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The influence of minor Mn additions on creep resistance of die-cast Mg–Al–RE alloys

S.M. Zhu[a,*], T.B. Abbott[a,b,c], M.A. Gibson[a,c,d], J.F. Nie[c], M.A. Easton[a]

[a] School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
[b] Magontec Limited, Sydney, New South Wales 2000, Australia
[c] Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
[d] CSIRO Manufacturing, Clayton, Victoria 3168, Australia

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ABSTRACT

Magnesium alloys normally contain minor amounts (~0.3%) of Mn to achieve improved corrosion resistance by controlling the level of Fe during melting. It has been reported recently that minor Mn additions can significantly enhance the age hardenability of die-cast Mg–Al–RE alloys. This paper reports that minor Mn additions also have a remarkable influence in improving the creep resistance of die-cast Mg–Al–RE alloys. The secondary creep rate of Mg–4Al–3La alloy at 175 °C/75 MPa is reduced by more than three orders of magnitude (from 5.9×10^{-7} s^{-1} to 3.0×10^{-10} s^{-1}) by the addition of 0.32% Mn. The improvement in creep resistance is associated with the dynamic precipitation of nanoscale Al–Mn particles during creep. The findings in this work shed new light on creep resistance of Mg–Al based alloys.

1. Introduction

Mg–Al–rare earth (RE) alloys are one of the families of magnesium die-casting alloys developed for elevated temperature applications. Two notable alloys are AE42 (Mg–4Al–2RE, wt%) and AE44 (Mg–4Al–4RE). AE42 exhibits superior creep resistance to AZ91 (Mg-9Al-1Zn) [1], but it tends to have hot tearing issues [2] and its creep resistance deteriorates rapidly at temperatures above 150 °C [3]. Adding more RE to AE42 was found to improve not only the creep resistance and but also the castability, which led to the development of AE44 [4]. Traditionally, RE was added in the form of misch metal, i.e. a mixture of several RE elements including Ce, La, Nd and Pr, with Ce being the most abundant element. This is because RE misch metal was initially produced by direct conversion of the ore without separating individual elements. However, with the high demand for Nd in magnetic applications in recent years, elemental La or Ce and the two-element misch metal (containing only Ce and La) have become considerably cheaper than the four-element misch metal. For this reason, work has been devoted to Mg–Al–RE alloys that contain either La [5,6] or Ce [7] or the La+Ce misch metal [8,9] in order to develop cheaper versions with comparable mechanical properties to the conventional four-element counterparts.

A thorough evaluation of castability, tensile properties and creep resistance has been conducted on AE42 and AE44, together with other speciality Mg casting alloys including AS31 (Mg–3Al–1Si), AJ52 (Mg–5Al–2Sr), MRI153A (Mg–9Al–1Ca–0.1Sr), MRI153M (Mg–8Al–1Ca–0.3Sr), MRI230D (Mg–6.5Al–2Ca–1Sn–0.3Sr), AXJ530 (Mg–5Al–3Ca–0.2Sr) and AM–HP2+ (Mg–3.5RE–0.4Zn) [9,10]. AE44, MRI230D, AXJ530 and AM–HP2+ are all comparable to the Al alloy counterpart in terms of creep resistance, but MRI230D, AXJ530 and AM–HP2+ have some issues with castability. The Mg–Al–RE alloys have very good room temperature ductility, but their yield strengths are relatively lower than those of MRI230D, AXJ530 and AM–HP2+.

It was found recently [11] that the strength of die-cast Mg–Al–RE alloys containing minor Mn additions can be improved significantly by ageing. For example, the yield strength of Mg–4Al–3La alloy with 0.32% Mn is increased by ~34 MPa (~26%) after ageing at 200 °C for 32 h without prior solution treatment. More interestingly, the remarkable improvement in strength after ageing is not accompanied by any significant loss in ductility. The age hardening is associated with the precipitation of nanoscale Al–Mn particles during ageing at elevated temperatures.

