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# Mg/TiC composites manufactured by pressureless melt infiltration

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## Abstract

Molten Mg was pressurelessly infiltrated into TiC preforms (56 vol.%) under flowing Ar at temperatures of 850, 900 and 950 °C. The rate of infiltration exhibited a strong temperature dependency. The mechanical strength of the composites increased from 172 to 233 MPa for processing temperatures of 850 and 950 °C, respectively.
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## 1. Introduction

Magnesium and its alloys are attractive candidates for automotive and aerospace applications due to their low density. Their moderate mechanical and physical properties, however, limit their proliferation in demanding applications such as structural and functional materials. The incorporation of suitable ceramic particles can compensate for many of these limitations leading to engineering materials with high specific properties, improved wear resistance and lower coefficients of thermal expansion [1,2].

A number of manufacturing techniques have been developed to produce metal matrix composites (MMCs). When high levels of reinforcement are required, the infiltration of liquid metal into porous ceramic preforms is preferred since it can yield near-net shape components with high stiffness and enhanced wear resistance. The driving force for infiltration the liquid metal is dictated by the affinity between the metal/ceramic couple in terms of wettability. Generally speaking this affinity is poor and worsened by the formation of oxides skins on the metal surfaces. Oxide layers in metals such as Al and Mg, represent a mechanical obstacle that has to be overcome before the inherent wettability of the system is exhibited. Whilst Al oxidises forming a compact and passivating layer, Mg forms a porous and non-protective oxide. When good wettability exists in a given metal/ceramic system, and under adequate conditions of temperature and atmosphere, the liquid metal may be drawn into the ceramic preform simply by capillarity.

TiC is a hard and stiff transition metal carbide with low density and has recently been dispersed in a Mg matrix via a master Al/TiC composite [3]. Sessile drop experiments revealed a non-wetting/wetting transition in the Mg/TiC system between 850 and 900 °C in Ar, without formation of new compounds at the interface, suggesting TiC is a stable reinforcement for Mg composites [4]. This study explores the feasibility of pressureless infiltration of molten Mg into TiC preforms. The effect of temperature on both, infiltration kinetics and mechanical properties were investigated.

## 2. Experimental procedure

Porous preforms were prepared by uniaxially pressing 18.5 g of TiC powder ($D_{50} = 1.2$ μm with a surface area of 2.32 m$^2$/g) at 8 MPa in a rectangular die to form green

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bars $\sim 65 \times 10 \times 10$ mm in size. The preforms were sintered at 1250 °C for 1 h in a tube furnace under flowing Ar, yielding porous preforms with 56% ±0.5 theoretical density, as measured by Archimedes' method (ASTM C373-00).

A thermogravimetric technique [5,6] was used to follow the infiltration behaviour at 850, 900 and 950 °C under an Ar atmosphere. The weight gained by the preforms, as a result of infiltration of liquid Mg into the TiC preforms, was continuously monitored to obtain characteristic infiltration profiles. The resulting composites were observed in a scanning electron microscope (SEM) attached to an energy-dispersive X-ray spectroscopy (EDX) system. X-ray diffraction (XRD) was used to identify the phases present by using Cu Kα radiation for $2\theta$ values between 20° and 90° with a scanning step of 0.02° and dwell of 2 s.

The natural frequency of vibration of the composites was measured using a Grindosonic MK5i (Lemmens) equipment and the elastic modulus of the composites was measured in a non-destructive fashion. The Mg/TiC composites were machined at low speeds on a lathe using carbide tools, to produce tensile specimens (ASTM E8M). Tensile tests were carried out, at room temperature, on a universal testing machine at a cross head speed of 0.016 mm/s. Fracture surfaces were observed using SEM. The hardness of the composites was measured by applying a 50 kg load with a Vickers indent. Porous regions were avoided when performing the indentations.

