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Synthesis of Al -TiC in-situ composites: Effect of processing temperature and Ti:C ratio

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Abstract

Al-TiC insitu composites are gaining increasing importance because of good wettability of TiC with Al melt and its favourable properties. However, incomplete reaction between the released Ti and C in Al melt leads to formation of undesirable phases like Al_3Ti which is detrimental to the properties. In this investigation, Al-TiC composites are processed at different temperatures from 700 °C to 1200 °C and with different Ti:C ratios to asses the effect of these two parameters on the formation of TiC particles. Microstructural features and X-ray diffraction results show that at temperatures below 1000 °C blocky type Al_3Ti forms. As the temperature is increased the blocky nature of Al_3Ti changes to needle like indicating release of Ti to a greater extent and as a result more and more TiC particles form. At 1200 °C there is no evidence of Al_3Ti formation after a reaction time of 30 minutes. Increasing the carbon content (Ti:C ratio) to two fold of the stoichimetric amount does not show any significant effect. Though a four fold increase in carbon content showed some promise, however, some amount of free carbon was found to remain.

1. Introduction

Metal matrix composites (MMCs) have gained wide acceptance because of their attractive properties such as high specific strength, stiffness, better wear resistance and improved elevated temperature properties compared to the conventional metals and alloys. Amongst metal matrix composites, discontinuously reinforced aluminium matrix composites (DRAMCs) have gained wide acceptance in past three decades due to their high specific strength and stiffness and improved wear resistance [1-4]. A number of processing routes have been developed for the manufacture of particle/ whisker/short fiber reinforced composites. Liquid metallurgy route is one of the most commonly applied techniques to manufacture particle reinforced composites. In this method reinforcement particles are introduced to the liquid metal ex-situ. The major difficulties in these processes are inhomogeneous distribution (clustering) and improper wetting of particles which lead to poor mechanical properties. This can be avoided if the reinforcement is produced in situ during processing. The in situ process involves synthesis of composites such that the desirable reinforcement(s) and the interfaces are formed during processing [5-7]. The resultant composites generally exhibit the presence of uniform distribution of reinforcement that tends to be fine and associated with a clean interface with the metallic matrix. It also gives rise to improved wettability and strong bonds between the reinforcement and the metallic matrix [8-10]. TiC is an attractive reinforcement for particulate composites because of its high elastic modulus and hardness. Furthermore, TiC particles also acts as nucleation sites during solidification and thus refines the grain size. This led to the development of Al-Ti-C master alloys for grain refinement of Al alloys [11-14]

The reaction kinteics for formation of TiC particles insitu in the Al melt depends on various factors like temperature, reaction time, Ti:C ratio. However, systemic studies on the effects of these parameters on formation TiC particles are limited. The aim of the present investigation is to process Al-TiC composites in situ and evaluate the effect of processing temperature and Ti:C ratio on the reaction kinetics of TiC formation. The processed composites are characterized for their microstructure and mechanical properties.

2. Materials and methods

Commercially pure aluminium was chosen as the matrix material. In order to form the TiC particles in-situ, K_2TiF_6 salt (CDH, India) and graphite powder (Lobachemie, India) of average particle size 50 μm was used. In the first set of experiments, required amounts of K_2TiF_6 salt and graphite powders were mixed corresponding to 5 wt.% of TiC. Commercially pure Al powder (SRL, India) of -325 mesh size was added to this mixture and thoroughly mixed in a plastic jar. Carbon content was kept at 1.3 times the stoichiometric amount to supplement the losses due to oxidation of graphite. Four samples of the powder blend was heated separately in a resistance-heated furnace under argon atmosphere and held at four different temperatures, 700, 800, 900 and 1000°C for 30 minutes. In each case the molten sample was quenched in water to freeze the microstructure. In the second set of experiments, Ti:C ratio was varied from 1.3 times the stoichiometric amount of carbon to four times the stoichiometric amount at 1000°C. Based on the out put of these experiments, Al-TiC composite was processed at 1200°C. K_2TiF_6 and graphite powders were mixed thoroughly and compacted in to pellets. Commercially pure Al was melted in a resistance-heated furnace and the K_2TiF_6 and graphite pellets were added with the help of a plunger. The reaction time in this case was also 30 minutes. The spent salt was decanted before pouring and the melt was cast in pre-heated cast irons molds. Sliced samples of composites were polished with emery paper up to 400 grit size, followed by polishing with Al_2O_3 suspension on velvet cloth. Finally samples were polished with 0.5 micron diamond paste. Kellers reagent was used as the etchant. Microstructural characterization was done using scanning electron microscope (SEM) and optical microscope. X-ray diffraction was carried out using Cu K_α radiation for confirming the formation of TiC particles and other phase analysis. The mechanical properties of the Al-TiC composite were evaluated by hardness and compressive tests. Microhardness of the composites was measured using a Vickers micohardness tester (WILSON WOLPERT). A load of 1 kgf and a dwell time of nine seconds was used. Room temperature compressive tests were carried out on an Instron machine at a strain rate of 10^{-3} sec^{-1} using standard ASTM cylindrical samples with an aspect ratio of 1.2.

