

In situ processing of TiC_p-Al composites by reacting graphite with Al-Ti melts

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Aluminum has been a key material, particularly in the aerospace and automotive industries, owing to its low density, high specific strength, good corrosion resistance and recyclability. Aluminum based metal matrix composites have also become attractive candidates for various applications where monolithic aluminum alloys cannot meet the strict design requirements. Recently, particulate reinforced aluminum composites have attracted a great deal of attention. Among various techniques which have been employed in the synthesis of these composites, incorporation of the reinforcing phase particles directly into the melt is practical and economic; yet it is not trouble-free. *In situ* processing of particulate reinforced composites, on the other hand, yields superior microstructures and thus better properties. In the present work, such a method to manufacture TiC_p-Al composites and the microstructures obtained thereof will be described. © 1999 Kluwer Academic Publishers

1. Introduction

In spite of a very attractive combination of properties, aluminum alloys can not meet the strict design requirements imposed by some advanced technology applications. When 'low density' is a critical issue for such applications, aluminum-based composites are the best alternative to be considered by design engineers. Among them, particulate-reinforced aluminum composites which provide only a modest improvement over the monolithic alloys, have nevertheless attracted a great deal of attention recently, owing to very reasonable processing costs, easy implementation and characteristic isotropic behavior.

The reinforcing phases are generally ceramic particles, namely carbides [1–3], nitrides [4] and oxides [5–8]. Particle sizes range from only a couple of microns to a millimeter and volume fractions up to 40% have been reported [9]. A variety of processing techniques have been employed to produce particulate-reinforced aluminum composites [10]. Yet, with the exception of a few, they fall within two broad categories: Solid-state (Powder Metallurgy Processing) and Liquid-state (Solidification Processing) methods. While the attributes of the former have long been recognized, the powder metallurgy methods are more expensive, more complicated and pose serious health and safety hazards as they involve handling of very fine metal/ceramic powders. Solidification processing, on the other hand, is particularly attractive as it is economical and practical. It can be easily implemented in the majority of the aluminum foundries and can be incorporated with the near-net shape casting technologies such as squeeze casting, die casting, etc.

Solidification processing is carried out in practice generally by direct introduction of the reinforcing phase particles into aluminum melts by mechanical means. A variety of techniques have been proposed to achieve a uniform distribution [11]. Mixing, however, is not always straightforward as the ceramic particles are poorly wet by aluminum melts. Hence, either the ceramic particles or the aluminum melts ought to be treated to promote wetting. These pre-treatments increase the manufacturing steps involved as well as the cost of processing. Furthermore, since the ceramic particles are usually not in equilibrium with aluminum, there is a potential risk of interface reactions which yield undesirable products at processing temperatures and lead to a substantial degradation of properties.

Many of the problems encountered in solidification processing of particulate-reinforced aluminum composites can be circumvented by an alternative approach which relies upon the *in situ* formation of reinforcing phase particles in aluminum melts [12]. Since the reinforcing phase so generated is thermodynamically stable, the matrix-particle interfaces tend to be clean, free from adsorbed gases, oxide films and detrimental reaction products and are thus much stronger.

The present work was undertaken to establish a simple method to manufacture TiC_p-reinforced aluminum composites by the *in situ* processing route. The emphasis was placed on the simplicity and the applicability aspects of the proposed method. Al-5Ti melts were reacted with graphite under favorable conditions and the microstructures obtained thereof were characterized.

2. Experimental procedures

2.1. Description of the method

Simply stated, the present method was designed to establish a chemical reaction between the titanium dissolved in molten aluminum and solid carbon which was introduced into the melt in the form of graphite. An Al-5Ti-0.2B alloy was used as the source of titanium as the carbide former and the aluminum matrix. This alloy is widely used in aluminum foundries in rod form and is the low-boron grade of tiber grain refiners which is very popular in the production of foil stock. Its microstructure typically consists of coarse Al_3Ti intermetallics and some tiny TiB_2 particles of only a couple of microns.

