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Phase Identification and Microanalysis in the Mg-Al-Ca Alloy System

Koray Ozturk and Zi-Kui Liu
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802, USA

Alan A. Luo
General Motors Research and Development Center
Materials and Processes Lab
30500 Mound Road, Warren, MI 48090-9055, USA

Phase identification and microanalysis were carried out on the Mg-Al-Ca system in order to construct its ternary phase diagram. Two alloys (Mg-4.5%Al-1.9%Ca and Mg-4.5%Al-3.0%Ca) were used in the present investigation. The alloy samples were sealed under an inert atmosphere and heat treated at 290 ºC and 370 ºC for one week. Crystal structure identification of the phases was made by X-ray diffraction (XRD) technique. The qualitative chemical analysis of the individual phases was performed on the bulk and replicas of the samples using energy dispersive X-ray spectroscopy (EDS) technique.

Introduction:

The addition of Ca to Mg-Al based alloys has been found to improve the high-temperature properties, such as creep resistance [1]. Although the similar effects have been observed in the case of rare earth elements addition, the use of lower-cost calcium is more desirable. Therefore, Mg-Al-Ca alloys have become promising materials for automotive powertrain applications. However, few studies have been done on the thermodynamics and phase relationships in this alloy system [1-4]. In previous studies, we investigated the solidification processes in the Mg-Al-Ca [5] and Mg-Al-Ca-Sr [6] systems. In the present work, the phase equilibria of two Mg alloys were studied experimentally and compared with the thermodynamic calculations. Thermodynamic calculations were based on the CALPHAD approach [7] and the Thermo-Calc software.

Table 1. Chemical Compositions of the Alloys (wt%).

Alloy	Chemical Composition							
	Al	Ca	Si	Sr	Mn	Fe	Ni	Cu
GM-B	4.5	1.9	-	-	0.27	0.003	<0.002	0.002
GM-C	4.5	3.0	-	-	0.27	0.003	<0.002	0.003

Experimental Procedures

Two alloys, Mg-4.5%Al-1.9%Ca (GM-B) and Mg-4.5%Al-3.0%Ca (GM-C), (all in weight percent unless otherwise specified), were supplied by General Motors R&D Center. They were made by die casting at Lexington Die Casting, Lakewood, NY. The melt temperature was controlled at around 677°C with the die surface temperature maintained at 350°C. The chemical analysis using ICP/AES (Inductively-Coupled Plasma/Atomic Emission Spectroscopy) techniques was performed, and the results are shown in Table 1.

Three types of samples were prepared for each alloy: a) as-cast, b) heat treated at 290 ºC, and c) heat treated at 370 ºC. The alloys were sealed under an inert atmosphere during the heat treatment for 1 week. At the end of the heat treatments, the samples were quenched into water to retain the equilibrium structure.

Microstructural observations were made using optical (Olympus BX60M) and scanning electron microscopes (Hitachi S-3500N and Philips XL20). Each sample was first cut from the as-cast and the quenched alloys using a regular lab scale diamond saw. The samples were then polished and etched using 4vol% Nital solution (HNO_3 in ethanol). For optical microscopy purpose, etching was performed only by applying the etchant on the surface for a short period of time (~10 s). This is because of the severe selective etching nature of these alloys. Primary Mg grains dissolve very quickly on contact with the etchant comparing with the secondary phase.

The selective etching nature of the samples was utilized during the phase identifications by XRD (Scintag PadV) and qualitative chemical analysis by EDS. The prolonged etching (~20 s) was performed by dipping the samples in the etchant to increase the surface area of the intermetallic precipitates and its intensity on x-ray spectrum.

