

## RESPONSE TO THERMAL EXPOSURE OF THE MECHANICALLY ALLOYED Al-Ti/C POWDERS

Yücel BİROL

Materials and Chemical Technologies Research Institute,  
Marmara Research Center, TÜBİTAK  
Gebze, Kocaeli, TURKEY

**ABSTRACT** Al-5Ti alloy powder was mechanically alloyed with carbon using a Spex 8000 laboratory mill. After 6 h of milling, the structure of the mechanically alloyed powder particles consisted of a more or less homogeneous mixture of Al and C and a very fine dispersion of Al<sub>3</sub>Ti particles. The mechanically alloyed Al-5Ti/C powders were heated in a differential thermal analysis cell under flowing argon in order to establish a chemical reaction between the carbon introduced into the particles and the Al<sub>3</sub>Ti phase. Al<sub>4</sub>C<sub>3</sub> was the first phase to form upon thermal exposure and has later reacted with Al<sub>3</sub>Ti to yield TiC. The latter reaction has started at approximately 850°C (at a heating rate of 20 K min<sup>-1</sup>) and has continued until complete conversion of Al<sub>3</sub>Ti to TiC.

**Keywords:** *TiCp-Al composites, mechanical alloying.*

### 1. INTRODUCTION

Discontinuously reinforced aluminium (DRA) alloys possess a spectrum of advantages with respect to their monolithic counterparts and have received a great deal of attention recently [1,2]. Aluminium alloys reinforced with titanium carbide particles are a prominent example of these hybrid materials which combine the ductility, toughness, electrical and thermal conductivity of the aluminium matrix with the strength, stiffness, hardness and wear resistance of the refractory carbides, leading to a unique combination of properties which cannot be achieved in either of the individual components by alloying and/or thermomechanical processing alone. TiC-reinforced aluminium composites are attractive candidates for a variety of applications, particularly in the automotive sector, as they offer, in addition to favorable mechanical properties, substantial weight savings [3].

A variety of processing techniques have been employed to produce aluminium alloys containing titanium carbide particles. Solidification processing route, which relies on introducing the carbide particles into aluminium melts, is particularly attractive as it is economical and practical; yet, it suffers in practice from the inability of aluminium melts to wet ceramic particles. A compocasting technique was proposed to overcome this difficulty [4]. Many of the problems encountered in solidification processing are overcome by an alternative approach which relies upon the in situ formation of TiC particles in aluminium melts [5-8]. Since titanium carbide particles so generated are 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. One such approach involves the formation of TiC particles by establishing a chemical reaction between a carbon-bearing gas and molten Al-Ti alloy [5] while in others, carbon is introduced into the Al-Ti melt in the form of powder [6] or bulk graphite [7].

Powder Metallurgy (PM) methods were also employed to synthesize TiCp-Al composites [9,10]. The process described in [10] relies on sintering a mixture of carbon particles, aluminium powder and the powder of an aluminium-transition metal intermetallic compound, the transition metal being a refractory carbide former such as titanium. In the present work, carbon was introduced into Al-Ti alloy powders by means of mechanical alloying (MA) and carbide particles were precipitated with a subsequent heat treatment. Preliminary results will be briefly outlined.

## 2. EXPERIMENTAL

Al-5Ti master alloy ingots were ground to powder using a vibratory mill and sieved with an ASTM No. 45 wire mesh screen in order to recover the fraction with a maximum particle size of 35 microns. The Al-5Ti alloy powder thus obtained was dry mechanically alloyed with carbon black in a Spex 8000 laboratory mill using hardened steel vial and balls for a total milling time of 6 hours. The ratio of Al-Ti powder to carbon black, on a weight basis, was approximately 10, substantially more than that required to achieve full conversion of Ti into TiC.

After 6 hours of milling, the mechanically alloyed samples were heat treated in a Setaram Differential Thermal Analysis (DTA) unit under flowing argon at a heating rate of 20 K min<sup>-1</sup>, in order to find out about their response to thermal exposure. The mechanically alloyed and heat treated samples were analyzed with X-Ray Diffraction (XRD) and metallographic techniques. A Shimadzu diffractometer equipped with CuK<sub>α</sub> radiation was used. Samples for metallographic analysis were prepared with conventional procedures and were examined with a Zeiss Axiovert Vario model optical microscope.

