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Characterization of the reactivity in Al-10wt.%TiC metal matrix composites by image analysis

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Abstract

A metal matrix composite was made by the addition of 10 wt.% of angular $TiC_{0.96}$ particles, $D_{50} = 18$ μm, to molten Al (99.9 wt.%). In order to evaluate the stability of TiC particles in Al at high temperatures, composite samples were placed in a pre-heated furnace, held for 48 hours between 600 ℃ and 1000 ℃ and air quenched. The as-cast and heat-treated samples were polished and imaged in a scanning electron microscope in backscattered mode. Quantitative metallography was performed using image analysis. The segmentation method was applied to samples that showed low reactivity, i.e. those exhibiting only TiC, Al and Al_4C_3. In highly reacted samples, a noise deconvolution method enabled reliable measurements of the TiC and Al_3Ti phases, which overlap in the gray level histogram. After a normalizing procedure, area fraction measurements showed that TiC reacts slowly in solid state and the reaction increases in liquid state with temperature to a maximum at 725 ℃. At higher temperatures, the reaction mechanism is different and it results mainly in the formation of Al_4C_3 suggesting that TiC is partially stable.

Key words: metal matrix composites, image analysis, microstructure, reactivity

1. Introduction

Metal matrix composites (MMC's) are attractive engineering materials that combine the ductility of "soft" metals with the stiffness and hardness of ceramic reinforcements. The reinforcement can vary in type and amount, thus leading to tailored physical and mechanical properties, unachievable by the single components. Due to its lightness, Al and its alloys are popular matrices for incorporating ceramic reinforcements; the result is MMC's with high specific strengths.

For Al matrices, non-expensive ceramics such as Al_2O_3 and SiC have been preferred as reinforcements [1]. Wettability and reactivity aspects are, however, major concerns during manufacturing and in the mechanical performance of the product. Good affinity between the liquid and the reinforcement in terms of wetting means an intimate bonding and no or limited reaction between both phases leads to a sound interface. A good interplay of both aspects guarantees an efficient transmission of the load across the interface, from the matrix to the reinforcement, enabling the mechanical response to be optimized. Whilst Al poorly wets Al_2O_3, SiC is readily degraded in Al melts, forming brittle and hydroscopic Al_4C_3 at the reinforcement-matrix interface. High silicon contents in the matrix are required to suppress the reaction [2–5].

More recently, attention has been turned to using TiC as a reinforcement for Al [6–9]. In addition to desirable physical and mechanical properties, TiC is an attractive reinforcement for Al, due to good wettability and epitaxy between the two phases [10, 11]. This results in strong interfacial bonding [8] and the resulting composites show larger increases in strength and stiffness than corresponding SiC additions [6].

Reaction is also observed in the Al-TiC system, and in this case the reaction products are $TiAl_3$ and Al_4C_3. The rate of reaction in the pure metal system

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*Corresponding author: tel./fax: (52) 443 3168355; e-mail address: composito@yahoo.com is, however, much slower and holding periods of over 48 hours are required for appreciable dissolution of the reinforcing phase at 700 ℃ [12], as opposed to 1 hour for a similar dissolution level of SiC at the same temperature [3]. TiC particles, unlike SiC, are stable in molten Al at higher temperatures. There are, however, discrepancies in the literature over the exact temperature above which TiC is stable, with values ranging between 693 and 1177 ℃ [5, 12–16]. The present study seeks to establish, from an experimental approach, the thermal conditions under which TiC particles of known stoichiometry are stable in pure Al melts. The knowledge gained from this study will enable optimization of the processing conditions of Al-TiC composites.

2. Experimental details

2.1. Materials and heat treatment

TiC particles were used, with a mean size of 18 µm, and, according to the specifications of the supplier (Kennametal, Latrobe, USA), a chemical composition, $TiC_{0.96}$. A metal matrix composite was made by the addition of 10 wt.% of these angular TiC particles to molten Al (99.9 wt.%) with the assistance of a K-Al-F flux [17]. The TiC particles were in contact with the melt, which was held at 780 ℃, for no more than 10 minutes before being cast into a 10 mm diameter steel mould. The casting was then divided into 10 mm long sections for experimental use.

In order to evaluate the stability of the TiC particles in Al at high temperatures, composite samples, resting on boron nitride-coated Al_2O_3 substrates, were placed in a pre-heated furnace and heat-treated at temperatures between 600 ℃ and 1000 ℃ for 48 hours. The heat treatment temperatures were accurate to ±4 ℃. After heat treatment the samples were removed from the furnace and allowed to cool to ambient temperature. Even after heat treatment at the highest temperature, the samples solidified in less than 1 minute.

