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METHOD OF MAKING MAGNESIUM-ZIRCONIUM MASTER ALLOY

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This invention relates to the introduction of zirconium into magnesium and magnesium base alloys and has as its special object the provision of a method of making a zirconium-magnesium mixture that can serve as a source of zirconium for a magnesium or magnesium alloy melt. Another object is to provide the zirconium-rich metallic body which will be substantially free from chloride inclusions. By substantially chloride-free I mean that it contains less than about 5% by weight of chloride.

Magnesium base alloys containing less than 1% zirconium by weight have attracted attention because of their favorable working characteristics and the improved properties at elevated temperatures which can be attained if a rare earth element is also present. The production of the zirconium containing alloys has been difficult, however, because of the low solubility of that element in magnesium and its low rate of solution therein. For example, it is almost impossible to alloy zirconium with magnesium by simply adding lumps of that metal to a magnesium melt and stirring the mixture, even though the melt is heated to a relatively high temperature. As a consequence, other modes of introducing the element have been employed in commercial operations, the most common one involving the use of certain decomposable zirconium compounds. The chloride has been employed for that purposes because of its low cost as compared to other zirconium halides and its rapid yet non-violent reaction with molten magnesium. However, it suffers from the disadvantage of yielding a considerable quantity of magnesium chloride as a reaction product and being vaporizable at the temperature of the molten metal. It is difficult to dispose of the mass of molten magnesium chloride or to treat it so as to minimize transfer with the molten metal. If globules of the chloride are allowed to remain in the allow they can cause corrosion in the cast or wrought products. Other zirconium halides have been proposed as a source of zirconium but they are too costly or the recovery of the metal is too low to justify the expense. In addition, they can give rise to undesirable reaction products.

I have overcome the foregoing difficulties by a novel method of making a zirconium rich body substantially free from chlorides, as defined herein, and using that composition as a source of zirconium for addition to magnesium and magnesium base alloys. Although the aforesaid body may contain some chloride as well as some oxide and the zirconium occurs as separate particles mixed with but not in solution in the magnesium it is convenient, nevertheless, to refer to it as being a master alloy. The process consists essentially in reacting a relatively large mass of zirconium chloride with magnesium or magnesium base alloy, lowering the temperature of the salt-metal mixture to at least partially solidify any molten metal, removing the reacted salt, reheating the metallic residue and removing any liquid alloy having a low zirconium content.

The process of making the master alloy consists of first providing a body of molten magnesium or magnesium

base alloy and maintaining it in that condition as the salt additions are subsequently made thereto. For the purpose of convenient reference such a body of magnesium or magnesium base alloy may be referred to as magnesic metal. A relatively large mass of zirconium chloride is added to and admixed with the molten metal, the weight of the zirconium chloride usually being equal to at least one-fourth the weight of the metal charge. Since zirconium chloride tends to vaporize at the temperature of molten magnesium it is generally advisable to mix it with an inert salt which, in combination with the chloride, will form a low melting point mixture. The inert salt addition should also form a low melting point mixture with the magnesium chloride resulting from the reaction of zirconium chloride and the magnesic metal. Suitable inert salts are the chlorides of sodium, potassium, barium and the like. Where such inert salts are employed it is advisable to observe the minimum proportion of zirconium chloride to the molten magnesium mentioned above in estimating the amount of salt mixture to be added to the molten metal charge. For best results the total amount of zirconium chloride or mixture containing that salt to be added to a given melt should be introduced in increments rather than as a single addition.

The temperature of the molten metal body should be maintained at a high enough level to permit fusion of the zirconium chloride-containing mixture as well as the chloride reaction product. In general, a temperature between 1350 and 1500° F. will answer the purpose but I prefer a temperature within the range of 1400 to 1450° F. To obtain as complete a reaction as possible with the magnesic metal the zirconium chloride should be well stirred into the metallic melt. The reaction occurs rather rapidly so that the stirring period need be of but relatively short duration, generally on the order of 2 to 10 minutes, after each addition of the zirconium chloride or mixture containing the same. The temperature of the metal-salt mass should be maintained within the above temperature range during the period the salt additions are made and in the following separation period.