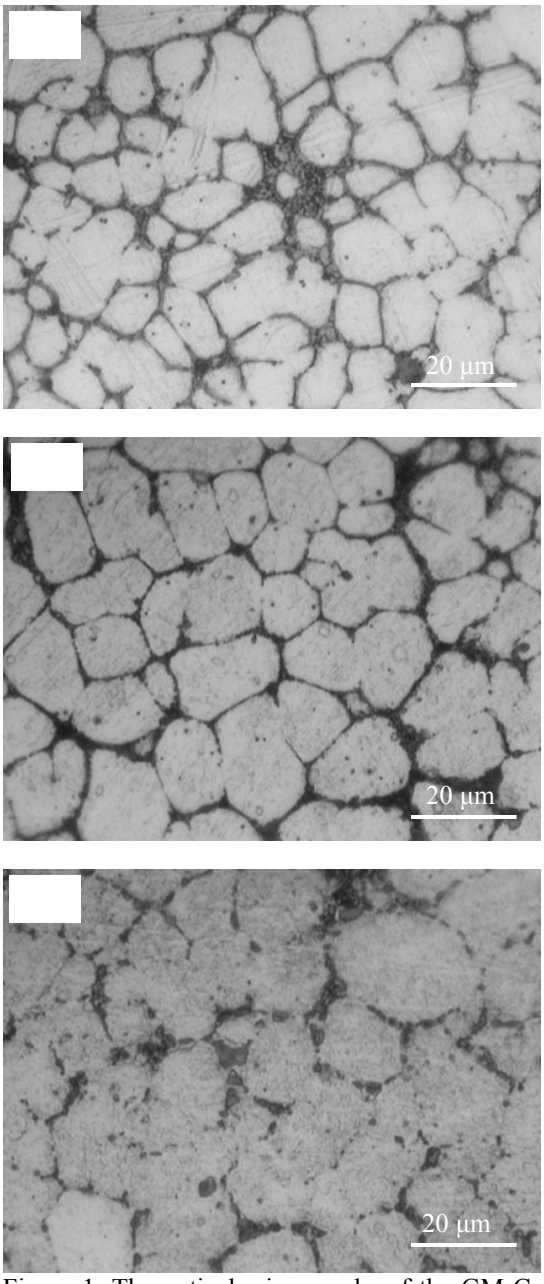

Figure 1. The optical micrographs of the GM-C sample (1725 X). (a)as-cast, (b)heat treated at 290 ºC for 1 week, and (c)heat treated at 370 ºC for 1 week.

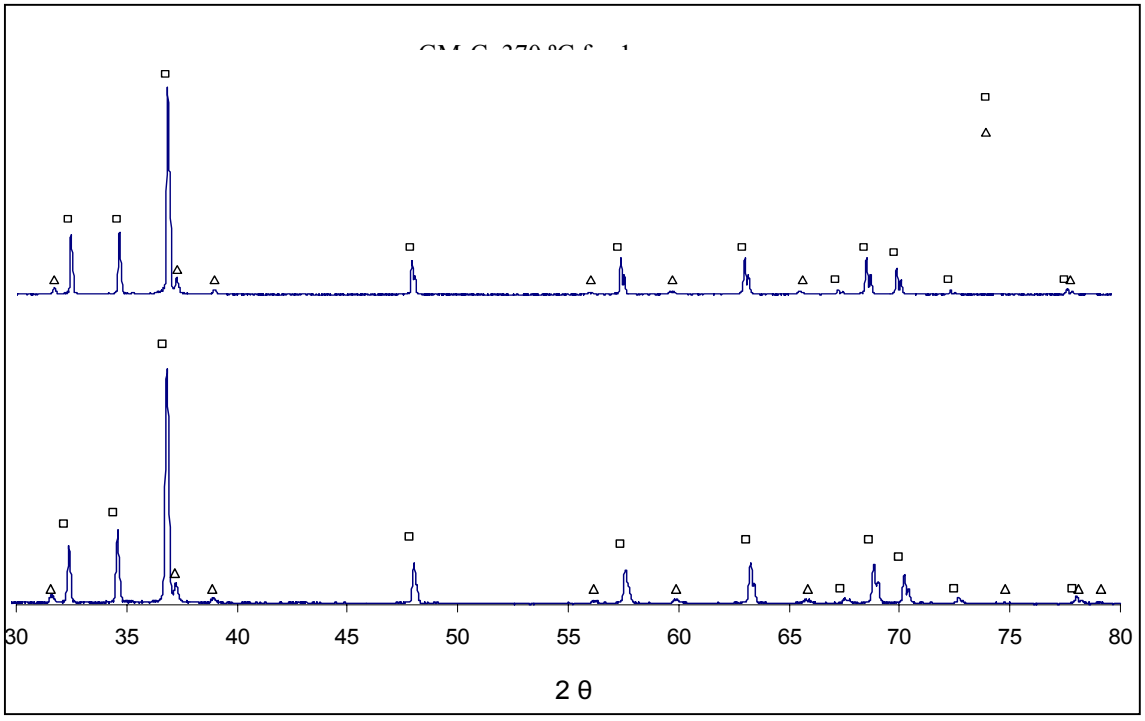

Figure 2. X-ray diffraction patterns showing the presence of Mg and Al_2Ca phase.

Chemical mapping and spot analysis was also performed using EDS technique. Both the bulk sample surfaces and their replicas were checked and compared with each other. Replicas were prepared from the etched samples by placing an adhesive carbon tape on their surface and detaching the tape from the samples.