2.2. Microstructural characterization

The as-cast and heat-treated samples were sectioned and samples were taken for metallography. Preparation for metallography was performed by mounting the samples in conductive bakelite, grinding on 240, 400, 800 and 1200 grit SiC papers, followed by polishing down to 1 µm. Throughout this procedure, the use of water was omitted in order to avoid the removal of any Al_4C_3 that might have been present.

A Jeol 6400 SEM operating at 10 kV was used in backscattered mode for metallographical examination of the samples. Energy dispersive X-ray analysis (EDX) was used to identify and calculate the approximate compositions of the reaction products in the heat-treated specimens. X-ray diffraction (XRD) analysis was performed on flat mirror-like polished samples, using a Siemens D500 diffractometer, with Cu Kα radiation, between 2θ angles of 20° and 140° at a scanning rate of 0.01°/s with a dwell time of 3 s. The traces were compared with standard spectra from powder diffraction files in order to identify the phases present in the as-cast and heat-treated samples.

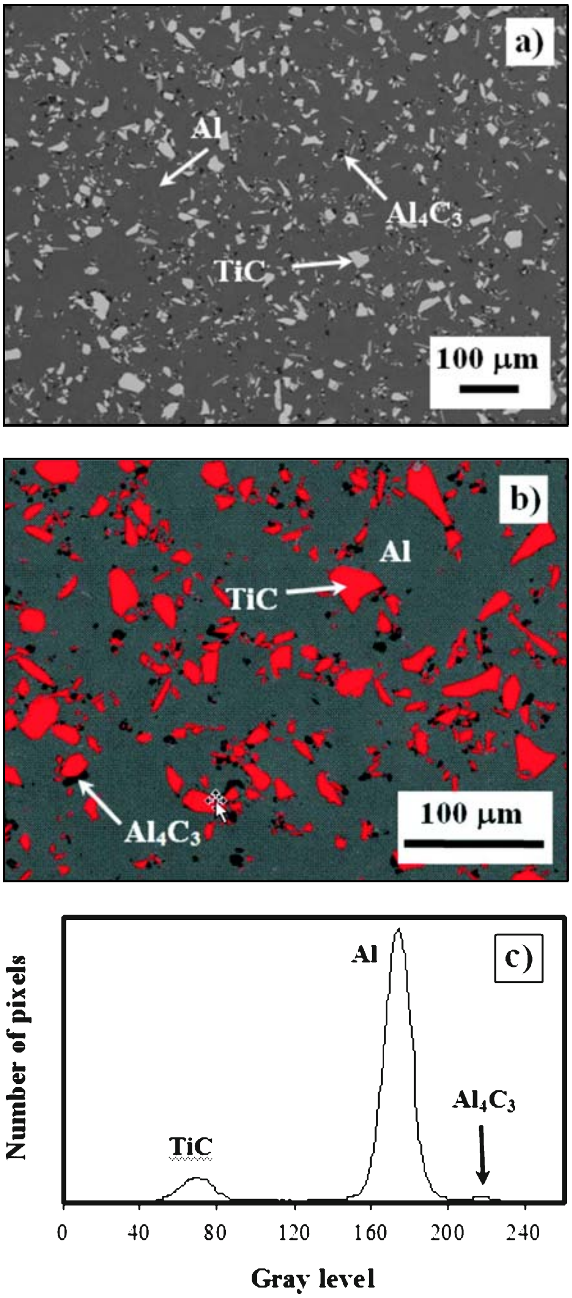


Fig. 1. a) Backscattered electron image of a sample held at 800 ℃ for 48 hours, b) segmentation of the TiC phase and c) histogram of the image.

