Magnesium Alloy and Method of Heat Treatment

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TITLE: MAGNESIUM ALLOY AND METHOD OF HEAT TREATMENT
Magnesium Alloy and Method of Heat Treatment

Field of the invention

The present invention relates to a magnesium casting alloy containing rare earth elements, and more particularly, to a magnesium alloy which is suited to heat treatment.

Background of the invention

The increased need for weight reduction of industrial materials is a driving force for the use of magnesium within the transportation industry, as it offers a good strength to weight ratio compared to many other materials. One focus of magnesium alloys containing rare earth elements is to produce good thermal stability at service conditions. Throughout this document the expression “rare earth” is to denote any element or combination of elements with atomic numbers 57 (lanthanum) to 71 (lutetium) inclusive. The rare earth elements are generally expensive, and alloys containing reduced rare earth contents while maintaining reasonable tensile and creep properties would be beneficial.

Castings of many different magnesium alloys are produced by a variety of procedures. These commonly include high pressure die casting, sand casting and permanent mould casting, although other types of casting such as atomization and strip casting are also conducted. Some alloys may be cast by several different procedures. Because of their relatively poor properties in the as cast condition, subsequent thermal processing is often conducted. In this processing the alloy or component is heated to a temperature appropriate for solution treatment, such as 450°C or 500°C, prior to quenching with water or some other cooling medium, and finally heating to an intermediate temperature for precipitation hardening to take place. One drawback of many magnesium casting alloys is a need for very long solution treatment times such as 6 to 24 hours, followed by ageing at reduced temperatures such as 200°C, also for very long times such as 12 to 24 hours. These features are an impediment to work
in progress in an industrial setting, and increase the cost of the manufactured component.

Another drawback of many magnesium alloys is that they undergo substantial grain growth during solution treatment at higher temperatures. Such growth is detrimental to properties of those alloys. Therefore it would be beneficial if the solution treatment time could be shortened to minimize grain growth while not compromising the precipitation hardening response and the development of properties.

Summary of the invention

In a first aspect the present invention provides a heat treatable magnesium based casting alloy, wherein the alloy is substantially free of iron and comprises:

(a) 0.5 to less than 2.1 wt% of a mixture of rare earth elements including from 0 to 1.39 wt% neodymium;
(b) 0.1 to 2 wt% zinc;
(c) 0.2 to 1 wt% zirconium;
(d) 0 to 0.1 wt % of at least one oxidation inhibiting element;
(e) 0 to less than 0.15 wt% of each of titanium and hafnium;
(f) 0 to less than 0.1 wt% of each of aluminium, copper, nickel, silicon, silver, yttrium and thorium;
(g) 0 to less than 0.005 wt% of strontium; and
(h) apart from incidental impurities, a balance of magnesium.

In a second aspect the present invention provides a heat treatable magnesium based casting alloy, wherein the alloy is substantially free of iron and comprises:

(a) 0.5 to less than 2.1 wt% of a mixture of rare earth elements including from 0 to 1.39 wt% neodymium;
(b) 0.1 to 2 wt% zinc;
(c) 0.2 to 1 wt% zirconium;
(d) at least one of manganese at up to 0.3 wt% and indium at up to 1 wt%;
(e) 0 to 0.1 wt % of at least one oxidation inhibiting element;
(f) 0 to less than 0.15 wt% of each of titanium and hafnium;
5 (g) 0 to less than 0.1 wt% of each of aluminium, copper, nickel, silicon, silver, yttrium and thorium;
(h) 0 to less than 0.005 wt% of strontium; and
(i) apart from incidental impurities, a balance of magnesium.

10 In preferred forms of the alloy of each of the first and second aspects of the invention, the rare earth content may range from 0.5 to 2.09 wt%, such as from 0.5 to 2.05 wt%. In suitable examples the alloy has a rare earth content of from 1.0 to 2.0 wt%.

15 Preferably the zinc content does not exceed 1 wt%.

The magnesium based alloy of the invention is able to be heat treated by being heated to a temperature appropriate for solution treatment, quenched in a suitable quenching medium and then heated to an intermediate temperature for precipitation hardening. However the alloy is amenable to a form of such heat treatment which departs from usual practice and which enables significant practical benefits to be obtained.

Thus, in a third aspect, the present invention provides a method of heat treating an article of a magnesium based alloy according to the first or second aspect of the invention, wherein the method includes the steps of:

1) heating the article:
   (i) to a temperature higher than for a normal solution treatment for a magnesium based alloy which differs in having a rare earth content in excess of 2.1 wt%, and
   (ii) for a period of time shorter than for said normal heat treatment;

2) quenching the article, from the temperature for step (1), into a suitable quench medium; and
(3) ageing the article, after quenching step (2), by holding the article for a period of time within an intermediate temperature range to achieve hardening or strengthening.