Finally, the identified phases were compared with the theoretical calculations. The ternary database was created for the calculations to predict the equilibrium phase diagram. The two isothermal sections were calculated at 290 ºC and 370 ºC.

Results and Discussion

Optical microscopy was employed at first to understand the microstructural evolution during the heat treatment of the alloys. Both GM-B and GM-C have similar microstructural features in them. Figure 1 shows the optical micrographs of GM-C alloy samples. The primary α-Mg grains are surrounded completely by the interconnected network of the grain boundary phase in the as-cast state. This grain boundary phase is formed during the eutectic solidification process. Therefore, it has a lamellar-type morphology (Figure 1-a). This morphology and the network nature of the grain boundary phase will experience the following changes during the heat treatment. After the homogenization at 290 ºC for 1 week, the network is somehow less complete and the lamellae become spherical shaped (Figure 1-b). This effect is more pronounced when the temperature is increased to 370 ºC (Figure 1-c). The same phenomena were also observed by Liu et al. [4]. The network of the grain boundary phase in the as-cast state collapsed and became a group of spherical particles scattered throughout the sample.

The microstructural evolution observation using optical microscope was followed by a crystal structure determination using XRD. The results for both alloys showed the formation of the fcc-Al_2Ca phase after the heat treatments (Figure 2).

On the other hand, the results from the as-cast sample showed no distinct peak belonging to Al_2Ca. Instead, there are some unknown peaks that are not matching to any known phases in the ternary Mg-Al-Ca system (Figure 3).

The detailed TEM investigation was made by Luo et al. on this lamellar-type grain-boundary phase [1]. They suggested that the intermetallic phase is a ternary solid solution phase in the hexagonal Mg_2Ca structure. It was represented by the chemical formula of $(Mg, Al)_2Ca$. Some

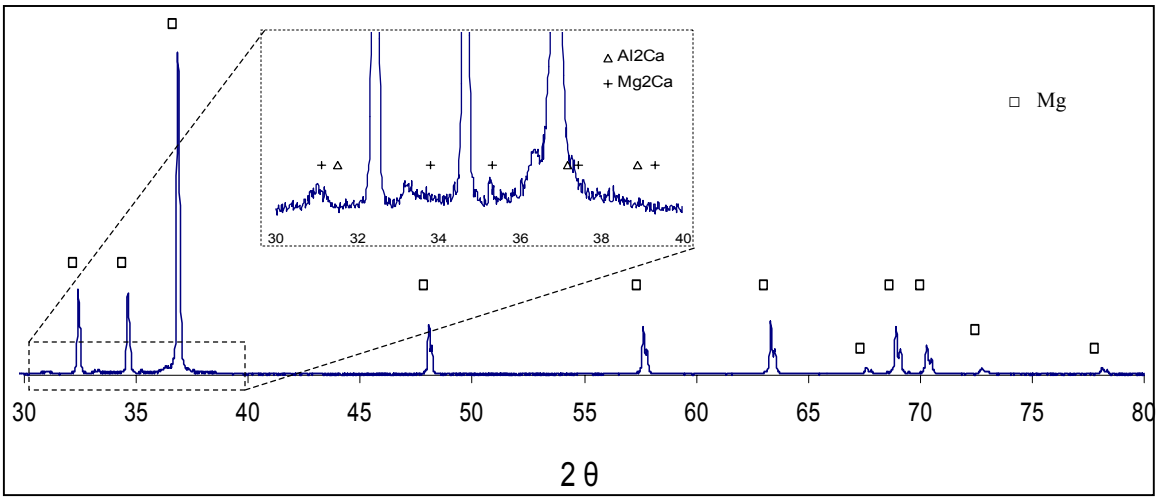

Figure 3. X-ray diffraction pattern of the as cast GM-C sample.

of the Mg atoms were replaced by the Al atoms in the crystal lattice. This result is in an agreement with the present EDS study although it is not a verification of the crystal structure. The replica of the as-cast sample was prepared. Figure 4 shows both the SEM image of the hollow lamellae and the EDS analysis at different spots. The matrix phase and the eutectic Mg was dissolved in the etchant leaving only the intermetallic phase.

The lamellae type phase in the as-cast state became particulate during the heat treatment processes. These particles are very small so that the actual EDS analysis on the bulk samples includes surrounding Mg phase because of electron beam spreading. This is clearly shown in Figure 5.

