United States Patent Office

2,788,271

Patented Apr. 9, 1957



2,788,271

# COMPOSITION FOR INTRODUCING ZIRCONIUM INTO MAGNESIUM AND METHOD OF MAKING SAME

Edward F. Emley, Clifton Junction, near Manchester, England, assignor to Magnesium Elektron Limited, Clifton Junction, near Manchester, England, a British company

No Drawing. Application January 5, 1953, Serial No. 329,744

Claims priority, application Great Britain January 9, 1952

7 Claims. (Cl. 75—93)

This invention relates to the production of magnesium base alloys which contain zirconium with or without other alloying constituents but in the absence of elements which combine with zirconium in molten magnesium to form insoluble compounds, alloys of this type being described in British Patent No. 511,137 assigned to the assignee of this application.

It is well-known that considerable difficulties are involved in alloying zirconium with magnesium.

These difficulties can largely be overcome by the method described in the specification of British Patent No. 652,230, also commonly owned by the assignee herein according to which a composition for alloying zirconium with magnesium consists of zirconium chloride and a large percentage of barium chloride and/or strontium chloride, some zirconium fluoride being also included, if desired, for the purpose of inspissating the chloride remaining after the alloying operation. However, this method also has certain disadvantages, namely (*a*) the alloying composition is hygroscopic and tends to give rise to porosity in castings made with alloys containing zirconium and zinc, with consequent reduction in tensile properties, and (*b*) the moisture which is absorbed by the composition decomposes the zirconium chloride and the composition soon becomes no longer satisfactory for introducing zirconium into magnesium. Furthermore, the hydrogen chloride liberated by this decomposition readily corrodes steel, and it has been found impracticable to store these alloying compositions even in airtight steel drums for any protracted period.

With a view to overcoming the difficulty due to hygroscopicity, it has been proposed in the specification of British Patent No. 652,224 to use an alloying composition containing a mixture of fluorides and in the specification of British Patent No. 652,227 it has been proposed to use alkali fluozirconates mixed with chlorides of alkaline earth metals and alkali metals. However, with these processes some difficulty is experienced in regularly obtaining the desirable high mechanical properties in sand castings. A further proposal according to the specification of British Patent No. 652,243 was to use an alloying composition consisting of one or more chlorides of alkaline earth metals including magnesium, together with zirconium fluoride, in the absence of potassium or sodium fluoride. With this process there appears to be no difficulty in readily obtaining high mechanical properties in sand castings provided the composition contains $MgCl_2$ or $CaCl_2$. It has, however, been found that if these chlorides are added in sufficient amount to convert all the $ZrF_4$ to $ZrCl_4$ considerable losses of $ZrCl_4$ due to volatilisation result. If, however, the quantity of magnesium chloride used is sufficient to convert only a part of the zirconium fluoride to zirconium chloride, the excess zirconium fluoride settles out of the molten mixture making it impracticable to manufacture large batches of the composition.

I have now found that it is possible to make a composition for introducing zirconium into magnesium which can be kept for comparatively long periods without undue absorption of moisture from the air and will enable sand castings to be produced with regular satisfactory mechanical properties and which is free from the other difficulties hereinbefore specified.



According to the present invention the composition contains both zirconium chloride and zirconium fluoride, potassium chloride, barium chloride and optionally magnesium fluoride in such proportions that the elements in the composition fall within the following percentage ranges, these salts being melted together in an anhydrous condition:

Zr____ 7–22½% (preferably not more than 20%.)
K____ 10–26½%.
Ba____ 6½–23% (preferably not more than 20%.)
Mg____ 0–6%.
F____ 5–22½%.
Cl____ 22½–42½% (preferably not more than 41%.)

The percentage of chlorine must be between 2 and 6% by weight of the composition greater than that chemically equivalent to metals other than zirconium present in the composition.

The proportions of the above specified salts in the composition fall within the following ranges:

$ZrCl_4$_____ 3 to 10%.
$ZrF_4$_____ 11–29%.
KCl_____ 19–51%.
$BaCl_2$_____ 10–35% (preferably not more than 30%.)
$MgF_2$_____ 0–15%.

It is possible that the final composition may contain a small amount of $BaF_2$ formed by slight reaction between the $ZrF_4$ and $BaCl_2$.