Minor Mn additions have been reported to have beneficial effects on creep resistance in Mg–6Al–2Sr–0.3Mn [12], Mg–6Al–3Ca–0.5Mn [13] and Mg–2Al–2Ca–0.3Mn [14] alloys. The improvements in creep resistance for these alloys were attributed to the presence and/or dynamic precipitation of nanoscale Al–Mn precipitates [12,13] or ordered GP zones [14]. Given that minor Mn additions significantly

* Corresponding author.
E-mail address: suming.zhu@rmit.edu.au (S.M. Zhu).

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enhance the age hardenability of die-cast Mg–Al–RE alloys [11], it is interesting to see how the creep resistance of Mg–Al–RE alloys will be affected by minor Mn additions. For this purpose, die-cast Mg–4Al–3La (ALa43) alloys with various Mn additions were prepared and their mechanical properties, especially creep resistance, were evaluated. It is worth mentioning that Mn is not an additional alloying element since Mg–Al–RE alloys, like other Mg alloys, normally contains about 0.3% Mn to reduce Fe during melting process for the improvement of corrosion resistance.

2. Experimental methods

ALa43 alloys with various levels of Mn additions, i.e. 0 (0Mn), 0.1% (0.1Mn), 0.3% (0.3Mn) and 0.5 wt% (0.5Mn), were used in the present study. The alloys were cast in a 250 t Toshiba cold chamber high pressure die casting machine using a 3-cavity die [15] to produce one rectangular dog-bone shaped tensile specimen (5.75 mm width and 3 mm thickness) and two cylindrical tensile bars (5.65 mm diameter). The alloy melts were produced in a resistance heated crucible and held at around 700 °C before casting. AM-cover (HFC-134a in CO_2 carrier gas) was used for melt protection during melting and holding. The temperature of the oil for heating up the die was set at 250 °C. The maximum ram velocity was 2.2 m/s and the intensification pressure was 120 MPa. The die cavity was filled in approximately 600 ms. The chemical compositions of the alloys were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and are shown in Table 1. There is a slight decrease in the Al content from the 0Mn alloy to the 0.5Mn alloy. A trace amount of Mn was also detected in the 0Mn alloy even though no Mn was added.

The cylindrical tensile bars were used to evaluate mechanical properties and creep behaviour of the alloys. The tensile tests were conducted at a crosshead speed of 5 mm/min and at both room temperature and 150 °C on a screw-driven Instron machine equipped with a heating chamber. At least three specimens were used for each test to ensure reproducibility. The constant load creep tests were conducted at 150 °C and 175 °C on creep testing machines. The specimens were immersed in heated silicone oil baths, with the temperature controlled to within ± 1 °C. Creep strain was measured by an extensometer that was attached directly to the gauge section of specimens. The tests were run until failure of the specimens or interrupted after 500 h.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) spectroscopy were used to characterize microstructure before and after creep testing. Foils for TEM examination were prepared by low-angle ion milling. For comparison, all microstructural examinations were carried out in the half-radius region within the gauge section of the tensile bars.

3. Results

3.1. Starting microstructure

SEM images of the as-cast ALa43 alloys with various Mn additions are shown in Fig. 1. The microstructure in these alloys is characterised by primary α-Mg dendrites surrounded by intermetallic phases in the interdendritic/grain boundary regions. Whilst the fibrous or lamellar-like intermetallic phase is predominant in all alloys, a few coarse, bulky particles are occasionally observed in the Mn-added alloy, especially 0.5Mn alloy. The intermetallic phases in the alloys were further examined by TEM, shown in Fig. 2. The fibrous phase is identified to be $Al_{11}La_3$ (body-centred orthorhombic, a=0.443 nm, b=1.314 nm and c=1.013 nm). The bulky intermetallic phase contains Mn in addition to Al and La, and is identified to be $Al_{10}La_2Mn_7$ (hexagonal, a=0.90 nm and c=1.30 nm). Similar intermetallic phases have been reported in other Mg–Al–RE alloys [7,8,16–18]. It is worth mentioning that the Al_2RE type intermetallic phase, which is common to Mg-Al-RE alloys, is not observed in the present ALa43 alloys. This observation is consistent with the previous work on permanent mould cast or die-cast Mg–4Al–(1–4)La alloys [5,6]. Zhang et al. [5] reported the presence of the Al_2La phase in an alloy with higher La content, i.e. Mg–4Al–6La, based on the X-ray diffraction analysis.

