United States Patent Office 2,919,190
Patented Dec. 29, 1959

2,919,190

ALLOYING OF MANGANESE AND ZIRCONIUM TO MAGNESIUM

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No Drawing. Application January 30, 1958
Serial No. 712,067

Claims priority, application Great Britain
February 6, 1957

8 Claims. (Cl. 75—168)

This invention relates to magnesium base alloys of the kind containing zirconium. As disclosed in the specification of British Patent No. 511,137 zirconium can be advantageously incorporated in magnesium base alloys in the absence of elements which form with zirconium inter-metallic compounds of high melting point. While manganese is correctly indicated in the aforesaid specification as forming such as inter-metallic compound it has nevertheless been found possible to include appreciable amounts of manganese in magnesium zirconium alloys provided that the zirconium content is controlled at a level well below that corresponding to full saturation in the absence of manganese. Such alloys containing both manganese and zirconium are described in the specifications of British Patents 759,411, 806,103 and 806,104.

It has also been found possible to incorporate small amounts of zirconium into alloys containing manganese although the manganese content is thereby much reduced.

In order to achieve the most desirable results it is necessary to achieve saturation of the alloy with zirconium and manganese, and satisfactory results are not obtained merely by adding to the magnesium as much zirconium and manganese as would each separately suffice to introduce the desired amounts of these elements. It is possible to achieve success by first incorporating a much larger amount of manganese than is intended in the final product and then adding zirconium until the desired levels of the two elements are obtained; or alternatively to saturate the alloy with zirconium and subsequently add sufficient manganese (for example in the form of Mg—2% Mn alloy) to reduce the zirconium to the desired level. Neither of these methods is however convenient nor easy to control in practice.

The main object of the present invention is to provide compositions by which manganese and zirconium can be simultaneously added to magnesium to produce either the required ultimate content of manganese and zirconium with magnesium or to introduce a much higher content so as to produce a master alloy which can be used for introducing the required content of manganese and zirconium into further quantities of magnesium.

According to the present invention manganese and zirconium are introduced simultaneously into magnesium by means of salt mixtures consisting of at least 5% by weight $MnCl_2$ and/or MnF_2 and at least 5% of $ZrCl_4$ together with at least one of the chlorides of the alkali and alkaline earth metals, the ratio of $ZrCl_4$ to $MnCl_2$ lying between 1.0 and 4.0.

When the mixture contains manganese and/or zirconium fluoride it is desirable that sufficient $MgCl_2$ should be present to be stoichiometrically equivalent to the fluoride.

Inert diluents may be included, e.g.: The salt mixture may for example contain—

	Percent
$ZrCl_4$	From 33 to 45
$MnCl_2$	From 33 to 12
KCl	From 33 to 45
$BaCl_2$	From 0 to 20

As already mentioned, the mixture may be used for producing a master alloy in which case the absence of fluorides is in general desirable. The master alloy should be capable of introducing these elements simultaneously in the right proportions. To be of practical value such a master alloy should also be capable of being used with melts in which the metal charge contains varying amounts of virgin ingot and alloy scrap. Such Zr—Mn master alloys have been prepared by simultaneous reductions with magnesium of salt mixtures containing $ZrCl_4$ and $MnCl_2$.

The optimum proportions of the salts used for making the master alloy depend on the manganese and zirconium contents desired in the final alloy.

The master alloy should contain the following three phases:

(*a*) Matrix phase consisting of magnesium or magnesium alloyed with one or more permissible elements, e.g. from 30 to 70 percent by weight of the master alloy.

(*b*) Metallic particles containing manganese and zirconium embedded in the matrix phase, e.g. from 20 to 60 percent of the master alloy.

(*c*) A salt phase consisting mainly of $MgCl_2$ with at least one alkali metal chloride and representing from 1–20 percent of the master alloy by weight.

According to a preferred form of the invention simultaneous introduction of manganese and zirconium is effected by means of a master alloy consisting of the three phases enumerated above and containing at least 10% Zr and 5% Mn, the ratio of zirconium and manganese lying between 1.0 and 4.0, the salt phase containing $MgCl_2$, preferably at least 1.0 percent by weight.

The use of the master alloy of this invention may be illustrated by way of the following example:

Master alloy analysis:	Percent
Mg	44.5
Zr	26.2
Mn	11.8

A 5% addition of the above master alloy was added to the following alloys and alloyed by stirring at 780° C.

Alloy A—Mg—3½% Th—2¼% Zn.
Alloy B—Mg—3½% Th—2¼% Zn—0.2% Zr—0.1% Mn.
Alloy C—Mg—3½% Th—2¼% Zn—0.5% Zr—0.2% Mn.

The zirconium and manganese contents after alloying were:

	Zr	Mn
Alloy A	0.47	0.17
Alloy B	0.51	0.18
Alloy C	0.63	0.16

The master alloy of the present invention may also be used in the production of alloys of the Mg—Mn, Mg—Th—Mn, Mg—RE—Mn (magnesium rare earth metals and manganese) types whereby fine grain is achieved.

We claim:

1. A process for producing magnesium base alloys containing manganese and zirconium wherein manganese and zirconium are introduced simultaneously into magnesium by means of salt mixtures consisting of at least 5% by weight of a compound selected from the class consisting of $MnCl_2$ and MnF_2 and at least 5% of $ZrCl_4$ together with at least one compound selected from the class consisting of alkali earth metal chlorides and alkaline earth metal chlorides, the ratio $ZrCl_4$ to $MnCl_2$ lying between 1.0 and 4.0.

2. A process as claimed in claim 1, in which a quantity of $MgCl_2$ is included in the mixture at least stoichiometrically equivalent to the fluoride.

3. A process as claimed in claim 1, wherein the salt mixture contains:

	Percent
$ZrCl_4$	From 33 to 45
$MnCl_2$	From 33 to 12
KCl	From 33 to 45
$BaCl_2$	From 0 to 20

4. A process as claimed in claim 1, wherein the mixture is used for producing a master alloy containing:

Manganese, from 5 to 25 percent by weight of the master alloy.

Zirconium, from 10 to 50 percent by weight of the master alloy.

5. A master alloy for introducing manganese and zirconium into magnesium comprising the following three phases:

(*a*) Matrix phase consisting of a metal composition selected from the class consisting of magnesium or a magnesium alloy;

(*b*) Metallic particles containing manganese and zirconium embedded in the matrix phase;

(*c*) A salt phase consisting mainly of $MgCl_2$ with at least one alkali metal chloride and representing from 1–20 percent of the master alloy by weight.

6. A master alloy as claimed in claim 5, wherein phase (*a*) is from 30 to 70 percent by weight of the master alloy and phase (*b*) is from 20 to 60 percent of the master alloy.

7. A master alloy as claimed in claim 5, containing at least 10% zirconium and at least 5% manganese, the ratio of zirconium and manganese lying between 1.0 and 4.0, the salt phase containing at least 1.0 percent $MgCl_2$.

8. A salt mixture for introducing manganese and zirconium into magnesium consisting of at least 5% by weight of a compound selected from the class consisting of $MnCl_2$ and MnF_2 and at least 5% of $ZrCl_4$ together with at least one compound selected from the class consisting of the alkali and alkaline earth metal chlorides, the ratio of $ZrCl_4$ to $MnCl_2$ lying between 1.0 and 4.0.

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