In a modification of the composition also according to the invention the barium chloride is replaced partly or wholly by one or more of the chlorides of strontium and rare earth metals, the latter being used only when the alloy to be made contains rare earth metals. The replacement by strontium chloride may be effected on the basis of 1% of strontium chloride being equivalent to 0.7% of barium. The replacement by rare earth metal chlorides may be effected on a 1:1 basis. Moreover, the potassium chloride may be partly or wholly replaced by sodium chloride and/or lithium chloride on a 1:1 basis. The composition may also contain reducible chlorides of one or more of the permissible alloying elements, i. e. Zn, Ag, Tl, Th, Cu, Bi, Pb, Be, Cd, in amounts chemically equivalent to not more than 12% $ZrCl_4$, the total of the $ZrCl_4$ content and the content of reducible chloride expressed in terms of its chemically equivalent $ZrCl_4$ content not exceeding 20% and preferably not exceeding 15% by weight of the composition, the relative proportions of the other constituents remaining unchanged. The total chlorine content will still exceed that chemically equivalent to the content of the metals other than zirconium, by between 2 and 6% by weight of the composition, this 2 to 6 percent of chlorine being the chlorine content of the 3 to 10% zirconium chloride.

Some magnesium fluoride which is chemically inert may be included in the composition for the purpose of stiffening the residue remaining after the alloying process.

By the use of this composition it is possible in effect to obtain the advantages of alloying by means of zirconium chloride, i. e. sand castings with optimum mechanical properties, but since the zirconium content of the composition is largely in the form of zirconium fluoride, the difficulties heretofore associated with the use of alloying compositions based on zirconium chlorides are avoided. The reason for this is that, during the reaction of the composition according to the present

invention with molten magnesium, a cyclic reaction takes place, whereby the zirconium chloride in the composition reacts with the molten magnesium to produce zirconium metal, which alloys with the magnesium, and also magnesium chloride, which then reacts with a portion of the zirconium fluoride to produce a further quantity of zirconium chloride. This $ZrCl_4$ in turn reacts with magnesium with regeneration of $MgCl_2$. The process continues in cyclic manner until the whole zirconium content of the composition has been reduced to the metallic form, the reaction always proceeding via zirconium chloride. Since the bulk of the zirconium chloride which ultimately reacts with the magnesium is formed in situ in a completely anhydrous condition from magnesium chloride which is itself liberated in completely anhydrous condition, porosity in zirconium containing alloy castings is effectively avoided. In general it is preferred that the composition shall contain zirconium fluoride in excess of the zirconium chloride. The proportion of zirconium chloride is not greater than 10% and the proportion of zirconium fluoride is preferably greater than 15%.

The final mixture will have a composition within the following limits:

| | |
|---|---|
| Zr....7–22.5 | |
| K....0–26.5 | |
| Na....0–26.5 | Total 10–26.5. |
| Li....0–26.5 | |
| Ba....0–23 | |
| RE....0–23 | $Ba + RE + \frac{5}{6} Sr = 6.5–23.$ |
| Sr....0–33 | |
| F....5–22.5 | |
| Cl....22.5–42.5 | |
| Zn....0–19 | |
| Ag....0–19 | |
| Tl....0–21 | |
| Th....0–16 | In total amount not exceeding more than 5% Zr (which latter corresponds to 12 percent $ZrCl_4$) |
| Cu....0–16 | |
| Bi....0–17 | |
| Pb....0–19 | |
| Be....0–1 | |
| Cd....0–15 | |

Whilst the composition may be made by melting the salts together in the above specified proportions this results in a marked tendency for the zirconium fluoride to settle out which renders the preparation of large batches of the composition impracticable. I have, however, now ascertained that the desired composition can be made in a form which is not only effective from the point of view of introducing zirconium into magnesium, but does not exhibit appreciable segregation even when produced in large batches.

According to this method the zirconium fluoride in the composition is produced in situ in the form of a very fine precipitate by reaction between zirconium chloride and potassium fluoride, insufficient potassium fluoride being however used to convert all to the zirconium fluoride in order that the resulting composition may contain 3–10% of zirconium chloride.

Accordingly in order to produce a composition in accordance with the invention the following salts in the proportions stated may be melted together:

| | Percent |
|---|---|
| $ZrCl_4$ | 18–50 |
| KF | 15–40 |
| KCl | 0–35 |
| $BaCl_2$ | 10–35 |
| $MgF_2$ | 0–20 |

the proportion of zirconium chloride exceeding that of potassium fluoride by 3–20% (preferably 3–18%).

The composition is preferably made by first melting the zirconium chloride with the potassium fluoride and, if desired, also with the potassium chloride but in the absence of barium chloride in order to avoid the direct formation of barium fluoride.