3. Results and discussions

3.1 Effect of temperature

Figure 1 shows the optical micrographs of the Al-TiC composites processed at different temperatures. At the lowest temperature used here (700°C), there is no sign of formation of TiC and only blocky type Al_3Ti particles are observed (Fig. 1 a). Similar observation can be made at 800°C also (Fig. 1 b). When the temperature was increased to 900°C, the blocky Al_3Ti particles are converted to needle shape and TiC particles start appearing at the grain boundaries (Fig. 1 c). This is also supported by the XRD results (Fig. 2) which show TiC peaks for 900°C sample but not for 700 and 800°C. These observations also provide some insights in to the reaction mechanism of TiC formation. K_2TiF_6 reacts with Al to form Al_3Ti according to the following reaction

$$3K_2TiF_6 + 4Al \rightarrow 3Ti + 3KAlF_4 + K_3AlF_6 \qquad (1)$$

$$Ti + 3Al \rightarrow Al_3Ti \qquad (2)$$

K_2TiF_6 is reduced by Al releasing Ti which dissolves in the Al and precipitates out as Al_3Ti as soon as its solubility limit is exceeded. This is also supported by the presence of peaks corresponding to $KAlF_4$ and K_3AlF_6 in the XRD pattern of 700°C sample. When the reaction temperature was increased to 800°C, the powder blend densified by liquid phase sintering and $KAlF_4$ and K_3AlF_6 salts generated by reaction (1) play a key role in the sintering process by cleaning the oxide layer from Al powders. Hence the XRD pattern (Fig. 2b) of the sample processed at 800°C is mainly dominated by Al_3Ti peaks while peaks of $KAlF_4$ and K_3AlF_6 are absent. As the processing temperature is increased to 900°C, the blocky shaped Al_3Ti turns in to needles and at the same time fine TiC particles appear at the grain boundaries. This indicates that at higher temperature Al_3Ti becomes unstable and Ti dissolves and wets the graphite particles to form TiC. The XRD spectrum of the 900°C (Fig. 2c) sample

