Thermodynamics of Phase Formation in Mg–Al–C Alloys Applied to Grain Refinement

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G. Deffrennes
Laboratoire des Multimatériaux et Interfaces, Université Claude Bernard Lyon 1, 22 avenue Gaston Berger, 69100 Villeurbanne, France

B. Gardiola
Laboratoire des Multimatériaux et Interfaces, Université Claude Bernard Lyon 1, 22 avenue Gaston Berger, 69100 Villeurbanne, France

M. Lomello
SYMME, Université Savoie Mont Blanc, Maison de la mécatronique 7 chemin de bellevue, 74944 Annecy le Vieux, France

J. Andrieux
Laboratoire des Multimatériaux et Interfaces, Université Claude Bernard Lyon 1, 22 avenue Gaston Berger, 69100 Villeurbanne, France

O. Dezellus
Laboratoire des Multimatériaux et Interfaces, Université Claude Bernard Lyon 1, 22 avenue Gaston Berger, 69100 Villeurbanne, France

R. Schmid-Fetzer
Institute of Metallurgy, Clausthal University of Technology, Robert-Koch-Str. 42, 38678 Clausthal-Zellerfeld, Germany

Abstract

Grain refinement of Mg-Al based alloys is challenging because it is known that Zr, which is extremely effective in many Al-free alloys, cannot be used. The addition of carbon through various routes by using carbon-containing sources is considered as an option. The grain refinement mechanisms are still under debate. The present work is focused on the ternary base system Mg-Al-C, including the potential nucleants Al4C3 and Al2MgC2, presently without consideration of Al2CO. The ternary carbide Al2MgC2 was synthetized and characterized using sealed Ta crucibles. The decomposition of the carbide was measured at 1290°C by Differential Thermal Analysis under a pressure of 8 bar. Practical difficulties, including high vapor pressure of Mg and high affinity of Mg with oxygen, as well as rapid hydrolysis of the Al2MgC2 carbide have been overcome.

Keywords

Al-C-Mg, Al_2MgC_2, Mg-Al alloys, Grain refinement

1. Introduction

A promising route to improve the mechanical properties of Mg and Mg alloys and to sustain the development of competitive magnesium based materials is the grain refinement of Mg alloys [1]. In fact, the Hall-Petch strengthening coefficient of magnesium is roughly four times greater than the one of aluminum [2]. Indeed, a refined microstructure enhances most of the mechanical properties of magnesium alloys [4, 3, 5, 6], including mechanical properties at higher temperature [7] as well as corrosion resistance [8].

Zirconium is widely accepted as the most successful and effective grain refiner currently known for magnesium [1]. However it is not a viable solution for Mg-Al alloys due to the formation of intermetallic phases with aluminum. Therefore, carbon addition methods have become the major industrial grain refinement technique for Mg-Al alloys [9]. The mechanism behind this grain refinement has raised many conflicting hypothesis over the last 15 years as the phases involved in the process such as Al_4C_3 and Al_2MgC_2 are micron-sized and may react strongly with water to form oxides [10] prior to characterization.

The most widely accepted hypothesis in the literature is that Al_4C_3 forms in the melt and leads to the heterogeneous nucleation of Mg grain during cooling [4, 5, 7, 11, 12, 13, 14, 15]. Indeed, Al_4C_3 would be a suitable nucleant for α-Mg [13]. The facts supporting this hypothesis is the systematic observation of micrometric Al-Mg-C-O particles in the final microstructure [4, 5, 6, 11, 12, 13, 14, 16, 17], notably in the center of the grains [4, 6, 13, 14, 16].

Several conflicting explanation of the refining phenomena are usually considered. Duplex nucleation theory was proposed considering Al_4C_3 as a nucleant for the Al_8Mn_5 phase in a first stage that would lead to the microstructure refinement in a second stage [7, 18]. Because of the presence of oxygen in the characterized particles, Al_2CO was considered as a potential nucleant [19]. However the formation of the oxide phase in the melt is not favorable from a thermodynamic point of view [13, 14, 20]. Jin et al. proposed that a segregation phenomenon of carbon would be the reason behind the refining by affecting the constitutional undercooling and restricting the grain growth during solidification [21]. This hypothesis was debated between Qian et al. [19] and Jin et al. [20].

