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ALLOYING COMPOSITION FOR INTRODUCING ZIRCONIUM INTO MAGNESIUM

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This invention relates to the production of magnesium base alloys containing zirconium, from which in accordance with British Patent No. 511,137, elements such as aluminium, 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, whilst other elements which we term "permissible alloying elements" such as zinc, cerium, silver, thallium, thorium, copper, bismuth, beryllium, lead, calcium and cadmium may be included.

Considerable difficulties have been experienced in alloying zirconium with magnesium, but this may be accomplished in accordance with the invention described in British Patent application No. 7,224 of 1945 by means of a master alloy which comprises at least the following three phases: (1) a metallic matrix phase consisting mainly of magnesium and/or one or more permissible elements, (2) a metallic phase consisting mainly or wholly of zirconium, the master alloy being substantially free from zirconium alloying inhibitor elements, and containing at least 1 per cent of zirconium and preferably at least three per cent zirconium, and (3) a salt phase comprising not more than 30 per cent (preferably less than 10 per cent) of the whole and consisting mainly or wholly of one or more halides.

Whilst this has been found to give satisfactory results as far as introduction of the required content of zirconium is concerned, it appears that if the salt phase consists solely of chlorides the final alloy is not sufficiently free from contamination with chlorides. If, however, the salt phase contains fluorides, it has been found difficult to disintegrate the master alloy rapidly when alloying with magnesium and consequently the melt requires stirring vigorously for a protracted period at high temperatures. If fluorides are used these must include one or more of the fluorides of the alkali and/or alkaline earth metals and as a result traces of these metals are found in the final alloy and produce disadvantageous results especially in reduction of mechanical properties particularly in the case of sand castings.

With a view to overcoming these difficulties, we have investigated the use of master alloys in which the salt phase consists of chlorides, including heavy metallic chlorides which are inert to magnesium such as barium chloride. For example, we endeavoured to produce a master alloy by the use of a mixture of barium chloride and sodium chlorozirconate but did not succeed in

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introducing sufficient zirconium chloride into this mixture because of its volatility. Continuing these experiments, we tried mixtures of barium chloride, potassium chloride and zirconium chloride, and found that such mixtures enable sufficient zirconium chloride to be introduced without undue volatilisation. Moreover master alloys made with such mixtures were used for alloying and were found to introduce adequate proportions of zirconium into the final magnesium alloy, which also was found to be much less prone to contamination with chlorides. Whilst the use of potassium chloride in the salt mixture is preferred, it will be possible to replace this partly or wholly by sodium chloride if precautions are taken to avoid volatilisation of the zirconium chloride—for example by melting the salts together in a closed vessel in which case even the sodium chloride may be omitted.

It would appear also that the barium chloride may be replaced partly or wholly by strontium chloride.

Instead of producing a master alloy which is then used for alloying with magnesium, we may use the mixture of salts directly for alloying with magnesium, this mixture being used either in molten condition or in solid prefused condition—for example in the form of small prefused pieces.

The salt mixture must contain a considerable proportion of barium and/or strontium chloride to ensure proper separation of the chloride reaction product from the alloy. The salt mixture also must contain a considerable proportion of zirconium salt to provide a practicable alloying process.

According to the present invention, therefore, magnesium is reacted with an intimate fused anhydrous mixture of salts comprising barium chloride and/or strontium chloride and zirconium chloride, the mixture containing at least 15 per cent of barium chloride or at least 20 per cent of strontium chloride or a mixture of barium and strontium chlorides in amounts equivalent to at least 15 per cent of barium chloride reckoning one per cent of strontium chloride as equivalent to 0.7 per cent of barium chloride, the mixture containing at least four per cent of zirconium. The mixture preferably also contains potassium chloride and/or sodium chloride. The mixture is used either directly for alloying or for producing a master alloy. The mixture of salts will preferably be used in the molten or prefused condition.