In the method of the invention, the solution treatment step (1) requires a higher temperature for a shorter period of time than for a normal heat treatment for an alloy which differs in having a rare earth content in excess of 2.1 wt%. In alloy heat treatments, an inverse relationship generally applies between the heat treatment temperature and the period of time at that temperature. However, in the method of the present invention, the reduction in the period of time typically is substantial compared to the limited scope for the possible higher temperature, relative to the period of time and the temperature for such normal heat treatment.

The upper temperature limit for a normal solution treatment usually is relatively close to the solidus melting temperature for a given alloy. Thus, there is a limited scope for a higher than normal solution treatment temperature as required by the present invention. The normal solution temperature is to enable solute elements to be substantially taken into solid solution, with the time at that temperature sufficient to enable this. An increase in temperature to the level required by the present invention necessarily is modest, such as for example an increase of about 30 to 60°C, due to the need to remain below the solidus. A reduction in time at that increased temperature permitted by the inverse relationship and for the same purpose of taking solute elements substantially into solid solution would similarly be modest, such as a reduction of about 5 to 15%. In contrast, the reduction in time at the increased solution temperature required by the present invention is substantial as it has been found that solute elements do not need to be taken substantially fully into solid solution. The reduction typically is in excess of about 40% and preferably in excess of about 60%. Thus, whereas magnesium casting alloys need very long solution treatment times such as 6 to 24 hours, the method of the present invention as applied to an alloy of the invention can necessitate a solution treatment time of less than four hours, preferably less than three hours, such as from about 1 to 2
hours and even as short as a few minutes. The solution treatment time can depend on the casting process and its effect on the as-cast microstructure.

Step (1) of the method of the invention enables a number of practical benefits to be obtained in the heat treatment of the alloy of this invention, or an article made of that alloy. A first benefit is in a very substantial cost saving resulting in part from a reduction in energy requirements for the solution treatment. That is, the additional cost due to a higher rate of energy consumption in using a higher than normal temperature is substantially exceeded by the reduced energy consumption resulting from the shorter than normal time for the solution treatment. There also are further significant cost savings, such as in labour, which result from the shorter than normal treatment time.

Once step (1) is understood and recognised as being beneficial, the cost saving detailed above becomes evident. However other practical benefits are surprising and contrary to expectations. The shorter than normal solution treatment time is insufficient to enable all solute elements to be taken into solution, despite the higher than normal temperature. This would be expected to result in a significantly less effective overall heat treatment, but this is found not to be the case. Rather, it is found that the kinetics of aging are enhanced, as also are the peak hardness and strength values obtainable with the overall method. In addition to these important benefits, the solution treatment of step (1) of the method results in a further important benefit. This is that detrimental grain growth usually encountered in solution treatment of magnesium alloys is able to be minimised to a significant extent and even substantially avoided. A still further benefit of step (1) of the method is an increased freedom in conducting the quenching of step (2).

In heat treatments used for other magnesium alloys, care has to be taken in quenching from the solution treatment temperature in order to prevent distortion of an article or casting. Thus, quenching usually is into hot water or hot oil in order to reduce the severity of the quench. These quenching media can be used in step (2) of the method of the invention. However, as a consequence of step (1) of the method, there is the added freedom and resultant cost benefit of
being able to quench into cold water with a substantially reduced risk of distortion. The ability to quench into cold water without distortion is of particular benefit for small to medium size castings and thin wall sections of larger castings. However, the ability also increases the size and complexity of castings which are able to be heat treated successfully without distortion being a problem.

The ageing step (3) of the method of the present invention also enables additional economic benefit. The period of time required at a given temperature within the required intermediate temperature range for ageing is able to be shorter than that required for an alloy differing in having a rare earth content in excess of 2.1 wt%, at least for the purpose of achieving a given level of hardening or strengthening.

**Brief Description**

In order that the invention may more readily be understood, description now is directed to the accompanying drawings, in which:

Figure 1 shows plots of hardness against ageing time for alloy according to the invention, following respective solution treatment conditions;

Figures 2(a) and 2(b) show the as cast microstructure for the alloy for Figure 1, in the as cast condition at respective magnifications;

Figure 3 shows the microstructure of the alloy for Figure 1 after a prior art solution treatment;

Figures 4 to 6 show the microstructure of the alloy for Figure 1 after a respective solution treatment according to the present invention;

Figures 7(a) to 7(d) correspond to Figures 3 to 6, respectively, and show the same microstructure at higher magnification; and
Figure 8 shows plots of hardness against ageing time for the alloy of Figure 1 after solution treatment for 2h at 558°C and quenching, with the ageing initially at respective times at a first temperature and then at a second lower temperature.