Following the final addition and stirring operation the fused mass should be allowed to remain quiescent to allow separation of the metallic and non-metallic components into layers according to their respective densities. Such gravitational separation will ordinarily take place in a matter of minutes, usually 2 to 10 minutes being sufficient. Upon standing at least two layers will be formed, the lowermost and heaviest being principally a mixture of magnesic metal and finely divided zirconium together with small amounts of chloride and oxide, while the top layer will consist of magnesium chloride and any salt which was introduced with the zirconium chloride. The liquid salt mass is generally of a thin freely pouring consistency, especially if the proportions of the salts are close to those of a eutectic mixture. In addition to the two distinct layers there is often an intermediate magnesium base alloy layer containing less than 1% zirconium that can be separated from the heavier master alloy at a later stage in the process.

When the separation into layers has been substantially effected the temperature of the mass should be lowered to a point where the magnesic metal either solidifies or becomes semi-solid. The temperature may be as low as 1000° F. but preferably should be about 1200 to 1250° F. At these temperatures the salt mass remains molten. From the standpoint of practical operation the cooling should be effected within the shortest time but the length of the cooling period is not of importance as far as solidification of the metal is concerned. Upon attaining the desired lower temperature the liquid salt is tapped or poured off leaving as little fused salt as pos-

sible. Since the metal portion is at least partially frozen, it is not difficult to physically remove the fluid salt layer. While it is desirable to eliminate the chlorides as completely as possible yet a certain amount can be tolerated providing special precautions are taken to remove them in the final product. If the process of stirring and separation is properly conducted the master alloy will contain not more than about 5% by weight of entrapped chlorides. Such a small amount is easily eliminated in making the final zirconium-containing alloy by following the usual magnesium melting practice of employing melting and refining refluxes. Any magnesium oxide entrapped in the master alloy will also be eliminated with the chlorides.

After removal of the salt, the mass remaining in the melting pot or other container should be reheated to a high enough temperature to melt any magnesic metal which solidified during the cooling step of the process. Reheating to a temperature above 1300° F. but below 1500° F. is generally sufficient. A rather fluid alloy, usually containing less than about 1% zirconium, accumulates on top of a heavy viscous mass, in most instances, which can be poured off and added to melts for making castings. It is sometimes helpful to work the metallic mass to facilitate release of any entrapped salt or fluid alloy. The thick plastic mass remaining in the container constitutes the master alloy to be employed for making additions of zirconium to other melts. Heating the master alloy to a higher temperature will not, ordinarily, increase its fluidity to any significant extent. However, it can be poured or scraped into suitable molds. The cast product can then be broken or cut into suitable size for addition to a melt.

The zirconium content of the master alloy may vary between 5 and 40% and is in finely divided form, the actual amount present in any case depending upon the quantity of zirconium chloride employed, the temperature of the melt, the effectiveness of the stirring and other factors. Generally, a zirconium content between 20 and 40% is preferred. In addition to the small amounts of non-metallic impurities mentioned hereinabove, the master alloy may contain alloying elements which have no adverse effect upon the decomposition of the zirconium chloride or which render the zirconium insoluble or otherwise non-available for subsequent alloying purposes. Zinc is often used in zirconium-containing alloys and hence it may be advantageous to include it in the initial metal body reacted with the zirconium chloride. Other alloying elements such as calcium and beryllium may also be included, if desired. Magnesium generally constitutes at least 50% of the alloy.

To use the master alloy it is only necessary to add the desired amount in solid or fused form to a magnesic metal and stir the melt as is normally done in making alloy additions. Following the addition the customary refining flux should be added to remove any oxide or chloride particles that may have been introduced by the master alloy. In this manner it is possible to obtain a high quality zirconium-containing alloy which is free from contamination with chloride particles or even oxide particles.

My invention is illustrated in the example where a zirconium chloride in salt mixture was employed consisting of 50% zirconium chloride, 25% sodium chloride and 25% potassium chloride. 112.5 pounds of the mixture were added to 65.1 pounds of a magnesium-5% zinc alloy melt heated in a melting pot to a temperature between 1370 and 1470° F. The metal salt mass was stirred for a period of 5 minutes. After standing for 4 to 5 minutes the melting pot and contents were withdrawn from the furnace and allowed to cool to 1200° F., whereupon the liquid salt layer was poured off. The pot was returned to the furnace, heated to 1350° F. and a liquid magnesium-zirconium alloy containing about 0.8% zirconium poured off. The viscous residue remaining in the bottom of the pot was then transferred to notch bar molds where it was allowed to freeze. The alloy thus produced was estimated to have a zirconium content of about 23% as determined by the recovery obtained in making a magnesium alloy containing 0.69% zirconium.

