REINFORCEMENT INFLUENCE ON PRECIPITATION PHENOMENA IN Ti_3Al INTERMETALLIC REINFORCED ALUMINIUM MATRIX COMPOSITES

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ABSTRACT

The influence of Ti_3Al particulate reinforcement on the precipitation kinetics and ageing behaviour of AA6061 and AA7015 based composites is studied. Composites were prepared by a solid-state process that combines powder metallurgy and extrusion. Composites were analysed by means of Differential Scanning Calorimetry (DSC) together with TEM observations and microhardness measurements. A different influence has been observed for the different composites in the sense that whereas for AA6061 composites there is a important influence of reinforcement on precipitation kinetics, for those based on AA7015 there is not.

1. INTRODUCTION

The presence of reinforcements in aluminium alloys with heat treating capabilities could have a very marked effect on kinetics and/or precipitation sequence of metastable phases. Although important research efforts have been performed in this field [1] conclusions of these studies could not be generalised nor be taken out of their own specific experimental details due to the fact that a vast number of parameters have to be considered (alloy family and composition, fabrication process, type, shape, size and quantity of reinforcement used, heat treatment parameters etc.) [2, 3]. Hence the study of precipitation phenomena is an important issue when dealing with aluminium matrix composites (AMCs).

On the other hand, when considering precipitation kinetics, there is generally an increase in precipitation rate of composites compared to the corresponding unreinforced alloys. There have been several studies in which heterogeneous nucleation is favoured by the presence of high amount of dislocations in the composite due to expansion coefficient mismatch between matrix and reinforcements. In fact, dislocations reduce incubation time for precipitates and increase diffusion rate. This produces reaching maximum hardening values for lower ageing time in composites [4-9]. In the case of homogeneous (as in AA6061 family, with β'' metastable phase) nucleation increased diffusion due to the presence of dislocations would explain faster growth of precipitates [10-12], although other studies showed that some heterogeneous nucleation of β' phase also appeared in dislocations [13, 14].

In this work, different intermetallic reinforced aluminium matrix composites are analysed, focusing on reinforcement influence on nucleation and growth of precipitates. The intermetallic used as reinforcement is Ti_3Al whereas two aluminium alloys have been selected as matrices: AA6061 and AA7015

2. EXPERIMENTAL PROCEDURE

Aluminium alloys selected for the fabrication of composites were high strength, heat-treatable alloys of the families Al-Mg-Si (AA6061) and Al-Zn-Mg (AA7015). AA6061 alloy composition was the following: 0.74% Si, 0.19% Mg, 1.00% Cu, 0.22 Cr, 0.06% Fe and Al bal. AA7015 alloy composition was the following: 5.96% Zn, 1.8% Mg, 0.3% Cu, 0.16% Zr, 0.16% Fe, 0.06% Si, and Al bal. Both alloys were primarily produced in powder form by ALPOCO (The Aluminium Powder Co., UK) through a gas atomisation process. Powders presented a spherical morphology with a maximum particle size of 75 μm and a mean value of about 30 μm. Particles of Ti_3Al intermetallic were used as reinforcements. These were produced by Se-Jong Materials (South Korea) through the hydride-dehydride process, which conferred them a polygonal morphology. Particle diameter ranged from few microns to a maximum value of 50 μm.

Processing of the composites consisted of a combination of powder metallurgy and extrusion techniques. This fabrication method guarantees both a good densification of the composite and a homogeneous distribution of the reinforcement in the matrix. Percentage of Ti_3Al reinforcement used was 5 and 10% in volume in both alloys. The fabrication procedure comprised of: mixing of alloy and intermetallic powders, cold compaction up to 250 Mpa, graphite lubrication of the green compact, heating at 500ºC for about one hour to homogenise the temperature and extrusion with a ratio of 25:1 and a ram speed of 1 mm/s [15]. At the end of the process, a bar of 5 mm of diameter of AMC was produced.

After extrusion, composites were heat treated. Heat treatments on AMCs consisted of solution treatment at 530ºC during one hour and water quenching at 20ºC. Ageing was conducted at 175ºC for different times. AMCs based on AA7015 were solution heat treated at 480ºC during one hour and water quenching at 20ºC. Ageing was conducted at 150ºC for different times.

DSC runs were performed for two kinds of analysis. The first one dealt with the assessment of the activation energy of formation of metastable precipitates through the method developed by Ozawa [16]. The second one was intended to study the growth of precipitates under ageing conditions. Also, to obtain a correlation between precipitation kinetics and hardening behaviour, a series of hardness tests were carried out simultaneously with the DSC runs. These tests were performed over similar samples (that is, in the same state of ageing) of those analysed in the DSC. On the other hand, ageing conditions were extended to higher times for some samples, in order to show in a clearer way the overaged stage.

Finally, precipitation evolution for the different composites was observed by means of Transmission Electron Microscopy (TEM). This technique enables the analysis of precipitates by focusing on morphology, size, quantity and distribution of these in the different stages of the ageing process, and its correlation with the phenomenology observed by the other techniques.

3. RESULTS & DISCUSSION

Composite AA6061-Ti_3Al.