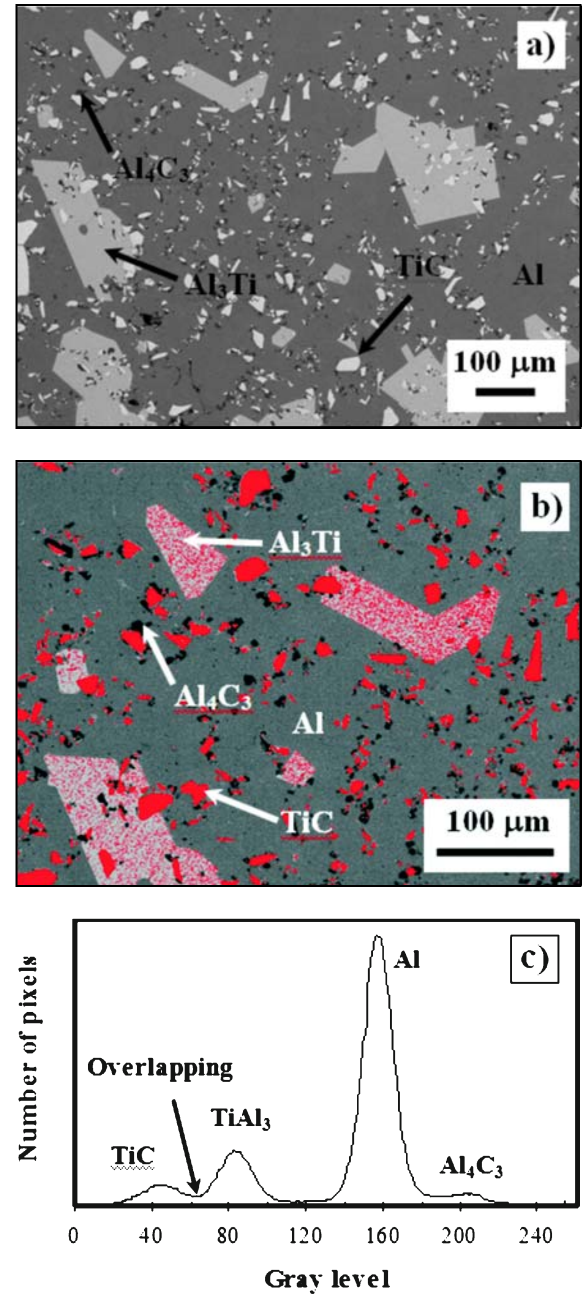


Fig. 2. a) Backscattered electron image of a sample held at 725 °C for 48 hours, b) segmentation of the TiC phase and c) histogram of the image.

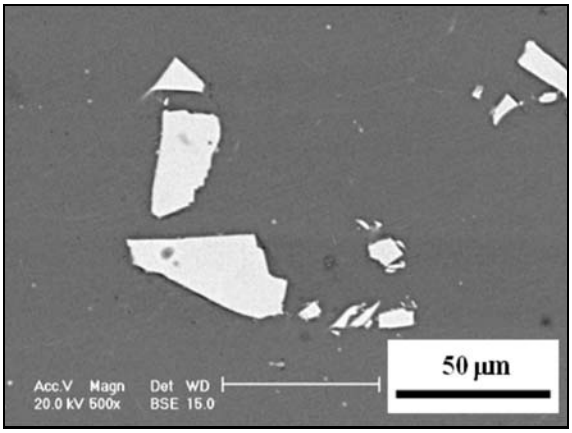


Fig. 3. Microstructural detail of the TiC particles embedded in the Al matrix for the as-cast composite.

2.3. Quantification of phases

Digital images of the microstructures of the samples were captured in backscattered mode. Quantitative metallography was performed, using Scion Image analysis software by highlighting the phases present, individually, and measuring the percentage area within the field of analysis. This technique, known as the segmentation or threshold method, was applied to samples that showed low reactivity, i.e. those exhibiting only TiC, Al and Al_4C_3 as shown in Fig. 1a. Figure 1b illustrates the thresholding process for the phases which is facilitated by the fact that the distribution of gray levels for the distinct phases does not overlap, as can be appreciated in the histogram shown in Fig. 1c.

In highly reacted samples, however, it was not possible to accurately separate the gray levels for TiC and Al_3Ti. Figure 2a shows an example for this microstructure and Fig. 2b clearly shows that thresholding the different phases would lead to erroneous quantifications. The histogram presented in Fig. 2c clearly shows overlapping in the gray level distribution for the phases present. To enable reliable measurements for these microstructures, a recently developed deconvolution method was employed [18]. This method involves separating the individual contributions of each phase to the gray-level histogram, assuming the range of gray levels for a given phase follows a Gaussian distribution. The individual contributions can be determined by knowing the mean gray level and standard distribution for each phase. These parameters are acquired from the image itself and thus after a best fitting iteration process the area fraction of each phase can be determined.

For both methods, representative quantification demanded the use of 6 images at 100 times magnification, analysing a total area of approximately 4.8 mm^2. In order to standardize the quantification procedure, the SEM operating parameters were kept constant.

