A Novel Mg–CaMgSn Master Alloy for Grain Refinement in Mg–Al-Based Alloys

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Abstract: A novel grain refinement method using a CaMgSn intermetallic phase was investigated via adding a Mg–CaMgSn master alloy to an AZ31 magnesium alloy. The results showed a remarkable grain refinement effect in as-cast AZ31, with the average grain size reduced from approximately 260–93 µm after adding 0.45 wt.% CaMgSn particles. The added CaMgSn phase was found in grain interiors and acted as heterogeneous nucleation sites during solidification. The edge-to-edge matching model confirmed a low mismatch value of 2.3% for the \{0002\}_Mg/\{211\}_CaMgSn close-packed plane, suggesting that \{211\}_CaMgSn was the possible matching plane for Mg nucleation. The microhardness and compressive yield strength were also improved by adding CaMgSn particles, confirming that adding Mg–CaMgSn master alloy was an effective method for refining the microstructure and improving the mechanical properties of Mg–Al-based alloys.

Keywords: casting; grain refinement; magnesium alloys; solidification

1. Introduction

Mg–Al-based alloys are the most commonly used commercial alloys for many industrial applications. The use of Mg–Al-based alloys for structural parts is receiving ever-increasing attention from automotive, aerospace, and power tools industries because of their attractive combination of low-density and high specific strength properties [1–3]. Thus far, Mg–Al alloys have been applied as instrument panels, seat frames, intake manifolds, shift towers, etc. [3]. However, compared with aluminum alloys and steel, the most common commercial Mg–Al-based alloys are still associated with low ductility and relatively lower strength, which limits further application. Grain refinement is a well-known method for improving mechanical properties and other qualities such as wear resistance [4–6] and corrosion resistance [7–10].

Inoculation has been considered an efficient and reliable technique to refine grain size in Mg alloys due to the fact of its low cost and high efficiency. So far, Zr has been used as an effective grain refiner in Al-free Mg alloys, since the addition of Zr to Mg–Al-based alloys would result in the formation of an Al3Zr phase, invalidating the Zr grain refinement based on the Mg–Zr peritectic reaction. Extensive work has been conducted to develop effective grain refiners for an Mg–Al system, and some grain refiners have been discovered such as SiC [11,12], AlN [13], C2Cl6 [14], Al4C3 [15,16], ZnO [17], Al3Ca [18,19], and Al2Y [20]. However, the application of these grain refiners is still limited due to the fact of various issues. For instance, the addition of SiC particles is limited by their effect on other properties such as ductility and corrosion resistance [11]. The grain refining
efficiency of AlN can only be achieved at high casting temperatures above 760 °C [13]. For ZnO, it can quickly fade in molten Mg alloys due to the fact of its instability, which reduces its refining efficiency [16]. For grain refiners with chlorine, such as C2Cl6, carbon powder, the preparation process is not always environmentally friendly [14]. Therefore, it is imperative to develop efficient and eco-friendly grain refiners for Mg–Al-based alloys. Compared with adding ceramic particles, Mg-based intermetallics with good grain refining efficiency are more desirable, as they tend to have better wettability with a Mg matrix during solidification.

It has been reported that additions of Ca to a Mg–Sn system can lead to grain refinement, which was attributed to the large constitutional undercooling of Ca in Mg alloys, as the growth restriction factor (Q-value) of Ca in Mg alloys is as high as 11.94 [21–24]. The addition of Ca in a Mg–Sn system results in the formation of the proeutectic CaMgSn phase in molten magnesium [25,26]. The CaMgSn intermetallic phase is with high thermal stability, and it is speculated that the CaMgSn phase may act as heterogeneous nucleation sites for Mg solidification [27]. Meanwhile, it is also reported that the addition of 1.0 wt.% tin to a Mg–3.8Zn–2.2Ca alloy not only results in the formation of a CaMgSn phase but also effectively refines the grains [28]. Compared with Ca, the Q-value of Sn is much smaller, just 1.47, which means the constitutional undercooling by Sn is limited. However, the role of the CaMgSn phase in grain refinement of Mg alloys is still not clear.