## 3. RESULTS & DISCUSSION

The Al<sub>3</sub>Ti intermetallic particles were distributed rather evenly among the Al-5Ti alloy powder particles and were generally smaller than those observed in the master alloy ingot (Fig. 1a). They have apparently undergone fragmentation during grinding, yielding particles of various sizes, some of which were as small as only a couple of microns. The optical micrographs of the Al-5Ti alloy powders revealed many sites where Al<sub>3</sub>Ti particles have fractured during grinding. Upon mechanical alloying with carbon, a layered structure typical of mechanically alloyed powders has formed after fairly short milling times (Fig. 1b,c). This layered structure has developed further, i.e. the layers have become finer, with increasing milling time before it was finally replaced, after 6 hours of milling, by a more or less homogeneous mixture of Al and C with a very fine dispersion of Al<sub>3</sub>Ti intermetallic particles (Fig. 1d). The Al<sub>3</sub>Ti particles have fractured further during the MA process and could hardly be resolved in the majority of the mechanically alloyed powder grains. No evidence for any carbide formation was available after milling for 6 hours.

The mechanically alloyed Al-Ti/C powder thus obtained was heated in order to establish a chemical reaction between the carbon introduced into the powder particles by MA and the Al-Ti intermetallic phase which has been substantially refined during the MA process. The DTA scans of the mechanically alloyed samples revealed, in addition to the endothermic peak associated with the melting of the matrix, two exothermic signals recorded right before and after the melting of the matrix, respectively, and an endothermic signal which starts at approximately 850°C (Fig. 2). The former two are believed to be generated by the same reaction which spreads over a range of temperatures, including that of the melting of the aluminium matrix. The change in the relative

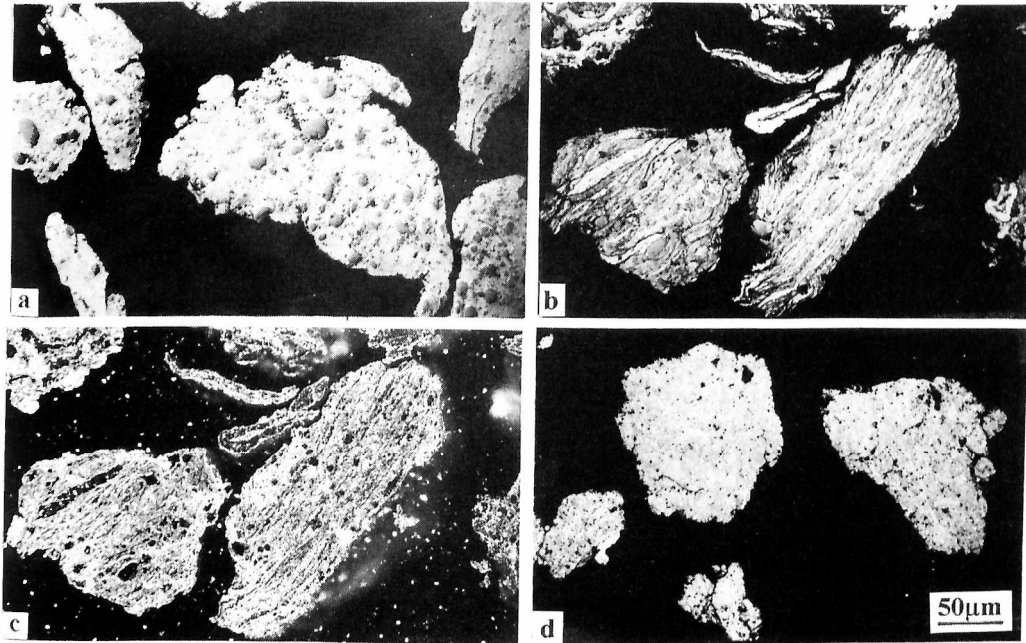


Figure 1. The cross-sections of (a) the ground Al-5Ti alloy powder, (b) bright-field and (c) dark-field optical micrographs of the mechanically alloyed Al-5Ti/C powder milled for 3 h and (d) for 6 h. Note that the  $\text{Al}_3\text{Ti}$  particles can be identified more easily in the dark-field micrographs.