3. Results

3.1. As-cast material

The TiC particles were reasonably evenly distributed in the as-cast MMC. Figure 3 shows the as-cast microstructure of the Al-10wt.%TiC composite. The

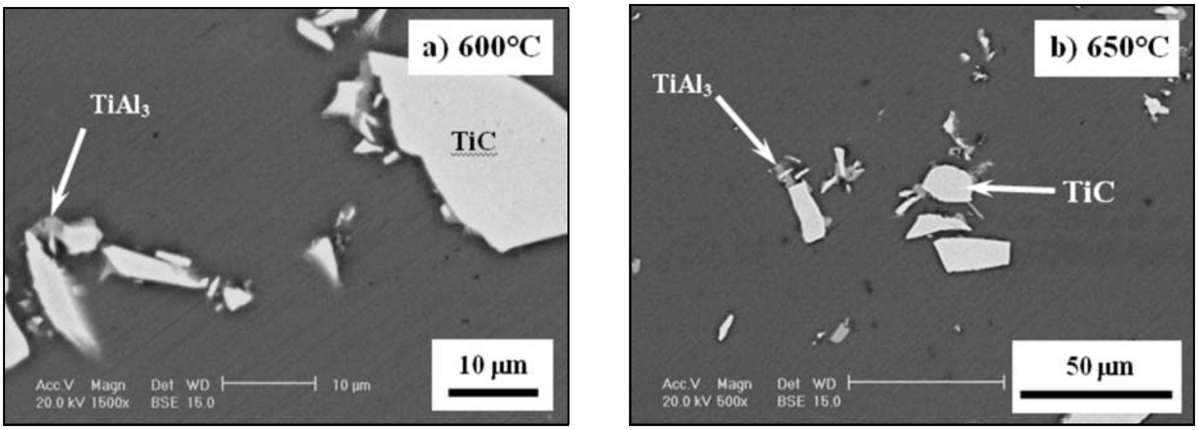


Fig. 4. SEM micrographs of composites held for 48 hours at: a) 600 ℃ and b) 650 ℃.

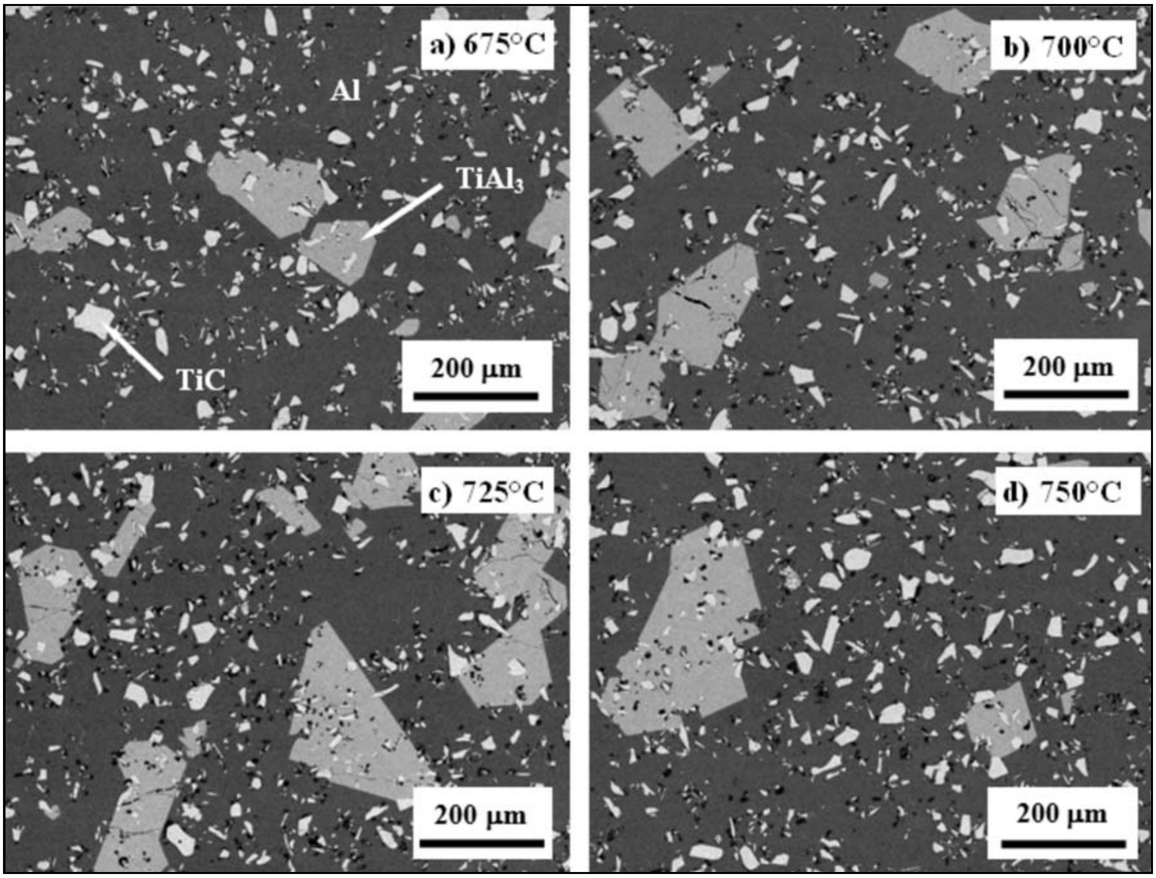


Fig. 5. SEM microstructures of composites held for 48 hours between 675 ℃ and 750 ℃.

micrograph indicates that after processing at 760 ℃ for 10 minutes followed by reasonably rapid cooling during casting, there is no evidence of reaction products either in the bulk of the matrix or at the interfaces.