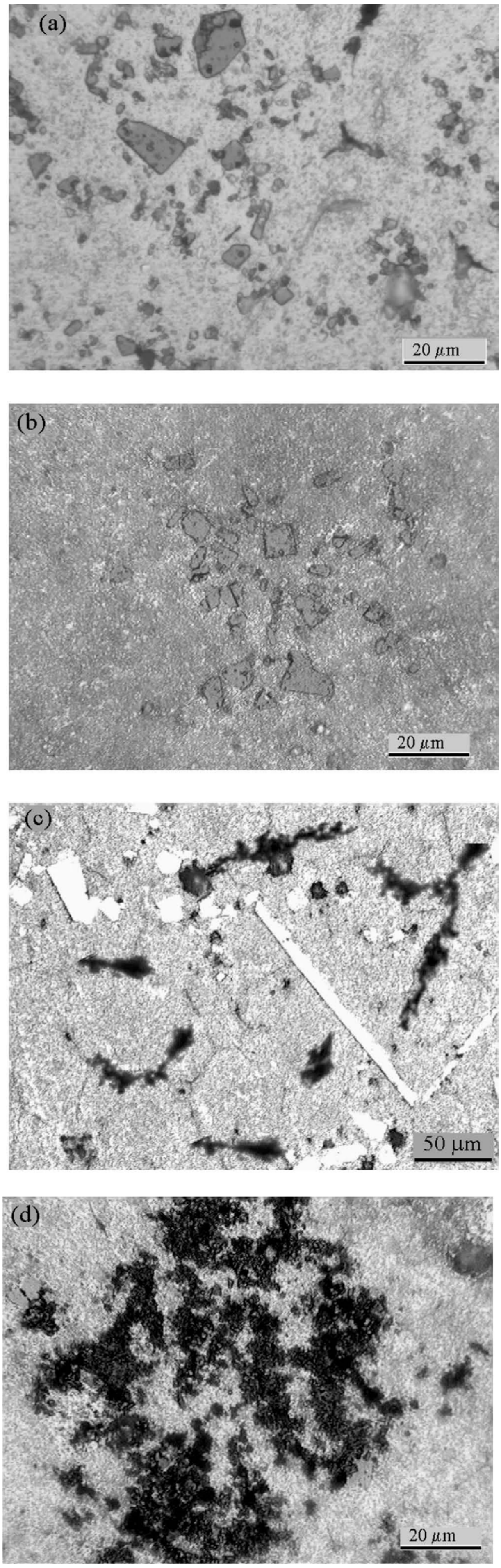

Fig. 1 : Optical micrographs of powder blends processed at (a) 700°C (b) 800°C (c) 900°C (d) 1000°C.

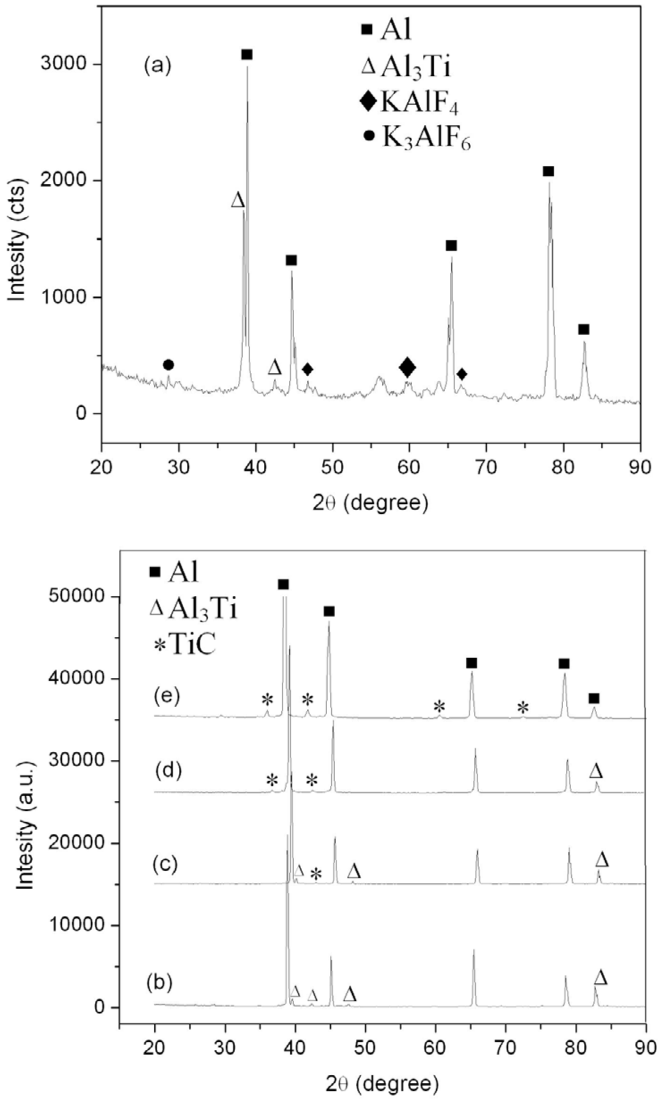

Fig. 2 : XRD plots of powder blends processed at (a) 700°C (b) 800°C (c) 900°C (d) 1000°C. (e) XRD plot of the composite processed at 1200°C.

also shows presence of TiC peaks while the intensity of Al_3Ti peaks reduces. The following reaction seems to be responsible for conversion of Al_3Ti to TiC.