## 3. Results and discussion

### 3.1. Microstructure and infiltration kinetics

Fine TiC powders were partially sintered to produce TiC preforms with ~44% interconnected porosity, with the microstructure shown in Fig. 1(a). Pressureless melt infiltration of molten Mg into these preforms was successfully achieved at temperatures of 850, 900 and 950 °C under flowing Ar. Fig. 1(b) shows a typical back-scattered electron micrograph of the resulting composites. The dark phase corresponds to Mg and the grey phase to TiC which clearly resembles the network observed in the sintered preforms. Although the full length of the bars infiltrated, some porosity was observed in the microstructure. Table 1 shows density measurements of the infiltrated composites and composites according to the rule of the mixtures with approximately 3% porosity were produced.

SEM examination and EDX analysis performed on the different samples did not show evidence of an additional phase, other than TiC and Mg. This was also corroborated by XRD, as shown in Fig. 2. XRD patterns of the composites infiltrated at different temperatures exhibited only the reflections for Mg and TiC with no apparent shift on their positions, which suggests that dissolution of the carbide or changes in its stoichiometry did not occur. This might be expected as the formation of Mg carbide is thermodynamically unfavourable. Also, Mg and Ti do not form intermetallics and the solubility of Ti in Mg is very limited under equilibrium conditions [7]. Thus, TiC can be considered stable in pure Mg melts.

Fig. 3 shows the infiltration profiles obtained for Mg/TiC composites infiltrated at different temperatures. Firstly, the temperature dependence of the infiltration rate is clear, the higher the temperature the faster the rate of infiltration. Secondly, there is an incubation period prior to stabilizing into parabolic-type infiltration curves. This incubation period, $t_0$, also seems to be temperature dependant. As the infiltrating temperature increases the incubation period becomes shorter, indicating that infiltration of liquid Mg in TiC preforms is
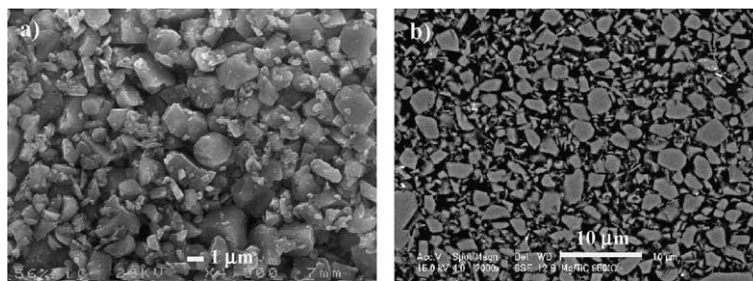


Fig. 1. (a) Morphology of the TiC preform and (b) Mg/TiC composite infiltrated at 950 °C.

Table 1
Porosity and density measurements of the composites (ASTM C373-00)

| Temperature (°C) | Open porosity (%) | Close porosity (%) | Density (g/cm³) | Theoretical density (%) |
|---|---|---|---|---|
| 850 | 0.4293 | 2.2296 | 3.4217 | 97.34 |
| 900 | 0.2648 | 2.3160 | 3.4245 | 97.41 |
| 950 | 0.2157 | 2.8430 | 3.4077 | 96.94 |
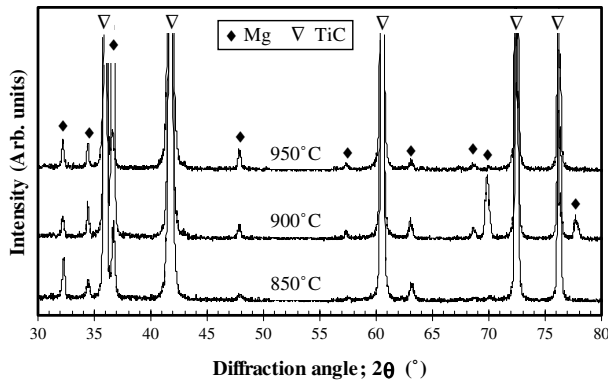
Fig. 2. XRD patterns for the infiltrated Mg/TiC composites.