For the purpose of producing a master alloy we find it preferable to melt the required halides

together, solidify the mixture and, whilst still hot, to pour on to it a molten magnesium-zirconium alloy. After stirring, the excess alloy is poured off, leaving a paste of master alloy and fluid chloride reaction product. The chloride mixture is then expressed as completely as possible by using a perforated plate with a handle attached to it at right angles. The magnesium used for this purpose does not necessarily contain zirconium but pure magnesium is less desirable as the magnesium will then take up some of the zirconium which is required to remain in the master alloy. The melting of the halide mixture may be effected in a crucible provided with a close fitting lid or with a chimney adapted to minimise loss of the zirconium chloride by volatilisation. The magnesium to be poured on to the halide mixture may incorporate one or more of the permissible alloying elements provided that sufficient magnesium is used to reduce the zirconium chloride.

Reducible salts of permissible alloying elements may be included in the halide mixture whether used for direct alloying or for the production of master alloy.

The master alloy will consist of an intimate fused mixture, having the following phases viz: (1) a salt phase including barium and/or strontium chlorides which phase does not exceed 30 per cent by weight of the composition, (2) a phase rich in magnesium or in a permissible alloying element, (3) a zirconium rich phase containing zirconium in a readily alloyable state; the composition being substantially free from fluorine and zirconium alloying inhibitor elements and containing at least 5 per cent of zirconium.

The total salt phase in the master alloy is less than 30 per cent and preferably between 1 and 20 per cent, e. g. 5 to 10 per cent. The first phase may contain one or more of the chlorides of potassium and sodium.

For the halide mixture the following composition is preferred:

	Per cent
Zirconium chloride	15 to 60
Potassium chloride at least	10
$BaCl_2$ at least	30

The remainder (if any) may be reducible halides of permissible alloying elements or zirconium fluoride.

A convenient method of procedure for producing the fused mixture is to mix the zirconium chloride in the form of the powdered salt or in lumps with a pre-fused solidified and milled mixture of barium chloride and potassium chloride in eutectic proportions. The total mixture is then fused. Alternatively, the solid zirconium chloride may be added to a molten mixture of the barium chloride and potassium chloride but this is less satisfactory.

Where the chloride mixture is to be used for direct alloying suitable steps may be taken to inspissate the mixture before and after the alloying reaction. If the mixture is to be inspissated before reaction, this should be effected by incorporating zirconium fluoride in the mixture. When the chloride mixture is to be used for the production of master alloy, the incorporation of zirconium fluoride or the use of any other inspissating agent should be avoided. For inspissating the chlorides remaining after the alloying reaction any of the following steps may be adopted:

1. The melt may be stirred by a power driven rotary device so as to effect separation of the metal from the salt residue whereupon the metal is poured off and refined with an inspissating salt flux.

2. Calcium fluoride or other known inspissating agent may be sprinkled on to the melt during alloying, and whilst stirring, so that as the stirring action brings the chlorides to the top of the melt, these salts are inspissated and can be separated from the metal.

3. The salt residue may be brought progressively to the surface of the melt by means of a flat horizontal plate mounted on a vertical handle, whilst an inspissating agent is continuously sprinkled on to the surface of the melt.

4. An inspissating mixture may be stirred into the melt, this mixture comprising a stiff paste of known inspissating agents and alkali or alkaline earth metal chlorides. This paste can be made for example by preparing a bath of molten chlorides and/or fluorides low in magnesium chloride at 850° C. and stirring calcium fluoride into it. This paste may be prepared in the crucible before alloying or may be separately prepared and added after cooling as lumps to the melt.

The alloying mixture should be as free as possible from zirconium alloying inhibitor elements and combined water. We have found that combined water has a strong inhibiting action on the alloying of zirconium with magnesium. Precautions should be taken to ensure that magnesium oxide is absent as far as possible during alloying. The alloy may be maintained in a quiescent state for say 15 minutes or half-an-hour after refining to allow any impurities or unalloyed material to sink to the bottom of the crucible.

