EFFECT OF PRASEODYMIUM ADDITION ON MICROSTRUCTURE AND HARDNESS OF CAST ZRE1 MAGNESIUM ALLOY

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ABSTRACT
The effect of 1 wt % Pr addition on ZRE1 cast alloy was investigated using Optical Microscope (OM), Scanning Electron Microscope (SEM), Energy-Dispersive Spectrum (EDS) and X-ray Diffraction (XRD). The purpose of this research is to investigate the variations in grain size and intermetallics formation with Pr addition, as well as their effect on hardness. The microstructure observations show that the grains became smaller with Pr addition, which lead to the increase of hardness of base alloy. EDS results showed that the base alloy mainly consists of α-Mg matrix and Mg-Zn-Ce as a second phase crystallized along the grain boundaries and when Pr was added, the Mg-Zn-Ce-Pr phase was formed, where Pr combined with the original second phase. The solubility of zinc and Pr in magnesium formed Zn-rich particles around grain boundaries.

Keywords: Magnesium alloy, rare earth, microstructure, hardness.

INTRODUCTION
Magnesium and magnesium alloys are used in a wide variety of structural and nonstructural applications due to they are light-weight, exhibit good strength and stiffness at both room and elevated temperatures and have high strength-to-weight ratios (tensile strength/density), comparable to those of other structural metals. Structural applications include automotive, industrial, materials-handling, commercial, and aerospace equipment. Magnesium alloys are also valuable for aerospace applications. Magnesium has relatively good electrical conductivity and thermal conductivity values. It also has a very high damping capacity, that is, the ability to absorb elastic vibrations (Kulekci 2008, Hirsch and Al-Samman 2013). Rare Earths (RE), such as Lanthanum (La) and Cerium (Ce) added to lightweight alloys to improve the high temperature strength, mechanical properties and creep resistance (Ahmad, Asmael et al. 2014, Mirza and Chen 2014, Yu, Chen et al. 2014). In addition, this RE usually added as mischmetal (MM) or didymium (Dm). Mischmetal is a natural mixture of the rare earths containing about 50 wt.% Ce, with the remainder being principally comprised of La and neodymium (Nd), and didymium is a natural mixture of approximately 85% neodymium (Nd) and 15% praseodymium (Pr). Addition of rare earth also reduce weld cracking and porosity in casting because they narrow the freezing range of the alloys (Davis 2001, Friedrich and Mordike 2006).

Recently developed alloys have contained separate rare earths. The properties of Mg-RE alloys are enhanced by adding zirconium to refine grain size and further increases in strength occur if zinc is present in the alloys as well. Higher creep strength at temperatures up to 250 °C has been achieved in the alloy ZRE1 (EZ33). (Ferro, Saccone et al. 2013). ELEKTRON ZRE1 is a magnesium-base casting alloy which combines excellent creep resistance up to 250 °C, with good room temperature properties. It is completely free from microporosity and very suitable for applications requiring pressure tightness. Elektron ZRE1 (EZ33) is used in aero engine components where improved creep resistance is required. In the aeroengine industry, magnesium alloys are being used successfully in both civil and military aircraft. Civil applications include intermediate casings for the engines and gearboxes, also in military aircraft, including the F16, Tornado and Eurofighter Typhoon, capitalize on the lightweight characteristics of magnesium alloys for transmission casings (Duffy 1996).

Previous studies showed that as-cast microstructure of ZRE1 magnesium alloy consist of α-Mg matrix and (Mg, Zn)2RE phase at the grain boundaries. The (Mg, Zn)2RE compound exhibited high stability of the chemical composition and morphology at temperature 150°C for 1000 hours. At 200 °C, the first stages of spheroidizing of the (Mg, Zn)2RE are observed, therefore the hardness of the ZRE1 alloy is slightly lower than that in the alloy annealed at 150°C. The degradation of the microstructure of the ZRE1 alloy at 400 °C is induced by the low oxidation resistance at this temperature. This effect causes the formation of the porous MgO layer and the oxidation of the (Mg, Zn)2RE compound. Thus, the mechanical properties of ZRE1 magnesium alloy decreased after heated at 200 °C, and cannot be heat treated above 400 °C. They also found that the alloy poured from 730°C shows the highest ultimate tensile strength (UTS) and hardness compared with the alloys poured from 780 °C and 830 °C (Rzychoń, Szala et al. 2012).