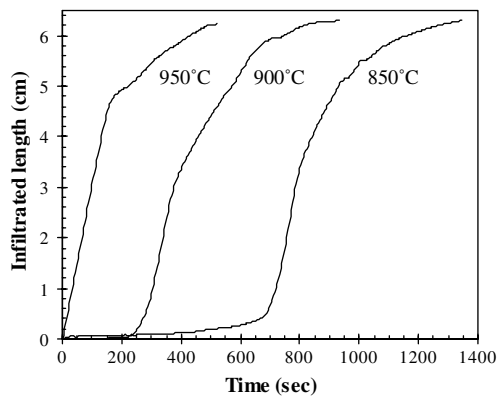Fig. 4. Wettability of liquid Mg on TiC [4].



Fig. 3. Characteristic infiltration profiles.

preceded by a thermally activated process. The presence of an incubation period has commonly been observed during the infiltration of TiC by Al and Al-alloys and has been ascribed to the unstable wetting behaviour in these systems [5,6], which involves the break up of the aluminium oxide film, followed by spreading driven by a chemical reaction at the interface [4,8,9]. This behaviour is typical of non-equilibrium systems.

A transient contact angle, $\theta$, has also been observed between liquid Mg and TiC, as shown in Fig. 4 [4]. Although the wetting behaviour is typical of non-equilibrium systems, the Mg/TiC interface was found to be free of reaction products and wetting is thought to be the result of the disruption of the MgO film on the drop surface aided by instantaneous Mg evaporation [9], and the subsequent establishment of chemical equilibrium bonds at the interface [4]. On this basis, the incubation
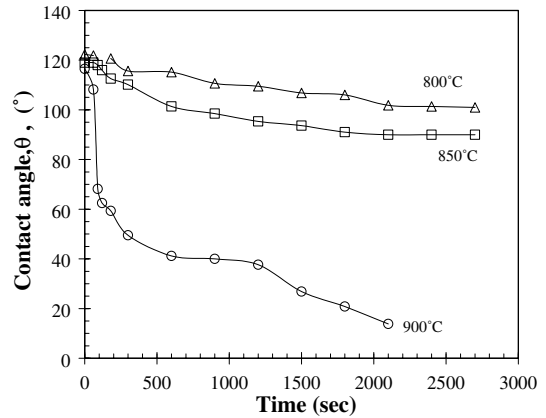
period in the infiltration of Mg in TiC can also be related to the time required for the Mg melt, in contact with the TiC preform, to achieve the threshold contact angle for infiltration to proceed at a given temperature. The condition for spontaneous infiltration, in theory, is given by $\theta < 90°$. The contact angle measured by the static sessile drop technique does not replicate the geometry and dynamics of a given infiltrating system, consequently, the transient period of the contact angle also does not accurately represent the time required prior infiltration. In this study, $t_0$ values are smaller than the times observed from the sessile drop experiments for $\theta$ to achieve a steady value. This fact might be explained by considering that the preform breaks through the MgO layer on top of the Mg melt when the preform is partially dipped into it, leading thus to direct contact between fresh liquid Mg and TiC.

Kinetic studies can be carried out on the infiltration profiles [5,6], as both the incubation period ($1/t_0$) and steady-state infiltration rate ($dl/dt$) are temperature dependent, the corresponding rate constants, $k$, can be determined at each stage at a given temperature. Arrhenius analysis is shown in Tables 2 and 3. The results revealed high activation energies, suggesting that mass transfer mechanisms control the infiltration process instead of viscous flow (for which activation energies fall in the order of about 10 kJ/mol [5]).

