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Segregation of Ca at the Mg/MgO interface and its effect on grain refinement of Mg alloys

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Abstract. It has been reported that native MgO particles in Mg alloy melts can act as heterogeneous nucleation substrates such that grain refinement of Mg alloys is achieved. A recent study showed the addition of Ca, combined with the native MgO particles, significantly improves grain refinement of Mg and its alloys. However, the mechanism underlying the grain refining phenomenon is not well understood due to the lack of direct experimental evidence. In this work, we investigated the segregation of Ca atoms at the Mg/MgO interface and its effect on grain refinement in Mg-0.5Ca alloys by utilizing advanced analytical electron microscopy. The experimental results focus on the chemical and structural information at the interface between MgO and the Ca solute. Adsorption layers rich in Al, N and Ca have been detected on $\{1\ 1\ 1\}$ facets of MgO particles, with the lattice structure resembling the structure of MgO. It is suggested that the significant grain refinement improvement can be attributed not only to the growth restriction due to the presence of Ca addition but also to the specific chemistry and structure of the adsorption layers.

1. Introduction

As the lightest structural metal, magnesium and its alloys have found a wide variety of applications in the industry due to their high specific strength and excellent castability [1,2]. The grain refinement of Mg alloys has received much attention over the past few decades since fine grain size is one of the factors improving the alloys' mechanical properties [3,4]. To achieve grain refinement, chemical and physical methods have been extensively studied from both experimental and simulation perspectives [5-7]. More than the improvement of mechanical properties, the addition of solute elements such as Al, Zr, Si and Ca is also a common and simple way to achieve grain refinement [8-10]. Among them, Ca produces a strong grain refining effect in pure magnesium [9], whose mechanism has been interpreted by the interdependence theory where Ca has the second highest growth restriction factor (Q) [10]. In Al-bearing Mg alloys, the intermetallic compound Al_2Ca was believed to act as a potent substrate for Mg nucleation, supported by the strong geometric misfit calculated in the edge-to-edge matching model [11].

Recently, Fan et al [12] reported the successful application of the native MgO particles found in Mg alloys as a grain refiner, with an extremely high number density of the oxide particles [13] well dispersed by the high shear melt conditioning (HSMC) device. This was corroborated by the experimental



observation of well-defined orientation relationships (OR) between the MgO particles and the Mg grain in both CP Mg and AZ91D alloys [12,14].

It is expected that the further addition of various alloying elements in Mg alloys would interact with the native MgO particles, as the local segregation of solutes has been shown to affect many properties such as wetting, catalysis, electronic structure, embrittlement of grain boundaries etc... Previous work on the manipulation of substrates by adsorption on the exposed surfaces showed that the structural or chemical variance brings about changes of nucleating potency [15-21]. Both the atomic structure and chemistry on the exposed surface play a key role in determining the nucleation potency. However, the interaction between MgO and alloying elements has been rarely studied; for example, Lee [8] found that the combined addition of MgO and strontium (Sr) in Mg-1Al alloys was more effective than the sole MgO or Sr addition. It was also demonstrated by Peng *et al* [22] that there was a significant decrease in the grain size following the marginal addition of Ca (0.01%). The authors suggested that a Mg₂Ca compound formed on the surface enhances the potency of MgO. However, the enhanced potency was not confirmed by atomic-level experimental results, *i.e.* the chemical and structural information at the interface between MgO/Mg.

So far, research on the interaction of MgO with different elements is still at an early stage. Few experiments and theoretical studies have been undertaken. In this study, the Mg-0.5Ca alloys were taken as an example to investigate the effect of the addition of Ca on the grain refining performance of MgO. Advanced electron microscopy is utilized to determine both the structure and chemistry of the Mg/MgO interface at atomic resolution, providing evidence to understand the mechanisms underlying the heterogeneous nucleation and grain refinement.

