ARC Centre of Excellence Design in Light Metals

The Corrosion Behaviour of HPDC Mg-RE Alloys

A.Südholz[1], N. Birbilis[1], M. Gibson[2], M. Easton[3], S. Zhu[2]

[1]ARC Centre of Excellence for Design in Light Metals, Department of Materials Engineering, Monash University, 3800, VIC, Australia

[2]CSIRO Materials Science and Engineering, Private Bag 33, Clayton South MDC, Clayton, VIC, 3169, Australia

[3]CAST Cooperative Research Centre, Department of Materials Engineering, Monash University, 3800, VIC, Australia

Introduction

Magnesium is a lucrative engineering material for the automotive and aviation sectors alike due to its excellent specific strength and castability. However Mg alloys are currently limited by poor corrosion resistance. This work investigates high pressure die cast (HPDC) alloys of binary rare-earth (RE) compositions in order to assess the effect of individual Ce, Nd and La in various concentrations.

Experimental Method

Alloying: Commercially pure Mg melt was formed under the protection of AM-cover (0.2wt.% tetrafluoroethane and 99.8wt.% nitrogen gas) and approximately 5ppmBe from a Al-5Be master alloy. Alloys were high-pressure die cast by Toshiba 250t cold chamber machine. Ram velocity of 2.25m/s was used with a maximum pressure of ~120MPa and a biscuit size of 40mm. Shot time ~600ms to fill the die cavity; and as a result of such rapid cooling rates, the microstructure of the castings is assumed to be uniform. Alloy composition was determined by ICP-AES (Table 1).

Electrochemical measurements: Electrochemical flat-cell (Figure 1) and micro-cell were connected to PAR 3Z potentiostat. Stable OCP was established within 10mins and potentiodynamic polarisation scanned at 1mV/s from 100mV<OCP to i=10mA/cm^2.

Imaging: Phillips XL-30 SEM (Figure 2) in BSE mode.

Figure 1. Electrochemical Flat cell

Figure 2. Phillips XL-30 SEM

Results

Each alloy was found to contain rare earth rich intermetallics within an α-Mg matrix, determined by TEM and summarised in Table 2. SEM imaging was carried out in BSE mode to reveal compositional contrast of rare earth intermetallics with respect to the α-Mg matrix. Figure 3 shows the effect of rare earth alloying on the microstructure of Mg. It can be seen from these images that increased weight percent of rare earth addition increases the volume fraction of the rare earth intermetallics. Microcell techniques facilitate potentiodynamic polarisation scanning of isolated phases (Figure 4) which demonstrate the noble nature of the respective intermetallics compared to Mg. This is further illustrated by a shift in electrochemical potential caused by the presence of more noble rare earth intermetallics in an active Mg matrix (Figure 5) and subsequent influence of corrosion kinetics (Figure 6).

Table 1. Elemental data of Mg-RE alloys determined by ICP-AES.

Alloy Series	La wt.%	Ce wt.%	Nd wt.%
1	0.51	0.53	0.47
2	0.94	0.93	0.76
3	1.71	1.48	1.25
4	3.44	2.87	2.60
5	5.07	4.76	3.53

Table 2. Structural details and densities of rare-earth intermetallics

Intermetallic	$Mg_{12}La$	$Mg_{12}Ce$	Mg_3Nd
Crystal Structure	tI26	tI26	cF16
Lattice Parameters (nm)	a = 1.03 c = 0.59	a = 1.033 c = 0.596	a = 0.741
Density (g/cm^3)	2.27	2.25	3.56

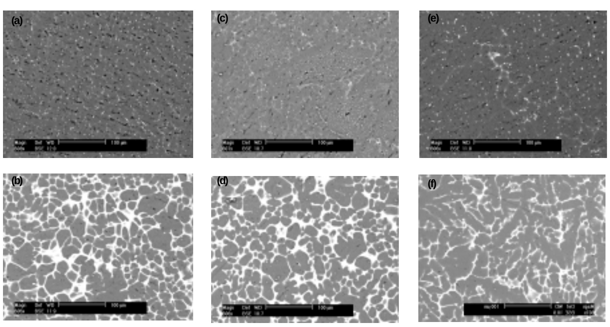

Figure 3. SEM (BSE mode) images: **(a)** Mg-0.53Ce **(b)** Mg-4.76Ce **(c)** Mg-0.51La **(d)** Mg-5.07La **(e)** Mg-0.47Nd **(f)** Mg-3.53Nd

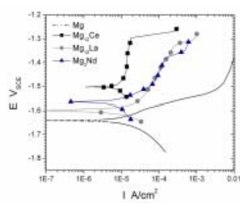

Figure 4. Potentiodynamic polarisation scans of intermetallics.

