

# The Influence of Ca-Additions on the Mechanical Properties of T300-C-Fibre/Mg(Al) Metal Matrix Composites

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## 1 Summary

The present paper deals with the issue of adding small amounts of Ca (up to 0.5% by weight) for melt protection during melt transfer in the squeeze casting process for the manufacturing of carbon fibre reinforced Mg based metal matrix composites. The influence of Ca-additions on melt oxidation, microstructure and (axial) tensile behaviour of a MgAl1-matrix alloy and UD Mg(Al1)/T300(C-fibres) composites is investigated. It is shown, that 0.3% of Ca is required for an effective melt protection. When added to the unreinforced MgAl1-matrix, Ca acts as a grain refiner and thus leads to a strength increase up to a Ca-content of 0.3%. In the composite, as a consequence of the addition of Ca, the tensile strength is reduced by 15%, to approximately 1200 MPa compared to the Ca-free MgAl1/T300 reference material. This tensile strength loss is attributed to the appearance of the Mg-Mg<sub>2</sub>Ca eutectic phase in the Ca-containing materials.

## 2 Introduction

Carbon fibre reinforced magnesium composites are candidate materials for the selective reinforcement of highly stressed magnesium castings [1,2]. Nevertheless, the mechanical performance of C-fibre/Mg composites is very sensitive to the fibre/matrix compatibility which in turn is affected by the interfacial reactivity of the material's constituents and by the related processing technique [3-5]. UD-T300 high strength C-fibre Mg composites with 1% addition of Al by weight produced by direct squeeze casting have proven to provide a good compromise between transversal and longitudinal tensile properties while being attractive from an economical point of view due to the use of low cost C-fibres and an established, high productivity processing technique [5].

The direct squeeze casting process, however, involves the transfer of liquid magnesium from the melting furnace to the casting die as well as a comparatively slow die filling procedure by pouring the melt directly into the die containing the fibre preform. Air turbulences arising from pouring of the hot liquid metal prevent an efficient use of protective gases such as SF<sub>6</sub>-mixtures. Moreover, because of the excessive global warming potential, the use of SF<sub>6</sub>-containing gas mixtures is becoming questionable [6,7]. Hence, during transfer and pouring, the melt must be protected against oxidation. Pure Mg and Mg alloys with a low Al content are particularly prone to oxidation in the liquid state. Besides Be, which is usually

added in very small quantities (to AZ91hp: 5-15 ppm), Ca has been known for years to reduce the susceptibility of liquid magnesium to oxidation when added in amounts of a few tenths of weight percents [7-9].

The goal of the present study is to investigate the potential of using small Ca-additions to a MgAl1 alloy to prevent oxidation during the squeeze casting process and to analyse the influence of Ca on microstructure and tensile properties of both the matrix alloy and the parent T300-C-fibre reinforced composite material.

### 3 Experimental

The MgAl1(Ca) alloys were melted from hp Mg (99.8), hp Al (99.99) and a Mg/Ca master alloy (70/30) provided by Timminco SA. in plain steel cylindrical crucibles under a SF<sub>6</sub>/CO<sub>2</sub> gas mixture protection; the melt temperature was set to 750°C. The Ca contents in the MgAl1-alloys were 0, 0.1, 0.2, 0.3 and 0.5% (chemical compositions in weight-%). Portions of 1dm<sup>3</sup> were prepared for each casting; the chemical composition was measured for each sample after casting by glow discharge optical spectrometry.

For the oxidation tests, approximately 0.15dm<sup>3</sup> of liquid metal were poured directly from the crucible into small steel cups (Ø 60 mm) preheated to 50°C and exposed to the laboratory atmosphere (air) until solidification.

Samples (120x80x20 mm) of the different unreinforced alloys were prepared by direct squeeze casting, i.e. the superheated melt (750°C) was directly poured (no gas protection) into the die (300°C) and squeezed under a maximum pressure of 130 MPa for 1 min. The composite samples (100x80x7 mm) were fabricated by squeeze infiltration of T300 C-fibre preforms preheated to 750°C under inert atmosphere (Ar), the remaining process parameters being the same as listed above. The preforms were produced by unidirectional filament winding; the fibre volume fraction  $v_f$  was set to 60 %.

For tensile testing of the unreinforced matrix alloys, 12 threaded cylindrical specimens with a gauge diameter of 6 mm and a gauge length of 30 mm were machined from each plate. Half of the specimens were subjected to a T6 heat treatment, i.e. 413°C/6hrs + 352°C/2hrs + 413°C/10hrs + oil quenching + 216°C/4hrs; the remaining specimens were tested in the as cast condition.

For tensile testing of the composite materials, smooth grip cylindrical specimens with a gauge length of 15 mm and a gauge diameter of 3 mm were machined (PCD tools) from the composite plates with the fibres being aligned in the axial direction. At least three tensile specimens were tested for each composition; they were clamped along the smooth surfaces in split collars. No heat treatment was performed on the composite materials.