2. Experiments

Commercial purity magnesium (Mg-0.04Al-0.02Mn-0.013Si) (all compositions are in wt.% unless specified otherwise) and pure calcium (99.9%) were used in this work. Grain-refining tests were followed by a standard TP-1 test [23] proving a consistent cooling rate of 3.5K/s. Pure Mg was melted at 680°C and protected by N₂ plus 0.5 vol pct SF₆; the addition of 0.5% Ca was followed by holding for 20mins. The melt was cast into a TP1 mould pre-heated to 350 °C. For alloys treated by high shearing, the high shear device was applied at a rotation speed of 4000 rpm for 10mins before casting. Specimens for grain size measurements were quantified by the mean linear intercept technique. The samples treated by HSMC are suffixed with ‘-HS’.

All the MgO particles for characterization were collected by a pressurized melt filtration technique [12]. The melt was first transferred to the pre-heated filtration unit isolated from air, and argon gas was then to force the liquid metal flowing through a filter at the bottom. The remaining melt in the crucible solidified steadily afterwards and left the concentrated oxides above the filter.

The morphology and chemistry of MgO particles were analyzed by scanning electron microscopy (SEM) using Carl Zeiss Crossbeam 340 and Super 35V microscopes, equipped with energy dispersive x-ray spectrometers (EDS). Conventional selected area diffraction (SAD) and high-resolution transmission electron microscopy (HRTEM) were conducted on a JEOL 2100F instrument operated at an accelerating voltage of 200 kV. For advanced characterization, scanning transmission electron microscopy (STEM) was carried out in a Nion UltraSTEM100 (operated at 100 kV) equipped with a Gatan Enfina electron energy loss (EEL) spectrometer. All high angle annular dark field (HAADF) images were collected under image detector semiangles of 89-195 mrad. All elemental peaks were identified following the reference [24]; chemical maps were produced by integration over a suitable window of the recorded intensity above the characteristic edge threshold for each element, after noise reduction by Principal Component Analysis (PCA) [25] and subtraction of the decaying background using a conventional power law model.

3. Results and discussion

3.1. Enhanced grain refinement by high shear melt conditioning and additions of Ca

Figure 1 shows the as-cast microstructures of CP-Mg and Mg-0.5Ca alloys, demonstrating the effect of Ca addition and HS treatment. As we can see, CP-Mg has a columnar grain structure with an average grain size of $816.4 \pm 95.9 \mu\text{m}$ (figure 1a). Moreover, either the addition of 0.5% Ca or the application of HS leads to the columnar-to-equiaxed transition (CET) and reduces the grain size to $296.6 \pm 34.1 \mu\text{m}$ in Mg-0.5Ca (figure 1b) and $235 \pm 18.1 \mu\text{m}$ in CP-Mg-HS (figure 1c), respectively. Furthermore, significant grain refinement was achieved by the joint effect of Ca addition and HS application, as the grain size of Mg-0.5Ca-HS is further decreased to $103.6 \pm 7.1 \mu\text{m}$ (figure 1d).

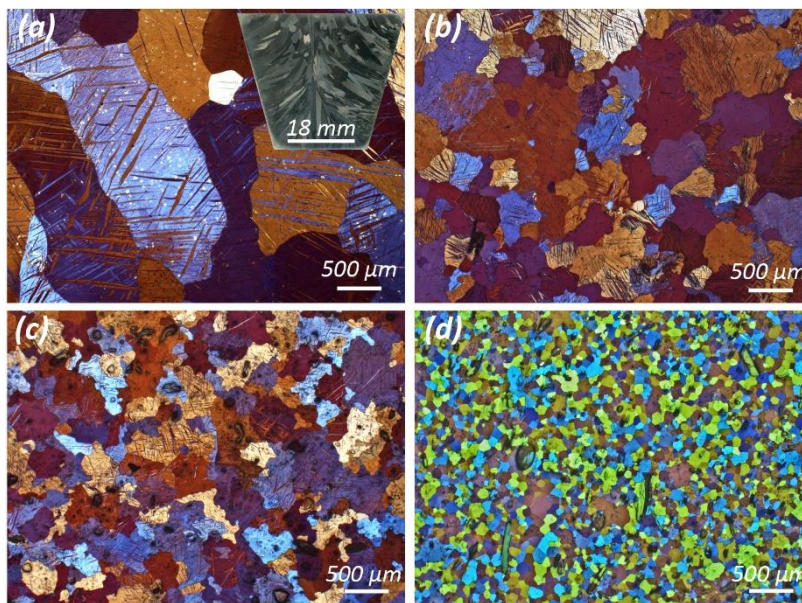


Figure. 1 Optical micrographs showing the microstructures of Mg-xCa alloys solidified in TP-1 condition. (a) CP-Mg; (b) Mg-0.5Ca; (c) CP-Mg-HS and (d) Mg-0.5Ca-HS.