Non-oxide ceramics exhibit a superficial oxide layer, the level of surface oxidation for TiC varies from an oxycarbide $TiC_xO_{1-x}$, to Ti suboxides to polymorphic $TiO_2$ [10]. The high affinity of Mg for oxygen suggests that during infiltration, an oxycarbide layer on the

Table 2
Activation energy estimated from the incubation periods

| $T_{inf}$ (°C) | $1/T$ (K) | Incubation time ($t_0$) | $1/t_0$ (s$^{-1}$) | $\ln(1/t_0)$ | Slope ($-E_a/R$) | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|---|
| 850 | 0.000890 | 680 | 0.00147 | −6.522 | | |
| 900 | 0.000852 | 240 | 0.00416 | −5.480 | −60,387 | 503.2 |
| 950 | 0.000817 | 8 | 0.125 | −2.079 | | |

Table 3
Activation energy estimated from the steady part of the infiltration profiles

| $T_{inf}$ (°C) | $1/T$ (K) | d$l$/d$t$ (cm/s) | ln(d$l$/d$t$) | Slope ($-E_a/R$) | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| 850 | 0.000890 | 0.0007003 | −7.264 | | |
| 900 | 0.000852 | 0.0064029 | −5.051 | −47,054 | 392.1 |
| 950 | 0.000817 | 0.0286099 | −3.554 | | |

surface of the TiC preform can be readily reduced by the advancing liquid magnesium front, and that this surface reaction is the possible driving mechanism for the infiltration process. Since no reaction products were seen on the infiltrated composites, it can be assumed that interfacial chemical interactions occur at a strictly nanoscale.

### 3.2. Mechanical strength

Table 4 summarises the mechanical properties for the composites. As expected, a significant increase in the elastic modulus is observed with regard to pure Mg ($E = \sim 45$ GPa). An increase is also seen by increasing the infiltrating temperature. In principle, and considering full infiltration, the elasticity modulus should be dependant on the volume fraction of the phases present rather than on processing temperature. Variations in density are less than 0.5% of theoretical value and they are not likely to be responsible for the significant variations in the general mechanical performance of the composites. Elasticity modulus measurements are also compared with a predicted value using the Halpin–Tsai model [11] for aspect ratios, $s$, of the reinforcing particles of 1 and 1.5. The values calculated from the model, which do not account for defects such as porosity, provides a slightly overestimated, but reasonable theoretical prediction, to the highest experimental value. Bearing in mind that porosity levels in the composites were low and comprised mostly of closed porosity, Boccaccini et al. model's [12] can be use to predict the elasticity modulus and estimate a theoretical value by taking into account this factor. Values predicted by this model fall within the minimum and maximum experimental values.

The ultimate tensile strength (UTS) and hardness values were also seen to be related to the infiltrating temperature. Whilst tensile testing evaluates the bulk of the specimens, hardness measurements, performed in confined, pore-free, volumes of the samples, provide an insight into the integrity of the particle–matrix interface which is directly related to the degree of intimate bonding achieved during processing. This aspect, therefore, has to be considered in relation to the mechanical response of the composites, since a good particle/matrix interfacial bonding improves load transfer, increasing stiffness and delaying the onset of particle/matrix de-cohesion. The contact angle in the Mg/TiC system exhibits a strong temperature dependency which is reflected in a reduction in the length of the incubation period and an increase in the infiltration rate when manufacturing at higher temperatures. It also appears to enhance bonding in terms of the work of adhesion, $W_a$ [4,9], as $W_a$ increases when $\theta$ decreases, according to $W_a = \gamma_{lg}(\cos\theta + 1)$, where $\gamma_{lg}$ is the liquid–gas surface tension, giving rise thus to a better mechanical performance, as seen in Table 4.

No necking was observed during tensile testing and no distinct yield point was seen in the stress-strain plots, suggesting that the composites failed rapidly after yielding. This observation, however, does not necessarily mean that the composites fully lack ductility. Fig. 5 shows SEM fractographs of composites processed at different temperatures. The fracture path is likely to have been dictated by the residual porosity, evidence of which is observed in Fig. 5(a). In the fully infiltrated regions, however, particle/matrix de-bonding can be appreciated (Fig. 5b–d), accompanied by scarce formation of micro-dimples. The limited presence of deep-circular cavities can be ascribed to the hcp crystal structure of Mg that restricts slip to the basal plane, forming elongated rather than circular dimples [13]. Furthermore, the slip behaviour of the Mg matrix during deformation is highly constrained by the high content of stiff particles, which in turn, imposes a high triaxiality of stress in the soft matrix [2]. These features indicate that the failure mechanism is related to matrix voiding, de-cohesion of TiC particles and the subsequent growth and coalescence of the corresponding micro-voids, rather than on shearing of the Mg phase impeded