$$Al_3Ti + C \rightarrow TiC + 3Al \quad (3)$$

However, in a recent study [15] it was shown that reaction (3) is not viable in the temperature range where Al_3Ti co-exist in the Al melt with graphite. TiC starts forming only when Al_3Ti dissolves in the melt with increasing temperature [15]. Therefore, the formation mechanism of TiC particles seems to be direct combination of Ti, which is released by the dissolution of Al_3Ti, to graphite.

$$Ti + C \rightarrow TiC \quad (4)$$

This is also supported by the optical micrograph of the powder blend processed at 1000°C (Fig. 1 d). It shows that TiC particles form at the Al-Al_3Ti interface where the dissolved Ti is available. At 1000°C more and more TiC particles form and as a result TiC peaks increases and Al_3Ti peaks decreases in the XRD spectrum (Fig. 2d). Since few Al_3Ti particles still remains even at 1000 °C, it was imperative to think of increasing the amount carbon at this temperature to see if Ti entirely diffuse to carbon dissolving Al_3Ti completely. The effect of carbon content (Ti:C ratio) is discussed in the next section.

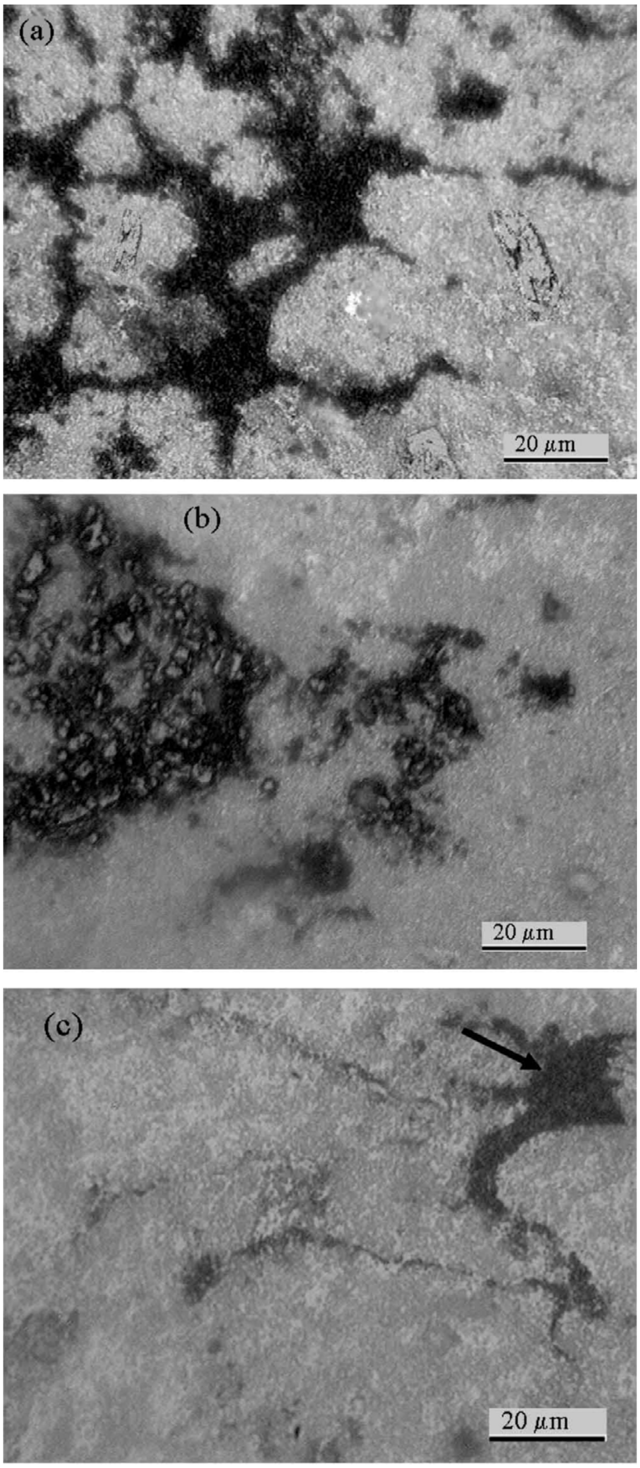

Fig. 3 : Optical micrographs of samples with different Ti:C ratio (a) 1.3C (b) 2C (c) 4C.