In this paper, a Mg–Ca–Sn master alloy containing CaMgSn phase particles was developed. This novel Mg–Ca–Sn master alloy was added into AZ31 Mg alloy as an effective grain refiner in Al-containing Mg alloys. The objective of this work was to investigate the effect of CaMgSn particles as an inoculant for microstructural refinement in Mg–Al-based alloys.

2. Materials and Methods

A Mg–3 wt.% CaMgSn master alloy was prepared in a mild steel crucible using a homemade resistance furnace at approximately 720 °C using Mg-20 wt.% Ca master alloy, pure Mg, and pure Sn with commercial purity. The chemical composition was measured using an XRF-1800 CCD X-ray fluorescence spectrometer (Shimadzu, Kyoto, Japan) and the results are shown in Table 1. The master alloy was subsequently extruded with an XJ-500t horizontal extruder (Wuxi Yuanchang Machine Manufacture Co., Ltd., Wuxi, China) to refine the size of the CaMgSn particles and improve their distribution.

| Master Alloy Ca Sn Mg |
|---------------------|---|---|---|
| Mg–3CaMgSn          | 0.61 | 1.88 | Bal. |

For grain refinement experiments, commercial Mg–3Al–1Zn (AZ31) alloy was melted and heated up to 720 °C in a steel crucible using an electric resistance furnace under a protecting gas mixture (1%SF6 and 99%CO2). Then, three different mass fractions of the Mg–3 wt.% CaMgSn master alloy (i.e., 0.21%, 0.45%, and 0.75%) were added to molten AZ31 alloy, respectively, and the melt was held for 15 min. Next, the melt was stirred for 30 s and then poured into a cylindrical mild steel mold with a diameter of 20 mm and a height of 100 mm. The steel mold was coated with boron nitride and preheated to 200 °C. The steel mold was fully filled to ensure the same size of each casting as well as the same cooling rate. The maximum cooling rate was approximately 0.2 °C.s−1 during solidification [18].

For microstructural analysis, samples were taken from the center of the ingot. For the optical microscope, the samples were polished to 2000 grit and etched in a solution of 6 g picric acid, 2 mL acetic acid, 100 mL ethanol, 0.5 mL phosphoric acid, and 1 mL distilled water. The etched specimens were examined using an Olympus optical microscope with polarized light to obtain color metallography (Olympus Optical Co. Ltd, Tokyo, Japan).
The grain size was measured by linear intercept measurement. Phase identification in the master alloy was studied by X-ray diffraction (XRD, Rigaku D/max, Tokyo, Japan). The morphology and distribution of the CaMgSn phase was characterized using scanning electron microscopy (SEM, TESCAN VEGA, Brno-Kohoutovice, Czech Republic) with an energy-dispersive X-ray spectrometer (EDS, INCA Energy).

For Vickers hardness testing, the samples with different amounts of CaMgSn particles were measured with an applied load of 0.5 N and a dwell time of 15 s. For compressive testing, the samples were machined by wire-electrical discharge machining (EDM) with a diameter of 15 mm and a height of 15 mm. The compression test speed was set as 1 mm/min. At least three samples were tested for each composition at each condition.

3. Results and Discussion
3.1. Characterization of Mg–3CaMgSn Master Alloy

Figure 1 shows the XRD patterns of as-cast and extruded Mg–3CaMgSn master alloy samples. It can be seen that the master alloy was composed of CaMgSn and α-Mg phases in both as-cast and extruded conditions. It is widely accepted that there are three possible second phases (i.e., Mg2Ca, CaMgSn, and Mg2Sn) formed in an Mg–Sn–Ca system [25]. The species of the second phase are controlled by the mass ratio of Sn to Ca. A mass ratio of Sn to Ca larger than three leads to the formation of CaMgSn and Mg2Sn. When the mass ratio is less than three, both CaMgSn and Mg2Ca will form. In this master alloy, the mass ratio of Sn to Ca was set as three, and the Mg–CaMgSn master alloy was successfully made.