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

1. The method of making a substantially chloride-free master alloy containing magnesium and zirconium comprising providing a body of molten magnesic metal, adding zirconium chloride thereto while maintaining said body in a molten condition, mixing said chloride with said molten metal whereby the reaction between the molten metal and zirconium chloride is substantially completed and a maximum amount of zirconium is introduced into the molten metal, terminating said mixing, allowing the mixture to stand and to gravitationally separate into metallic and non-metallic layers without substantial change in temperature with respect to that prevailing during the period of adding and mixing the zirconium chloride, lowering the temperature of the layered mass to a level where at least some of the molten metal solidifies, removing substantially the entire non-metallic layer, reheating the remaining metallic portion at least to a temperature at which the previously frozen magnesic metal again melts and thereafter removing any liquid alloy.

2. The method of making a substantially chloride-free master alloy containing magnesium and zirconium comprising providing a body of molten magnesic metal, adding zirconium chloride thereto in the proportion of at least one-fourth the weight of the magnesic metal while maintaining said body in a molten condition, mixing said chloride with said molten metal whereby the reaction between the molten metal and zirconium chloride is substantially completed and a maximum amount of zirconium is introduced into the molten metal, terminating the mixing, allowing the mixture to stand and separate into layers according to the relative densities of the metallic and non-metallic components while maintaining the temperature at a level such that no molten metal is allowed to freeze, lowering the temperature of the layered mass until at least some of the molten metal freezes, removing substantially the entire layer of the non-metallic component, reheating the remaining portion to at least a temperature at which the previously frozen metal again melts, and thereafter withdrawing any liquid alloy having a low zirconium content.

3. The method of making a substantially chloride-free master alloy containing magnesium and zirconium comprising providing a body of molten magnesic metal, adding zirconium chloride thereto in the proportion of at least one-fourth the weight of the magnesic metal while maintaining said body in a molten condition, mixing said chloride with said molten metal whereby the reaction between the molten metal and zirconium chloride is substantially completed and a maximum amount of zirconium is introduced into the molten metal, terminating the mixing, allowing the mixture to stand and separate into layers according to the relative densities of the metallic and non-metallic components while maintaining the temperature at a level such that no molten metal is allowed to freeze, lowering the temperature of the layered mass until at least some of the molten metal freezes, removing substantially the entire layer of the non-metallic component, reheating the remaining portion to at least a temperature at which the previously frozen metal again melts, allowing any liquid alloy of low zirconium content to accumulate on top of the zirconium-rich alloy and thereafter removing said liquid alloy.

4. The method of making a substantially chloride-free master alloy containing magnesium and zirconium comprising heating a body of magnesic metal to a temperature between 1350 and 1500° F., adding zirconium chlo-

ride to and mixing it with said magnesic metal while maintaining the temperature of the mass within the said temperature range whereby the reaction between the molten metal and zirconium chloride is substantially completed and a maximum amount of zirconium is introduced into the molten metal, terminating the mixing, allowing the mixture to stand and separate into metallic and non-metallic layers without substantial change in temperature, lowering the temperature of the layered mass to level where at least some metal freezes but not below 1000° F., removing substantially the entire non-metallic layer, reheating the remaining mass to 1300 to 1500° F. and removing any liquid metal having a low zirconium content.

5. The method of making a substantially chloride-free master alloy containing magnesium and zirconium comprising heating a body of magnesic metal to a temperature between 1350 and 1500° F., adding thereto a mixture of zirconium chloride and at least one inert salt, the zirconium chloride being added in a proportion equal to at least one-fourth the weight of the magnesic metal body, stirring said zirconium chloride-salt mixture into said metal body while maintaining the temperature of the mass within the aforesaid temperature range whereby the reaction between the molten metal and zirconium chloride is substantially completed and a maximum amount of zirconium is introduced into the molten metal, terminating the stirring, allowing the mixture to stand

and separate into metallic and non-metallic layers without substantial change in temperature of the mass, lowering the temperature of the layered mass to a level where at least some metal freezes but not below 1000° F., removing substantially the entire non-metallic layer, reheating the remaining mass to 1300 to 1500° F. and removing any liquid metal having a low zirconium content.

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