Table 4
Mechanical properties of the Mg/TiC composites

| Temperature (°C) | $E$ (GPa) | $E_{Halpin–Tsai}$ (GPa) | $E_{Boccaccini\ et\ al.}$ (GPa)[a] | UTS (MPa) | Vickers hardness |
|---|---|---|---|---|---|
| 850 | 123 | 138 ($s = 1$) | 123–136 | 172 | 183–191 |
| 900 | 130 | 153 ($s = 1.5$) | 123–137 | 200 | 194–197 |
| 950 | 136 | | 122–135 | 233 | 205–212 |

[a] Aspect ratio of the pores = 1, orientation factor $(\cos^2 \alpha_d) = 0.31$.
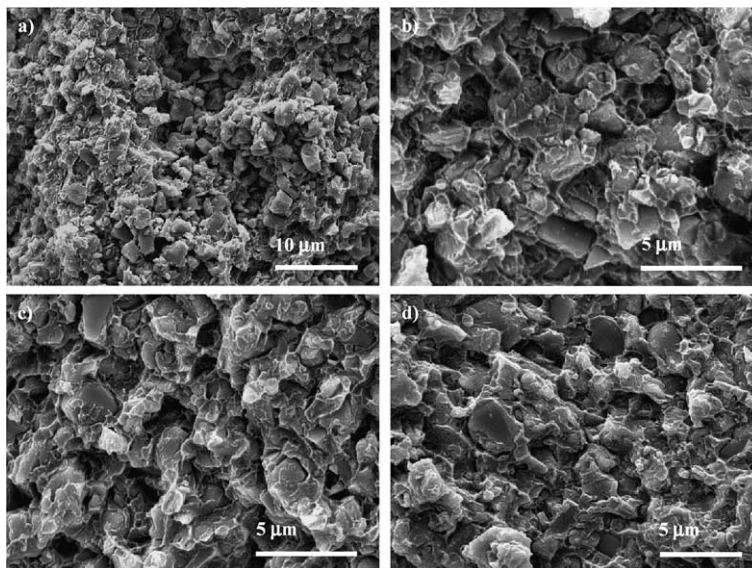
Fig. 5. Fractographs of the composites infiltrated at: (a, c) 900 °C, (b) 850 °C and (d) 950 °C.

by the TiC particles. The later mechanism was seen in Al/58%TiC composites with extensive formation of dimples [14].

A number of fractured TiC particles are also observed, and although most of them are larger than the average particle size, this is an indication of good particle–matrix bonding. TiC breakage is most likely to have been triggered by the presence of micro-cracks on the as-received powders or cracks created during compaction of the preforms. A discrete increase in the number of broken particles was observed when increasing the infiltrating temperature, although, the fracture mechanism was seen to be the same irrespective of this parameter. It is thought that this is due to improved particle/matrix adhesion, achieved at higher infiltrating temperatures.

## 4. Conclusions

Molten Mg was successfully pressurelessly infiltrated into TiC preforms under an inert Ar atmosphere at temperatures ranging between 850 and 950 °C. Composites free from reaction products, with less than 3% porosity, were obtained. Prior to steady-state infiltration, characteristic infiltration profiles exhibited an incubation period, which was temperature dependant and related to the dynamic wetting behaviour previously observed in the Mg/TiC system. High activation energy values suggest that the infiltration process is controlled by an interfacial mass transfer mechanism. The mechanical properties of the composites exhibited a trend to increase with infiltrating temperature, this ten-

dency, was related to the improved wetting achieved when manufacturing at higher temperatures. Matrix voiding and interfacial de-cohesion followed by growth and coalescence of the corresponding micro-voids was found to be the failure mechanism.

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