3.2 Effect of Ti:C ratio

Three different carbon content in amounts of 1.3C (1.3 times the stoichiometry), 2C (double the stoichiometry) and 4C (four times the stoichiometry) were used to vary Ti:C ratio in the powder blends. The effect of the varying Ti:C ratio is analyzed in the light of microstructure (Fig. 3) and XRD analysis (Fig. 4). Optical micrographs in Fig. 3 (a), (b) and (c)

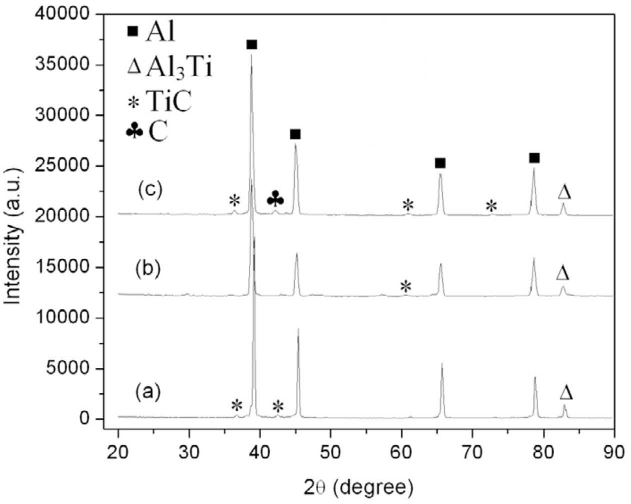

Fig. 4 : XRD plots of samples with different Ti:C ratio (a) 1.3C (b) 2C (c) 4C.

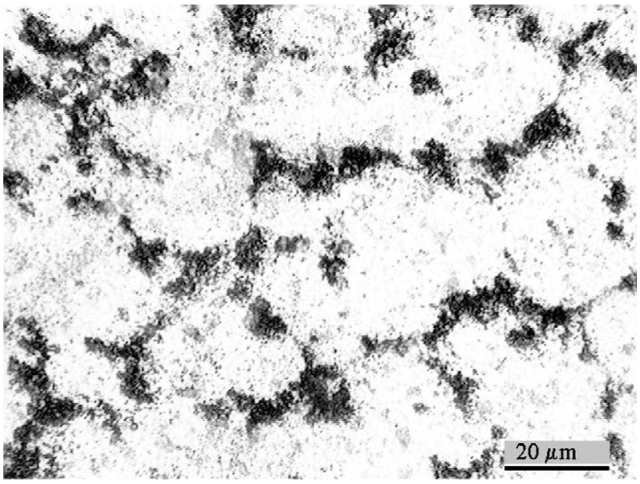

Fig. 5 : Optical micrograph of the Al-TiC composite processed in Al melt at 1200°C.

show the microstructure of 1.3C, 2C and 4C samples respectively. It can be seen that 1.3C sample produces the best results in terms of formation and distribution of TiC particles. On the other hand, although the intensities of Al-TiC peaks were little higher in the 4C sample, however, some amount of free carbon was observed (arrow in Fig. 3d) along with TiC particles due to the excess carbon which did not react. This is also supported by the XRD analysis (Fig. 4).

Based on these observations, an Al-TiC composite was processed at 1200°C with 1.3C carbon and 30 minutes of reaction time. This composite was used to investigate the effect of TiC particulates on mechanical properties. Optical micrograph of this composite in Fig. 5 shows no sign of Al_3Ti particles. The SEM micrograph in Fig. 6 (a) also shows uniform distribution of TiC particles and the EDXA taken on one such particle confirms these particles to be TiC (Fig. 6b). This is also supported by the XRD plot of the composite (Fig. 2e). It can be noted that the Al peaks of the samples processed from Al powder (Fig. 2 b–d) are shifted from corresponding peak in the melt-processed Al-TiC composite (Fig. 2e). This can be attributed to the residual stresses developed due to quenching of the powder samples to freeze the microstructure. The surface of the sample cools with a much higher cooling rate due to quenching compared to the interior. As a result tensile stresses are developed at the surface and interior is subjected to compressive stresses.