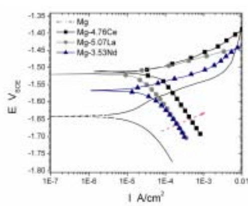

Figure 5. Potentiodynamic polarisation scans of Mg-RE alloys.

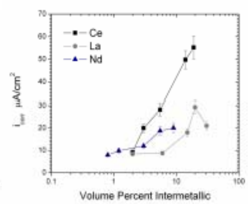

Figure 6. Corrosion current of alloy as a function of volume % intermetallic.

Potentiodynamic polarisation scans reveal two key electrochemical parameters: E_{corr} and i_{corr}. The corrosion potential (E_{corr}) gives a relative measure of the thermodynamic stability of the surface and the corrosion current density (i_{corr}) gives a measure of the rate of the corrosion reaction. Both parameters were found to be influenced by weight percent addition to pure Mg of each respective rare earth element (Figure 7).

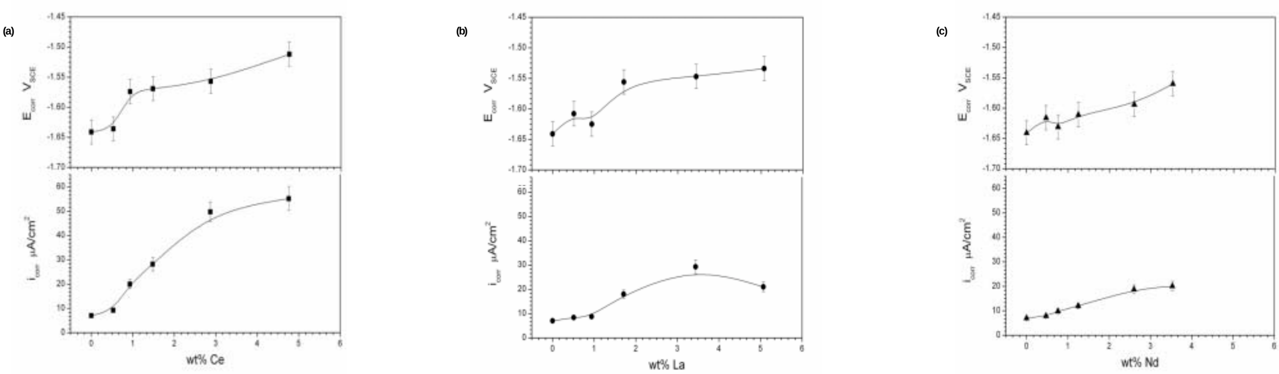

Figure 7. Variation of electrochemical parameters E_{corr} and i_{corr} with wt% rare-earth: **(a)** Mg-Ce series **(b)** Mg-La series **(c)** Mg-Nd series

Discussion

- This work represents a detailed investigation into the effects of Ce, La and Nd additions on the corrosion behaviour of HPDC alloys. Electrochemical characterisation of individual phases has been achieved.
- Additions of Ce, La and Nd elements to commercial purity Mg form stable intermetallic species; $Mg_{12}Ce$, $Mg_{12}La$ and Mg_3Nd respectively. These phases affect the corrosion behaviour of the alloy.
- Intermetallics formed by the addition of rare earth elements present a more noble phase within an active matrix. This leads to micro-galvanic coupling between intermetallic and matrix. Increased galvanic coupling enhances the overall corrosion rate of the alloy.
- Consequently, increased volume percent of each respective intermetallic, and therefore increased cathodic activity, progressively increases the corrosion current density (i_{corr}) of the respective alloy with increasing weight percent of alloying addition.
- This work aims to serve as a design tool in the development and assessment of HPDC alloys.

Future Work

- Investigate combined effects of rare-earth elements in ternary alloy systems.
- Integrate this knowledge into rational alloy design.

Acknowledgements

Funding provided by the Australian Research Council Centre of Excellence for Design in Light Metals is gratefully acknowledged, together with funding from the Victorian State Government (DIIRD) for the establishment of the Victorian Facility for Light Metals Surface Technology. The CAST Co-operative Research Centre was established under, and is funded in part by, the Australian Governments Co-operative Research Centres Scheme.