3.2. Native MgO particles as endogenous grain refiners

The positive effect of HS on grain refinement had been investigated by Fan *et al.* [12] who proposed that the enhanced grain refinement comes from the dispersion of native MgO particles in CP-Mg and AZ91D [12,14]. As presented in figure 2a, MgO particles are indeed present with an irregular morphology, with some distinct facets being observed in particular particles (as circled). A previous study [14] had suggested that all such particles would have octahedral shapes bounded by $\{111\}$ facets. Here, their observed morphology was only negligibly affected by the addition of 0.5Ca, as

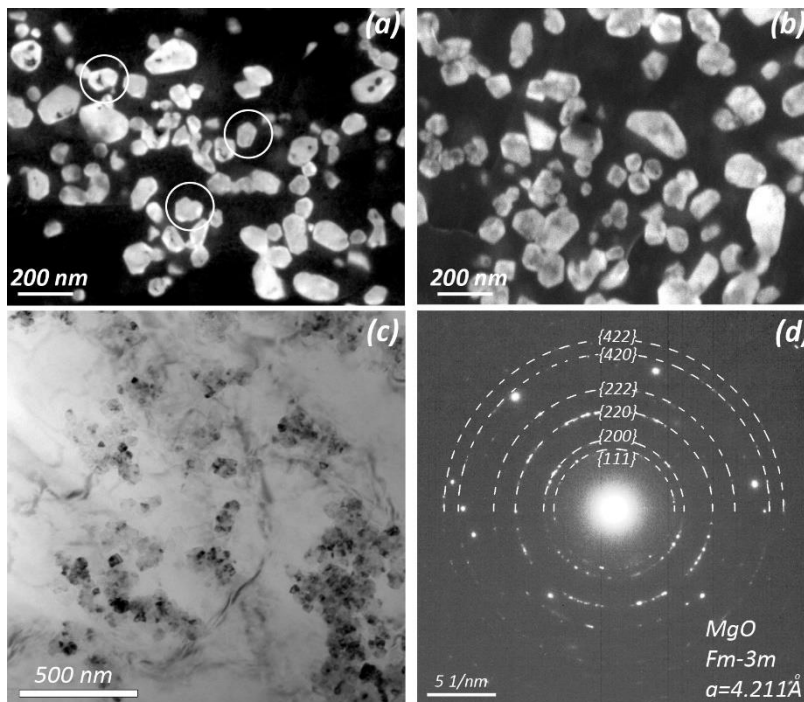


Figure. 2 (a, b) SEM images showing the native MgO particles in CP Mg and Mg-0.5Ca, respectively; (c) TEM bright field image of MgO particles involved in part of a large MgO film; (d) the related SAD pattern taken from the area covering the major part of (c).

consisting of discrete particles in Mg-0.5Ca alloy. The corresponding SAD pattern acquired on the oxide film (figure 2d) has the feature of diffraction rings which can be indexed as MgO (F m-3m, $a=4.211\text{\AA}$ [26]). It indicates that the oxide film is composed of discrete MgO particles in random orientations.

Further characterization on over a hundred of particles in this study never detected the presence of any possible CaO particles or other oxides. It is thus believed that the MgO particles are the only oxide type in the melt of Mg and Mg-0.5Ca. Moreover, considering the casting condition of both alloys in this work, MgO is expected to be the predominant inclusions outweighing other particles like nitrides or fluorides [27] due to the high affinity of Mg with oxygen. So it is reasonable to suggest that the inoculant in both melts should be native MgO particles during solidification, at least as the dominant species.