On the other hand, using the replica sample, it was found that the precipitates in the heat treated samples contain only Al and Ca. In the replica, the interference of Mg matrix phase in the EDS spectra was avoided and the true chemical constituents were detected (Figure 6). This result is a strong support of the XRD analysis for the existence of Al_2Ca phase in the heat treated samples.

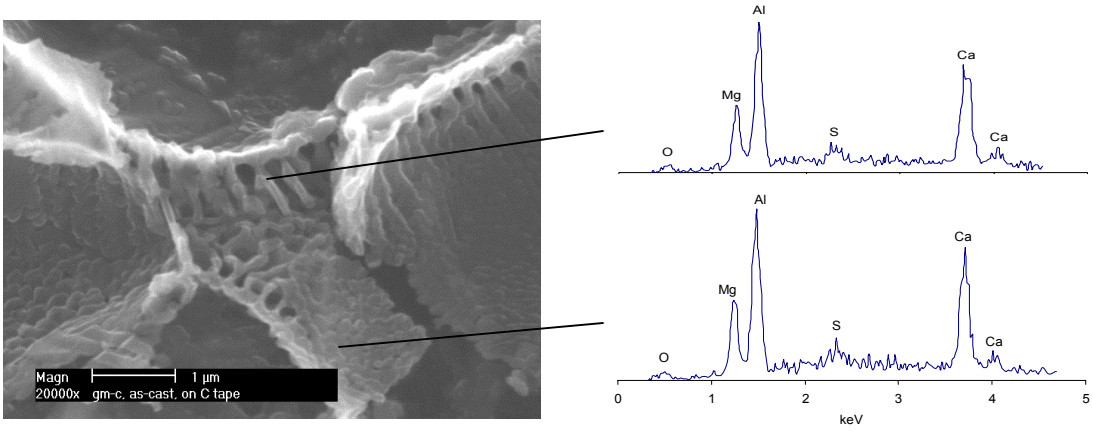

Figure 4. SEM image and EDS analysis of the lamellae-type grain boundary phase from a replica of GM-C sample on a carbon tape.

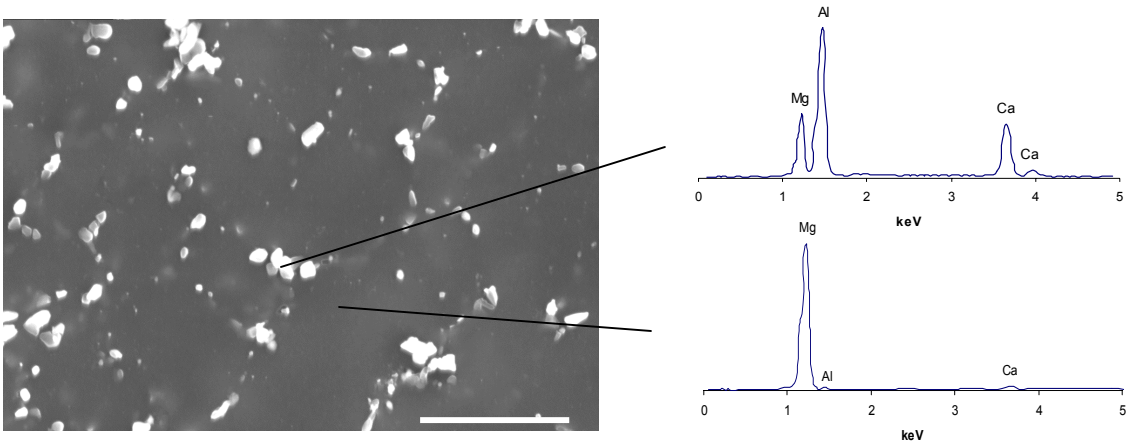

Figure 5. SEM image and EDS analysis of both the particulate grain boundary phase and the matrix phase from a bulk GM-B sample after heat treatment at 370 ºC for a week.

The above experimental results were compared with the theoretical calculations in order to confirm the phase identifaction. The prediction made by the computational thermodynamics approach is validated by this comparison. Two isothermal sections of the Mg-Al-Ca system at 290 ºC and 370 ºC were calculated. Since the chemical compositions of the alloys are mostly Mg, only the Mg-rich corner of the ternary phase diagram is shown in Figure 7. Given the experimental compositions and the conditions, the stable phases were already predicted by the calculations.

The fact that the Mg-Al-Ca ternary phase in the as-cast microstructure decomposes into Al_2Ca after long-term exposures at 290 ºC or 370 ºC does not suggest any instability of this termanry phase in the operating temperatures of automotive powertrains (< 250ºC). In fact, the metallurgical stability and the ternary $(Mg, Al)_2Ca$ and its interfacial coherency with the Mg matrix are reported to be responsible for improved creep resistance in Mg-Al-Ca alloys [1].