The tiber rods were induction melted in a silicon carbide crucible. A graphite susceptor was used to achieve an efficient melting. The melt was superheated to 1150°C at a rate of $10^\circ\text{C}/\text{min}$, to aid the dissolution of the Al_3Ti particles and to promote wetting of graphite by the Al-Ti melt. Once the temperature of the melt was fixed at 1150°C , a specially designed rotor manufactured from porous graphite was immersed into the melt. It was fixed to a motor-driven shaft, also made of graphite. The speed of the shaft could be adjusted precisely in the range 50–400 rpm. Caution was exercised to perfect the eccentricity of the shaft so as to avoid formation of vortexes and disturbance at the melt surface. The surface of the melt was covered with a thick layer of a high melting-point salt flux in order to protect the melt from oxidation. The flux was replenished occasionally to compensate for the amount lost as a result of burning. The rotor shaft was treated with a special coating at the melt line to avoid excessive burning. The rotor was rotated inside the melt at 100 rpm throughout the experiment. The stirring action provided by induction melting and the rotating graphite shaft ensured continuous exposure of unreacted Ti to carbon. A schematic drawing of the experimental set-up used for *in situ* processing of TiC_p -Al composites is given in Fig. 1. The operation was terminated after 60 min and the melt was skimmed and thoroughly mixed with graphite rods. Then it was poured into a permanent mold and squeezed into rectangular plates with a plunger.

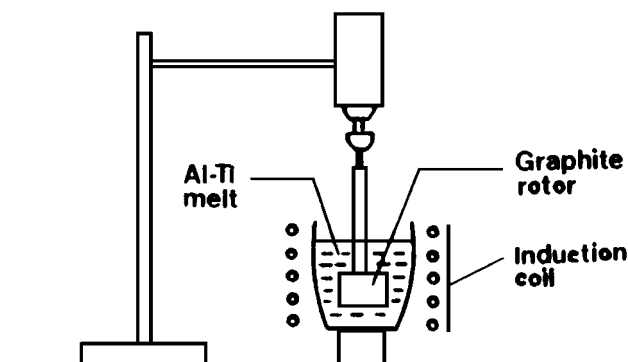


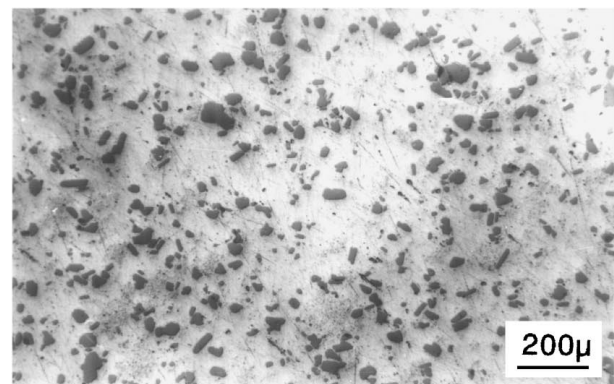
Figure 1 A sketch of the experimental set-up used for *in situ* processing of TiC_p -Al composites.