One method which we have used for preparing the master alloy will now be described by way of example. A molten salt mixture is produced of the following approximate composition, 7 kgs. of barium chloride, 3 kgs. of potassium chloride, 10 kgs. of zirconium chloride, by addition of the zirconium chloride to a molten mixture of barium chloride and potassium chloride in the proportions of 70 parts by weight of barium chloride to 30 parts by weight of potassium chloride. This salt mixture is then cooled, solidified and broken up into lumps of convenient size.

Approximately two thirds of this salt mixture is placed at the bottom of a red hot crucible. We then pour into the crucible magnesium or a magnesium alloy containing about 0.7 per cent of zirconium at a temperature of about 730° C., sufficient metal being poured to cover the lumps of salt mixture. For example, about 12.5 kgs. of magnesium alloy may be used. The total mixture is allowed to stand for a few minutes to ensure complete reaction and the remaining quantity of the lumps of salt mixture is then added and after standing for a further short period, the total mixture is thoroughly stirred. The result of the process comprises a stiff pasty mass of master alloy together with excess chlorides in fluid condition and a small quantity of excess magnesium or magnesium alloy. We now pour off the excess chlorides and magnesium alloy, and express as much as possible of the residual salt residue from the pasty master alloy using a flat perforated disc with handle attached. This recovered salt residue is then poured off and the master alloy remaining in the bottom of the crucible is scraped out into suitable moulds so as to form moulded pieces of convenient size.

The master alloy so produced should be kept in sealed containers until required for alloying and should be preheated to a temperature of about 400° C. before introduction into the molten magnesium.

If desired one or more of the rare earth metals, for example mischmetall, may be incorporated in the master alloy. For this purpose the rare earth metals may be added in metallic form to the master alloy just before it is scraped out of the crucible. On adding the rare earth metals to the master alloy, the mixture is covered with a suitable flux which should be free from magnesium chloride and preferably free from fluorides, and which preferably contains barium and/or strontium chloride. When rare earth metals are introduced in this way, a graphite crucible should be used because of the solubility of iron in rare earth metals. Graphite tools should also preferably be used.

The master alloy may contain other permissible elements, for example, cadmium and/or zinc, and may be entirely free from magnesium. When incorporating zinc or cadmium it will also in this case be desirable to use a graphite crucible and tools. A graphite crucible may also be used for the initial melting of the zinc or cadmium or alloys containing these metals to avoid contamination with iron, if it is desired to add them in a molten form.

The salt mixture whether for direct alloying or for the production of a master alloy may also contain one or more reducible chlorides of permissible alloying elements.

After carrying out the final alloying operation, the remaining heavy fluid chloride residue may be stiffened by any of the methods above described.

The chlorides may be partly or wholly replaced by bromides or iodides but not by fluorides.

Impurities in the form of zirconium alloying inhibitor elements or other impurities which militate against introduction of zirconium into magnesium will be avoided as far as possible.

The magnesium used for making the master alloy or for making the finished alloy may be degassed to remove hydrogen for example by introducing hexachlorethane into it.

The master salt and master alloy are specially suitable for replenishing the zirconium content of remelted magnesium alloys.

The magnesium-zinc-zirconium alloys made by means of the master alloy of this invention possess certain remarkable properties.