3.2. Microstructures of the heat-treated samples

Figure 4 shows backscattered SEM micrographs of samples heat-treated in solid state for 48 hours. As shown in Fig. 4a, high magnifications were required to observe a light phase forming on the surface of the particle at 600 ℃, whilst at 650 ℃ the presence of this phase is more evident and vestiges of a black phase can also be seen.

Figure 5 shows that heat-treating in liquid state between 675 ℃ to 750 ℃ results in extensive reaction. Large and angular blocky shapes of the light phase are observed throughout the samples accompanied by

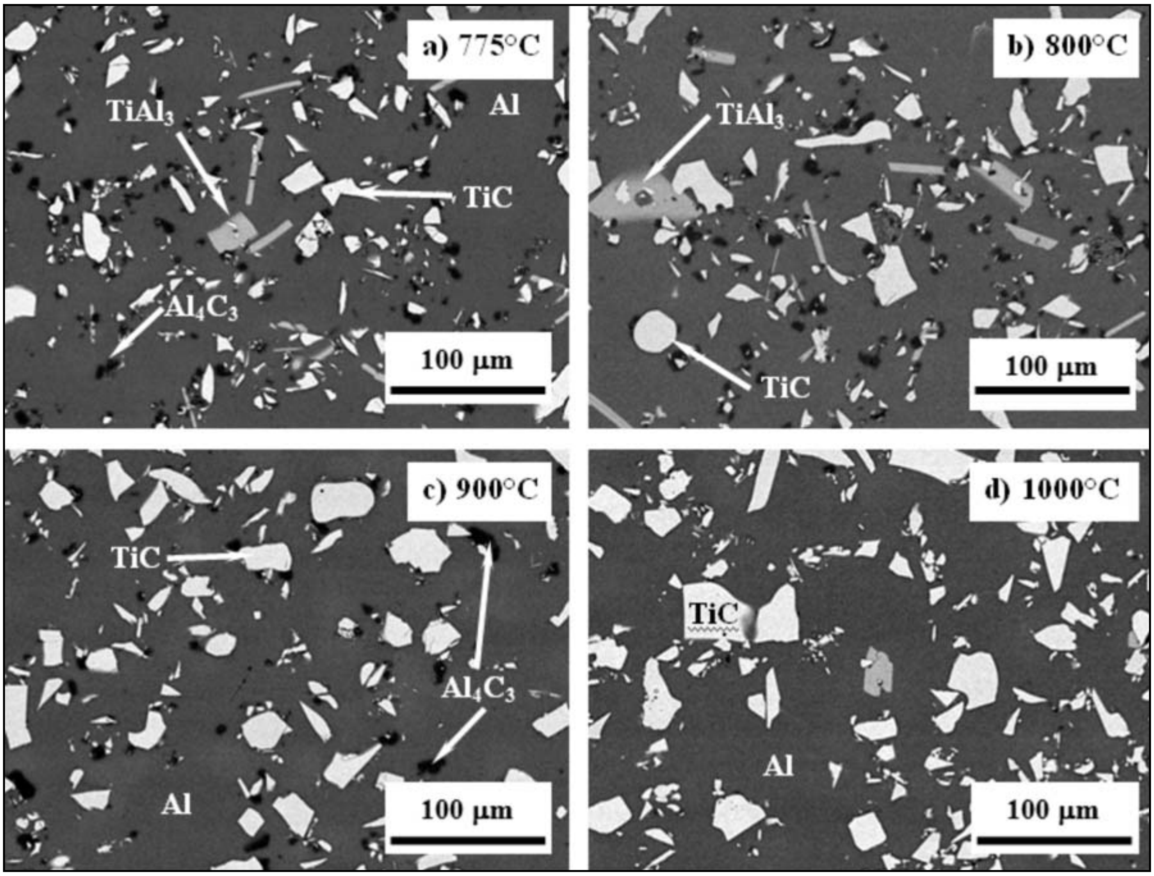


Fig. 6. Microstructures of Al-TiC composites held for 48 hours between 775 ℃ and 1000 ℃.

a smaller, black reaction phase that is associated with the TiC particles, precipitating at the particle-matrix interface. According to EDX analysis, as expected, the light and black phases were identified as Al_3Ti and Al_4C_3. The formation of blocky Al_3Ti intermetallics in the melt means that the maximum solubility of Ti in Al has been exceeded at the corresponding temperatures. Increased levels of the reaction products can be appreciated up to 725 ℃.