2.2. Characterization of microstructures

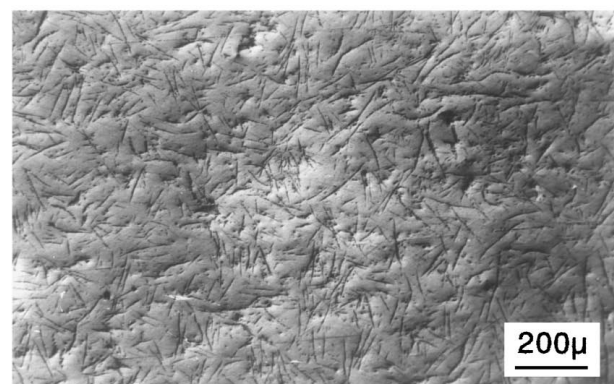
Samples of approximately 10 grams were taken from the melt at the start and in the course of processing and then quenched. The analysis of these samples proved very useful in identifying the phase structure of the melt and the reactions in progress. The squeeze-cast rectangular plates were sectioned and mechanically polished together with the samples taken in the course of the experiment. They were examined with a Reichert MeF_2 optical microscope and a JEOL JSM 840 scanning electron microscope equipped with Energy Dispersive Spectroscopy (EDS). Phase identification was possible in most cases, in the as-polished condition. However, samples for optical microscopy were lightly etched with a 0.5% HF solution to improve contrast when necessary. X-Ray Diffraction (XRD) patterns were also obtained using a Phillips Diffractometer equipped with $\text{CuK}\alpha$ radiation.

3. Results and discussion

The as-received Al-5Ti-0.2B alloy reveals a homogeneous distribution of coarse Al_3Ti intermetallics with nearly equiaxed morphologies and very few tiny TiB_2 particles (Fig. 2a). On the other hand, the microstructure of the sample which was quenched from the melt at 1150°C , right before *in situ* processing has started, shows some distinctly different



(a)



(b)

Figure 2 The microstructure of the Al-5Ti-0.2B alloy (a) as-received and (b) as-quenched from the melt at 1150°C .

features (Fig. 2b). Al_3Ti particles in this sample are no longer equiaxed but instead acicular. They must have decomposed completely by the end of the heating cycle and have apparently recrystallized in the form of coarse needles upon quenching. Also worth noting in this sample is the lack of TiB_2 particles. It is assumed that the TiB_2 particles have agglomerated and were then removed from the melt possibly by settling at the bottom of the crucible. The tendency of TiB_2 particles to agglomerate and to form clusters after long holding times is well established [13]. It is fair to conclude from these observations that the melt was essentially a binary Al-Ti liquid solution at the start of *in situ* processing.

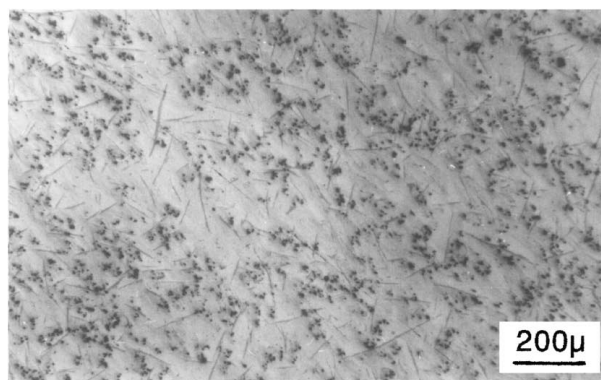
The microstructures of samples quenched from the melt at the start and in the course of processing and that of the rectangular plate squeeze-cast at the end of this operation are illustrated in Fig. 3. After 10 minutes of processing, one can see, in addition to sharp Al_3Ti needles which appear light gray in optical micrographs, a number of TiC particles which are much darker (Fig. 3b). These TiC particles are very small, generally less than $3\ \mu\text{m}$ in size while the Al_3Ti needles are up to several hundred microns long. It appears that TiC starts to form soon after graphite is introduced into the melt, thanks to a very good wetting of graphite by Al-Ti melts. It has been reported in a recent work [14] that titanium improves wetting substantially owing to its strong reactivity towards carbon and that wetting of graphite by Al-Ti melts occurs almost immediately at 1150°C .