Recently, strong experimental evidences [22] suggest that the formation of Al_2MgC_2 particles in the melt would lead to the heterogeneous nucleation of Mg grain in a later stage. In addition, first-principles calculations conducted by Wang et al. emphasized that Al_2MgC_2 is a suitable crystal nucleus for α-Mg [23]. From a thermodynamic point of view the work of Viala et al. [10] also support this hypothesis as the authors found that at 727°C alloys containing from 0.6 to 19 wt.%Al were in a two-phase equilibrium with Al_2MgC_2. Indeed, the carbon inoculation process temperatures found in the literature for Mg-Al alloys vary from 700 to 790°C and the alloy composition range from 3 to 9 wt.%Al. It is to note that equilibrium between Mg-Al liquid and Al_4C_3 is only reached above 19 wt.%Al at 727°C [10].

Despite the interest of grain refinement of Mg-Al alloys by carbon inoculation the Al-C-Mg system is not satisfactorily assessed as the carbide phase Al_2MgC_2 is presently not described in any thermodynamic database for Mg alloys [24, 25]. Currently, the only information available related to Al_2MgC_2 are an isothermal section at 727°C [10] as well as the structure of the allotropic form of Al_2MgC_2 stable above 727°C determined by Rietveld refinement from X-ray powder diffraction data [26, 27]. This lack of experimental data is a common issue for any magnesium-based system above 1000°C. It is a direct consequence of the high vapor pressure of Mg coupled with its high reactivity making experimental work delicate. In addition, Al_2MgC_2 strongly reacts with water, making extraction and characterization even more difficult.

An extensive knowledge of phase equilibria between carbon and Mg-Al alloys as well as the determination of the structural, thermal and thermodynamic properties of Al_2MgC_2 is compulsory to

make a reliable thermodynamic assessment of the Al-C-Mg system and, in fine, to sustain the development of grain refined Mg-Al alloys. In the present study Al_2MgC_2 was synthesized and the thermal decomposition of the carbide was characterized by DTA.

2. Experimental procedure

2.1. Materials

Samples used in the study were prepared from commercial powders of magnesium (purity > 99,8 wt.%, grain size 150 < d < 850 µm, Alfa Aesar), aluminum (purity > 99,8 wt.%, grain size 44 < d < 420 µm, Alfa Aesar) and graphite (synthetic, d < 20 µm, Sigma Aldrich).

2.2. Sample preparation

The powders were ball-milled during 20 min in a tungsten carbide mortar and cold-pressed under 250 MPa. All the preparation steps were performed under protective Ar atmosphere. Due to the high vapor pressure of Mg, reaching almost 6 bar at 1350°C [28], as well as the high reactivity of Mg regarding oxygen, the syntheses were carried out using sealed Ta crucibles (h=8mm, d=7mm, thickness=0.5mm, purity > 99,95wt.%, Concept Metal) arc welded under 0.6 bar of Ar. Thermal shields made of Ta were placed over the sample in order to protect magnesium from the radiations during the welding of the crucible lid that would otherwise lead to evaporation of Mg.

2.2. Synthesis and thermal treatments

For the thermal treatments made at 1000(+/-4)°C the Ta crucibles were sealed inside silica vessels under 0.2 bar of Ar in order to avoid oxidation of the Ta crucibles during the thermal treatment and to offer a second protection in case the crucibles would fail under the Mg vapor pressure. A conventional horizontal tube furnace with Eurotherm controller was used as heat source. Owing to the small volume of the crucibles the vapor pressure of Mg could be reached without altering the initial sample composition, as less than 0.1wt.% of Mg was needed to supply the vapor phase at 1000°C. At the end of the isothermal heat-treatments the silica vessels were broken in water as soon as being driven out of the furnace so that the samples were efficiently quenched.

2.3 SEM-EDS

Quenched samples were cut using a diamond saw without adding any lube, and polished using a water-free polishing procedure to prevent the hydrolysis of Al_2MgC_2. SEM observations were performed directly after polishing on a Zeiss SEM under a high voltage of 10kV and at a working distance of 8.5 mm. Mass fraction of the three elements were obtained from electronic standards.