Praseodymium (Pr) is a rare earth metal, and used to alloying agent with magnesium to create high-strength metals that are used in aircraft engines. The formation and mechanical properties of Mg97Zn1RE2 alloys with long-period stacking ordered (LPSO) structures investigated by (Kawamura and Yamasaki 2007). Some cast ingots were soaked at 500 °C for 10 hours in air. The yield strength and ultimate tensile
strength of Mg$_{97}$Zn$_1$Pr$_2$ were more than 350 MPa, and elongation was at 3%. The elevated-temperature tensile properties of the wrought Mg$_{97}$Zn$_1$RE$_2$ alloys showed that the yield strength and ultimate tensile strength of Mg$_{97}$Zn$_1$Pr$_2$ alloy were more than 200 MPa, and elongation was around 25%. SEM micrographs of the as-cast Mg$_{97}$Zn$_1$RE$_2$ alloys showed a secondary phase with a lamellar contrast was observed in the grain boundaries and dendrite arm boundaries for RE = Y, Dy, Ho, Er and Tm. The secondary phase of Mg$_{97}$Zn$_1$RE$_2$ cast alloys with RE = Y, Gd, Tb, Dy, Ho, Er and Tm exhibited pale contrast in the vicinity of bright contrast at the cell boundaries. X-ray diffraction patterns showed that the alloys were composed mainly of α-Mg and Mg-RE intermetallic compounds for RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Yb.

(Cui, Liu et al. 2010) studied effect of Pr additions on microstructure and mechanical properties of die-cast AZ91D magnesium alloy, by the addition of 0.4, 0.8, and 2 wt.% Pr separately into the base alloy, which were prepared by high-pressure die-casting technique. They investigated the effects of Pr on the microstructures of die-cast Mg-9Al based alloy by XRD and SEM. They found that the mass fraction of Pr at around 0.8% is considered to be suitable to obtain the optimal mechanical properties. The optimal mechanical properties are mainly resulted from grain boundary strengthening obtained by precipitates and solid solution. The UTS, yield strength, elongation, and hardness of Mg-9Al-xPr alloys are improved, while Pr content increases from 0.4% to 0.8%. When the Pr addition increases to 1.2%, the ultimate tensile strength, yield strength, elongation, and hardness have a slight decline. When analyzing the microstructures of Mg-9Al-xPr alloys, they mainly composed of α-Mg matrix and Mg$_{17}$Al$_{12}$. With single Pr addition, Al$_{13}$Pr$_3$ and Al$_3$Mn$_2$Pr phases can be found in the microstructure. It was discovered that increasing of Pr content caused increase of the sizes of Al$_6$Mn$_2$Pr and Al$_{11}$Pr$_3$ phases quickly. The increase of Al$_6$Mn$_2$Pr and Al$_{11}$Pr$_3$ phase size can cause a decline in mechanical properties. The mass fraction of 0.8% Pr is considered to be suitable to obtain the optimal mechanical properties. The aim of this study is to extend the investigations concerning the microstructure, phase constitutions and mechanical properties of as-cast ZRE1 magnesium alloy, after the addition of an individual rare earth metal, Pr, which has low solubility in magnesium solid solution. Further addition of Pr into the ZRE1 (Mg–Zn–RE–Zr) alloy is to produce distinct effect on the properties of the base alloy by an individual rare earth metal.

**EXPERIMENT PROSEDURE**

ZRE1 magnesium cast alloy was used as the base alloy. Table-1 shows chemical composition of the as-cast ZRE1 magnesium alloy.

<table>
<thead>
<tr>
<th>RE</th>
<th>Mg</th>
<th>Zn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>2.0</td>
<td>3.0</td>
<td>2.5</td>
</tr>
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The 1 wt.% Pr RE was added into the melt. Melting of the base alloy was conducted in an electrical resistance furnace, with a steel crucible under a cover gas mixture of Ar and 2% SF$_6$. 1 wt.% Pr was added as small pieces after the base alloy melted around 730 °C, and then the temperature was kept at 730 °C with stirring for a view minutes to ensure dissolution of alloying elements, then pouring in a steel mold (preheated up to 500 °C) at 730 °C. Specimens were prepared for microstructure analyses and hardness by wet grinding on silicon carbide papers and a final grinding was done by 1200 /2400 grit papers, followed by polishing with 0.3 micron α-alumina. The microstructure was characterized by optical microscope, SEM/EDS (JEOL- JSM-6380LA), and XRD. IMT iSolution DT V12.0 image analyser was used to examine the microstructure, mean area of grain plane section (grain size) was measured using the intercept method specified in ASTM E112. The hardness test was carried out by (Matsuzawa DVK-2) Vickers hardness tester using 5 Kg load, and each reading represents an average of seven measurements.

