**Aluminium-Rich Coring Structures in Mg-Al Alloys with Carbon Inoculation**

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**Abstract.** A homogeneous microstructure of as-cast magnesium alloys is necessary to improve the formability during their subsequent thermomechanical processing. In Al-containing magnesium alloys, the grain refinement by carbon inoculation is considered to be the best approach until now. However, the mechanism of grain refinement is unclear. The present work investigates the coring microstructure in Mg-Al alloys inoculated with carbon using FIB, SEM and TEM techniques. In each grain one or more “hillocks” exist, enriched with carbon, manganese and aluminium. This is possibly related to the inhomogeneous nucleation of alpha-magnesium. The precipitates in these “hillocks” are always surrounded by the aluminium-rich zones. These characteristics of microstructure observed in Mg-Al alloys with carbon inoculation are compared with that observed in Al-free magnesium alloys inoculated by zirconium. The similarities between them are discussed. A novel mechanism is suggested to explain the grain refinement in Mg-Al alloys inoculated by carbon.

**Introduction**

For Al-containing magnesium alloys, carbon inoculation is considered to be the most successful process to refine the casting microstructure at present [1]. Carbon inoculation can be carried out by adding materials such as graphite, wax, C\(_2\)Cl\(_6\), and SiC particles etc. While the efficiency of C inoculation is well known, the mechanism of grain refinement by carbon inoculation is still unclear. Due to the fact that carbon inoculation only functions with the existence of aluminum, the enhanced nucleation of alpha-magnesium on the surface of Al\(_4\)C\(_3\) particles was popularly treated as the reasons responsible for the grain refinement [2-4]. Unfortunately, the presence of this phase was never proven by experimental techniques. The conclusion was drawn based on the indirect experimental results and sometimes thermodynamic calculations. Besides that, other explanations were suggested for the mechanism of grain refinement by carbon inoculation. Jin et al. attributed the resultant grain refinement to the segregation of carbon that occurred during solidification [5]. This hypothesis was regarded not to be so persuasive [2], and not commonly accepted. Another speculation is the modified version of Al\(_4\)C\(_3\), which was suggested by Yano et al. [3]. They interpreted Al-C-O particles as Al\(_2\)CO, acting as the nucleants for the grain refinement by carbon inoculation.

Recently, it was reported that the grain refinement in Mg-Al alloys inoculated by carbon is associated with (Al,Mn)-containing intermetallics. Kim et al. suggested that carbon inoculation changed the morphology of these intermetallics, and thus the grains are refined because they considered these intermetallics are the effective nucleants [6]. However, the investigations performed by Han et al. indicated that the (Al,Mn)-containing intermetallics has a low efficiency as nucleants for alpha-Mg [7]. They claimed that Al\(_4\)C\(_3\) has an affinity for these intermetallics and...
form in the shape of a coating around these intermetallics. The grains are refined by the enhanced nucleation of alpha-Mg on the surface of these Al4C3-coated (Al,Mn)-containing intermetallics.

The present work investigates the microstructure of Mg-Al alloys inoculated with carbon agents using X-ray diffraction or transmission electron microscopy. A novel grain refinement mechanism is proposed i.e. the enhanced nucleation of alpha-Mg on the surface of Al2MgC2 phase, which is different from the previous Al4C3 hypothesis.

Results and Discussion

The detailed experimental procedures about the materials preparations and microstructural characterizations can be found in the previous literatures [8-9].

Figure 1. Optical micrographs, (a) Mg-3Zn, 568±423 µm and (b) Mg-3Zn-0.3SiC, 252±171 µm.

Figure 2. Identification of second phases in Mg-Al alloys with the addition of low content SiC.

Figure 3. Microstructural observations of the as-cast Mg-3Al-0.3C alloy.

Morphologies of grains. After inoculated by the carbon or SiC particles, the grain size of Mg-3Al alloy largely decreases and is distributed more homogeneously [9]. There is no much difference in the grain size between the alloys with the addition of carbon and SiC particles. The grain size decreases from 420 µm to about 140 µm after inoculation by carbon or SiC particles. As observed in Mg-Al alloys, the addition of small amounts of SiC also reduces the grain size of Mg-3Zn alloys (Figure 1). However, it should be noted that the efficiency of grain refinement by SiC is lower in Mg-Zn alloys than in Mg-Al alloys.

Results of X-ray diffractions. Figure 2 shows the XRD patterns from the Mg-Al alloys inoculated by low-content SiC particles. Like in Mg-Al alloys inoculated with 10% SiC [8-9], the phases such as Mg2Si, Mg7Al12 and Al2MgC2 are identified. Previous investigations on Mg-3Al-10SiC also show the formation of the ternary phase Al2MgC2 [8-9]. Detailed information and discussion about the phase analysis can be obtained in the previous literature [8, 10]. Different from the previous results [11], the ternary compound Al2MgC2 is identified instead of the binary compound Al4C3 in the Mg-Al alloys inoculated with SiC particles. Recent investigations by Schiff et al. also show the formation of this ternary compound Al2MgC2 in Mg-Al-SiC alloys [12].