In summary, it can be said that a Ti:C ratio close to 4:1 and a processing temperature of 1200°C are required to obtain Al-TiC composites without Al_3Ti intermettalics. This is in agreement with previous studies which used liquid metallurgy route to process Al-TiC master alloys and composites [12,15,16,17].

3.3 Mechanical properties

3.3.1 Microhardness

Table 1 shows the microhardness values of unreinforced Al and Al-5wt%TiC composite. The composite shows higher hardness than the base metal. The matrix of composites contains higher dislocation density as a result of dislocations generation due to large difference in thermal expansion coefficient between the matrix and reinforcement [18-21]. This leads to higher hardness in the composites. Presence TiC particles refines the grain size and thus finer grain size in the composite also leads to higher hardness.

Table 1 : Vickers hardness values (HV_1) and 0.2% proof stress (compressive) of pure Al and Al-5%TiC composite.

Material	*Hardness (HV_1)*	*0.2% Proof stress (MPa)*
Pure aluminum	24	42
Al-5%TiC	37	75

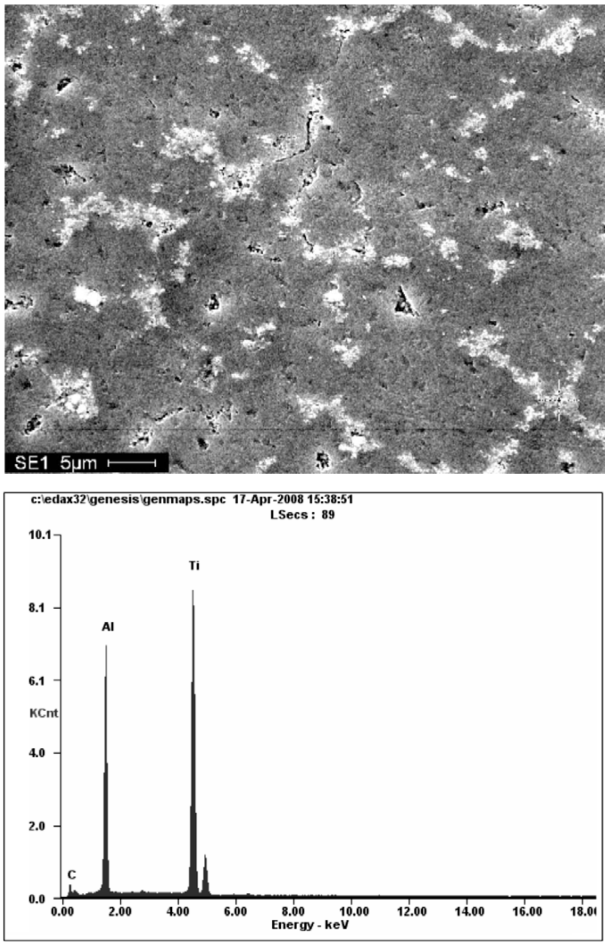

Fig. 6 : (a) SEM micrograph of the Al-TiC composite processed at 1200°C showing uniform distribution of TiC particles. (b) EDAX taken on one such particle.

3.3.2 Compressive strength

Results of compressive test are also summarized in Table 1. It can be seen that the composite exhibits higher 0.2% proof stress compared to the unreinforced base metal. Main strengthening in composites comes from effective transfer of load from the matrix to the reinforcement via the interface. Therefore the interfacial bonding between the particle and matrix must be strong. As described above, the insitu composites generally have good bonding between the reinforcement and the matrix due to generation of interfaces during the process itself. This gives rise to higher strength in the Al-TiC composite. The higher dislocation density and resistance to dislocation motion by the TiC particles are also responsible for the higher strength in the composite.

4. Conclusions

The effect of processing temperature and Ti:C ratio on the reaction kinetics of TiC formation in Al was investigated. A processing temperature of 1200°C is required for complete dissolution of Al_3Ti particles and completion of reaction between released Ti and C. Ti:C ratio of 4:1.3 (1.3C carbon) yields the best result in terms of formation and distribution of TiC particles. The processed Al-5wt%TiC composite shows higher hardness and 0.2% proof stress (compressive) compared to the unreinforced pure Al.

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