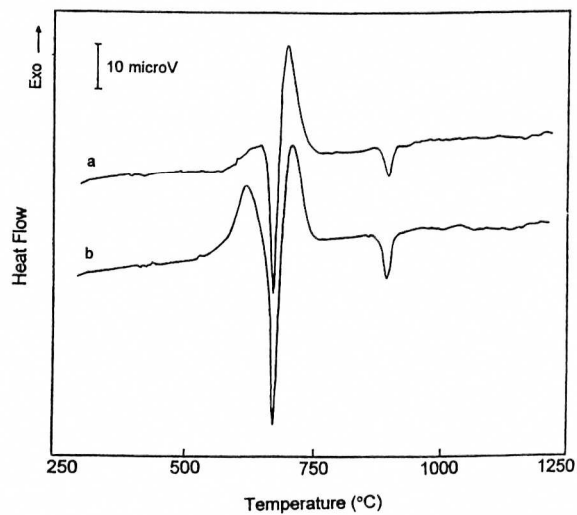


Figure 2. The DTA thermograms of the mechanically alloyed Al-5Ti/C samples milled for (a) 3 h and (b) 6 h, recorded at a heating rate of  $20 \text{ K min}^{-1}$ .

intensities of these two exothermic peaks suggests that this reaction is shifted to lower temperatures with increasing milling time. The endothermic peak at 850°C, on the other hand, seems to be unaffected by the milling history of the sample and has remained undisplaced.

Several MA powder samples were consecutively heated in the DTA cell to the end of each one of these thermal signals and then suddenly quenched. They were then analyzed with XRD and metallographic techniques in order to identify the reactions responsible for these signals. The XRD pattern of the sample heated to 620°C, just before the onset of melting of the aluminium matrix, is illustrated in Fig. 3d and reveals reflections of the  $\text{Al}_4\text{C}_3$  phase in addition to those of aluminium and the  $\text{Al}_3\text{Ti}$  phase. This suggests that the first peak in the DTA scan is generated by the solid-state carburization of the aluminium matrix. The  $\text{Al}_4\text{C}_3$  reflections are quite weak and rather diffuse, suggesting that the amount of precipitation is limited and that the carbide precipitates at this stage are very fine. The carbide precipitation is evident also from the optical micrographs of this sample which shows that the matrix has responded to etching and has developed a darker contrast after the heat treatment (Fig. 4a). The  $\text{Al}_4\text{C}_3$  particles inside the individual powder particles are apparently too small to be resolved at these magnifications.

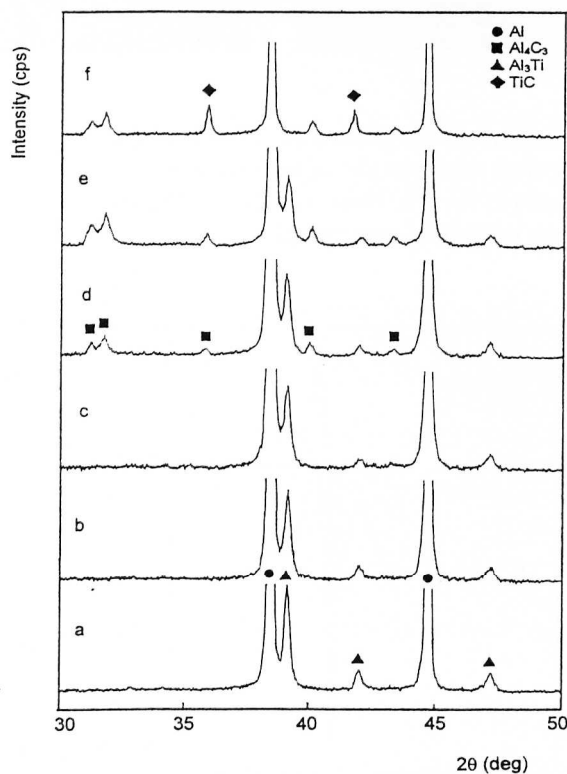


Figure 3. X-ray diffraction patterns of (a) the ground Al-5Ti alloy powder, the mechanically alloyed Al-5Ti/C powder milled for (b) 3 h, (c) 6 h, and of the mechanically alloyed samples heated to (d) 620°C, (e) 750°C and (f) 1000°C at 20 K min<sup>-1</sup> and then quenched.