SEM observations and EDX analysis. In Mg-Al alloys inoculated by carbon or SiC particles, there exist one or several precipitates (they look like “hillock”) inside each grain (Figure 3). The microstructures for Mg-Al containing low content of SiC have been presented elsewhere [8-9]. All EDX line-scan analyses show the similar results for the precipitates in Mg-Al alloys with the addition of carbon or SiC. These precipitates are enriched with Al, Si, C, O and sometimes Mn. Even in Mg-Al alloys inoculated with carbon, the precipitates inside the grain always have a high
content of Si. Near these precipitates, a region with the enrichment of Al was observed (Figure 4 and [9]). In Mg-3Zn alloy inoculated with 0.3SiC, the situation is different. Although sometimes precipitates were observed at the centre, they were identified as SiO$_2$ (Figure 5) or Mg-Zn intermetallics. No precipitates enriched with carbon were found.

Figure 4 EDX line-scan analysis, (a) Mg-3Al-0.3C, (b) Mg-3Al-10SiC.

Figure 5 SEM micrographs showing some second phases inside the grains of Mg-3Zn-0.3SiC alloys, (a) microstructure and (b) EDX line-scan analysis.

TEM observations. The precipitates inside the “hillock” were sectioned by the Focused Ion Beam (FIB) cutting technique and then observed by TEM. The observations on several precipitates show similar results. Figure 6 presents the typical morphology of one “hillock”. The phases inside the “hillock” include Mg$_2$Si, Mg$_{17}$Al$_{12}$ and an Al-Mn containing phase. Among them, Mg$_2$Si and Al-Mn phases are surrounded by Mg$_{17}$Al$_{12}$ phase. The Mg$_2$Si phase is located on the top of the “hillock”. Based on the XRD results (Figure 2) and EDX line-scan analysis indicating the carbon enrichment for these “hillocks” (Figure 4), the carbon-containing ternary phase Al$_2$MgC$_2$ is expected to exist inside these “hillocks”. The small particles inside the region of Mg$_{17}$Al$_{12}$ are likely to be the ternary phase Al$_2$MgC$_2$ (see arrows in Figure 6(b)).

Short comments. The most characteristic feature of the microstructure of Mg-Al alloys with a small amount of carbon or SiC addition is the presence of the distinct “hillocks” enriched in Al with the majority containing a cluster of particles. They are normally located in the central region of grains, and are similar to the Zr-rich cores in the Mg-Zr alloys reported by Qian et al. [13]. The comparison between Al-rich and Zr-rich coring structures may help to understand the grain refinement mechanism occurred in Mg-Al-(C or SiC) alloys. Both Al-rich coring structures observed in the present work and Zr-rich coring structures have a similar size scale in the range of 2 to 5 µm. They are observed not only in the center of grains but also sometimes on the grain boundaries. The Zr-rich coring structures sometimes also contain several phases such as pure Zr and Fe-containing phase [13]. Due to the similarities of Al-rich and Zr-rich coring structures, the Al-rich coring structures may also have formed through a peritectic reaction. Detailed investigations such as the thermodynamic simulation are further needed to confirm this conclusion. In Mg-Zr alloys, the Zr phase in the Zr enriched coring structure is normally in direct contact with the magnesium matrix. In contrast, in the Al-rich coring structures of Mg-Al-(C or SiC) alloys, some of the potential nucleants Al$_2$MgC$_2$ are surrounded by the Mg$_{17}$Al$_{12}$ phase. This difference may explain why the nucleation efficiency of alpha-Mg by Zr inoculation in non-aluminum magnesium alloys is much higher than by carbon inoculation in Al-containing magnesium alloys.
Figure 6 TEM observations of the phases located on the “hillock” inside the grains, (a) Mg-3Al-0.3C, the phases inside a “hillock”, and (b) smaller particles in the region of the Mg_{17}Al_{12} phase.

Conclusions

When Mg-Al alloys inoculated with carbon or SiC, their grain size largely decreases. Inside each grain one or more precipitates are observed, which have a morphology of “hillock”. These precipitates are enriched with Al, Si, C, O and sometimes Mn. Near these precipitates, a region with higher Al content exists. These “hillocks” contain several phases Mg_{2}Si, Mg_{17}Al_{12}, Al-Mn intermetallic and Al_{2}MgC_{2}. The Mg_{2}Si phase locates on the top of “hillocks”. The ternary phase Al_{2}MgC_{2}, which is the potential nucleant, is surrounded by Mg_{17}Al_{12} phase.

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References