# INFLUENCE OF REINFORCEMENT ON THE REACTIVITY LAYER FORMATION IN Ti-Al INTERMETALLICS DISCONTINUOUSLY REINFORCED Al-Cu-Si-Mg ALLOYS

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**SUMMARY:** The effects of type and volume fraction of particulate Ti-Al intermetallic reinforcements on the reaction layer formation in aluminium metal matrix composites (MMCs) was investigated. MMCs were prepared in the laboratory by following a powder metallurgy route and hot extrusion was used as consolidation process. Isothermal heat treatments regarding time were carried out at a fixed temperature of 530ºC and at different times of 1, 6, 12 and 24 hours in order to emphasise the diffusion processes between matrix and reinforcement. Several analysis were performed (SEM, EDX, microhardness) in order to study the development of the reaction layers as well as cycle polarisation test to evaluate the corrosion resistance. Formation of the interphase layers showed an increased reactivity because of the presence of silicon in the matrix. Also, the nature of the reaction layers was influenced by differences in the composition and processing technique of the intermetallics used as reinforcements as well as the volume fraction in the composite. The influence of the reaction layer in the corrosion behaviour of Ti-Al/6061 Al metal matrix composites (MMCs) was evaluated following the variation in the primary passivation potential (Epp) as well as in the pitting potential (Eb). Specimens were examined after exposure to the sodium chloride solution employing scanning electron microscopy and micro pitting corrosion was observed.

**KEYWORDS:** aluminium matrix composite, titanium intermetallics, heat treatment, reactivity layer, interface, interphases, powder metallurgy

## INTRODUCTION

Aluminium matrix composites reinforced with ceramic particles have been the centre of attention of many investigations in the past years. Different reinforcements of this nature have been investigated (comprising oxides, carbides and nitrides), although most of the research done by the scientific community has focused on either alumina ($Al_2O_3$) or silicon carbide (SiC). Today, their overall benefits and limitations are well known and some applications have been manufactured in an production basis [1-5].

Yet, the advances made in high performance materials like intermetallics have open new possibilities of development in the MMC field. Intermetallics have very interesting properties to be used as reinforcements in aluminium based composites: high strength, modulus, and thermal stability [3]. One of the first investigations on this combination was made by Varin [6] and continued by other authors [7-11] but were primarily focused in the use of $Ni_3Al$ intermetallic particles. In a further work by the authors [12] titanium aluminides were presented as a quite promising reinforcement.

On the other hand, aluminium alloys of interest are those with increased strength by means of precipitation hardening. Hardening processes involve the use of relatively high temperatures, mainly in the solution treatment and have an important influence over the matrix-

reinforcement interface [9-12]. It is accepted that for obtaining a sound composite whichever the reinforcement is, the interfacial bond strength between particle and matrix has to be maximised in order to ensure the correct transmission of stresses [6,13,14]. Thus, the aims of the present work is to continue the study on the development of reaction layers at the matrix-reinforcement interface in aluminium matrix composites reinforced with two types of titanium aluminide intermetallics: $Ti_3Al$ and TiAl.

## EXPERIMENTAL PROCEDURE

An Al-Cu-Si-Mg aluminium alloy with the composition 1.0 % Cu, 0.74% Si, 0.19 %Mg and Al bal. was used in this study. This alloy was primarily produced in powder form by ALPOCO (The Aluminium Powder Co., UK) through a gas atomisation process. The powder presented a rounded morphology with a maximum particle size of 75 μm and a mean value of 31 μm.

$Ti_3Al$ and TiAl intermetallics were used as reinforcements. $Ti_3Al$ intermetallics obtained by two different fabrication processes. The first one was based in a hydride-dehydride process which conferred them a polygonal morphology and were produced by Se-Jong Materials (South Korea). The particle size distribution ranged from few microns to a largest particle size of 50 μm. The other $Ti_3Al$ powders together with the TiAl ones were argon atomised, manufactured by Crucible Materials Corp. (USA). This process produced particles of spherical morphology, being screened those of size ranging from 25 to 50 μm. Figure 1 shows a SEM image of the morphology of the intermetallic powders used.