The  $\text{Al}_4\text{C}_3$  precipitation was accelerated once the aluminium matrix has melted owing to the much higher diffusion rates in the liquid state. After heating the mechanically alloyed powder to  $750^\circ\text{C}$ , to the completion of the exothermic signal, the  $\text{Al}_4\text{C}_3$  reflections have become more prominent (Fig. 3e). The microstructure, on the other hand, has changed very little with the matrix becoming only slightly darker (Fig. 4b). It is still very difficult to identify the individual  $\text{Al}_4\text{C}_3$  particles in the optical micrographs. The  $\text{Al}_3\text{Ti}$  intermetallic phase has survived and no  $\text{TiC}$  has formed in this temperature range as evidenced by the XRD and metallographic work. It is well known from the in situ processing of  $\text{TiC}_p\text{-Al}$  composites that it takes temperatures as high as  $1000^\circ\text{C}$  for the  $\text{TiC}$  to form due to the stability of the  $\text{Al}_3\text{Ti}$  phase which dissolves only above  $1000^\circ\text{C}$  [ ].

The XRD pattern of the mechanically alloyed sample, heated beyond the second endothermic signal, was substantially different (Fig. 3f). Diffraction lines of the  $\text{TiC}$  phase were noted for the first time while those of the  $\text{Al}_3\text{Ti}$  intermetallic phase have vanished. It is also of interest to note that  $\text{Al}_4\text{C}_3$  reflections have somewhat diminished over this temperature range. The  $\text{Al}_3\text{Ti}$  phase was apparently consumed completely and the  $\text{Al}_4\text{C}_3$  phase partially, in a reaction which has produced the  $\text{TiC}$  phase. The reaction of  $\text{Al}_3\text{Ti}$  with  $\text{Al}_4\text{C}_3$ , under favorable conditions, yields  $\text{TiC}$ ; i.e.



and thus provides a plausible account of the observed microstructural changes. The above reaction is endothermic and becomes thermodynamically possible, that is the accompanying free energy change is negative, starting at approximately  $800^\circ\text{C}$ . Considering the peak shift that must have taken place at the heating rate used to obtain the DTA traces in the present work ( $20 \text{ K min}^{-1}$ ), it is fair to state that the onset of the second endothermic signal measured from the DTA scans ( $850^\circ\text{C}$ ) is in