Detailed Description of Drawings

As an example of the ability to conduct short heat treatments of an alloy composition according the invention without detriment to the alloy is provided in the following. The composition of the test alloy, as given by ICP analysis, is shown in Table 1. For hardness testing and ageing responses, a 15mm thick section of a stepped sand cast casting block was sectioned into hardness test pieces approximately 2cm*2cm in size.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Mg</td>
<td>(balance)</td>
</tr>
<tr>
<td>% La</td>
<td>0.27</td>
</tr>
<tr>
<td>% Ce</td>
<td>0.49</td>
</tr>
<tr>
<td>% Nd</td>
<td>1.30</td>
</tr>
<tr>
<td>% Zn</td>
<td>0.58</td>
</tr>
<tr>
<td>% Zr</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Ageing studies were conducted at 215°C from different solution treatment conditions examined, and these are shown in Figure 1. The solution treatment conditions were: (a) 16h at 525°C, (b) 1h at 558°C, (c) 2h at 558°C and (d) 4h at 558°C. The condition (a) of 16h at 525°C was considered to be a baseline measure of what may be considered to be a usual or typical solution treatment schedule, whereas the conditions (b), (c) and (d) illustrate the method of the invention for rare earth containing alloys of the invention. From Figure 1 it is observed that both the kinetics of ageing and the peak hardness values reached are enhanced when the alloy is solution treated at 558°C for 1 or 2
hours. Following an optimum solution treatment time of 1 to 2h at, for example, 558°C, the kinetics of ageing at 215°C are enhanced such that useable functional properties are gained after only 1 or 2 hours ageing. Additionally, it should be noted that the time required to substantially overage at 215°C, comparative to the peak hardness of alloy solution treated for longer times, is relatively long.

To examine the effect on microstructure of the solution treatment conditions, in particular the continuity of rare earth containing grain boundary phases and zirconium containing regions within the grains, samples were examined optically from each of the solution treatment conditions (a) to (d) described above with reference to Figure 1. Both of these features are known to be advantageous to high temperature thermomechanical deformation, and the retention of these structures was found to be highly desirable. All samples were taken adjacent to each other from the 15mm step of a step plate, and then were polished normally and etched using a solution of 1% HNO₃, 24% H₂O and 75% glycerol. The as-cast microstructure is shown in Figure 2 at two magnifications. Note the grain boundary phase is mostly continuous. It is also noted that the grain size in the as-cast condition ranges from about 50um up to about 300um diameter.

Figure 3 shows the microstructure following solution treatment of 525°C for 16h and, as can be seen, the rare earth containing grain boundary phase is semi-continuous and spheroidised around grain boundary triple points. Also, the dark grey phases discernable in Figure 3 are Zr containing particles at the centers of grains.

Figure 4 shows the microstructure following solution treatment for 1h at 558°C. Grain boundary phases are semi-continuous and spheroidised. Grain boundary phases appear slightly finer than in Figure 3 and are dispersed along grain boundaries. The zirconium containing regions of the microstructure are again evident from the rosette shaped features in the center of grains.
Figure 5 shows the microstructure following solution treatment for 2h at 558°C. Grain boundary phases are again semi-continuous and spheroidised, being similar to those for Figures 3 and 4.

Figure 6 shows the microstructure following 4h at 558°C. Grain boundary phases are no longer continuous but grain boundaries are lined by spheroidised phases.

For comparison purposes, higher magnification micrographs from Figures 3 to 6 are repeated in Figure 7 for easy evaluation. Despite the higher temperature of solution treatment, the grain size is still little different to that noted in the as-cast microstructure of Figure 2.

Little difference is observed between material solution treated 16h at 525°C and material solution treated 1 or 2h at 558°C, in regards to the rare earth and zirconium containing phases present. Solution treating for 4h, at the solution temperature of 558°C, breaks up too much of the grain boundary phases and zirconium containing phases present in the structure to be of practical use at moderately elevated temperatures, and this is also reflected in the ageing kinetics of this condition, which is reduced. Optimum ageing conditions are solution treatment 1-2h at 558°C followed by ageing from 1.5h to 3h at 215°C. This produces an increase in hardness of approximately 16% compared to the standard condition of 16h at 525°C for the alloy for a substantial time reduction in solution treatment.

Alloy treated under solution treatment conditions of 1h at 558°C and 2h at 558°C (corresponding to conditions (b) and (c) respectively above) was then aged for 2h at 215°C, and tensile properties determined. Tensile properties over multiple samples were found to be:

<table>
<thead>
<tr>
<th>Condition</th>
<th>0.2% proof stress (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Failure %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b)</td>
<td>128</td>
<td>170</td>
<td>2</td>
</tr>
<tr>
<td>(c)</td>
<td>123</td>
<td>181</td>
<td>3</td>
</tr>
</tbody>
</table>
These strength properties are comparable to the 0.2% proof stress of some other higher rare earth content magnesium alloys. Also, alloys AZ63 and AZ91 heat treated to the T6 temper typically display lesser 0.2% proof stress values of 110 and 120Mpa, respectively. Additionally, unlike the yttrium containing alloys such as WE54, the alloy of the present invention does not display substantial detrimental secondary precipitation that causes embrittlement at intermediate temperatures such as 65°C, and therefore has good intermediate temperature precipitate stability. This is illustrated in Figure 8.

Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the spirit or ambit of the invention.

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Effect of solution treatment

Fig 1
Fig 7
Fig 8
References

--None--