The number as well as the size of Al_3Ti needles progressively decrease upon further processing suggesting that more and more of the dissolved Ti had been consumed in the formation of TiC , thus depleting the melt of Ti. This is also reflected by an ever increasing population of TiC particles with time. It is claimed that TiC forms by the reaction of dissolved Ti with carbon on the surface of the graphite rotor. This is the only place in the present system where carbon is available since the solubility of carbon in molten aluminum is practically nil. The stirring action provided by magnetic as well as mechanical means ensure continuous exposure of graphite to unreacted Ti. Once nucleated, TiC particles start to grow on the surface of the rotor until they reach a critical size. They are detached from the surface when they can no longer reside on the rotor due to vigorous stirring and are finally dispersed in the melt. Coarsening of the TiC particles dispersed in the melt is highly unlikely due to lack of any dissolved carbon in the melt. Evidence for this claim is available in the metallographic work which showed that the majority of TiC particles were nearly equal in size which remained more or less constant throughout the process. The above argument is a plausible account of the evolution of microstructure in the course of processing.

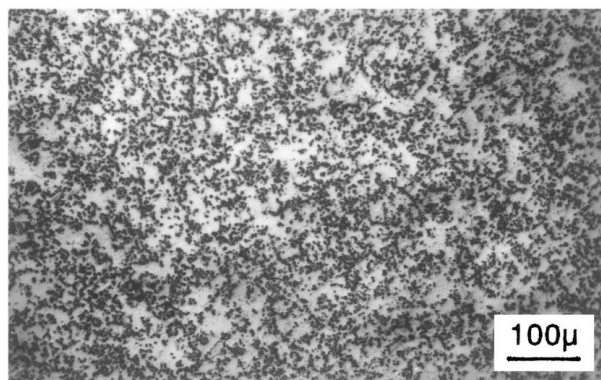
Finally, after 60 minutes of processing, the cross-section of the squeeze-cast plate reveals a uniform distribution of TiC particles inside the $\alpha(\text{Al})$ matrix (Fig. 3c). A couple of very small Al_3Ti particles can also be detected, however, at still higher magnifications (Fig. 4). These particles which were as long as a frac-



(a)



(b)



(c)

Figure 3 Optical micrographs of the samples quenched from the melt (a) before the start, (b) 10 minutes from the start and (c) at the end of *in situ* processing ($t = 60$ minutes).

tion of a millimeter at the start of processing are now reduced nearly to the size of TiC particles.

The optical microscopy work is paralleled by the results of the XRD analysis. The XRD patterns obtained from a series of samples which represent the entire range of processing are illustrated in Fig. 5. The spectrum of the sample quenched from the melt before *in situ* processing has started reveals, in addition to the $\alpha(\text{Al})$ matrix, only the Al_3Ti phase and is almost identical to that of the as-received alloy. Additional peaks

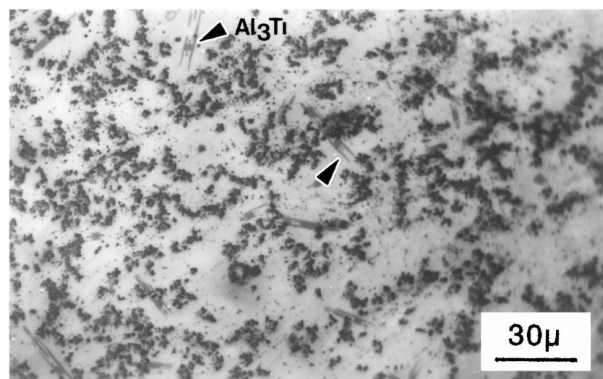


Figure 4 Optical micrograph of the squeeze-cast plate showing Al_3Ti intermetallics in addition to TiC particles.