Typical microstructures of as-cast and extruded Mg–3CaMgSn master alloy samples are presented in Figure 2. For the as-cast sample in Figure 2a, the second phases were distributed along the grain boundaries, and some bright particles were found among the eutectic phases. According to the EDS result of point A, this phase was with Ca and Sn, and the atomic ratio of Sn to Ca was 0.8, close to 1, inferring it was the CaMgSn second phase. In Figure 2b, after extrusion, the CaMgSn second phases were broken into small pieces and dispersely distributed along the extrusion direction. The length of the broken particles was approximately 10–20 μm, and the thickness was approximately 2–5 μm.
The grain refinement effect of Mg–3CaMgSn master alloy was present in Figure 3. The grain size was revealed by the color metallography. For AZ31 without CaMgSn addition, the grains were irregular in shape and with an average grain size of approximately 270 μm. With 0.21 wt.% CaMgSn addition, the grain morphology was still irregular with no obvious grain refinement effect. The average grain size was approximately 260 μm. With the further addition of CaMgSn to 0.45 wt.%, a remarkable refinement was achieved. The grains become uniform with an average size of just 93 μm. When the addition was up to 0.75 wt.%, it also presented a refined microstructure; however, the average grain size slightly increased to 101 μm. The results show that CaMgSn particles can effectively refine Mg–Al alloys. However, the grain refinement of Mg–3%CaMgSn was limited at large additions (above approximately 0.75 wt.%). This may be caused by the cluster of CaMgSn particles in the liquid when the addition was above 0.75%. This cluster of inoculants will decrease the effective heterogeneous nuclei and reduce the grain refinement [19,29].
3.3. Grain Refinement Mechanism

It is evident that the addition of CaMgSn mater alloy leads to an obvious grain refinement, but it is still not clear whether this grain refinement is from the nucleation of CaMgSn particles or constitutional undercooling of Ca. In order to clarify the role of the CaMgSn phase during solidification, the as-cast AZ31-0.75% alloy was characterized by XRD as shown in Figure 4. From the XRD patten, in addition to Mg17Al12 and α-Mg, the CaMgSn phase was also detected in as-cast AZ31-0.75% alloy. Due to the small addition of CaMgSn, the peaks of CaMgSn were quite low. However, the peaks of CaMgSn were quite distinguished from that of Mg17Al12 and α-Mg, especially from 20 to 30 °C. The result indicates that the CaMgSn intermetallic particles survived in the molten Mg during casting.

![Figure 4. The XRD diffraction pattern of AZ31-0.75%CaMgSn alloy.](image)

The distribution of CaMgSn particles in the as-cast AZ31-0.75% alloy was detected in a backscattered electron (BSE) image as shown in Figure 5a. In order to reveal the grain boundary, the sample was solution treated at 400 °C for 6 h to dissolve the eutectic phase. There was a particle clearly located near the center region of the grain, likely acting as the nucleation site. The sample was carefully checked by BSE, and the found CaMgSn particles were always located inside of the grains, which confirms the distribution of the CaMgSn particles. The EDS analysis of particle A is presented in Figure 5a. According to the EDS results, particle A in the central part of the grain was enriched in Mg, Ca, and Sn. Moreover, the atomic ratio of Sn to Ca was close to 1, which is consistent with the chemical composition of CaMgSn. Combining the XRD result in Figure 4, it is reasonable to infer that this particle was the added CaMgSn from the Mg–CaMgSn master alloy. The results indicate that the CaMgSn phase was thermally stable and acted as an inoculant in molten Mg and promoted the grain refinement of the AZ31 alloy.

![Figure 5. Backscattered electron image of the AZ31-0.75% alloy (a) and the EDS analysis of the bright particle A (b).](image)
Theoretically, a crystallographic matching relationship between CaMgSn and α-\(\text{Mg}\) is needed if the CaMgSn intermetallic is to be a nucleation site. The edge-to-edge matching model proposed by Zhang et al. \([30–32]\) has been successfully used to understand the grain refinement mechanism and efficiency in both Al and Mg alloys. According to this model, a metallic compound can be the potential grain refiner for the matrix alloy when the mismatch \(f_\text{e}\) between the potential matching plane pairs and the misfit \(f_\text{t}\) between the potential matching direction pairs in the matching planes are less than 10\%. The potential matching plane pairs are normally the close packed or nearly close packed planes, and the matching direction pairs are the close packed or nearly close packed direction in the matching planes.