**RESULTS AND DISCUSSION**

**Microstructure**

The microstructures of ZRE1 and ZRE1 + 1 wt.% Pr alloys under optical microscope are shown in Figure-1. It can be seen that the microstructure of the base alloy has been changed when Pr was added, and by comparing the two images in Figure-1, the average grain sizes of base alloy and base alloy + 1 wt.% Pr were determined to be 72.40 μm and 45.41 μm, respectively. Therefore, it can be concluded that Pr addition to ZRE1 alloy is effective to refine grains of the alloy. Table-2, shows the grain sizes of base alloy and base alloy + 1 wt.% Pr.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>0 wt.% Pr</th>
<th>1 wt.% Pr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size, μm</td>
<td>72.40</td>
<td>45.41</td>
</tr>
</tbody>
</table>

As seen, the grain size of the base alloy decreased with the Pr addition. Therefore, it is observed that Pr addition to ZRE1 alloy is effective to refine grains of the alloy. (Zhiyong, Jingjing et al. 2014) found that the addition of 1.20 wt.% Pr into AZ61 magnesium alloy lead to reduce grain sizes of the alloy about 50%. SEM observations showed that the microstructure of base alloy consists of α-Mg grains surrounded by second phase...
crystallize along the grain boundaries as a kind of massive morphology (Figure-2).

The EDS results showed that second phase was composed of magnesium, zinc, and cerium, Figure-2 (point 2), and the matrix contains magnesium, zinc and a small amount of zirconium, Figure-2 (point 1). It can be seen that the base alloy consisted of two phases, the $\alpha$-Mg matrix and Mg Zn Ce intermetallic compound. (Rzychoń, Szala et al. 2012) have been written molecular formula of the second phase as (Mg, Zn)$_{12}$Ce.

**Figure-1.** Microstructures images of magnesium alloys: (a) untreated alloy and (b) 1 wt.% Pr containing alloy.

**Figure-2.** (a) SEM micrograph image of base alloy with EDS analysis (b) and (c) of phases marked as (point 1. Mg-Zn-Zr) and second phase (point 2. Mg-Zn-Ce) respectively.

SEM observations and EDS results of ZRE1 + 1 wt.% Pr alloy are shown in Figure-3. It can be seen that Pr combined with the intermetallic phases, which continuously distributed along the grain boundaries. Combination of alloying rare earths with elements decreasing the solubility of rare earths in Mg and simultaneously forming thermally stable plate shaped particles on the basal planes is clearly a promising method of developing creep resistant magnesium alloys. The solid solubility of Zn and Pr in Mg is very low and reduces with the decrease of the temperature of the melt, where zinc is added to reduce the solubility of the expensive rare earth.
The low solid solubility of Zn in the presence of RE elements releasing Zn bound in intermetallic particle. It can be seen from SEM image and EDS that the formed particles have a high concentration of Zn (around 63 wt.%) and distributed inside the grain boundaries, where these intermetallic particles could be reinforced the grain boundaries.

The XRD patterns of ZRE1 and ZRE1 + 1 wt.% Pr alloys are shown in Figure-4. It can be seen that no new phases were formed. Moreover, the peak intensities of Mg-phase decreased with the Pr addition, however, Mg RE-phase slightly increased. These results are related to very low solubility of Pr in solid solution. Thus, during solidification, rare earth elements form (Mg, Zn) RE phase, until the remaining RE were used without any formation of other phases.

Figure-3. (a) SEM micrograph shows Zn-rich particles inside the grain boundary, (b) EDS microanalysis of the particle marked with the white arrow (Mg-Zn-Ce-Pr).

Figure-4. XRD patterns of ZRE1 and 1 wt.% Pr containing alloys.

Hardness test

Figure 5 shows hardness of the base alloy and base alloy + 1 wt.% Pr. It can be seen that the hardness is improved with 1 wt.% Pr, which increased from 47 HV for base alloy to 58.5 HV. The increase in hardness value of base alloy with the addition of Pr may be explained by grain refinement, where the grain size reduced and also improved by the effect of second phase (Mg-Zn)_{12} RE and intermetallic compound (Mg-Zn-Ce-Pr), (Yang et al. 2008) showed that Mg_{12}RE is a strengthening phase of MEZ (Mg-Zn-RE) alloys.

The hardness result is in agreement with (Zhiyong, Jingjing et al. 2014), where they found that the Pr addition improves the mechanical properties of AZ61 alloys, and with the addition of 2 wt.% Pr into AZ61, the hardness of as-cast AZ61 alloy is improved from 50 HB to 57 HB.

Figure-5. Effect of Pr addition on hardness of ZRE1 alloy.

CONCLUSIONS

The effect of the Pr addition on microstructure and hardness of ZRE1 cast alloy was investigated and the following can be summarized:
The addition of Pr has favorable effect on reducing the grain size of ZRE1 alloy around 37%.

The addition of Pr reduced solubility of Zn, which led to the formation of Zn-rich particles at grain boundaries and formed Mg-Zn-Ce-Pr during the solidification.

The hardness value of ZRE1 improved by 24 %, with 1 wt.% Pr addition.

ACKNOWLEDGEMENTS
This research is funded by Exploratory Research Grant Scheme (ERGS), vot number E023, Ministry of Higher Education, Malaysia.

REFERENCES