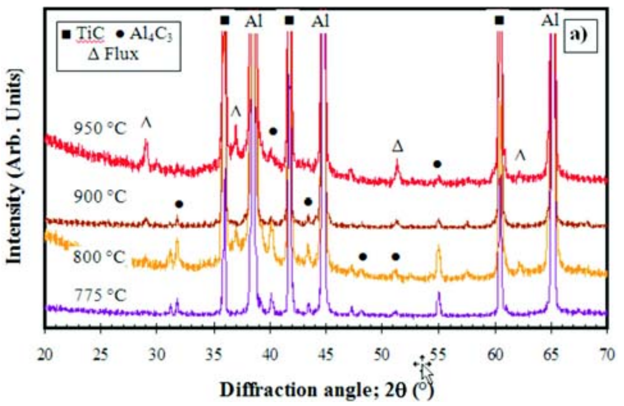
Figure 6 shows that after holding between 775 ℃ to 850 ℃, the large blocky intermetallics have not formed. Instead, scarce small blocks and a needle-like phase, with a small aspect ratio, are now observed. The presence of small Al_3Ti blocks suggests that the solubility limits of Ti in Al are just exceeded in the 775–850 ℃ interval after a 48 h hold. Al_4C_3 is, however, still formed in appreciable levels. At 900 ℃ and above, very few aluminides were observed and although Al_4C_3 was still present at 900 ℃ and 950 ℃, very little was observed at 1000 ℃, as is evident in Fig. 6d.

Progressive reaction of the composites was also investigated using XRD. The results are shown in Fig. 7. The patterns for the samples at 600 ℃ and 650 ℃ were found to be similar to that for the as-cast material, in which only the reflections corresponding to Al and TiC were present, indicating that the low level of reaction observed in the SEM is well below the resolution limit of the XRD instrument, approximately 1–2 wt.%. Between 675 ℃ to 750 ℃, the presence of Al_3Ti and Al_4C_3 is clearly confirmed.

A quantitative analysis of the phases present cannot be obtained from these XRD patterns since preferential orientations were observed throughout the samples for a number of reflections. High intensities for diffraction peaks corresponding to Al_3Ti were seen for the sample heat treated at 750 ℃ for 2θ angles higher than the interval shown in Fig. 7. Above 750 ℃, reflections for Al_3Ti were not present, indicating that the levels of intermetallics observed in the SEM are below the detection limit of the instrument. At 775 ℃ and 800 ℃ Al_4C_3 peaks are clearly exhibited and at 900 ℃ and 950 ℃ Al_4C_3 peaks are barely detectable. In some of the heat-treated samples, XRD analysis showed the presence of residual flux from the composite manufacturing method.

3.3. Quantification of phases

Quantitative image analysis of the phases present is shown in Table 1. There are clearly some inconsistencies in the measured volume fractions as some of



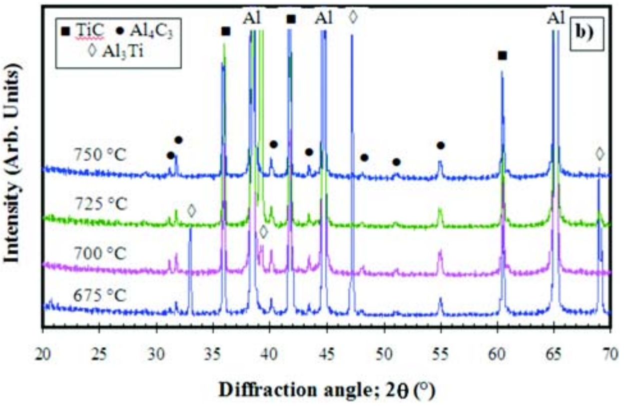


Fig. 7. XRD patterns for the Al-10wt.%TiC composites heat-treated between: a) 950 °C and 775 °C and b) 750 °C and 675 °C for 48 hours.

