to be made between the same size and type of casting.

Having thus described my invention and an embodiment thereof, I claim:

1. A method of refining the grain size of magnesium and magnesium base alloy castings and materially reducing the non-metallic impurity content thereof involving melting the metal, introducing into the melt 0.01 to 0.3 percent by weight of at least one halogenated hydrocarbon compound which is solid at room temperature and thereafter casting the metal.

2. A method of refining the grain size of magnesium base alloy castings containing from 3 to 12 per cent aluminum and materially reducing the non-metallic impurity content thereof involving melting the alloy, heating it to a temperature between about 1300 and 1550° F., introducing into the melt 0.01 to 0.3 per cent by weight of at least one chlorinated hydrocarbon compound which is solid at room temperature, and thereafter casting the alloy.

3. A method of refining the grain size of magnesium base alloy castings containing from 3 to 12 per cent aluminum and materially reducing the non-metallic impurity content thereof involving melting the alloy, heating it to a temperature between about 1300 and 1550° F., introducing 0.01 to 0.3 per cent by weight of hexachlorobenzene into the melt, and thereafter casting the alloy.

4. A method of refining the grain size of magnesium base alloy castings containing aluminum and materially reducing the non-metallic impurity content thereof involving melting the alloy, introducing into the melt 0.01 to 0.3 per cent by weight of at least one halogenated hydrocarbon compound which is solid at room temperature, and thereafter casting the alloy.

5. A method of refining the grain size of magnesium base alloy castings containing aluminum and materially reducing the non-metallic impurity content thereof involving melting the alloy, introducing into the melt 0.01 to 0.3 per cent by weight of at least one chlorinated aromatic hydrocarbon compound which is solid at room temperature, and thereafter casting the alloy.

6. A method of refining the grain size of magnesium and magnesium base alloy castings and materially reducing the non-metallic impurity content thereof involving melting the metal, adding a salt flux thereto, introducing into the melt 0.01 to 0.3 per cent by weight of at least one halogenated hydrocarbon compound which is solid at room temperature, and thereafter casting the metal.

7. A method of refining the grain size of magnesium base alloy castings containing aluminum and materially reducing the non-metallic impurity content thereof involving melting the alloy, adding a refining salt flux thereto, introducing into the melt 0.01 to 0.3 per cent by weight of at least one halogenated hydrocarbon compound which is solid at room temperature, and thereafter casting the alloy.

8. A method of refining the grain size of magnesium and magnesium base alloy castings involving melting the metal, introducing into the melt 0.01 to 0.3 percent by weight of at least

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one halogenated hydrocarbon compound which is solid at room temperature, and thereafter casting the metal.

9. A method of refining the grain size of magnesium or magnesium base alloy castings containing aluminum involving melting the alloy, introducing into the melt 0.01 to 0.3 percent by weight of at least one halogenated hydrocarbon compound which is solid at room temperature, and thereafter casting the alloy.

10. A method of refining the grain size of magnesium base alloy castings containing from 3 to 12 percent aluminum involving melting the alloy, introducing into the melt 0.01 to 0.3 percent by weight of at least one chlorinated hydrocarbon which is solid at room temperature and thereafter casting the alloy.

11. A method of refining the grain size of magnesium base alloy castings containing from 3 to 12 percent aluminum involving melting the alloy, heating it to a temperature between about 1300 and 1550° F., introducing 0.01 to 0.3 percent by weight of hexachlorobenzene into the melt, and thereafter casting the alloy.

12. A method of refining the grain size of magnesium base alloy castings containing from 3 to 12 per cent aluminum involving melting the alloy, introducing into the melt 0.01 to 0.3 per cent by weight of a chlorinated hydrocarbon compound which is solid at room temperature and thereafter casting the alloy.

13. A method of refining the grain size of magnesium base alloy castings containing from 3 to 12 per cent aluminum involving melting the alloy, heating it to a temperature between 1300 and 1450° F., introducing 0.01 to 0.3 per cent by

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weight of hexachlorobenzene into the melt, and thereafter casting the alloy.

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