The close-packed or nearly close-packed planes of magnesium and CaMgSn were identified by empirical examination of the powder X-ray diffraction intensity data available from the PDF file \([33]\). For Mg, the close packed planes were identified to be \(\{0002\}\), \(\{10\overline{1}1\}\), and \(\{10\overline{1}0\}\). For CaMgSn with a primitive orthorhombic structure, they were \(\{211\}\), \(\{102\}\), and \(\{111\}\). The corresponding matching planes are listed in Table 2. It was found that there were two plane pairs of mismatched values less than 10\%: \(\{0002\}_\text{Mg}/\{211\}_\text{CaMgSn}\) and \(\{10\overline{1}0\}_\text{Mg}/\{211\}_\text{CaMgSn}\). The result suggests the \(\{211\}_\text{CaMgSn}\) of CaMgSn can be a potential matching plane of the Mg matrix.

### Table 2. The matching plane pairs between α-\(\text{Mg}\) and CaMgSn.

| Potential Matching Plane | \(f_\text{d}\)% | Potential Matching Plane | \(f_\text{d}\)% | Potential Matching Plane | \(f_\text{d}\)% |
|-------------------------|----------------|-------------------------|----------------|-------------------------|----------------|
| \(\{0002\}_\text{Mg}/\{211\}_\tau\) | 9.1 | \(\{10\overline{1}1\}_\text{Mg}/\{211\}_\tau\) | 15.9 | \(\{10\overline{1}0\}_\text{Mg}/\{211\}_\tau\) | 2.3 |
| \(\{0002\}_\text{Mg}/\{102\}_\tau\) | 46.6 | \(\{10\overline{1}1\}_\text{Mg}/\{102\}_\tau\) | 55.8 | \(\{10\overline{1}0\}_\text{Mg}/\{102\}_\tau\) | 37.5 |
| \(\{0002\}_\text{Mg}/\{111\}_\tau\) | 39.9 | \(\{10\overline{1}1\}_\text{Mg}/\{111\}_\tau\) | 48.2 | \(\{10\overline{1}0\}_\text{Mg}/\{111\}_\tau\) | 31.1 |

The atomic configurations in the \(\{211\}_\text{CaMgSn}\) are graphically plotted in Figure 6 to calculate the misfit, \(f_\text{t}\) value along the matching direction pairs. \(\{1\overline{1}1\}_\text{CaMgSn}\) and \(\{01\overline{1}\}_\text{CaMgSn}\) were contained in the close-packed plane \(\{211\}\) of CaMgSn. As a simple hexagonal close-packed (hcp) structure, magnesium has three possible close or nearly close-packed directions: \(\{1\overline{1}0\}_\text{Mg}\), \(\{10\overline{1}0\}_\text{Mg}\), and \(\{1\overline{1}1\}_\text{Mg}\). Those matching planes involve four corresponding qualified direction pairs: \(\{1\overline{1}0\}_\text{Mg}/\{1\overline{1}1\}_\text{CaMgSn}\), \(\{1\overline{1}0\}_\text{Mg}/\{1\overline{1}1\}_\text{CaMgSn}\), \(\{1\overline{1}1\}_\text{Mg}/\{1\overline{1}1\}_\text{CaMgSn}\), and \(\{1\overline{1}0\}_\text{Mg}/\{1\overline{1}1\}_\text{CaMgSn}\). Thus, the proposed initial orientation relationships \(\text{ORs}\) are given by:

![Figure 6. Atomic configurations of CaMgSn on its close-packed plane \(\{211\}_\text{CaMgSn}\).](image-url)
OR1: \([10\overline{1}0]_{\text{Mg}}/[1\overline{1}1]_{\text{CaMgSn}} : \{0002\}_{\text{Mg}}/[211]_{\text{CaMgSn}}\)

OR2: \([11\overline{2}0]_{\text{Mg}}/[1\overline{1}1]_{\text{CaMgSn}} : \{0002\}_{\text{Mg}}/[211]_{\text{CaMgSn}}\)