Table 1. Concentration of phases as measured by image analysis (vol.%)

Temperature (°C)	TiC	Al_4C_3	Al_3Ti
As-cast	1.9725	0	0
600	1.5611	0	0
650	1.6334	0	0.3479
675	8.4062	1.5110	4.0424
700	7.5684	2.1531	7.0641
725	7.3805	3.3090	10.0244
750	8.5126	2.9849	5.1288
775	10.4172	3.0907	0.4027
800	11.4072	2.3507	0.4204
850	11.2307	1.9853	0.3316
900	11.3826	1.7793	0.0938
950	10.5945	1.5459	0.0514
1000	17.8249	0.2604	0.1359

Table 2. Normalized concentration of phases present as measured by image analysis

Temperature (°C)	$\frac{TiC_{[t]}}{TiC_{[0]}}$	$\frac{Al_4C_{3[t]}}{TiC_{[0]}}$	$\frac{Al_3Ti_{[t]}}{TiC_{[0]}}$
As-cast	1	0	0
600	1	0	0
650	0.9646	0.0467	0.2054
675	0.88028	0.1582	0.4233
700	0.8228	0.2340	0.7680
725	0.7467	0.3347	1.0142
750	0.7903	0.2771	0.4761
775	0.8166	0.2422	0.0315
800	0.8651	0.1782	0.0318
850	0.8820	0.1559	0.0260
900	0.8942	0.1397	0.0073
950	0.9005	0.1314	0.0043
1000	0.9890	0.0144	0.0075

them are above those in the starting composite, 0.06. These deviations are due to variations in volume fraction in the starting samples and due to sedimentation effects whilst holding. A normalising procedure was carried out to eliminate these discrepancies. The procedure assumes that the reaction occurring is:

$$13/3\mathrm{Al} + \mathrm{TiC} = \mathrm{Al_3Ti} + 1/3\mathrm{Al_4C_3}, \qquad (1)$$

thus, all the reacting carbon forms Al_4C_3, which is not unreasonable as the solubility of C in Al is very low, i.e. 1.3×10^{-3} ppm at 660 °C and 8.8 ppm at 982 °C [19–21]. By knowing the masses of TiC and Al_4C_3 at any time, t, the initial amount of stoichiometric TiC before reaction, $TiC_{[0]}$, can be calculated from:

$$\mathrm{TiC}_{[0]} = \mathrm{TiC}_{[t]} + 1.25\ \mathrm{Al_4C}_{3[t]}. \qquad (2)$$

Equation (2) can be converted to a more convenient expression, in terms of the volume fractions, by substituting the densities of TiC and Al_4C_3. In this case the constant becomes 0.7566. Thus the quantity of TiC present can be expressed as a ratio of that present at any time, t, compared to the original quantity, $TiC_{[t]}/TiC_{[0]}$.

The normalized data are presented in Table 2. Figure 8a plots the fraction of TiC particles remaining after each heat treatment, that is the ratio of TiC in the sample to that present at $t = 0$. It is clear that from 650 °C onwards, a consistent reduction in the fraction of TiC particles remaining can be observed until a minimum is reached at 725 °C. Beyond this point, and up to 800 °C, the fraction of TiC reacted decreases sharply and then steadily to about 90 % at 950 °C. At 1000 °C the fraction of TiC remaining is close to unity.

The ratios of reaction product quantities to initial TiC concentration are depicted in Fig. 8b. Using the density of TiC, Al_3Ti and Al_4C_3 (4.91, 3.357 and 2.972 g cm^{-3}, respectively), the mass fraction of reaction products has been normalized with regard to the corresponding initial concentration of titanium

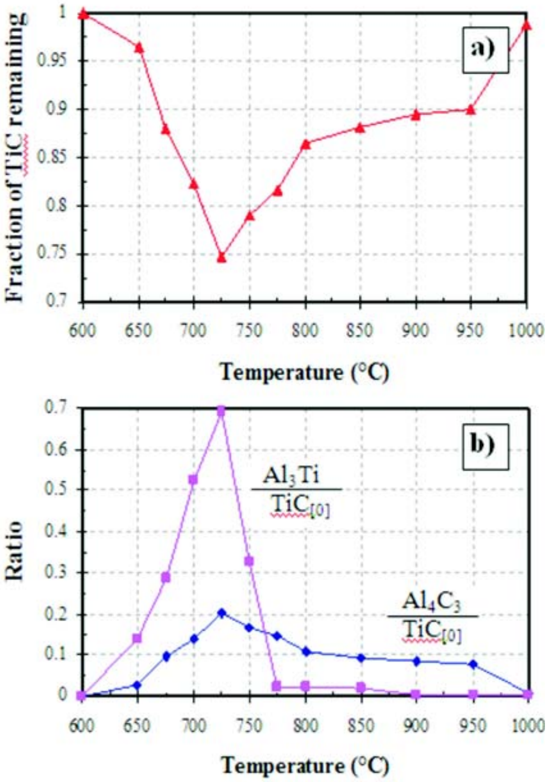


Fig. 8. Quantitative progression of reaction: a) fraction of TiC remaining and b) ratios of reaction products to initial TiC concentration.

carbide, $TiC_{[0]}$. Generally speaking, the concentration of the reaction products is inversely proportional to the fraction of TiC remaining. This trend is not, however, followed by Al_3Ti from 750 °C to 950 °C; instead, the intermetallic phase is present well below the level expected at 750 °C to nearly disappear at 775 °C and above.