2.4 Differential Thermal Analysis

Thermal analysis was performed from room temperature to 1350°C in a Setaram TAG92 using a B-type Pt-Rh DSC sensor. The sensor was slightly deformed to match the Ta crucible geometry, and an yttrium oxide paste was used to prevent any reaction at the crucible/DSC-sensor interface. As reference a cylinder made of tungsten with a thermal mass (mCp) as close as possible to that of the sample was used. The DSC was calibrated in temperature using gold standard.

3. Results and discussion

3.1 Synthesis of Al_2MgC_2

The synthesis of the Al_2MgC_2 carbide was carried at 1000°C during 240 hours from the composition 70Mg – 19Al – 11C wt.%. After the synthesis stoichiometric Al_2MgC_2 crystals were obtained inside a 98.9Mg-1.1Al at.% matrix as well as with unreacted graphite located at the carbide – matrix interface as shown in Fig. 1. Smaller crystals were hexagonal-shaped whereas largest ones were rectangular-shaped. As witnessed by Viala et al. [10] Al_2MgC_2 hydrolysis was observed and was found to be significant after half an hour in air. Huang et al. [22] proposed the following hydrolysis reaction:

$$2Al_2MgC_2 + 8H_2O = 2MgAl_2O_4 + 4CH_{4(g)} \quad (1)$$

Phases were characterized by EDS and results are displayed in Table 1. Al_2MgC_2 composition was determined from a set of crystals selected so that oxygen lies below the detection limit. No solubility of carbon could be measured in the matrix within the detection range.
The fact that the matrix was very poor in aluminum suggests that thermodynamic equilibrium have been reached. Plus the composition of 1.1 wt.%Al for the liquid involved in the three-phase equilibria with graphite and Al_2MgC_2 at 1000°C is coherent with the value of 0.6 wt.%Al obtained at 727°C by Viala et al. [10].

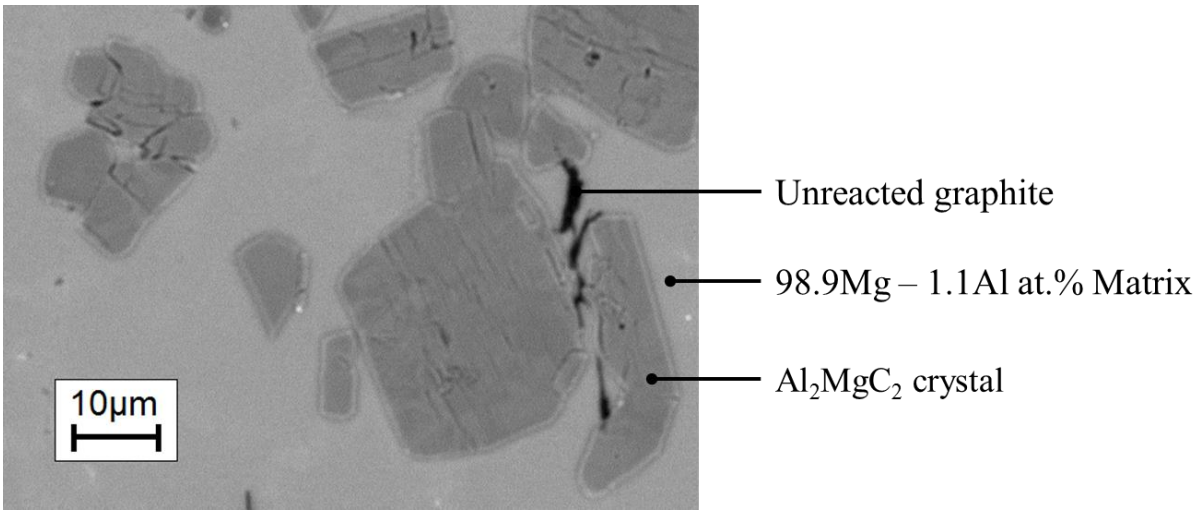

Fig. 1 SEM observation of a 70Mg – 19Al – 11C wt.% sample heat-treated 240 hours at 1000°C. The microstructure is characterized by Al_2MgC_2 crystals, unreacted graphite and a 98.9Mg-1.1Al at.% matrix.

Table 1 Composition in at.% of the phases formed in 70Mg – 19Al – 11C wt.% samples heat-treated 240 hours at 1000°C.