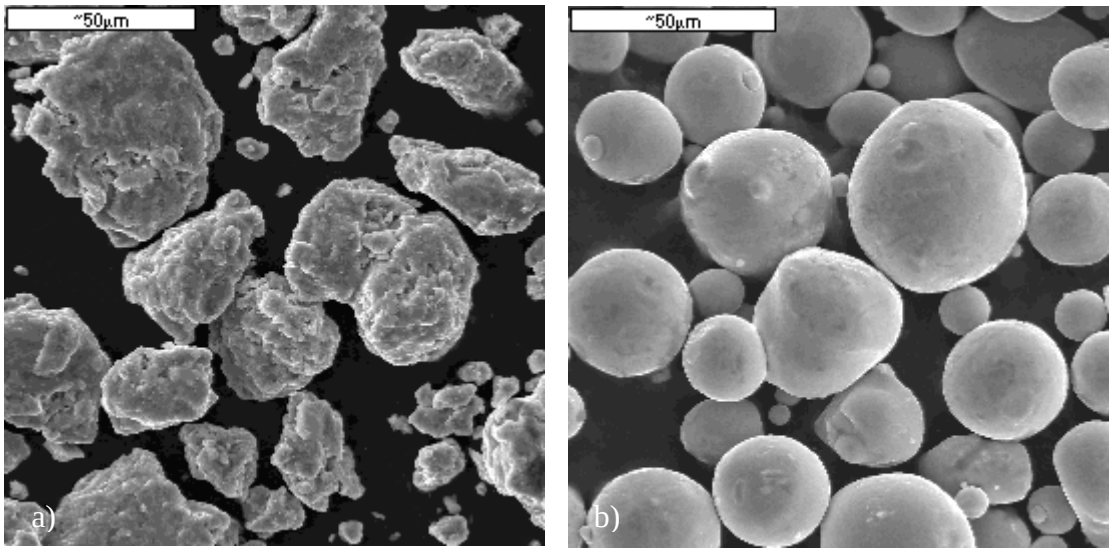


Fig.1 Morphology of intermetallic particulates used as reinforcements in the present study. a) $Ti_3Al$ obtained from the Hydride-Dehydride process. b) $Ti_3Al$ obtained by the argon atomisation process.

The fabrication procedure comprised: mixing of alloy and intermetallic powders, compaction (250 Mpa), graphite lubrication, heating at 500ºC for an hour to homogenise the temperature and extrusion with a ratio of 25:1 and a ram speed of 1 mm/s [7]. At the end of the process, a bar of 5 mm of diameter of MMC was produced. As mentioned earlier, three different reinforcements were used (two diversely produced Ti3Al and a TiAl intermetallic) in two percentages (5 and 10 vol. pct.), for a total of six combinations as follows:

| Denomination | Composites studied |
|---|---|
| A-5%$Ti_3Al$-HD | Al alloy + 5 vol. pct. $Ti_3Al$ hydride-dehydride process |
| A-10%$Ti_3Al$-HD | Al alloy + 10 vol. pct. $Ti_3Al$ hydride-dehydride process |
| A-5%$Ti_3Al$-RST | Al alloy + 5 vol. pct. $Ti_3Al$ gas atomised |
| A-10%$Ti_3Al$-RST | Al alloy + 10 vol. pct. $Ti_3Al$ gas atomised |
| A-5%TiAl-RST | Al alloy + 5 vol. pct. TiAl gas atomised |
| A-10%TiAl-RST | Al alloy + 10 vol. pct. TiAl gas atomised |

The different composites so produced were subjected to isothermal heat treatment at a fixed temperature of 803K (530°C) for different times in order to emphasise the diffusion processes between matrix and reinforcement. The elapsed times selected were 1, 6, 12 and 24 hours. In this study, optical (Nikon Microphot FX) and scanning electron microscopy (JEOL 6300) with X-ray microanalysis (Link Isis EDX) were used to determine the growth and nature of the reaction layer. Also, Vickers microhardness measurements on matrix, reaction layer and reinforcements were made with Matsuzawa MHT2 apparatus, applying a load of 10gf for 15 seconds.

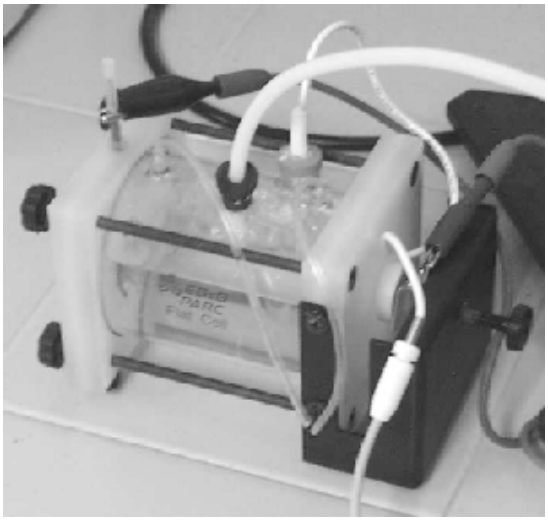

Fig. 2. Corrosion cell for study of cyclic polarisation.

Corrosion tests on heat treated composites were also performed. Samples 2 mm thick and mounted in an epoxy resin with an exposed area of 0.2 $cm^2$, were tested on a 3.5 wt% NaCl solution. Deaerated solution with 25 ml/min of $N_2$ was selected for the potentiodynamic study. The cyclic polarisation curves were obtained using an AgCl/Ag reference electrode and a Pt counter-electrode. Experiments were carried out at an EG&G flat cell (fig. 2) and potentiostat. Further details about these electrochemical measurements are found in [15]. Different potentials were measured: corrosion potential ($E_{c1}$), primary passivation potential ($E_{pp}$) and pitting potential ($E_b$), as well as the amplitude of the passive zone ($E_{pp}$-$E_b$). After testing, samples were washed in an ultrasonic bath to clean the corrosion products.

