Patented Feb. 14, 1950 2,497,537

UNITED STATES PATENT OFFICE

2,497,537

ZIRCONIUM CARRYING ALLOYING SUBSTANCE

Edward Frederick Emley and Alfred Claude Jessup, Clifton Junction Works, near Manchester, and Philip Andrew Fisher, Flixton, England, assignors to Magnesium Elektron Limited, London, England, a British company

No Drawing. Application June 14, 1947, Serial No. 754,766. In Great Britain May 17, 1946

2 Claims. (Cl. 75—168)

1

This invention relates to magnesium base alloys which contain zirconium.

The addition of zirconium to magnesium or magnesium base alloys facilitates the production of castings and wrought goods having a fine grained crystalline texture and desirable mechanical properties.

However, considerable difficulties have been experienced in alloying zirconium with magnezium in such a manner as to produce alloys having the most desirable mechanical properties. Research on this problem resulted in the invention described in British Patent No. 511,137 according to which, elements such as aluminum, silicon, tin, manganese, cobalt, nickel, and antimony, which form high melting point compounds with zirconium, and which we term "zirconium alloying inhibitor elements," are omitted from the alloy whilst other elements (which we term "permissible alloying elements") such as zinc and cadmium may be included.

In order to introduce the zirconium into alloy we have experimented with the addition of zirconium chloride and various other compounds or mixtures which, however, are attended by various disadvantages.

Amongst other substances we have tried mixtures or compounds consisting of zirconium fluoride with potassium and/or sodium fluoride. We have found however that when these substances are used in the form of powder considerable burning of the magnesium occurs, and very little zirconium is taken up in the alloy. If however these substances are added to the magnesium in the molten form or in the form of prefused lumps, reaction is still more violent, and indeed frequently results in dangerous explosions.

We discovered, however, that such mixtures or compounds when mixed with certain chlorides can be reacted with molten magnesium without violent reaction. This even applied when the chloride employed is that of the same alkali metal, the fluoride of which has been incorporated in the alloying mixture, i. e. potassium chloride will inhibit the violent reaction in the presence of potassium fluoride and similarly sodium chloride will inhibit the violent reaction in the presence of sodium fluoride.

This discovery formed the basis of the invention described in co-pending British patent application No. 20,870 of 1945, according to which an alloying substance to introduce zirconium into magnesium consists of mixtures of one or more chlorides of alkali and alkaline earth metals including magnesium with the aforesaid mixtures

2

or compounds of zirconium fluoride with potassium or sodium fluorides.

In view of the fact that nearly all chemical reactions proceed more readily when the reagents are in a liquid or dissolved state rather than in a solid state and inasmuch as the introduction of potassium fluoride and/or sodium fluoride resulted in dissolving the zirconium fluoride, it had been thought that the presence of an alkali fluoride was essential to the satisfactory introduction of zirconium with magnesium by methods based on the use of zirconium fluoride.

We have, however, now ascertained that if potassium and sodium fluorides are omitted from the alloying substance, satisfactory alloying conditions can nevertheless be obtained including absence, of any violent reactions, provided that at least one of the alkaline earth metal chlorides (including magnesium chloride) is added to the zirconium fluoride. It is found that some types of zirconium fluoride (including oxyfluorides) if used for alloying, either alone or when mixed with other fluorides, result in violent reactions but even these types react quietly when used in conjunction with alkaline earth metal chlorides.

According to the present invention therefore the alloying substance consists essentially of one or more of the chlorides of the alkaline earth metals including magnesium together with zirconium fluoride.

If desired, some potassium and/or sodium chloride may also be incorporated in the alloying substance which assists in reducing loss by volatilisation of zirconium chloride which is formed by reaction. Preferably, the composition of the alloying substance is selected so that the chloride content alone is fluid at a temperature of 850° C. or less in order to facilitate the alloying reaction at comparatively low temperatures.

The chlorides are preferably melted together before adding the zirconium fluoride thereto.

The alloying composition made from the following ingredients is quoted by way of example:

	Per cent.
Zirconium fluoride	25
$MgCl_2$	27.5
$BaCl_2$	17.5
KCl	30

If desired, halides of permissible alloying elements may also be incorporated in the alloying substance.

The term zirconium fluoride used herein is intended to include a group of chemicals, the precise composition of which is not easy to deter-

mine, but which essentially include zirconium and fluorine in combination and may also include oxygen or oxygen and hydrogen, but which are preferably free from compounds of inhibitor elements.

The chlorides are preferably treated to reduce the water content before adding them to the zirconium fluoride. For example they may be heated to at least 800° C. and then cooled to a suitable temperature, say 750° C., for addition to the zirconium fluoride.

Sufficient zirconium fluoride should be used to enable the alloying substance to contain at least 4 per cent of zirconium in the form of the chloride or fluoride.

The alloying substance preferably also includes at least 10 per cent of barium or at least 15 per cent of strontium or a total of barium and strontium in amounts equivalent to at least 10 per cent barium reckoning 3 per cent of strontium as equivalent to 2 per cent of barium, the barium and/or strontium being present in the form of chlorides or fluorides.

The alloying may be effected by adding the magnesium or magnesium base alloy in solid or molten form to the alloying substance which also may be in either solid or molten condition. When both the metal and alloying substance are molten they are stirred to effect dissolution of the zirconium in the alloy. Alternatively the alloying substance may be added to the molten metal before stirring. These processes may be used for restoring the zirconium content of remelted zirconium-containing magnesium base alloy.

We claim:

1. A zirconium-carrying alloying substance, excluding alkali metal fluorides, consisting of zirconium fluoride in amount equivalent to at least 4 per cent of zirconium, and at least one chloride of a metal from the group consisting of alkaline earth metals including magnesium, the chloride component being in amount to enable the alloying substance as a whole to melt at the alloying temperature.

2. An alloying substance as claimed in claim 1 wherein at least one chloride of the group consisting of potassium chloride and sodium chloride is also included.

EDWARD FREDERICK EMLEY.
ALFRED CLAUDE JESSUP.
PHILIP ANDREW FISHER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,235,508	Von Zeppelin	Mar. 18, 1941
2,250,687	Von Zeppelin	Julyl 29, 1941
2,261,906	Nelson et al.	Nov. 4, 1941
2,267,862	Hanawalt et al.	Dec. 30, 1941
2,373,515	Stroup et al.	Apr. 10, 1945
2,418,408	Heath et al.	Apr. 1, 1947
2,452,914	Emley et al.	Nov. 2, 1948

FOREIGN PATENTS

Number	Country	Date
489,700	Great Britain	Aug. 2, 1938
115,655	Australia	July 31, 1942

OTHER REFERENCES

Beck: ""Technology of Magnesium and its Alloys," 1940, page 317, pub. by F. A. Hughes and Co., London, England.