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Strengthening by the percolating intergranular eutectic in an HPDC Mg–Ce alloy

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ABSTRACT

Dual beam FIB tomography was used to create a 3D model of the percolating intergranular (α-Mg)–$Mg_{12}Ce$ eutectic in a Mg–0.51 at% Ce alloy and its tensile deformation behaviour assessed using finite elements. The eutectic itself was modelled as a fibre reinforced composite, with the elastic constants of the $Mg_{12}Ce$ intermetallic determined using a first principles approach. The 3D eutectic network exhibited a very low structural stiffness, akin to that of bending-dominated cellular structures. Such high compliance implies that the 3D structure may contribute to the alloy's strength while sustaining limited damage by cracking, hence extending the reinforcing without compromising the ductility, up to strains in excess of 1%. Elastic stretching of the 3D network adds ~25 MPa to the overall strength of the alloy at 0.2% offset strain, a value comparable to the strengthening expected from a similar volume fraction of dispersed (isolated) elastic particles. Flash anneal of the alloy to break up the spatial interconnection confirmed that the strengthening introduced by the eutectic stemed from the combination of network reinforcement and dispersion hardening.

1. Introduction

Cerium, in the form of Ce-rich mischmetal, is currently used to increase the creep strength of high pressure die casting (HPDC) Mg alloys. Due to its low solubility in the solid state, and like other Rare Earth (RE) elements, Ce is considered a “eutectic forming” solute. During solidification the Ce atoms concentrate in the liquid ahead of the solidification front, creating a large fraction of eutectic liquid which ultimately forms a percolating intergranular network of Mg–$Mg_{12}Ce$, particularly near the casting surface, or casting skin [1,2]. The volume fraction of eutectic in commercial Mg–RE alloys can be very significant, up to ~22% [1], and a sizable contribution to the casting's strength and strain hardening can thus be expected from it.

Dual beam FIB 3D tomography by Nagasekhar et al. [3] and a subsequent FE analysis by Zhang et al. [4] provided detailed insights of the 3D configuration and deformation behaviour of the percolating intermetallic in HPDC AZ91D alloy. These studies concluded that the profuse spatial interconnection should account for a measurable fraction of the alloy's strength in addition to the dispersion hardening effects. Compared to the Mg–Al alloy system, in which Al is highly soluble, Mg–Ce alloys can be expected to exhibit a limited amount of solid solution strengthening because of Ce's low solid solubility. Indeed, microprobe concentration profiles across the α-Mg grains of an (mass%) HPDC Mg–11RE–4Zn–1Al alloy[3] indicated that the as-cast microstructure corresponds to that of a composite made of a nearly pure Mg matrix reinforced by an intergranular network of eutectic (α-Mg)–$Mg_{12}Ce$ [5]. That is, the lack of solid solution hardening turns HPDC Mg–Ce alloys into ideal model materials to assess the contribution of the 3D eutectic network to the overall strength of the matrix alloy, in this case fine grained, nearly pure Mg. By extension, a straightforward comparison with the analytical estimate of the strengthening expected through dispersion hardening of a similar volume fraction of isolated (i.e., non-spatially interconnected) intermetallic particles [4,6] should be possible.

The aim of this work was to assess the deformation behaviour of the 3D percolating eutectic microstructure (hereafter called *3De*) and, by extension, its contribution to the strength, of cast-to-shape tensile specimens of an HPDC Mg–0.51 at% Ce alloy of a prior study by Chia et al. [1]. Dual beam FIB 3D reconstruction data

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[3] RE denoted in this case a Ce-rich misch-metal containing 51.7 mass% Ce, 23.1 mass% La, 18.6 mass% Nd, and 6.5 mass% Pr.

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were collected to create a numerical image of the percolating eutectic, and the tensile deformation behaviour of the 3D structure subsequently modelled through a finite element (FE) code. Although there have been extensive studies on the properties of Mg–RE intermetallics (e.g., [7–9]), values for the $Mg_{12}Ce$ intermetallic elastic constants required for the FE modelling appeared not to be available. Therefore, values for these constants were obtained via a first-principles approach calculation (described in Appendix A). Those values were then used to calculate the weighted average modulus for the (α-Mg)–$Mg_{12}Ce$ eutectic using a standard metal matrix composite approach.

The calculated contribution to the total strength was validated against experimental data in two ways: a short (1 h) solution heat treatment (hereafter called flash-anneal) aimed at breaking up the spatial interconnection of the eutectic was applied to some tensile specimens and their strength compared with that of the as-cast specimens; the strength of the as-cast specimens was compared with that of similarly cast specimens of a dilute (eutectic-free) Mg–0.09 at% Ce alloy, used to represent the eutectic-free matrix alloy in which the percolating eutectic of the Mg–0.51 at% Ce alloy was embedded.