## RESULTS AND DISCUSSION

The solid state processing technique used for the fabrication of the composites ensured the absence of any kind of reaction layer between any of the intermetallics utilised and the aluminium matrix. This fact facilitates the subsequent analysis on development of the reaction layers during heat treatments. Furthermore, the composites obtained through this method have a quite good quality, with a homogeneous distribution of reinforcements and nearly a total densification.

After heat treatments, a reaction layer was developed at the reinforcement-matrix interface. Figures 3 and 4 show the final appearance of the composites reinforced with $Ti_3Al$ intermetallics after a heat treatment of 24 hours at 803K. These micrographs give a qualitative idea of the influence that both type (in relation to the fabrication process) and percentage of reinforcement have on the reaction layers formed.

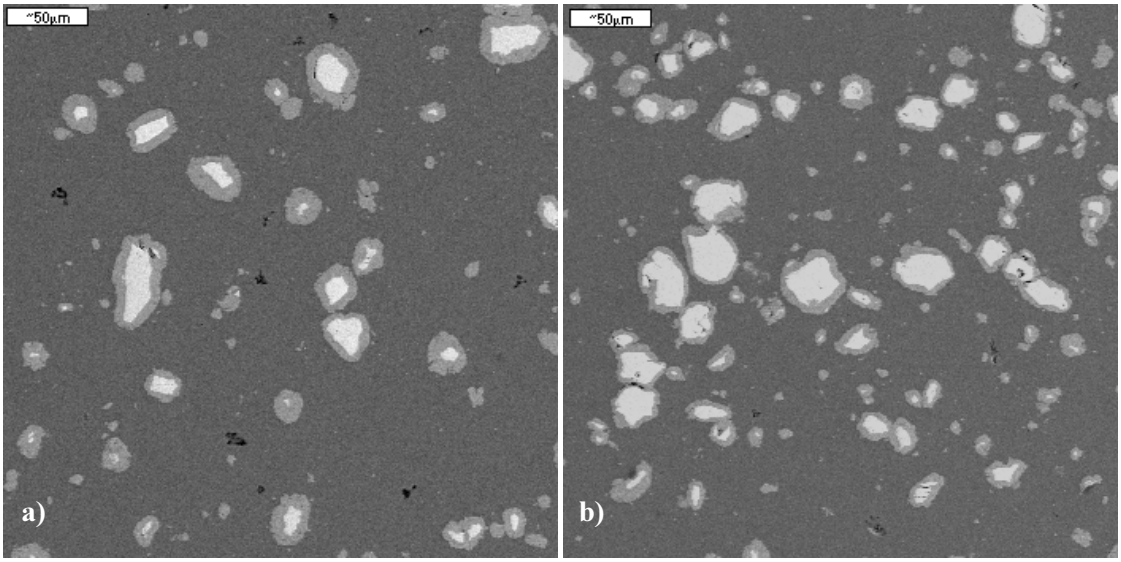


Fig. 3. Composites reinforced with $Ti_3Al$ intermetallic produced by the Hydride-Dehydride process after heat treatment at 803K for 24 hours. a) 5% reinforcement. b) 10% reinforcement.