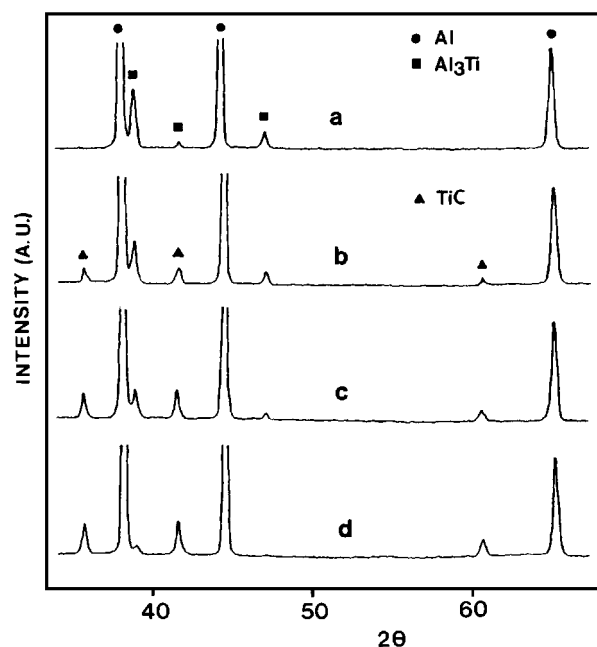


Figure 5 XRD patterns of the samples quenched from the melt at 1150°C (a) before the start, (b) 10 minutes, (c) 40 minutes after the start and (d) of the rectangular plate squeeze-cast at the end of *in situ* processing ($t = 60$ minutes).

which belong to the TiC phase are noted after 10 minutes of processing. TiC peaks become more prominent with time in contrast to those of Al_3Ti . Finally after 60 minutes of processing, Al_3Ti peaks are replaced almost entirely by those of TiC and a two-phase composite with $\alpha(\text{Al})$ and TiC is established.

While there are several binary (Al_4C_3 , TiC) and ternary (Ti_2AlC , Ti_3AlC) carbides which have been reported to be in equilibrium in the Al-Ti-C system [15–18], there was no evidence for those other than TiC under the processing conditions described in the present work. Al_4C_3 , which has been claimed to precipitate out of the melt first when a similar Al-Ti melt was treated with a carbonaceous gas [12], was observed only at longer processing times. It is inferred from the as-quenched microstructures of several melt samples reacted with graphite further ($t > 60$ minutes), that Al_4C_3 starts to form when the melt is nearly saturated with TiC, i.e. when it is almost devoid of Ti. Further evidence showing that TiC is the first phase to form when

Al-Ti melts of similar compositions are allowed to react with carbon has been presented by other investigators as well [14, 19].

Among the binary and ternary carbides of the Al-Ti-C system, TiC is thermodynamically the most stable. This explains why TiC forms first instead of Al_4C_3 . Aluminum starts to react with graphite only when the melt is nearly depleted of Ti. The microstructure of the squeeze-cast plate which is crowded with TiC particles reveals evidence also for some Al_3Ti as well as for some Al_4C_3 suggesting that the precipitation of Al_4C_3 gets underway before complete conversion of Ti into TiC. Hence, it is best from a practical standpoint, to terminate processing before the dissolved Ti is totally consumed in order to avoid the risk of getting some Al_4C_3 in the cast plate. Al_4C_3 is certainly not a desirable constituent in the composite as it is a brittle compound which decomposes readily when exposed to atmospheric moisture. Furthermore, the fluidity of the melt was found to be severely impaired when it was processed into the Al_4C_3 -formation range. Unreacted Ti which crystallizes in the form of Al_3Ti needles upon solidification, on the other hand, can be tolerated when it is present in the melt only in very small quantities (Fig. 4).

4. Summary

When the molten Al-5Ti alloy was allowed to react with bulk graphite at a processing temperature of 1150°C , TiC formed by the reaction of dissolved Ti with graphite at the melt-graphite interface. Once, nucleated, TiC particles grew to a certain size and were detached from the surface of the graphite rotor and were dispersed in the melt. After 60 minutes of processing, the melt was nearly saturated with TiC particles and the operation was terminated at this point before Al_4C_3 started to form. The TiC particles were distributed rather uniformly inside the $\alpha(\text{Al})$ matrix and were generally smaller than $3\ \mu\text{m}$. With the exception of a few Al_4C_3 particles which have formed in the later stages, no carbides other than TiC were revealed in the squeeze-cast plate under the processing conditions described in the present work.

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