The tensile tests were performed at a constant crosshead speed of 0.5 mm/min and the macroscopic strain was measured with an extensometer.

The microstructure of the different materials was investigated by light microscopy.

## 4 Results and discussion

### 4.1 Chemical analysis & oxidation tests

Although over-alloyed by 30% during melt preparation, the Ca content is slightly below the target values (Tab. 1). This effect is attributed to a pronounced oxidation of Ca.

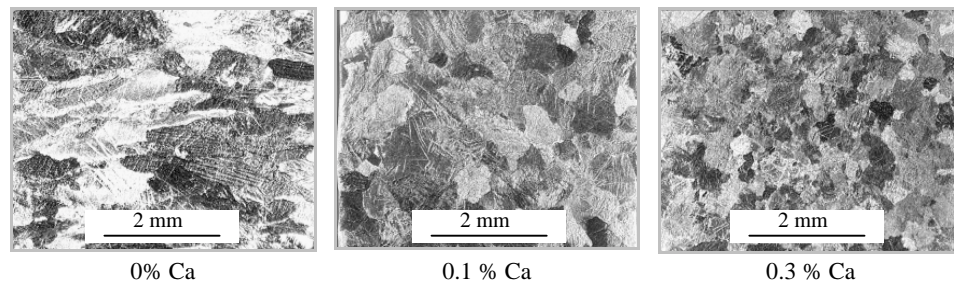
**Table 1.** Ca- and Al-contents of the different squeeze cast materials (weight-%)

| target | unreinforced matrix alloy |          |          |          | T300 C-fibre reinforced material |          |          |          |
|--------|---------------------------|----------|----------|----------|----------------------------------|----------|----------|----------|
|        | Al1Ca0                    | Al1Ca0.1 | Al1Ca0.3 | Al1Ca0.5 | Al1Ca0                           | Al1Ca0.1 | Al1Ca0.2 | Al1Ca0.3 |
| Al     | 1.18                      | 0.92     | 1.19     | 1.08     | 0.98                             | 1.18     | 1.07     | 1.06     |
| Ca     | 0.001                     | 0.06     | 0.28     | 0.42     | 0.001                            | 0.06     | 0.16     | 0.19     |

The Ca-free MgAl1 alloy oxidizes during melt pouring and starts burning rapidly in the absence of the protective gas. When adding 0.3% (i.e. 0.28%) Ca, oxidation is completely suppressed and upon solidification the surface appearance turns to gold.

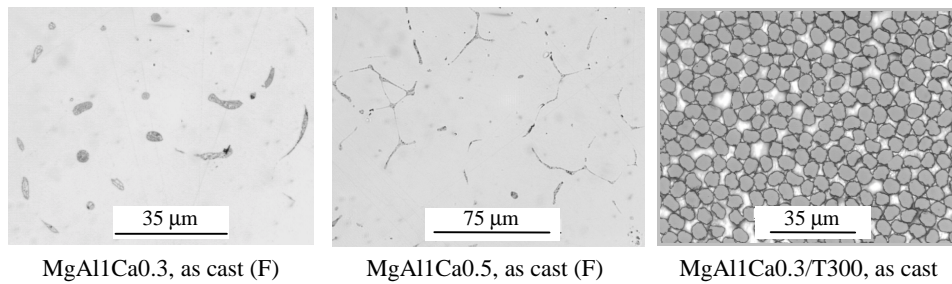
### 4.2 Microstructure

Adding Ca to alloy MgAl1 continuously reduces the grain size of the squeeze cast microstructure as shown in Fig. 1, thus confirming similar statements made in [8,9]. Ca-additions beyond 0.3% did not show any further effect in grain size refinement.



**Figure 1.** Influence of Ca-additions on grain size in the unreinforced squeeze cast matrix alloy (F)

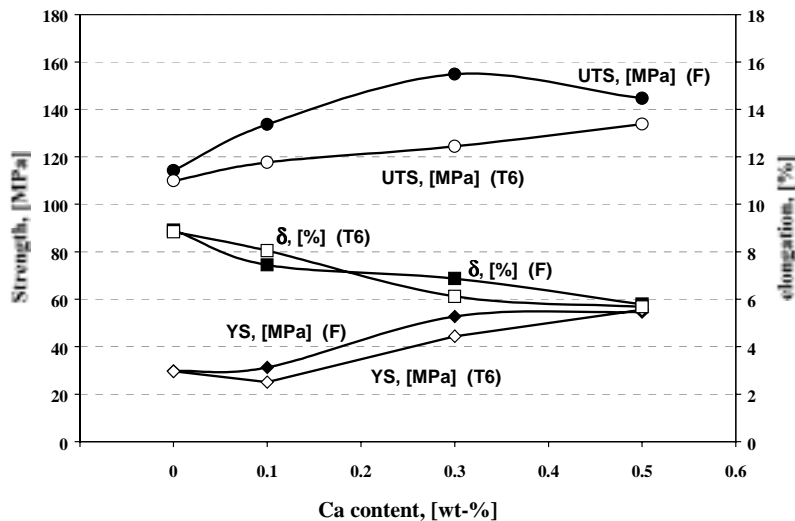
Ca-additions also lead to the formation of the eutectic  $Mg_2Ca$ -phase; at low Ca concentrations (0.1, i.e. 0.06%) this phase appears as small spherical droplets (1-5  $\mu m$ ). With increasing Ca content, the shape of the eutectic phase tends to be more elongated until it is continuously formed along the grain boundaries at 0.5% Ca (Fig. 2). The eutectic phase is not affected by solution heat treating; the microstructure in the T6 temper does not significantly differ from the "as cast" one. The composite material is well infiltrated and the fibre distribution is shown to be homogeneous, but also quite dense; the high fibre volume fraction (>60 %) leads to multiple fibre/fibre contacts (Fig. 2). No eutectic phase is visible in the inter-fibre regions by optical light microscopy.