Summary

In conclusion, the heat treatment causes the decomposition of the lamellae-type ternary grain boundary phase in the alloys. The equilibrium phases under given conditions are primary Mg matrix and Al_2Ca. The network of the grain boundary phase in the as-cast state collapsed to form more scattered Al_2Ca particles throughout the alloys during the homogenization process. The experimental results are in good agreement with the theoretical calculations.

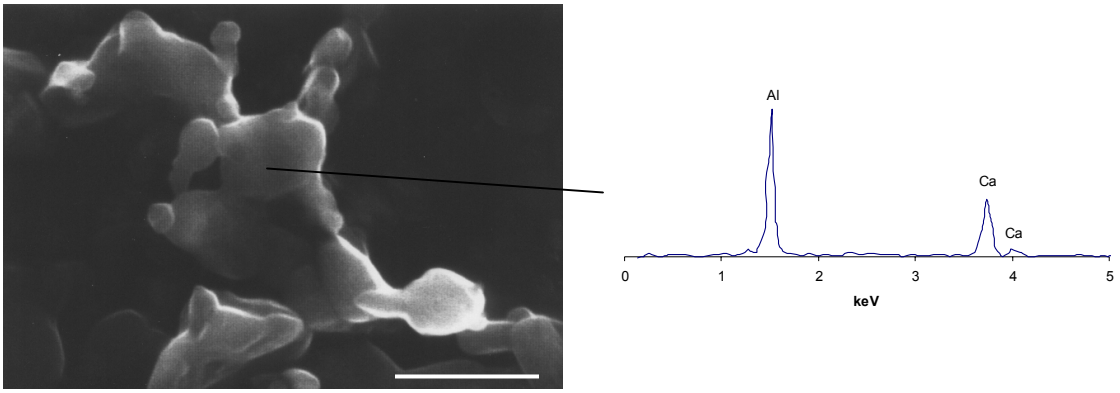

Figure 6. SEM image and EDS analysis of the particulate grain boundary phase from a replica of GM-B sample after heat treatment at 370 ºC for a week. The particles are on a carbon tape.

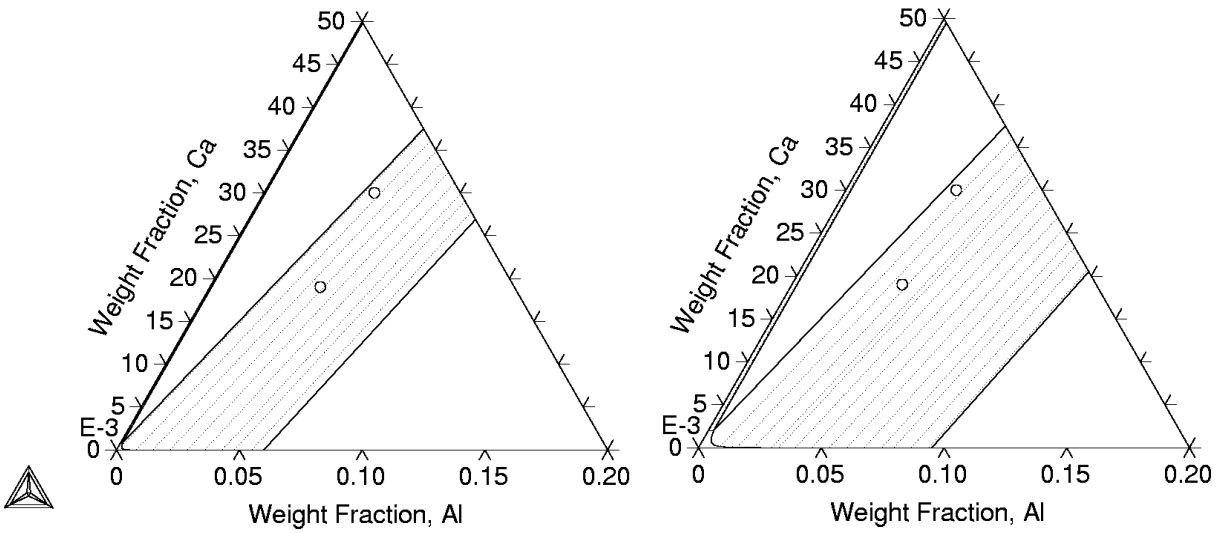

Figure 7. Calculated isothermal sections of the Mg-Al-Ca ternary phase equilibria at 290ºC and 370 ºC.

Acknowledgements

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