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METHOD OF PRODUCING MAGNESIUM BASE ALLOYS

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1 Claim. (Cl. 75—168)

This invention relates to magnesium base alloys containing zirconium and thorium, the zirconium being within the range 0.1–1% and the thorium being present from 0.5 up to 8%. I have described alloys of this kind in my pending British patent applications Nos. 13,845/50 and 10,919/51.

In the commercial production of articles from such alloys it is necessary to remelt the alloys and at the same time to introduce a further quantity of zirconium in order to offset losses of zirconium which occur on remelting to thus raise the zirconium content to the maximum value. In order that this additional zirconium may be effectively introduced into the alloy, a process which we term "revivification," it is very desirable to puddle the melt at a temperature of the order of 800° C., e. g. 775–850° C. However, I have found in the course of experiments that considerable losses of the expensive thorium content of the alloy are experienced; for example, with alloys containing 3% thorium I have found the losses to be from 0.4–1% for each revivification process. It is well known that losses of rare earth metal are encountered in the processing of magnesium alloys containing these alloying elements. The losses arise from reaction between the rare earth metals and $MgCl_2$ present in the fluxes normally used. There is no appreciable tendency for rare earth metals to be lost by preferential oxidation, and if a molten magnesium alloy containing, say, 3% of rare earth metal is stirred for some time in the absence of flux, the rare earth content is not appreciably lowered. In view of the close analogies between the actinide and lanthanide group of elements, it would be expected that thorium would react with $MgCl_2$ in the same way as rare earth metals, so that by use of $MgCl_2$-free fluxes losses of thorium would be prevented. I have found however that even with great care in fluxing and stirring and use of fluxes free from $MgCl_2$ it is not possible to reduce the thorium loss below about 0.35% for each revivification process, indicating that the thorium shows little tendency to react with fluxes containing $MgCl_2$, and we have confirmed this conclusion directly.

Continuing our investigations into the causes of these losses I have found that, also unlike the corresponding case of magnesium alloys containing rare earth metals, thorium can be readily lost from the molten alloys by preferential oxidation, although burning may not be visible.

Furthermore, I have found that loss of thorium can proceed indirectly via $MgCl_2$, provided MgO is also present, namely, by the reaction to a slight extent of the thorium with magnesium chloride in the flux, producing a small amount of thorium chloride, which then reacts with magnesium oxide formed by burning of the magnesium and/or present as a constituent in the flux. This causes further thorium to enter the flux phase so as to maintain the equilibrium concentration of thorium chloride, the reaction thus proceeding in cyclic manner until very appreciable thorium losses from the metal phase have occurred. It would at first sight appear desirable to

avoid the incorporation of magnesium chloride in fluxes, but the presence of at least 5% is, however, desirable as this improves the wetting characteristics of the molten flux and reduces oxidation during revivification. It is, therefore, desirable to avoid including magnesium oxide in the flux and to avoid oxidation of the magnesium of the alloy. For the latter purpose the use of inert atmospheres appeared to be desirable. However, the use of argon for this purpose is generally too expensive. The only other possibilities appeared to be sulphur dioxide and chlorine. Unfortunately, sulphur dioxide, although capable of affording protection against oxidation to molten magnesium in quiescent condition up to nearly 800° C., reacts violently with magnesium when this is stirred at temperatures above about 730° C. Chlorine is also unsuitable since this reacts with the iron crucible at the temperature in question whereby there is a strong tendency for iron to be taken up by the magnesium alloy which results in a loss of zirconium. Nitrogen would not normally appear to be suitable because it is well known to react with molten magnesium and this reaction cannot be prevented entirely by flux application when the alloy is vigorously puddled. However, in spite of this I have now found that the melting and revivification of the alloys at the temperature in question can be effected without much preferential loss of thorium by applying a flux containing less than 5% MgO (if any) in the presence of more than 5% magnesium chloride and effecting the stirring of the alloy in the presence of a zirconium alloying substance and under the inert atmosphere consisting mainly or wholly of nitrogen.

This method not only reduces the total loss of thorium from the alloy but also prevents or minimises preferential loss of thorium so that the highly desirable result is achieved of maintaining the relative proportions of thorium and magnesium practically constant. Thus in six revivification tests carried out at 800° C. on an alloy containing 2.5% thorium, the average reduction in thorium content per test was 0.35%, whereas under the same conditions but using a jet of nitrogen directed on to the metal surface, the average reduction in thorium content was only 0.09% per test.

The fluxes used for the purpose of the invention preferably contain at least 5% magnesium chloride and are free from magnesium oxide. Fluxes of this type made in accordance with British patent specification No. 652,234 are, for example, suitable and in particular a flux which has been used with good results has the following composition:

	Percent
$BaCl_2$	40
$MgCl_2$	30
KCl	10
CaF_2	20

In carrying the invention into practice we may provide a steel crucible, for example, suitable for the melting of 300 lbs. of alloy. This crucible can be fitted with a hood which hood has a comparatively small opening for the introduction of flux. A small tube extends through the hood and serves for the introduction of nitrogen into the space above the metal in the crucible. The hood may have another opening through which passes the stem of a puddling tool. The opening for the flux may be at the side adjacent the lip of the crucible whilst the opening for the puddling tool may be at or near the top of the hood. Some flux is strewn on the bottom of the crucible and then the ingots of the magnesium-zirconium-thorium alloy are placed in the crucible together with any scrap metal of suitable composition which it may be desired to remelt and an appropriate quantity of a zirconium alloying composition agent.

The hood of the crucible is fixed in position and the charge is melted in the usual way with application of flux as required to prevent burning. If desired a stream of nitrogen may be passed through the apparatus during the melting of the metal charge. When the charge is fully melted, the temperature is raised to 800° C., the supply of nitrogen is turned on, and the melt is puddled to introduce the zirconium into the alloy, flux being applied as required to minimise burning. After the alloying process is complete the hood is removed from the crucible and the melt is cast in the normal manner. If desired the lid or hood may be permanently attached to the crucible and a stream of nitrogen may be passed through the hood during the actual casting operation. If desired also a deep crucible may be used in place of a crucible of the normal shape, fitted with a hood. The deep crucible may be of height equal to at least one and a half times (e. g. twice) its diameter, in which case the nitrogen may be directed on to the metal surface through a steel tube and burning prevented in this way without the need for a special lid to the crucible. In this case, however, consumption of nitrogen will be greater.

Means may be provided to distribute the nitrogen and/or fluxes uniformly over the surface of the melt.

The zirconium alloying composition may be made in accordance with British Patent No. 652,227.

I claim:

A process for the treatment of magnesium base alloys containing thorium and zirconium comprising stirring the alloy at a temperature of 775 to 850° C., in the presence of (*a*) a flux cover containing 0.0 to 5% MgO and 5% to 100% $MgCl_2$, (*b*) a substance capable of introducing zirconium solubly into molten magnesium and (*c*) an inert atmosphere consisting mainly of nitrogen.

References Cited in the file of this patent

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OTHER REFERENCES

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