Phases	at.% Mg	at.% Al	at.% C
Matrix	98.9	1.1	-
Al_2MgC_2	20.9	40.3	38.8

3.2 Thermal decomposition of Al_2MgC_2

Differential Thermal Analysis was performed on samples (70Mg – 19Al – 11C wt.% powder compact equilibrated at 1000°C during 240 hours, Section 3.1). The as-quenched samples were made of Al_2MgC_2, unreacted graphite and a 98.9Mg – 1.1Al at.% matrix (Fig. 1). Results are displayed in Fig. 2. Melting of the matrix was observed at 615.8°C during heating and the solidification started at 640.12°C during cooling. Those temperatures are coherent with the matrix composition found before (Table 1) and after (Table 2) DTA as they correspond to the fusion and solidification of a 98Mg – 2Al at.% alloy [28]. In addition, a sharp exothermic signal was detected at 1290°C.
The exothermic signal found at 1290°C was attributed to the decomposition of Al_2MgC_2, and the reaction of decomposition is proposed as follows:

$$Al_2MgC_2 = Al_4C_3 + C + L \quad (2)$$

Eq. (2) denotes a four-phase equilibrium, a ternary peritectic on cooling, as opposed to the stoichiometric reaction equation in eq. (1). It is interesting to note that after the DTA the Al_2MgC_2 crystals morphology changed significantly compared to the synthesis carried out at 1000°C. Indeed Al_2MgC_2 crystals were one order of magnitude bigger after the thermal analysis and platelet-shaped instead of being hexagonal-shaped or rectangular shaped. This new morphology was very similar in both size and shape to the Al_4C_3 crystals that would be obtained by the authors when performing synthesis with Al rich liquids. As a matter of fact, in the center of the biggest Al_2MgC_2 crystals the Al_4C_3 carbide could be found after the thermal analysis as shown in Fig. 3 as a record of the decomposition reaction. Al_4C_3 crystals contained 5.0 at.% of Mg present in solid solution similarly to the findings of Viala et al. at 727°C [10].
One should note that the decomposition of Al_2MgC_2 was measured under a pressure of 8 bar, half of it being due to the vapor pressure of Mg and the other half to the Ar pressure initially filled during arc-welding of the crucible increasing with the temperature as an ideal gas.