The level and distribution of solutes within the α-Mg dendrites for 0Mn and 0.3Mn alloys were analysed by TEM EDX analysis, shown in Fig. 3. The presence of Mn solute is detected in 0.3Mn alloy but not in 0Mn alloy. There is an increase in Al concentration from the centre of the dendrite towards the boundaries. This is what is expected for non-equilibrium solidification in die-casting. However, there appears an opposite trend in Mn concentration in 0.3Mn alloy. The reverse segregation of Mn has been reported in AZ31 and AM50 [19,20] and is known to be related to the peritectic nature of Mn in Mg–Al–Mn system [21]. It is noted that the Al concentration near the boundaries of the dendrite is ~2.0 wt% for the 0.3Mn alloy, slightly lower than that for the 0Mn alloy, which is ~2.6 wt%. Since the solubility limit of Al in Mg is ~3.3 wt% at 175 °C according to the Al-Mg phase diagram [22], no formation of $Mg_{17}Al_{12}$ would be expected in both alloys during creep at 175 °C. However, as shown later, this is not the case.

Table 1
Chemical composition of the die-cast Mg–4Al–3La alloys in this study.

Alloy	Al%	Mn%	Ce%	La%	Nd%	Fe ppm	Si ppm
0Mn	4.37	0.013	< 0.005	3.12	< 0.005	150	400
0.1Mn	4.1	0.11	< 0.005	2.91	< 0.005	90	300
0.3Mn	4.07	0.32	< 0.005	2.92	< 0.005	100	500
0.5Mn	4.05	0.52	< 0.005	2.97	< 0.005	110	300

3.2. Tensile properties and creep properties

Representative tensile curves of the as-cast alloys tested at room temperature and 150 °C are shown in Fig. 4 and the tensile properties such as the 0.2% yield strength, tensile strength and elongation to failure are listed in Table 2. It appears that the tensile properties at room temperature are not affected by the minor Mn additions. A pronounced effect is evidenced at 150 °C, with the yield and tensile srength increased whilst the ductility decreased with increasing Mn addition up to 0.32%. However, a further increase in Mn addition from 0.32% to 0.52% does not lead to any obvious changes in tensile properties, suggesting that 0.3% is probably the optimum Mn addition for the present alloys.

A remarkable improvement in creep resistance by the minor Mn additions is observed, as shown in Fig. 5. For example, upon loading at 150 °C and 90 MPa, the 0Mn specimen failed in less than 10 h with a secondary creep rate of $1.9\times10^{-6}\ s^{-1}$ whilst the 0.5Mn specimen sustained 500 h without failure (test interrupted at this point) and the secondary creep rate was $1.2\times10^{-10}\ s^{-1}$. It is to be noted that the secondary creep rate is decreased rapidly with increasing Mn addition up to 0.32%, but it drops moderately with further increase in Mn addition to 0.52%. The tests at 175 °C and 75 MPa show a similar trend in creep properties.

3.3. Microstructure after creep

To uncover the cause of the remarkably improved creep resistance by minor Mn additions, the microstructure in the creep specimen tested at 175 °C and 75 MPa to failure or for 500 h was examined for the four alloys. The SEM observations of the crept specimens are shown in Fig. 6. As compared with the as-cast state, the $A1_{11}La_3$ phase appears to be stable during creep testing, with no obvious change in shape or size observed. This is consistent with the previously reported studies for die-cast Mg–4Al–(1–4)La alloys [5,6] and AE44 [23,24].