3.3. Nature of the adsorption layer

Recent studies have demonstrated that the alloying element can affect nucleation *via* the adsorption onto the surface of nucleation particle [16, 28]. It is therefore essential to investigate the possible interaction between Ca and MgO. This was examined by chemically sensitive HAADF imaging and EELS spectroscopy performed using a Cs-corrected Nion UltraSTEM100. The HAADF image (figure 3a) shows an adsorption layer with a thickness of around 1 nm being observed at the Mg/MgO interface, which appears in a relatively lower contrast compared with MgO. The EELS spectra acquired from different positions (figures 3b&c, averaged over the regions indicated by coloured boxes) suggest the composition of the adsorption layer differs from MgO and Mg matrix: it contains Ca, N and Al, and seems mostly devoid of O since the strengths of O K EELS edge from the interface and Mg matrix are nearly the same (figure 3b), likely only arising from the native oxide at the surface of the thin TEM sample.

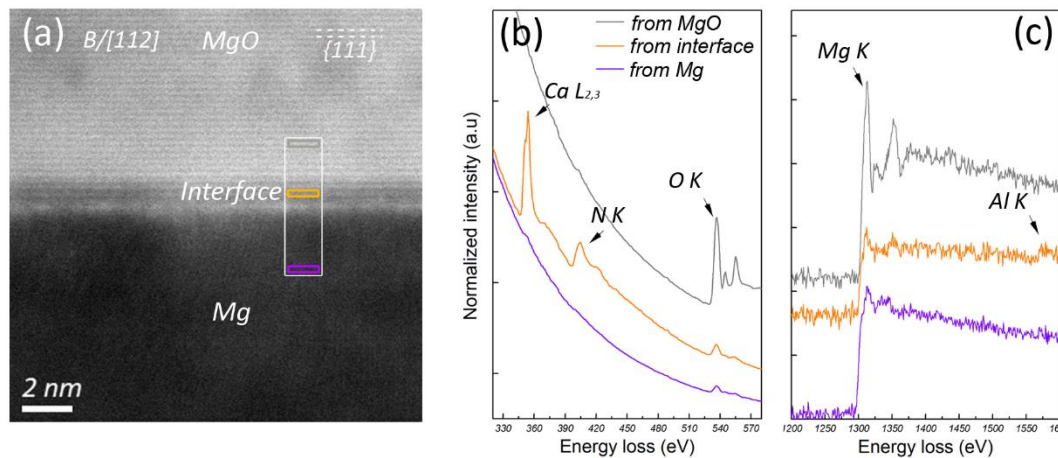


Figure. 3 (a) STEM-HAADF image presenting an adsorption layer at the interface; (b, c) the spectra extracted from different areas in (a). Note that background subtraction had been applied for the spectra in (c).

It has been shown in previous studies that crystallographic misfit plays an important role in determining the grain refining potency of a particle [29-32], which makes it important to determine the precise lattice structure of the adsorption layer at the interface. As shown in figure 4a, the faceted MgO particle shows the adsorption layers on both $\{1\ 1\ 1\}$ facets. HRTEM images corresponding to both facets reveal that the adsorption layer has the same structure as the adjacent MgO (figures 4b and 4c). Therefore, the lattice misfit between MgO with adsorption layers and Mg remains, the same as that between normal MgO and Mg (8.19% [14]). This suggests that the nucleation potency should also remain unchanged from the crystallography point of view.

According to the adsorption and the epitaxial model [18,29], it is possible for the segregated atoms to form an ordered solid phase on the substrate surface with mono- or multi- layers (less than critical thickness) which resemble the structure of the substrate even at a temperature above the alloy liquidus.