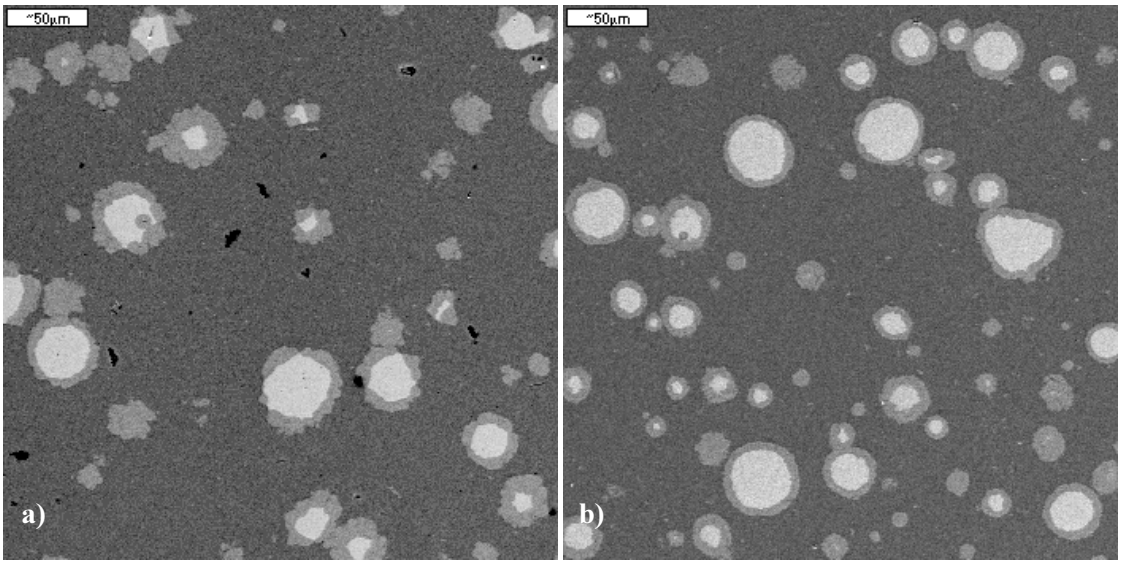


Fig. 4. Composites reinforced with argon atomised $Ti_3Al$ intermetallics after heat treatment at 803K for 24 hours. a) 5% reinforcement. b) 10% reinforcement.

Regarding the influence of the processing technique used for the fabrication $Ti_3Al$ reinforcements, a higher growth rate of the reaction layers in the composite reinforced with argon atomised intermetallics is observed. After different measurements on the particles with an apparent thinner reaction layer (that should be related to that of the equatorial section of the particles), a graph of the thickness growth of the reaction layers against time of heat treatment can be plotted. The results are plotted in figure 5, confirming the observations made above. On the other hand, the influence of reinforcement content on development of the reaction layers is also observed in figure 5. It shows how as the reinforcement content is reduced, the thickness of the reaction layers is higher. Furthermore, both types of reinforcements are influenced similarly.

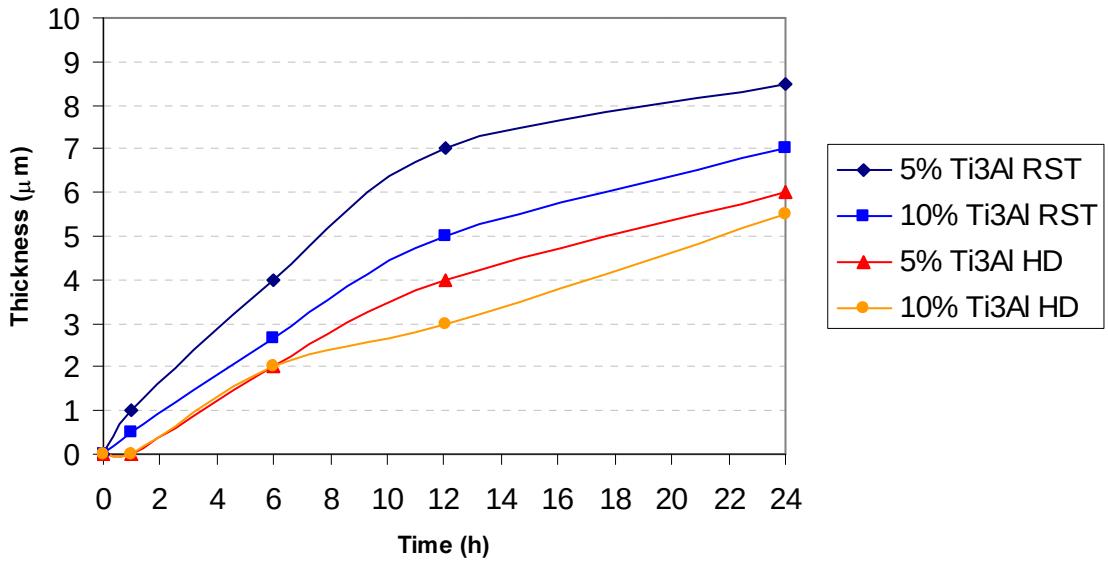


Figure 5. Plot of layer growth (diametral thickness in particles) as a function of heat treatment time for the composites reinforced with $Ti_3Al$ intermetallics.

To establish the nature of the interphases developed at the reaction layers, several qualitative and semiquantitative EDX-ray analysis were carried out. In a previous work by the authors [12], it was described how the alloying elements influence the development of reaction layers in these kind of composites. In fact, the aluminium alloy of this study was chosen with the aim of putting together some of the most important alloying elements of aluminium alloys (Cu,Si,Mg) to assess the influence of them on the formation of these reaction layers.