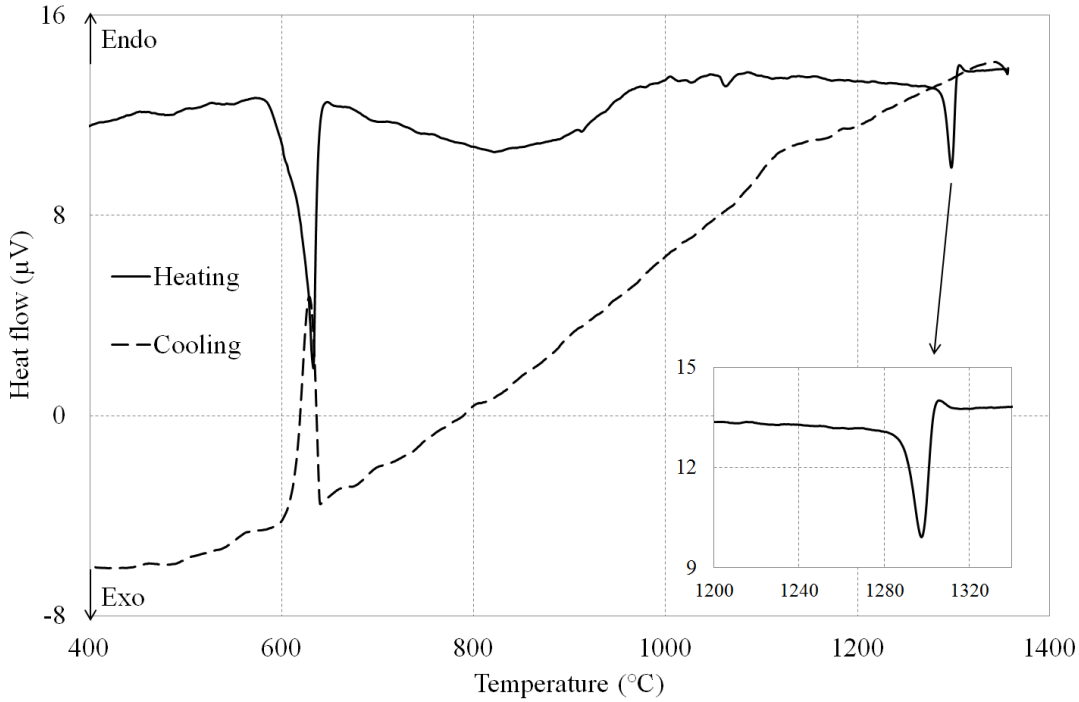

Fig. 2 Heat flow versus temperature for thermal analysis performed on a sample of composition 70Mg – 19Al – 11C wt.% equilibrated at 1000°C during 240 hours.

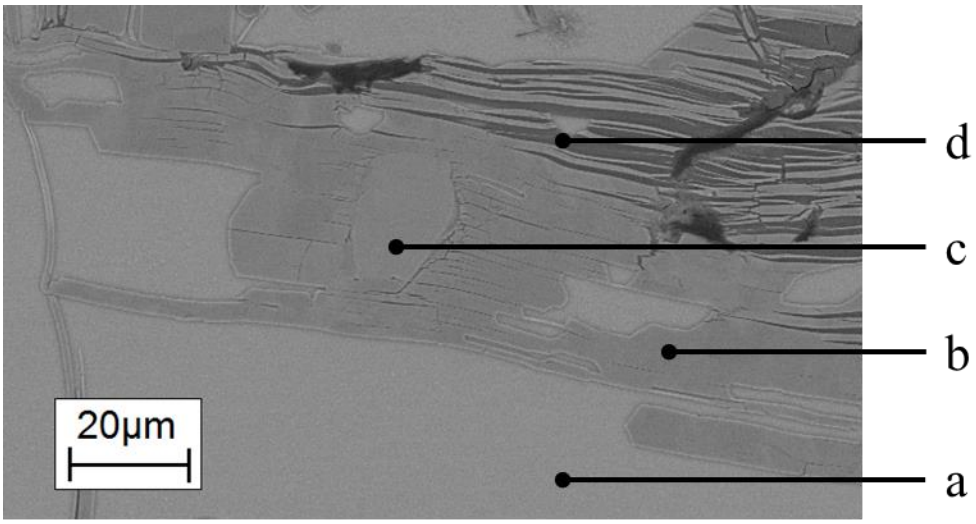

Fig. 3 SEM observation of a 70Mg – 19Al – 11C wt.% sample equilibrated 240 hours at 1000°C after DTA. The microstructure is characterized by (a) 98.4Mg-1.6Al at.% Matrix, (b) Al_2MgC_2 crystals, (c) Al_4C_3 crystals in the center of the biggest Al_2MgC_2 crystals and (d) Al_2MgC_2 crystals undergoing oxidation. EDS results are displayed in Table 2.

Table 2 Composition in at.% of the phases formed in a 70Mg – 19Al – 11C wt.% sample heat-treated 240 hours at 1000°C after DTA was performed.

Phases	at.% Mg	at.% Al	at.% C	at.% O
Matrix (a)	98.4	1.6	-	-
Al_2MgC_2 (b)	20.3	39.3	40.4	-
Al_4C_3 (c)	5.0	52.7	42.3	-
Al-C-Mg-O (d)	8.2	19.1	5.0	67.7

4. Conclusion

The Al_2MgC_2 phase has been synthesized in sealed Ta crucibles capable of withstanding up to 15 bar of internal pressure. The ternary carbide decomposition temperature in (Mg,Al) liquid was measured at 1290°C by DTA. The developed experimental procedure is promising as it allowed working with magnesium at temperatures up to 1350°C where the pressure inside the crucible reaches 10 bar. Further experiments including the determination of phase equilibria at 1000°C and 1290°C are being carried out by the authors to provide a complete thermodynamic description of the Al-C-Mg system. Indeed, the thermodynamic modeling of the Al_2MgC_2 carbide is of interest to support grain refining of Mg-Al alloys by carbon inoculation under optimized processing conditions by quantitative simulations.

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