It is worth noting that after heat-treating in the solid state, although some reaction was observed in the SEM, XRD did not detect the presence of new phases. This indicates that the reaction products are present in quantities below the limit of detection of the instrument, approximately 1–2 wt.%. Similarly, for composites heat-treated between 675 °C and 750 °C the quantities of Al_4C_3 and Al_3Ti present are above, and between 775 °C and 950 °C Al_3Ti is below the level of detection by this technique. The results from quantitative metallography agree well with these observations indicating that it, and the normalising procedure, are reliable methods for quantifying the progression of the reaction.

4. Discussion

Samples of an Al-10wt.%TiC composite, in the as-cast condition, without visible signs of reaction, were heat-treated between 600 °C and 1000 °C and solidified quickly so that their high temperature microstructures were retained. After heat-treating the composites for 48 hours, at 600 °C and 650 °C, in the solid state, very slight signs of reaction were observed. Although extremely slow, it is known that reaction occurs in the solid state [22–24] and holds up to 496 hours at 640 °C are needed to produce significant contents of reaction products [24]. In the fully liquid state noticeable levels of reaction were measured, increasing with holding temperature up to 725 °C, where the highest degradation of the TiC particles was observed. Previously [5, 25], a maximum in reactivity was observed in the liquid-state at 750 °C, in close agreement with the present study, where TiC decomposes to form Al_4C_3 and Al_3Ti.

According to thermodynamics, an invariant four-phase equilibrium between Al, Al_4C_3, Al_3Ti, and TiC exists, at 693 °C [26], 754 °C and 797 °C [13], and 812 °C [25], according to different authors. Frage et al. [26] proposed that heat-treating stoichiometric TiC at 727 °C resulted in C depletion from the TiC_x structure until $x = 0.885$. In this study Al_4C_3 and large blocks of Al_3Ti were present up to 750 °C and indeed, Al_4C_3 and small blocks of Al_3Ti were still found at 800 °C, meaning that the findings of the present work match more closely the temperatures predicted in references [13] and [25] for the invariant transformation.

In the present study, however, TiC was seen to be partially stable above 775 °C and Al_4C_3 was the main product of the reaction, being present in low and decreasing levels as the heat-treating temperatures increased, suggesting that reaction is taking place albeit reasonably slowly. The absence of large or small intermetallic blocks in the microstructure suggests that the solubility limits are not exceeded during holding at temperature and that the needle-like intermetallics observed were formed during cooling.

Based on the experimental evidence presented in this study, it can be postulated that TiC particles are not stable in molten Al at temperatures below 775 °C and react according to the following mechanism:

$$3TiC + 13Al(l) \rightarrow Al_4C_3 + 3TiAl_3 \,. \tag{3}$$

It was previously reported [5], and corroborated in the present work, that the decomposition of TiC in molten Al did not regularly increase with temperature, after reaching a maximum, it decreased. This behaviour is due to the invariant transformation [5, 27]. The rate of reaction was slower at 750 °C than at 725 °C, but still, significant volumes of Al_3Ti were found. Increasing the heat-treating temperatures further showed only the presence of Al_4C_3 in decreasing levels. This behaviour suggests a different mechanism of reaction at higher temperatures. The reaction kinetics and mechanism will be dealt with, in detail, in a subsequent manuscript.

5. Conclusions

The reactivity in Al-10wt.%TiC metal matrix composites was studied by holding samples for 48 h at temperatures between 600 ℃ to 1000 ℃ and image analysis was used as a reliable tool to measure the extent of reaction. Experimental findings revealed that TiC reacts slowly in solid state and the reaction increases in liquid state with temperature to a maximum at 725 ℃. At higher temperatures, the reaction slows down. Between 800 ℃ and 1000 ℃, the dissolution of TiC yields only Al_4C_3 at decreasing levels, as the temperature increases. This suggests that the dissolution mechanism at temperatures higher than 775 ℃ is different to that at lower temperatures and it results mainly in the formation of Al_4C_3.

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