Figure 6 shows a X-ray line analysis trough the reaction layer developed in the A-10%$Ti_3Al$-RST composite after 12 hours of heat treatment. The curves of the relative counts regarding the elements involved along the analysis line are plotted at the right side. Cu spectrum is not present as it was found to have no influence in the formation of the reaction layer in Ti-Al reinforced composites [12]. The spectra shows that there is an important silicon enrichment in the intermetallic phase formed. The relative counts show a very intense and constant increase throughout the reaction layer for this element in comparison to the matrix. The results from the semiquantitative X-ray analysis showed that the composition of the main intermetallic phase formed is close to $(Al,Si)_3Ti$, where silicon substitutes aluminium in the $Al_3Ti$ intermetallic binary system, in agreement with the work performed by Das et al.[16]. In early stages of layer development, a ternary interphase with a composition close to $(Al,Si)_2Ti$ is also formed. However, this intermetallic is not always found in every reacted particle of reinforcement, and the phase seems to progress quickly to the more stable $(Al,Si)_3Ti$ phase.

On the other hand, it has been observed that the silicon content present in the $(Al,Si)_3Ti$ phase changes with the time of heat treatment, that is, with the thickness of the reaction layers developed. Figure 7 below shows the variation of silicon content (as at. pct) in the composites reinforced with both types of $Ti_3Al$ intermetallics in relation to heat treating time. All of them follow a similar pattern, with a first stage in which silicon content increases markedly, reaching a maximum, and then decreasing. Regarding reinforcement content, the highest increase of silicon content is found in the composites with a lower percentage (5%). Also, this increase is more acute for the intermetallic produced by gas atomisation. This result can be interpreted as follows. As the silicon content in the aluminium alloy matrix is

limited and not very high, it is much readily available for the intermetallic particles of composites with a lower content of the same. Because of that both composites with a 5% of reinforcement show interphases with a higher content (higher peaks) than composites with 10%. Moreover, it seems that the higher the content of silicon is available, the faster is the formation and growth of the reaction layer. On the other hand, the presence of a reinforcement made by gas atomisation plays also in favour of this effect. It seems that the fine grained microstructure of the particles could enhance the interfacial diffusion of alloying elements and so the formation of the Al-Si-Ti ternary phases found. For this reason, the kinetics of Si enrichment in the reaction layer is faster for composites with gas atomised reinforcements, being independently of the percentage of reinforcement content (peaks at similar heat treatment times).

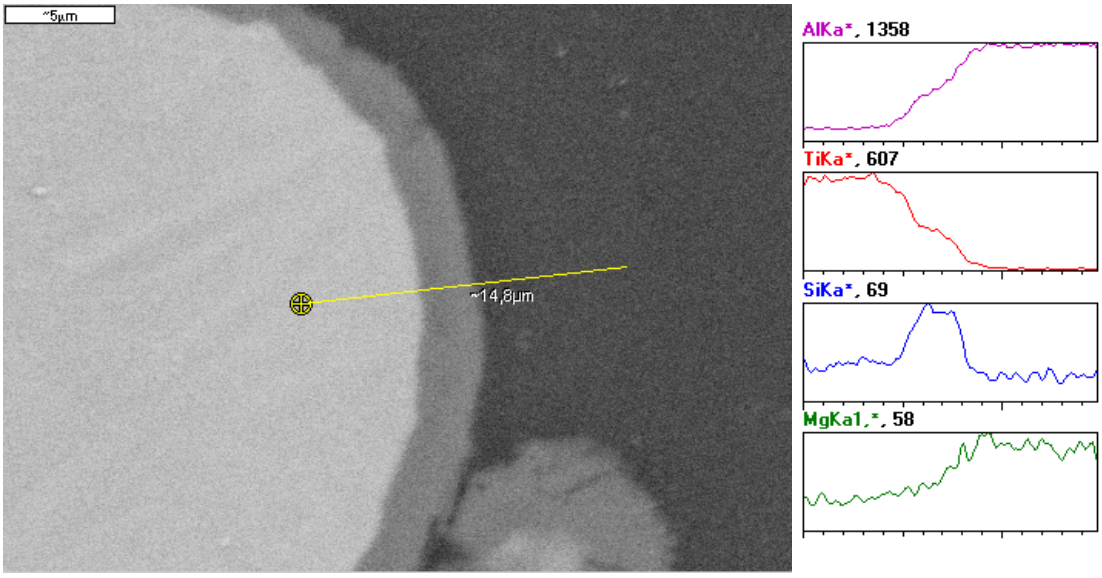


Figure 6. X-ray line analysis for A-10%$Ti_3Al$-RST composite heat treated for 12 hours at 803K. Right, relative spectra of the most important elements.