In the specification of British Patent No. 511,137 one alloy quoted by way of example contains 0.7% zirconium, 4% zinc and 2% cadmium, for which the following properties are quoted:

Tensile Strength, Kgs./sq. mm.		Yield Point (0.2%), Kgs./sq. mm.		Elongation, Per cent	
Before Heat Treatment	After Heat Treatment	Before Heat Treatment	After Heat Treatment	Before Heat Treatment	After Heat Treatment
16.5	17.2	9.8	12.2	8.6	4.8

We have found however that figures as high as these were not obtainable from test bars cast in green sand moulds. For the purpose of comparative tests, we used sand cast test bars made in accordance with D. T. D. Specification No. 289B. We are well aware that higher mechanical figures can be achieved by other methods

e. g. by testing miniature test bars by the use of sand cast test bars which are cast to shape and subjected to test in the unmachined condition and by the use of die moulds and dried sand moulds. A noticeable increase also occurs in figures quoted on the basis of 0.2% proof stress, whereas we base our tests on the more usual standard of 0.1%.

A further difficulty was encountered in endeavouring to obtain sand cast articles other than test bars i. e., articles shaped for normal commercial purposes having high mechanical properties in so far as much poorer properties were obtainable from bars cut from these articles, this disparity between the mechanical properties obtained from cast articles and test bars being much greater than is observed with the magnesium base alloys normally used for castings, e. g. containing 8% aluminium.

It will be appreciated that comparative figures for examination of this aspect of the casting properties must be based on average results for corresponding sections taken from the cast articles.

On increasing the zinc content to above four per cent we found that the above mentioned disparity between the mechanical properties obtained from cast articles and test bars was further notably increased.

This disparity is mainly associated with microporosity and was so serious that it appeared that there was no advantage to be gained in pursuing research on this type of alloy any further. It is true that considerable diminution of the microporosity was achieved by additions of rare earth metals, but this unfortunately only introduced another disadvantage namely a brittle grain boundary phase accompanied again by considerable reduction in mechanical properties.

We have, however, given much attention to these problems and have found that the difficulties arise largely from hydrogen in the melt or the presence of traces of more electro-positive metals which may give rise to hydrogen by reaction with green sand moulds. This hydrogen results in microporous sand castings possessing much reduced mechanical properties.

We have now found that this tendency to microporosity can be considerably reduced if the quantity of "soluble zirconium" in the alloy is at least 0.6% and preferably at least 0.7%. By "soluble zirconium" we 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 in an aqueous solution of hydrochloric acid consisting of 30 ccs. of HCl (specific gravity 1.16) to 85 ccs. of water, sufficient acid being added during dissolution to maintain the initial concentration.

With a view to further reducing this tendency we have tried in various ways to introduce into the alloys as high a content of soluble zirconium as possible while at the same time minimising contamination of the melts with hydrogen. We have found that the process of the present invention will regularly introduce sufficient soluble zirconium into magnesium without giving rise to traces of objectionable electro-positive elements. We have, therefore, devoted much attention to the elimination of hydrogen from alloys prepared in accordance with the present invention.

When the above described precautions against moisture in the alloying materials are taken and

the master alloy of the present invention is prepared from the chloride mixture while the latter is molten or just solidified and still hot, use of this master alloy gives rise to magnesium-zinc-zirconium alloys characterised by special properties. These properties which are most pronounced when the master alloy is used to restore zirconium lost by remelting the alloys instead of for direct production of the final alloys from magnesium, are as follows:

(*a*) Remarkably high proof stress in the range 4¼ to 5¾% zinc rising from 7.5 tons per sq. inch in the as cast to 12.5 tons per sq. inch in the fully heat treated state. For maximum proof stress we heat treat for prolonged periods at 100° C.

(*b*) High proof stress combined with high ultimate tensile stress in sand castings. The following mechanical properties are obtainable.

	0.1% Proof Stress, Tons/sq. inch	Ultimate Tensile Stress, Tons/sq. inch
As cast at least	7½	at least 15½
Heat treated at least	9	at least 16½

(*c*) High proof stress combined with high elongation is obtainable in die castings (viz castings made in metal moulds), the following properties being obtainable:

	0.1% Proof Stress, Tons/sq. inch	Ultimate Tensile Stress, Tons/sq. inch
As cast at least	8	at least 14
As heat treated at least	9½	at least 14

For the purpose of obtaining the combination of properties referred to above under (*b*) and (*c*) the alloy should contain at least 0.6% soluble zirconium, at least 4¼% and not more than 5¾% zinc, not more than 0.05% sodium, and not more than 0.03% of other alkali or alkaline earth metals, the required soluble zirconium content and reduction of content of sodium and other alkali and alkaline earth metals being obtainable as hereinbefore described.