Thus I may add the zirconium chloride to a molten mixture of the potassium fluoride and potassium chloride, whereafter the barium chloride is added to the melt. Alternatively, I may add the potassium fluoride to a molten mixture of the zirconium chloride and the potassium chloride before adding the barium chloride.

As a further alternative I may make a mixture of the solid zirconium chloride, potassium chloride and potassium fluoride and melt them together and then add the barium chloride to the melt. The $ZrCl_4$ and the KCl may be melted together in a preliminary stage, cast into lumps, and then remelted with the KF. Melting may be carried out in a crucible with a heavy well fitting lid or if desired in an autoclave. The magnesium fluoride may be added at any desired stage.

The composition of the present invention may be used for introducing zirconium into magnesium in several different ways. For example, the constituent salts of the composition may be melted together in a crucible whereupon molten magnesium or magnesium alloy may be poured into the crucible or solid magnesium or magnesium alloy may be introduced into the crucible and melted therein. Alternatively, the composition may be added in solid or molten condition to the molten magnesium or magnesium alloy. Preferably I add the composition in the form of solid lumps to the magnesium or magnesium alloy in a crucible shortly after the charge has begun to melt. In all cases alloying is effected by puddling the melt at a temperature of 700–900° C., e. g. 800° C. The following experiment carried out in accordance with the invention is quoted by way of example:

*Example I*

6½ lbs. of a $ZrCl_4$ containing melt (50% $ZrCl_4$, 50% KCl) and 1¾ lbs. KF were melted down in a steel crucible fitted with a heavy lid. When this charge melted 1¾ lbs. $BaCl_2$ were added and stirred in. The mixture was then cast into a shallow tray and the solid melt broken into approximately 2 inch lumps. 1.5 lbs. of these lumps were added to a 10 lb. melt of magnesium base alloy containing 4½% zinc and 0.1% Zr. The melt was puddled for one minute at 800° C. Average tensile properties on three vertical D. T. D. sand cast bars made from this melt after heat treatment for 2 hrs. at 330° C. followed by 24 hrs. at 180° C. were as follows:

| 0.1% P. S., t. s. i. | U. T. S., t. s. i. | Percent El on 2" |
|---|---|---|
| 10.4 | 17.0 | 5.0 |

The grain size at the centre of a 1 inch diameter chill cast bar was 0.018 mm.

The alloy on analysis showed a total zirconium content of 0.8% of which 0.7% was in soluble condition: by "soluble" I mean that part of the zirconium content which has dissolved in the magnesium and which is distinguishable from the remainder of the zirconium by being readily soluble (together with the magnesium which contains it) in an aqueous solution of hydrochloric acid consisting of 30 cc. of HCl (specific gravity 1.16) to 85 cc. of water, sufficient acid being added during dissolution to maintain the initial acid concentration.

1¼ lbs. of the above alloying composition were added to a 10 lb. melt of magnesium base alloy containing 2.8% R. E. (rare earth metal), 2.5% Zn and 0.1% Zr. The melt was puddled for 2 mins. at 800° C. Average tensile properties on 3 vertical sand cast test bars poured from this melt were as follows:

| 0.1% P. S., t. s. i. | U. T. S., t. s. i. | Percent El on 2" |
|---|---|---|
| 5.6 | 10.4 | 5.0 |

Comparative hygroscopicity tests were carried out with this melt and with a prefused alloying salt containing

equal weights of $ZrCl_4$ and KCl. In 40 mins. exposure to air of approximately 80% relative humidity the latter salt picked up 2.5% moisture, but the salt according to the present invention described in this example picked up barely 0.5%.

*Example II*

An alloying substance was prepared with the following chemical composition.

| | Percent |
|---|---|
| $ZrCl_4$ | 8 |
| $ZrF_4$ | 26 |
| KCl | 26 |
| $BaCl_2$ | 27 |
| $MgF_2$ | 13 |

This was divided into three portions, two of which were exposed in a humidity chamber maintained at 80% relative humidity. Each portion was used to prepare a Mg-Zn-Zr alloy containing 4½% Zn, and the average tensile results on D. T. D. test bars cast from each melt were as follows:

| Time of exposure in humidity chamber | Tensile properties after Heat Treatment for 16 hrs. at 180 C. | | |
|---|---|---|---|
| | 0.1% P. S., t. s. i. | U. T. S., t. s. i. | Percent El on 2" |
| Nil | 9.8 | 17.0 | 9.0 |
| 24 hrs. | 9.9 | 17.7 | 10.5 |
| 48 hrs. | 9.6 | 17.0 | 8.0 |