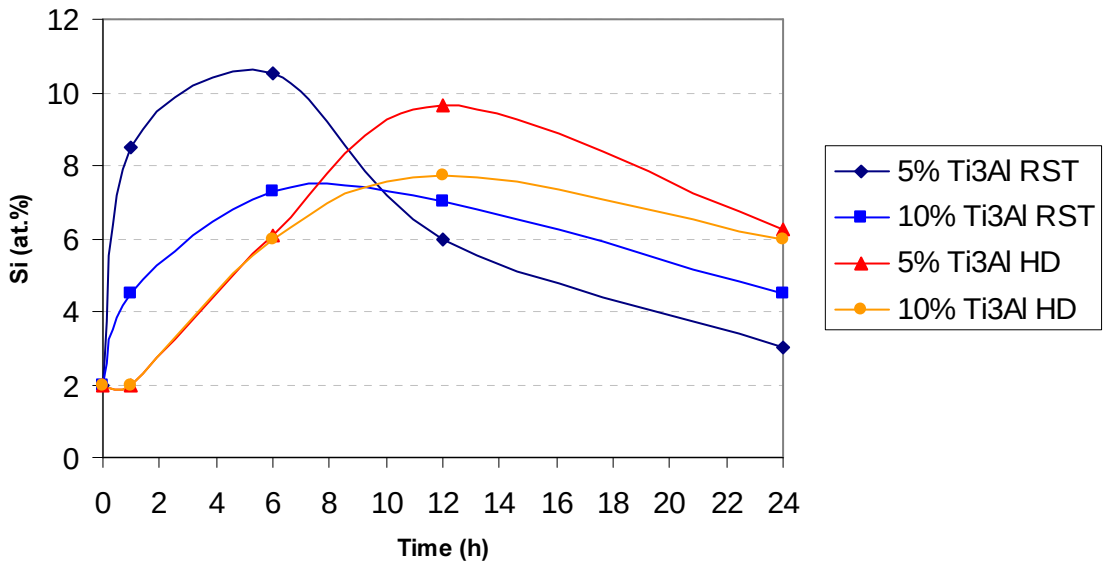


Figure 7. Plot of silicon content (at. pct.) in the reaction layers against time of heat treatment at 803K. $Ti_3Al$ reinforced composites.

When considering the composites reinforced with TiAl intermetallics, the development of reaction layers after similar heat treatments was much lower, although the interphase formed was similar in nature: $(Al,Si)_3Ti$ . As seen in figure 8, after 24 h. of heat treatment at 803K, the reaction layer developed is much smaller, than, for instance, that developed for the $Ti_3Al$ reinforced composites after 12 hours (fig. 7).

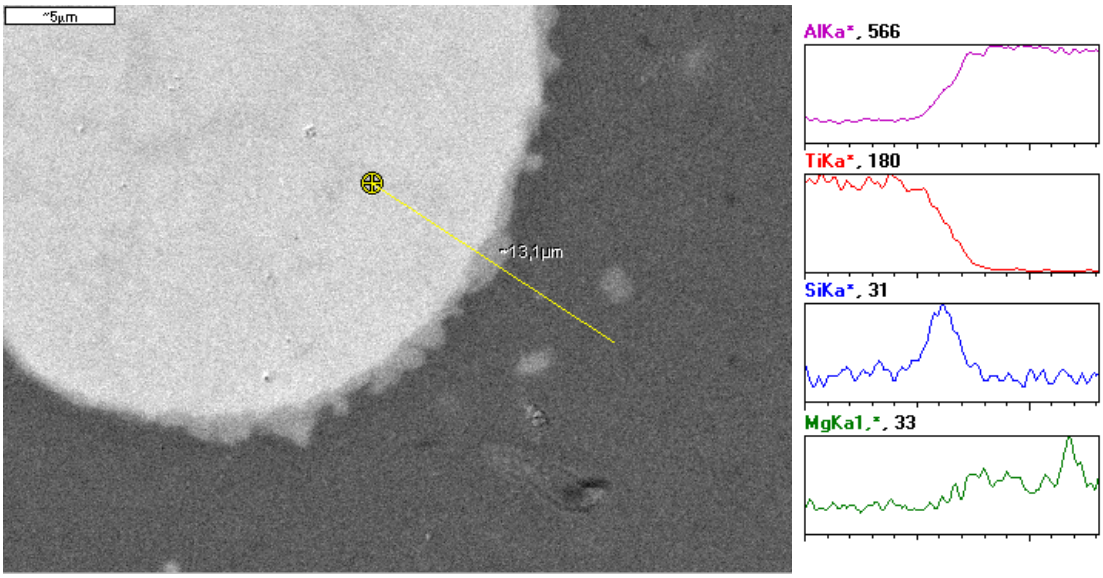


Figure 8. X-ray line analysis for A-10%TiAl-RST composite heat treated for 24 hours at 803K. Right, relative spectra of the most important elements, showing again an increase on the silicon content of the interphase formed.

