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The role of crystallography and thermodynamics on phase selection in binary magnesium–rare earth (Ce or Nd) alloys

M.A. Easton [a,b,*], M.A. Gibson [a,c], D. Qiu [a,d], S.M. Zhu [a,b], J. Gröbner [e], R. Schmid-Fetzer [e], J.F. Nie [a,b], M.-X. Zhang [a,d]

[a] CAST Co-operative Research Centre, University of Queensland, St. Lucia, Brisbane QLD 4072, Australia
[b] Department of Materials Engineering, Monash University, Clayton, Australia
[c] Division of Process Science and Engineering, CSIRO, Clayton, Australia
[d] Division of Materials, School of Mechanical and Mining Engineering, University of Queensland, St. Lucia, Brisbane QLD 4072, Australia
[e] Clausthal University of Technology, Institute of Metallurgy, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany

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Abstract

In-depth understanding of secondary-phase selection during solidification and ageing is a crucial factor underpinning microstructure design and alloy development. Experimental observations show significantly different behavior of secondary phase selection between the Mg–Nd and Mg–Ce systems. Mg–Nd alloys show a significant degree of metastability of secondary phase selection during solidification, with $NdMg_{12}$ forming upon slow cooling and $NdMg_3$ upon fast cooling. However, at high heat treatment temperatures and long enough times, Nd_5Mg_{41} forms. In contrast, Mg–Ce alloys form $CeMg_{12}$ under a wide variety of casting conditions, and this phase remains stable even after long annealing times at high temperatures. However, both Mg–Ce and Mg–Nd alloys undergo a similar precipitation sequence during ageing. Based on recently developed thermodynamic data and crystallographic matching calculations, the phase selection in these two alloy systems under different processing regimes is well explained by the competition between the driving force (reduction in bulk Gibbs energy) and the nucleation energy barrier (increment of surface energy). The approach used here can be also applied to similar phase selection problems in other alloy systems.

Keywords: Magnesium alloys; Rare-earth; Phase transformations; Eutectic solidification

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1. Introduction

Magnesium–rare earth (RE) systems appear to be the best candidates for highly creep resistant and castable high pressure die cast (HPDC) Mg-based alloys [1,2]. In order to be able to produce alloys that are not prohibitively expensive, it is desirable that the RE elements used for alloying are those most common in misch-metal, i.e. Ce, La and Nd. Recent research indicates that each of these RE elements has its own specific characteristic effects on the properties of Mg–RE alloys. Of great importance to high temperature applications, creep resistance is found to be significantly higher in Nd-containing alloys than those rich in either Ce or La [3–5]. To further optimize these alloys, thermodynamic characterization of the Mg–Ce–Nd system has recently been undertaken [6].

One of the interesting things about Mg–RE systems is that the Mg–Nd alloys have what appear to be complex phase relationships, while Mg–Ce alloys do not. The stable intermetallic phase in hypoeutectic Mg–Nd alloys is Nd_5Mg_{41} [7,8], but this is only ever observed after alloys have been cooled particularly slowly or heat treated for a long time. Casting alloys tend to contain $NdMg_{12}$ [7,9] at relatively slow cooling rates [10] or $NdMg_3$ if the cooling rate is particularly rapid, as in high-pressure die casting

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* Corresponding author at: Department of Materials Engineering, Monash University, Clayton, Australia. Tel.: +61 3 9905 3895; fax: +61 3 9905 4940.
E-mail address: mark.easton@monash.edu (M.A. Easton).

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[11] or in gravity casting with a large steel die [12]. However, it has also been reported that $NdMg_3$ was found in a sand-cast Mg–2.7Nd–1.2Gd alloy [13]. In contrast, in the Mg–Ce system or Ce-rich alloys, $CeMg_{12}$ is always formed irrespective of the solidification rate, and appears to be stable after long-term heat treatments [10]. Since $REMg_{12}$ and $REMg_3$ appear to affect the properties of the alloys in slightly different ways [11,14], understanding their formation is important for property optimization.