The present work differs from the earlier one [4] on AZ91D alloy in one important aspect: in the AZ91D the eutectic intermetallic can be detected independently of the eutectic α-Mg during the FIB sectioning. This is so partly because the Mg–Al eutectic is divorced, hence the intermetallic phase is quite sizable, and partly due to Zn being incorporated into the $Al_{12}Mg_{17}$ intermetallic, thus enhancing the phase contrast with the surrounding Mg–Al solid solution [3]. For the present alloy, TEM examination [1] showed that the eutectic α-Mg assumes a very fine fibrous form enclosed by the $Mg_{12}Ce$ phase. This peculiar configuration makes the identification of the intermetallic virtually impossible in the SEM at the magnifications used in the FIB sectioning and reconstruction. The 3D image in the Mg–Ce alloy thus represents the percolating eutectic instead of just the intermetallic as in the AZ91D alloy. In more practical terms: whereas in the AZ91D alloy the reinforcement effects can be traced down to the percolating intermetallic phase, in the Mg–Ce the reinforcement effects can only be ascribed to the percolating (α-Mg)–$Mg_{12}Ce$ eutectic composite.

2. Data for analysis

2.1. Tensile data, flash-anneal

Tensile testing data for the 0.51 at% Ce and the 0.09 at% Ce as-cast specimens were sourced from Chia et al.'s earlier[4] work [1]. Several as-cast cylindrical tensile specimens of the original 0.51 at% Ce alloy batch were (flash-) annealed at 520 °C for 1 h and water quenched, and subsequently tensile tested following the procedure described in the original work. SEM backscattered electron (BSE) micrographs of the microstructure in the skin region and the tensile stress–strain flow curves of the flash-annealed specimens were compared with those of the as-cast ones.

3. 3D microstructural characterization

Dual beam focused ion beam (FIB) tomography was used to characterize the 3D microstructural features of a rectangular cross section, cast-to-shape tensile specimen of the Mg–0.51 at% Ce alloy of the prior study by Chia et al. [1]. A volume adjacent to a corner of the cross section, chosen to represent the finest microstructure of the casting's skin was serially sectioned into 0.2 μm thick slices on an FIB machine. The images were subsequently aligned, followed by sequential segmentation and reconstruction, to create an image of the 3D microstructure of the eutectic (α-Mg)–$Mg_{12}Ce$. Table 1 lists the relevant parameters of the FIB tomography. Further details of the overall procedure can be found in [3].

Table 1
Parameters of the FIB tomography.

FIB tomography			Sectioned slices		
Source	Voltage	Current	Resolution	Slice thickness	No. of slices
Ga^+ ions	30 kV	1.0 nA	1024 × 884	0.2 μm	100

3.1. Elastic constants of the $Mg_{12}Ce$ intermetallic

The calculations are described in Appendix A.

3.2. Damage by cracking

Brittle fracture of the eutectic $Mg_{12}Ce$ phase was assumed to occur at a tensile strain of 0.7%. This strain value was adopted based on existing experimental results [10,11] concerning stress accumulation in dispersion hardened alloys and the tensile fracture of directionally solidified eutectics, as per the arguments detailed below.

Bauschinger effect experiments in dispersion hardened cast alloys [12] indicate that the stresses in the dispersed particles increase linearly with the applied plastic strain up to a strain of ~0.7%. Past that point, loading of the embedded particles increases at the much reduced rate of forest hardening due to the activation of extensive recovery by cross slip and secondary slip at the head of dislocation pile-ups against the particles. For the eutectic of the present alloy, matrix plastic relaxation was assumed to start at 0.7% (local) strain. This assumption implies a very low yield strength for basal slip and ignores any micro plasticity effects prior to full plastic relaxation. By setting the intermetallics' cracking strain also at 0.7% strain, the model naturally made evident the combined effect of matrix stress relaxation and damage by cracking of the most stressed eutectic micro-trusses. The value adopted for the cracking strain is consistent with experiments showing that unidirectionally solidified in-situ eutectic composites fail in tension at a strain of about 1% [10,11]. A 1% strain bound was applied also to the maximum average strain in the present simulations.

3.3. Finite element modelling

Meshing of the *3De* was done using 4-node tetrahedral elements (C3D4) through the built-in tools of the commercial Amira 5.3™ package software [13]. The software package ABAQUS 6.10™ was subsequently used to assess the deformation behaviour.

4. Results

4.1. 3D microstructural features

Fig. 1a shows the FIB-sectioned reconstructed volume. The lighter (green) and darker (blue) areas represent, respectively, the α-Mg and the eutectic (α-Mg)–$Mg_{12}Ce$. The eutectic, shown in

[4] In Chia et al.'s work the present alloys were labelled using the mass% concentration as 2.87Ce and 0.53Ce, respectively.