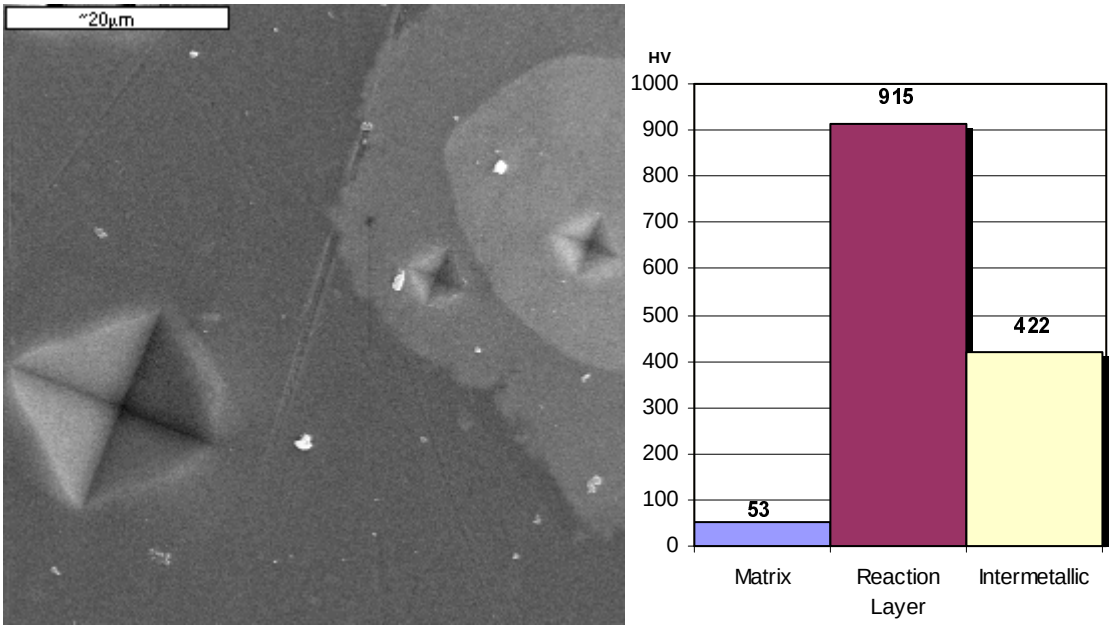


Figure 9. Micrograph showing Vickers microhardness indentation on matrix, reinforcement and reaction layer for the composite A-5%$Ti_3Al$-RST after 24 h. at 803K. Right, Vickers hardness values.

To asses the relative strength of the different constituents, microhardness measurements were carried out. Figure 9 shows the test indentations and hardness values obtained. It is clear from these results that the interphase formed $(Al,Si)_3Ti$ has a relatively higher strength than

both the matrix and original reinforcement particle. Varin [6] established that the interfacial zone in Al-intermetallic MMCs should be ductile, so this would have a non positive effect on the mechanical properties of the composite.

*Corrosion Tests.*

Susceptibility of aluminium and aluminium alloys to pitting corrosion in chloride environments is studied commonly by evaluating $E_b$, namely the potential value above which pits will initiate and bellow which they will not. It is also important to know the effectiveness of the passive layer by calculating the amplitude of passive region as the difference between $E_b$ and $E_{pp}$ (passivation potential). Figure 10 shows $E_b$, $E_{pp}$ and $E_{c1}$ values, found for the MMC with the potentiodynamic polarisation tests as a function of the type of reinforcement employed. Only slight differences were observed in values measured on the different composites, around 100-150 mV. In all cases, a cathodic displacement of potential values was observed for the composites due to the potential difference between matrix (acting as an anode) and reinforcement (acting as a cathode). This fact favours generalized corrosion. Analysing content and type of reinforcement employed, it was verified its influence in corrosion behaviour. Whereas high values in the reinforcement content are associated with smaller potential values, the opposite tendency is followed by TiAl particles.

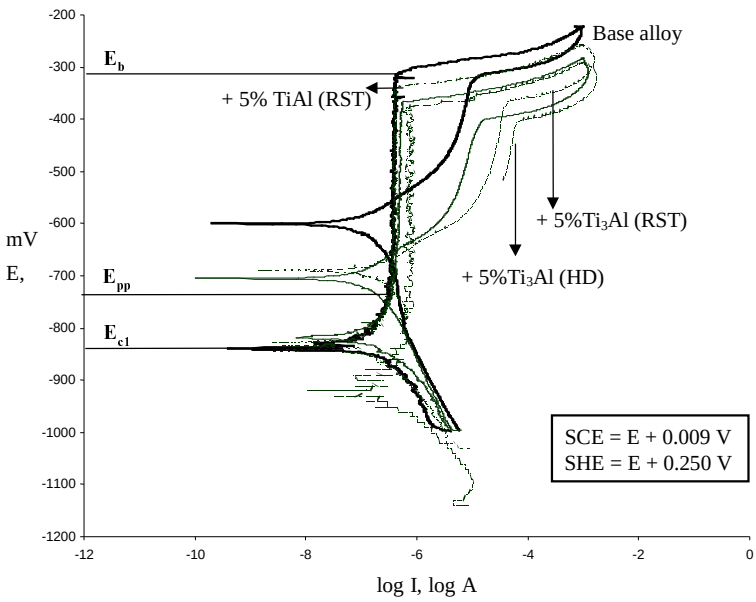


Figure 10. Cyclic polarization curves for unreinforced matrix and composites developed.