**Figure 2.** Microstructure of the MgAl1(Ca) matrix-alloys and the parent composite material

### 4.3 Tensile properties

In the as cast condition, the tensile strength of the MgAl1(Ca) matrix alloy continuously increases with increasing Ca-content. However, beyond 0.3% Ca the yield strength increase becomes less pronounced and the ultimate tensile strength declines. In parallel, increasing the Ca-content leads to a marked loss in elongation to fracture (Fig. 3).



**Figure 3.** Influence of the Ca-content on the tensile properties of the MgAl1(Ca) matrix alloys. (open symbols: T6 treatment, closed symbols: as cast condition, F)

In T6-condition strength gradually increases and elongation decreases with increasing Ca-content up to 0.5%. The T6-tensile properties are inferior to the "as cast" ones.

The increase of strength upon addition of Ca up to 0.3% is attributed to the related grain size decrease; beyond 0.3%, grain size is no further reduced and strength stagnates.

The fracture surfaces of the matrix alloys feature some evidence of intergranular fracture; this phenomenon becomes more pronounced with increasing Ca-content. Although Ca-additions are reported to favour hot tearing [7,8,10], no evidence of hot tearing was found in the squeeze cast specimens, which is most probably due to the elevated process pressure. Nevertheless, as revealed by metallography, the  $Mg_2Ca$  phase is shown to segregate along the grain boundaries and may thus lead to local intergranular failure. As a consequence of this, strength decreases once a critical amount of intergranular eutectic phase is formed and elongation is markedly reduced as well, thus confirming observations made in [7,9].

The Mg<sub>2</sub>Ca phase cannot be dissolved by the solution heat treatment employed in this study (413°C). Similar observation is made in [11] where it is reported that even after solution heat treatment at 460°C for 48 hrs this phase remains unaffected.

The tensile strength of the composite materials is obviously adversely affected by the addition of Ca, as shown in Tab. 2. But it is also observed, that for 0.3% Ca the standard deviation is quite small compared to the reference alloy which leads to a similar minimum in tensile strength values. The fracture surfaces are characterized by pronounced pull-outs of fibre and fibre bundles; failure generally occurs by matrix shear deformation in the inter-fibre spaces, thus confirming a good interfacial fibre/matrix bonding. Although not visible by light microscopy, it is presumed that at least some amount of microscopic Mg-Mg<sub>2</sub>Ca eutectic is formed along the fibre/matrix interfaces. This phenomenon is already known from other continuous fibre reinforced Al- and Mg-based composites with matrix compositions prone to form eutectic phases and was shown to degrade the tensile properties of these materials [12].

**Table 2.** Influence of Ca additions on the tensile strength of MgAl1/T300-C-fibre composites (F)

| Ca-content, [%]    | 0    | 0.1  | 0.2 | 0.3  |
|--------------------|------|------|-----|------|
| UTS, [MPa]         | 1471 | 1229 | 999 | 1181 |
| standard deviation | 269  | 184  | 297 | 39   |

## 5 Conclusions

1. Small Ca-additions to a MgAl1-alloy are shown to effectively prevent melt oxidation during the squeeze casting process; the optimum amount is 0.3 wt-%.
2. Up to 0.3% Ca, the grain size of the MgAl1-alloy is reduced by one order of magnitude and the tensile strength increases accordingly; an increase of the Ca-content beyond this level has no further beneficial influence on grain size.
3. Ca-additions lead to the formation of the eutectic Mg<sub>2</sub>Ca phase which tends to form continuous networks along the grain boundaries, which is particularly pronounced for Ca-contents above 0.3%. As a consequence, both strength and elongation are adversely affected and partial intergranular fracture appears. The Mg<sub>2</sub>Ca eutectic phase cannot be dissolved by a solution heat treatment at 413°C and remains also unaffected with respect to its morphology.
4. In the C-fibre composite material, Ca additions reduce the tensile strength by 15% compared to the mean value of the Ca-free reference material. However, due to the markedly lower standard deviation at 0.3% Ca, the minimum tensile strength values of both materials are comparable, i.e. 1150 vs 1200 for 0.3 and 0% Ca respectively.

## 6 Acknowledgements

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