Mg–Nd alloys show a greater propensity to age hardening than Mg–Ce alloys because of a greater maximum solid solubility and, consequently, a larger supersaturation of solute can be obtained during either solidification or solution heat treatment which can then be exploited at typical ageing temperatures [4,10]. In contrast to the very different phase selection of Ce-rich and Nd-rich Mg-based alloys during solidification, they have a very similar response during ageing, i.e. Guinier–Preston (GP) zones forming first, followed by β'', β' and then the stable β-phase [15–18]. It has been shown that $REMg_3$ forms as a coherent or semi-coherent metastable phase (β'' and β') before the "more" stable $REMg_{12}$. Similar precipitation sequences have been found in Mg–Y–Gd and Mg–Y–Nd alloys, although it was noted that the habit plane of the early stage precipitates affects the later phase selection [19,20].

Therefore, it is of interest to understand phase selection in Mg–RE alloy systems. To facilitate this, two factors need to be considered: thermodynamic stability and surface energy of the phases. The classical theory of phase transformations suggests that the free energy change ΔG for a phase transformation can be summarized by Porter et al. [21]

$$\Delta G = -V\Delta G_v + A\gamma(+V\Delta G_s) \tag{1}$$

ΔG consists of three terms, the first of which is related to the volume V of the new phase that is formed, which causes a free energy reduction ΔG_v. This is counteracted by the free energy required to create a surface area A of new phase with a particular surface energy, γ. For solid–solid phase transformations, a third term is added related to the volume misfit strain energy ΔG_s between the matrix and the new phase. In both solidification reactions and solid–solid phase transformations, nucleation usually occurs on heterogeneous sites and consequently surface energy and thermodynamic driving forces are key for both types of phase transformation [22,23]. Such heterogeneous nucleation sites can include inoculant particles [24] or the mold wall [25] during solidification, or crystal defects such as grain boundaries, dislocations, solute clusters or vacancies in a solid-state transformation [21]. By manipulation of the driving force, through temperature or cooling rate, and the potency of heterogeneous sites, phase selection has been shown to vary considerably, including the formation of metastable phases during both solidification [26,27] and ageing [18]. As noted by Biloni and Boettinger [28], metastable phases can often have favorable nucleation characteristics compared with stable phases, and consequently form preferentially at high undercooling during solidification. Examples can be found in cast irons [29] and other systems [30,31].

It has long been recognized that one of the key factors affecting the surface energy, and consequently phase transitions, is the lattice matching between the phases in both solidification [32–34] and solid-state reactions [21,35]. The edge-to-edge matching (E2EM) approach [36–39] is a recent breakthrough that enables matching planes and directions to be identified, along with a measure of interatomic and interplanar misfit. In the past decade, the E2EM model has been successfully applied to understanding and predicting the crystallographic features between adjacent crystalline phases, including precipitate/matrix [40], grain refiner/matrix [41] and epitaxial layer/substrate [42]. This approach has been very powerful in explaining solid–solid, such as martensitic, transformations and in identifying new grain refiners for solidification reactions. This paper uses the results from a recent CALPHAD study of phase relationships in the Mg–Ce–Nd system [6] and results from the E2EM model to explain phase selection in binary Mg–Ce and Mg–Nd systems.

2. Experimental observations of phases and phase relationships

2.1. Intermetallic phases formed as eutectic during solidification

Binary Mg–4.76 wt.% Ce and Mg–8.05 wt.% Nd alloys used in this study were produced by HPDC, which is described in detail elsewhere [11]. In addition, a sample of each melt used for HPDC was taken and poured into a steel permanent mold to cast a disk 10 cm in diameter and 2 cm thick. To investigate whether or not the intermetallic phases are metastable, some samples were annealed at 500 °C for 96 h. Phase identification was conducted by transmission electron microscopy (TEM) in a Philips CM20 instrument equipped with an Oxford INCA energy dispersive X-ray spectrometer. The TEM foils were prepared by low-angle ion milling using a Gatan precision ion polishing system.

TEM bright-field images and micro-beam diffraction patterns of the intermetallic phase in HPDC Mg–4.76 wt.% Ce alloy [11] are shown in Fig. 1. In the as-cast condition, the eutectic consisted of rod-like α-Mg within the intermetallic phase. From the indexing of electron diffraction patterns, the intermetallic phase was identified to be $CeMg_{12}$. The 500 °C annealing led to aggregation and coarsening of the intermetallic phase, but did not change its crystal structure, suggesting that $CeMg_{12}$ is the equilibrium phase in the Mg–Ce system at temperatures at least up to 500 °C, which fits with previous observations of this system.

Identification of the intermetallic phase in HPDC Mg–8.05 wt.% Nd alloy [4] is contained in Fig. 2. The intermetallic phase was observed to have a partially divorced mor-