The passive amplitude measured for the composites was smaller than the one obtained for the unreinforced matrix. This result implies the existence of a less resistant passive layer when considering MMCs.

After solution heat treatments, a change in potential values was detected. In all cases, it was found an increment in potential values (in noble or anodic direction) as the heat treatment time increased until an optimal solution time and following this time, potential values return to more cathodic values. A possible explanation of this behaviour is the formation of reaction products at the interface matrix/reinforcement as a result of heat treatment. As referred above, it was found by X-ray microanalysis the presence of $(Al,Si)_2Ti$ and $(Al,Si)_3Ti$ intermetallic phases in the reaction layer. $(Al,Si)_2Ti$ phase transforms in $(Al,Si)_3Ti$ with heat treatment time, and the optimal solution time associated with the highest potential values was

found when $(Al,Si)_2Ti$ phase was still present. So it was concluded that the formation $(Al,Si)_2Ti$ intermetallic phase enhance the pitting resistance for AA6061/Ti-Al composites.

After exposure to cyclic polarisation, localised corrosion in the samples was studied by SEM. Small pits were observed, figs. 11 and 12. Some differences were found between composites before and after heat treatments. At short heat treatments, the aspect of samples is similar to figure 11, where it can be observed the holes developed around reinforcement particles.

Considering elevated heat treatment times a higher degree of pitting was observed in the surface. As shown in figure 12, the pits extended by the matrix without affecting reinforcement particles or reaction layer. Therefore intermetallic phases restrict pit propagation to the matrix zones that surround them.

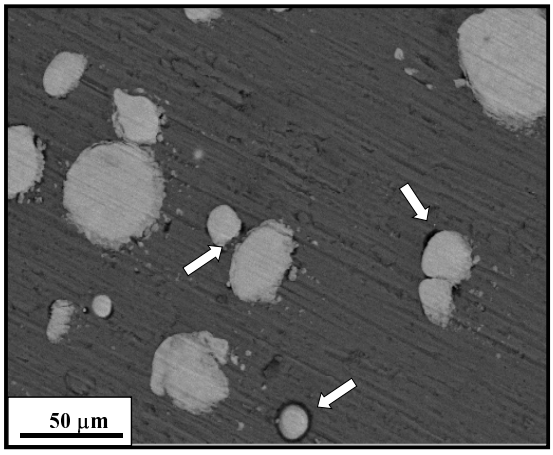


Fig. 11. Corrosion surface on composite with 5% of TiAl intermetallic.

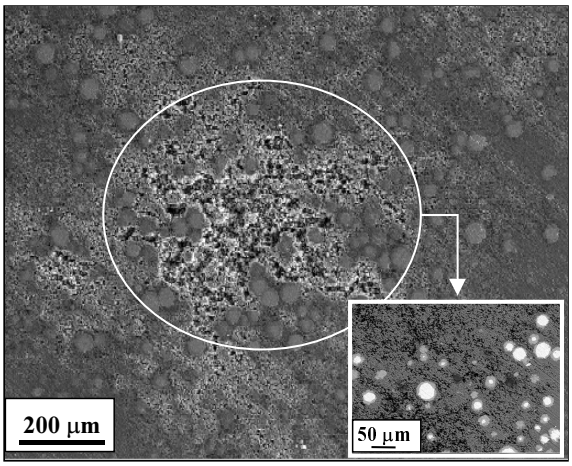


Fig.12. Corrosion surface on composite with 5% of $Ti_3Al$ after 12 hours at 803K. Pitting detail.

## CONCLUSIONS

Intermetallics processed by argon atomisation technique show a higher activity in the formation of reaction layers. Composites with a lower percentage of reinforcement show a higher reactivity as silicon is more available for the formation of stable Al-Si-Ti interphases. Reactivity of TiAl reinforced composites is much lower than $Ti_3Al$ reinforced ones. When present the reaction layer, the composition is similar to that of the other composites and near to the ternary intermetallic $(Al,Si)_3Ti$. The interphase formed has a high strength nature, that would impair the mechanical properties of the composites.

Pitting resistance of AA6061/Ti-Al can be improved composites by performing solution heat treatments. There is an optimal solution time associated with the highest potential values obtained for the composites. Corrosion morphology is affected by solution heat treatments. Elevate times implies high pit contents, restricted to matrix zones surrounding reinforcement and reaction layer developed.

Future work will focus on microstructure/mechanical properties relationship through mechanical and tribological characterisation. Also, the study on the influence of matrix alloying elements over the formation of the reaction layer will be continued together with a deeper analysis on corrosion behaviour.

## ACKNOWLEDGEMENTS

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