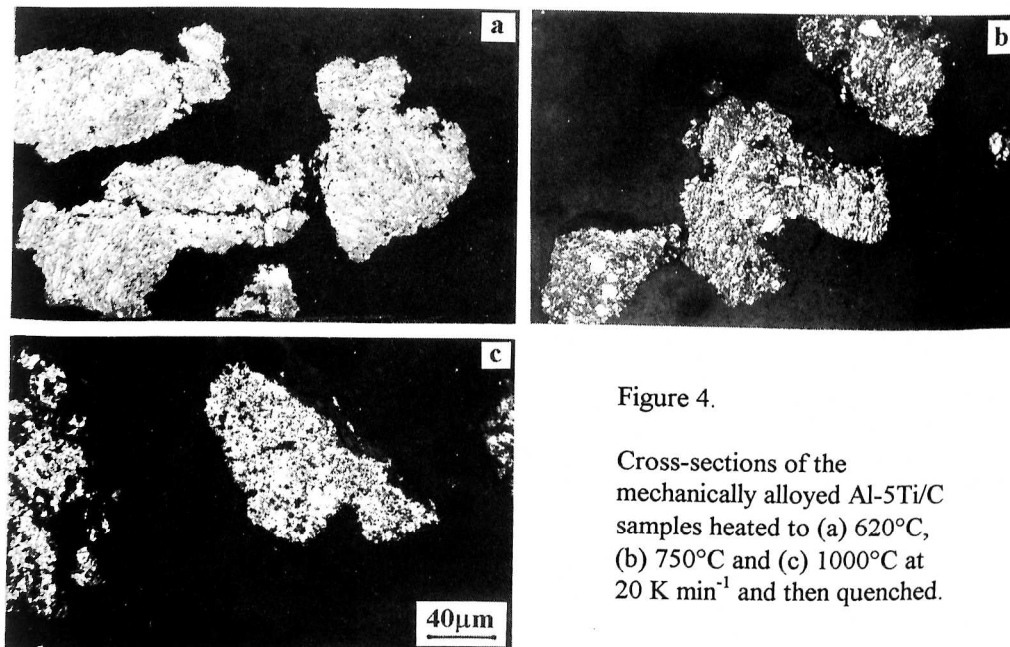


Figure 4.

Cross-sections of the mechanically alloyed Al-5Ti/C samples heated to (a)  $620^\circ\text{C}$ , (b)  $750^\circ\text{C}$  and (c)  $1000^\circ\text{C}$  at  $20 \text{ K min}^{-1}$  and then quenched.

reasonable agreement with that estimated for reaction (1) from the thermodynamic calculations. Since the amount of carbon used in the mechanical alloying experiments was far greater than that required to achieve full conversion of the  $\text{Al}_3\text{Ti}$  phase to  $\text{TiC}$ , a substantial portion of the  $\text{Al}_3\text{Ti}$  which has formed earlier has remained unreacted. The intra-grain structure of the mechanically alloyed sample heated to  $1000^\circ\text{C}$  is illustrated in Fig. 4c. The carbide particles can now be identified inside the powder grains while no evidence for the  $\text{Al}_3\text{Ti}$  intermetallic particles is available.

#### 4. SUMMARY

$\text{Al-5Ti}$  alloy powder was mechanically alloyed with carbon using a Spex 8000 laboratory mill. After fairly short milling times, a layered structure typical of mechanically alloyed powders has formed inside the particles. This layered structure has developed further with increasing milling time before it was finally replaced, after 6 h, by a more or less homogeneous mixture of Al and C and a fine dispersion of  $\text{Al}_3\text{Ti}$  particles. The mechanically alloyed  $\text{Al-5Ti/C}$  powder thus obtained was heated in a DTA cell under flowing argon in order to establish a chemical reaction between the carbon introduced into the particles by MA and the  $\text{Al}_3\text{Ti}$  phase.  $\text{Al}_4\text{C}_3$  was the first phase to form inside the particles upon thermal exposure and was too small to be identified with the optical microscope. The precipitation of  $\text{Al}_4\text{C}_3$  started in the solid state and was accelerated once the aluminium matrix has melted. The  $\text{Al}_4\text{C}_3$  particles have survived until  $850^\circ\text{C}$  where they have started to react with  $\text{Al}_3\text{Ti}$ . A very fine dispersion of  $\text{TiC}$  particles was thus generated inside the powder particles.

#### Acknowledgements

It is a pleasure to thank O. Çakır, O. Arısoy, E. Karabeyoğlu and M. Berk for their help in the experimental part of this work.

#### REFERENCES

1. A. I. Nussbaum, *Light Metal Age*, February (1997), 54.
2. I. A. Ibrahim, F. A. Mohamed and E. J. Lavernia, *J. Mater. Sci.*, 26(1991), 1137
3. P. Rohatgi, *JOM*, 43(1991), 10.
4. A. Sato and R. Mehrabian, *Metall. Trans.*, 7B(1976), 443.
5. S. Khatri and M. Koczak, *Mater. Sci. Engng*, A162(1993), 153.
6. A. Banerji and W. Reif, *Met. Trans.*, 17A(1986), 2127.
7. Y. Birol, submitted to *J. Mater. Sci.*
8. A. Jarfors, H. Fredriksson and L. Froyen, *Mater. Sci. Engng*, A135(1991), 119.
9. G. W. Halldin, Y. He and T. H. Tsai, in *Progress in Powder Metallurgy*, Vol. 38 (eds.) J. G. Bewley and S. W. McGee, Montreal, Quebec, Canada, 24-27 May 1982, p. 593
10. U.S. Patent No. 4,402,744.