(*d*) Mechanical properties in bars cut from sand cast articles which closely approach and indeed frequently exceed figures obtained from D. T. D. type of test bars in contrast to standard magnesium base casting alloys which normally exhibit somewhat reduced mechanical properties in actual sand castings as compared with test bars.

Magnesium base alloys containing zirconium cannot be remelted and cast in the normal way, since on remelting, much of the zirconium passes into an ineffective state with consequent loss in mechanical properties. All such remelted alloy has hitherto required addition of more alloying agent in order to restore the mechanical properties.

Contrary to all expectations it has been found that magnesium-zinc-zirconium alloys containing between 4¼% and 5¾% of zinc and prepared in the above described manner can be remelted and recast with only a slight loss in mechanical properties, and that 0.1 per cent proof stress as high as 7.0 tons per square inch in the as cast and 9.0 tons per square inch when heat treated at 180° C. can frequently be obtained.

It is not possible for a maximum permissible hydrogen content to be specified for alloys prepared in accordance with the present invention;

the substantial absence of hydrogen is, however, ensured by use of the alloying procedure and precautions cited.

Small amounts of permissible alloying elements may be tolerated in the alloy including cadmium and are earth metals but the latter are generally undesirable on account of their adverse effect on elongation.

For best results, it is desirable that the contents of any alkali or alkaline earth metals other than sodium which may be present should neither individually nor collectively exceed 0.01% and should not in any event exceed 0.03%. The sodium content is preferably less than 0.02% and should not exceed 0.05%.

The alloys may contain cadmium up to 3% without materially affecting their mechanical properties. They may also contain rare earth metals up to 3%; this will tend somewhat to reduce the mechanical properties but will result in alloys which are specially serviceable where pressure tight qualities are desired.

The alloys of the present invention preferably contain at least 85 per cent of magnesium, not more than 1.0% total zirconium, the remainder being only permissible alloying elements.

We claim:

1. An alloying composition for introducing zirconium into magnesium consisting of an intimate fused anhydrous mixture of zirconium chloride in quantity at least 15% and at least one chloride selected from the group consisting of the chlorides of barium and strontium in quantity equivalent to at least 30% barium chloride reckoning 1% of strontium chloride as equivalent to 0.7% of barium chloride.

2. An alloying composition as claimed in claim 1 which also contains at least one chloride selected from the group consisting of potassium and sodium.

3. An alloying composition as claimed in claim 2 which also contains at least one substance selected from the group consisting of the chlorides of zinc, cadmium, cerium, silver, thallium, thorium, copper, bismuth, and lead.

4. An alloying composition for introducing zirconium into magnesium, consisting of an intimate fused mixture having the following phases, viz: (1) a salt phase constituting between 1% and 30% of the composition and selected from the group of chlorides consisting of the chlorides of magnesium, potassium, sodium, barium and strontium, said salt phase containing at least some magnesium chloride and containing at least one of the chlorides of barium and strontium in quantity at least equivalent to 30% barium chloride reckoning 1% of strontium chloride as equivalent to 0.7% of barium chloride; (2) a matrix phase consisting essentially of at least one of the metals selected from the group consisting of magnesium, zinc, cadmium, cerium, silver, thallium, thorium, copper, bismuth, beryllium, lead, and calcium and (3) a metallic zirconium rich phase embedded in phase 2 and containing zirconium in a readily alloyable state; the composition containing at least 5% of metallic zirconium and being substantially free from aluminum, manganese, tin, silicon, cobalt, nickel and antimony.

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