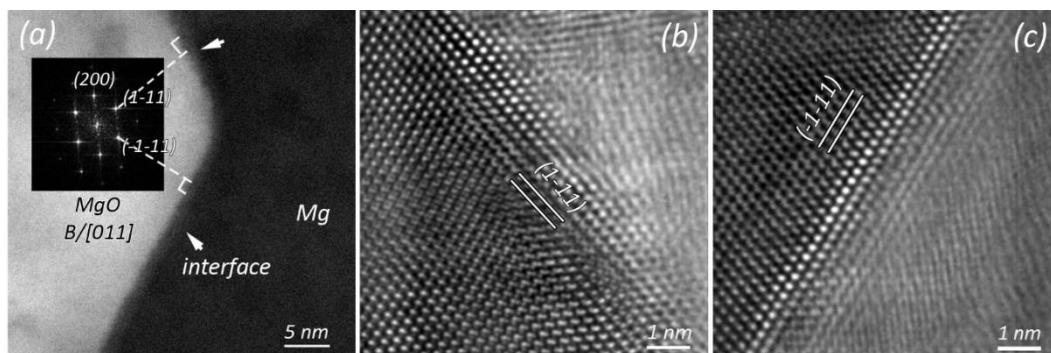


Figure. 4 (a) ADF image of a $\{1\ 1\ 1\}$ faceted MgO (inset: the related FFT pattern) with adsorbed layers; (b, c) the corresponding HRTEM images taken from the facets in (a).

3.4. The enhanced grain refinement under the combined effect of Ca addition and HS application

As shown in figure 1, without application of HS, the addition of 0.5 Ca provides growth restriction and the constitutional undercooling at the solidification front, promoting MgO particles to nucleate and then decreases the grain size (figure 1b). Coupled with the dispersion of native MgO particles by HS, more particles could be activated for grain initiation and hence more significant grain refinement as shown in figure 1d. Comparing figures 1c and 1d shows that the presence of Ca in the Mg melt is important to provide sufficient constitutional undercooling to promote heterogeneous nucleation by activating more MgO particles, which have been well dispersed by HS. However, the previous study by Peng *et al.* [22] has demonstrated that further addition of Ca in Mg melt from 0.5 to 1% produces marginal further grain

refinement effect only. This implies that, besides providing growth restriction and constitutional undercooling affecting the growth process of solidification, the presence of Ca in the Mg melt may also have effects on the solidification process.

From the experimental results presented in Section 3.3, it is revealed that the interaction between Ca and MgO results in the formation of isostructural adsorption layers on the surface of MgO particles. The atomically thin layer seems to have a relatively small effect on the grain initiation process based on the free growth model [33]. This model suggests that the grain initiation is a deterministic process and the undercooling for free growth is inversely proportional to the particle size. In the current study, the size of the MgO particles, including the adsorption layer (itself only around 1nm in thickness), did not vary significantly: the undercooling for free growth should thus be constant.

Nevertheless, it is now well recognized that the adsorption layers will affect the nucleation potency of substrate particles, as reported by Fan *et al* and Wang *et al* [16,28]. Although elucidating the precise mechanism at play in the current work requires further effort, a few hypotheses can be proposed. One possibility is that the potency of MgO for heterogeneous nucleation is changed due to the change of surface roughness [34], which might be induced by the presence of different elements in the adsorption layers. Wang *et al.* [28] showed that a mono-layer of Ti₂Zr forms on the surface of TiB₂, which induces surface roughness and then impedes the heterogeneous nucleation of Al [28, 34]. However, it is still unclear whether or not the surface roughness of the MgO increases or decreases with adsorption based on current results. Another possibility is that the surface energy of MgO particles could be decreased by the solute segregation in the form of adsorption layers. This decrease of surface energy could cause further dispersion of MgO particles during HS application, which may further increase the number density of MgO particles available for nucleation, leading to significant grain refinement.

In summary, it is proposed that the enhanced grain refinement produced by the combined effect of Ca addition and HS application can be attributed not only to the growth restriction generated by Ca partitioning but also to the formation of an adsorption layer on the surface of MgO particles.

4. Conclusions

1. Combining the application of HS and Ca addition can produce significant grain refinement in commercial pure Mg alloys.
2. Ca atoms tend to segregate at the Mg/MgO interface. The interaction between Ca and MgO results in the formation of distinct adsorption layers at the interface with a thickness of around 1nm, containing Ca, N and Al. The crystal structure of the adsorption layer resembles the lattice structure of the MgO particle.
3. It is suggested that the considerable grain refinement induced by HS application and Ca addition is the result from not only the growth restriction but also from the formation of the adsorption layers caused by the interaction between Ca and MgO particles.

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