OR3: \([11\overline{2}0]_{\text{Mg}}/[01\overline{1}]_{\text{CaMgSn}} : \{0002\}_{\text{Mg}}/[211]_{\text{CaMgSn}}\)

The ORs between \(\{0002\}_{\text{Mg}}/[211]_{\text{CaMgSn}}\) need to be further refined by applying the \(\Delta g\) theory in order to finalize the rotation angle of the matching planes relative to each other about the matching direction [32–35]. By using the \(\Delta g\) theory, the actual OR1 that were predicted between CaMgSn and the Mg matrix in real materials and the corresponding habit planes can be obtained. They were:

\(\text{OR1: } \{0002\}_{\text{Mg}} \pm 8.49^\circ \text{ from } \{211\}_{\text{CaMgSn}}, [10\overline{1}0]_{\text{Mg}}/[1\overline{1}1]_{\text{CaMgSn}}\)

JEMS software was used for generating the theoretical electron diffraction patterns by considering the kinematic approximation. Figure 7 shows the simulated spot diffraction patterns along the \([10\overline{1}0]_{\text{Mg}}/[1\overline{1}1]_{\text{CaMgSn}}\) zone axis for OR1. The habit plane is indicated by the dashed line and a set of parallel \(\Delta g\)'s were found. Similar superimposed diffraction patterns for the OR2 and OR3 can also be constructed. From the crystallographic calculation discussed above, a potential matching relationship between CaMgSn and Mg was found, which provides theoretical support for CaMgSn as a heterogeneous nucleation site of the Mg matrix during the solidification process.

Figure 7. Simulated diffraction patterns of the Mg matrix and CaMgSn along the zone axis \([10\overline{1}0]_{\text{Mg}}/[1\overline{1}1]_{\text{CaMgSn}}\) showing a set of parallel \(\Delta g\)'s. The dashed line indicates the habit plane where the superscript “C” denotes CaMgSn and the superscript “M” denotes Mg.

### 3.4. Hardness and Mechanical Properties

The microhardness and compressive yield strength of as-cast AZ31 with different additions of CaMgSn are shown in Figure 8. The microhardness of the as-cast sample was 45 HV, and it gradually increased with the increasing addition of CaMgSn. With 0.75% CaMgSn addition, the microhardness improved to 56 HV. For the compressive yield strength (CYS), similar to the microhardness, the added CaMgSn led to an increase from 75 MPa of as-cast to 117 MPa with 0.75% addition. The increased hardness and compressive yield strength were attributed to grain refinement, according to the Hall–Petch relationship. In addition, the added CaMgSn particles themselves contributed to the increased hardness and yield strength. The grain size of AZ31-0.45% was close to that of AZ31-0.75%, while the hardness and yield strength were both improved with the further addition of CaMgSn. This further improvement of hardness and CYS has been reported in previous studies [36–38].
In addition to being a nucleation site, the added particles also impede the movement of dislocation and contribute to the hardness and strength.

![Figure 8. Microhardness (a) and compressive yield strength (b) of AZ31 with different amounts of CaMgSn addition.](image)

4. Conclusions

In this study, a novel Mg–3CaMgSn master alloy was fabricated and applied to refine the grain structure in an as-cast AZ31 Mg alloy. The role of the CaMgSn phase in the grain refinement mechanism in Mg alloys during the casting process was investigated. The related conclusions are summarized as follows:

1. The addition of Mg–3CaMgSn master alloy provided significant grain refining efficiency for AZ31. With the addition of 0.45 wt.% CaMgSn particles, the grain size was reduced from 270 to 93 µm in as-cast AZ31 alloy samples;
2. The added CaMgSn particles survived in molten Mg and acted as heterogeneous nucleation cites for α-Mg during solidification;
3. The crystallographic matching relationship between CaMgSn and α-Mg was evaluated by an edge-to-edge matching model. Based on the calculated interatomic spacing misfits along the matching planes, it was concluded that the \{211\}CaMgSn plane of CaMgSn potentially matched the \{0002\}_Mg plane of the Mg matrix for the heterogeneous nucleation cites of α-Mg.

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