I claim:

1. A composition suitable for introducing zirconium into magnesium having the following ingredients:

| | Percent |
|---|---|
| $ZrCl_4$ | 3 to 10 |
| $ZrF_4$ | 11 to 29 |
| KCl | 0 to 51 |
| NaCl | 0 to 51 |
| LiCl | 0 to 51 |
| $BaCl_2$ | 0 to 35 |
| $ReCl_3$ | 0 to 35 |
| $SrCl_2$ | 0 to 50 |
| $MgF_2$ | 0 to 15 |

Reducible chlorides of at least one of the metals Zn, Ag, Tl, Th, Cu, Bi, Pb, Be, Cd: from nil to a quantity not exceeding that chemically equivalent to 12 percent of the $ZrCl_4$ in the composition; the total of the $ZrCl_4$ and the quantity of other reducible chlorides, if any expressed in $ZrCl_4$ equivalency not exceeding 15% by weight of the composition; the composition including at least 19 percent but not more than 51 percent of the chlorides of potassium, sodium, and lithium in total; the composition also including at least 10 percent but not more than 35 percent of the sum of the barium chloride, rare earth metal chlorides, and seven-tenths of the strontium chloride.

2. A composition as claimed in claim 1 wherein the zirconium chloride content is at least 4 percent and the sum of the barium chloride and seven-tenths of the strontium chloride is less than 30 percent.

3. A composition as claimed in claim 1 wherein the proportion of zirconium chloride is less than that of the zirconium fluoride which exceeds 15 percent.

4. A method of making a composition as claimed in claim 1 wherein the zirconium chloride and the potassium fluoride are first melted together, and then the barium chloride is added to form the zirconium fluoride in situ in the condition of a fine precipitate.



5. A method of producing a composition suitable for introducing zirconium into magnesium wherein the following salts in the proportions stated are melted together:

| | Percent by weight |
|---|---|
| $ZrCl_4$ | 18 to 50 |
| KF | 15 to 40 |
| KCl | 0 to 35 |
| $BaCl_2$ | 10 to 35 |
| $MgF_2$ | 0 to 20 |

the proportion of zirconium chloride exceeding that of potassium fluoride by 3 to 20 percent, whereby reaction occurs between the KF and the $ZrCl_4$ and $BaCl_2$.

6. A method as claimed in claim 5 wherein the zirconium chloride is melted with the potassium fluoride with or without the potassium chloride, and the barium chloride is added subsequently, whereby reaction occurs between the KF and the $ZrCl_4$ and $BaCl_2$.

7. A composition suitable for introducing zirconium into magnesium consisting of:

| | Percent |
|---|---|
| Zr | 7 to 22.5 |
| K | 0 to 26.5 |
| Na | 0 to 26.5 |
| Li | 0 to 26.5 |
| Ba | 0 to 23 |
| Re | 0 to 23 |
| Sr | 0 to 33 |
| F | 5 to 22.5 |
| Cl | 22.5 to 42.5 |
| Zn | 0 to 10 |
| Ag | 0 to 19 |
| Tl | 0 to 21 |
| Th | 0 to 16 |
| Cu | 0 to 16 |
| Bi | 0 to 17 |
| Pb | 0 to 19 |
| Be | 0 to 1 |
| Cd | 0 to 15 |
| Mg | 0 to 6 |

the percentage of chlorine being between 2 and 6% by weight of the composition greater than that chemically equivalent to the metals other than zirconium present in the composition; the fluorine being present in combination with at least one of the metals and at least partly with the zirconium to form at least 15% $ZrF_4$ by weight of the composition; the composition including at least 10 percent but not more than 26.5 percent of potassium sodium and lithium in total; the composition also including at least 6.5 percent but not more than 23 percent of the sum of the barium, rare earth metals, and five-sixths of the strontium; the quantity in total of Zn, Ag, Tl, Th, Cu, Bi, Pb, Be, Cd and Mg not exceeding a total quantity which is chemically equivalent to 5 percent zirconium, all of the elements in the composition being combined in the form of chlorides and fluorides.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,497,531 | Ball et al. | Feb. 14, 1950 |
| 2,497,537 | Emley et al. | Feb. 14, 1950 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 624,304 | Great Britain | June 2, 1949 |
| 652,222 | Great Britain | Apr. 18, 1951 |
| 652,226 | Great Britain | Apr. 18, 1951 |