The first group of DSC runs for this group of composites dealt with the assessment of the activation energy of formation of metastable precipitates. These were carried out by a precipitation kinetics analysis of solid state transformations by the Ozawa plot. This is a non-isothermal method based on running the DSC analysis with a constant heating rate. By doing these tests over similar samples with the same initial conditions and at different heating rates, and after analysing the precipitation peaks related to the precipitates to study, an easy graphic construction gives an estimation of the activation energy of precipitation.

These analyses were carried out on samples of the extruded alloy and the composites with a 5 and a 10% of Ti_3Al. On the other hand, analogue studies were done on a commercial wrought AA6061 alloy, for comparison. Any sample was analysed immediately after quenching in water at about 20ºC, in order to minimise any kind of precipitation at ambient temperature. The solution heat treatment was 1 hour at 530ºC.

Although the activation energy value obtained by this method is only approximate, it is very interesting its estimation on the relative comparison between the materials under study. Figure 1 shows DSC plots of the materials referred above. In this case, a heating rate of 20ºC/min has been used.

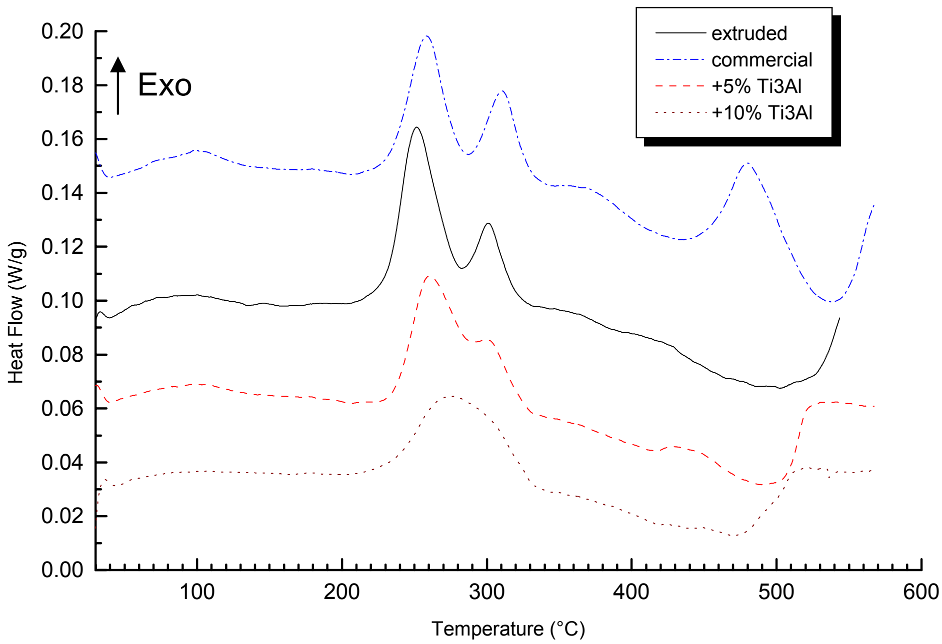

Figure 1. DSC plots of the materials studied after quenching in water. Heating rate: 20°C/min. Curves are displaced over y-axis for better display.

Precipitation of metastable precipitates of equilibrium phase β (phases β'' y β') is confirmed by the presence of two similar exothermal peaks in both extruded and commercial wrought AA6061 [13]. In these curves the influence of reinforcement presence in precipitation kinetics is already clear. In fact, there is is a displacement of the peak associated to the precipitation of metastable phase β'' towards the one of β' as percentage of reinforcement increases, up to a point where both peaks are overlapped. On the other hand, peak temperature of the following phase (β') is not affected by the percentage of reinforcement present. This agrees with the activation energy (AE) values obtained after several DSC runs at different heating velocities and applying the Ozawa plot for all of them: whereas for β'' those values are different, for β' are similar (Table 1)

Table 1. Activation energies (AE) of phase β precursors.

Material	AE β'' (kJ/mol)	AE β' (kJ/mol)
AA6061 extruded	84±5	122±4
AA6061+5%Ti_3Al	79±6	120±2
AA6061+10%Ti_3Al	69.5±3	-----
AA6061 commercial	95±7	125±3

A reduction in the value of activation energy of formation of metastable phase β'' is observed as the amount of reinforcement present increases. Also, the AE value for the extruded alloy is inferior of that of the commercial alloy. Nevertheless, as stated before, β' values are similar either for the extruded, commercial and 5% reinforced alloy. For the composite with a 10% of reinforcement, the overlapping peaks prevent the assessment of this value.

Once the analyses in the "as quenched" condition were performed, some experiences in different states of ageing were carried out to study the growth of precipitates during ageing. For this purpose a second series of DSC runs were carried out. DSC runs were done on samples with different ageing times at 175ºC, after the solution heat treatment of 1 hour at 530ºC and quenching in water at 20ºC. Elapsed times considered were 15', 30', 1 h, 2 h, 4 h, 8 h y 16 h, in order to encompass all precipitation sequence stages, up to overageing.

Figures 2 and 3 show the peaks of formation of metastable precipitates β'' and β' after ageing for 30 min. and 1 hour. An important precipitation of phase β'' for the two composites and base alloy considered is observed in the first one after only 30' of ageing. This is justified by the decrease in the relative intensity of the first peak in these curves, corresponding to β''. This peak is much lower in the aged condition for any material considered when compared with the same peak in the "as quenched" condition (Fig. 1). Nevertheless, the presence of a small exothermic peak indicates that there have been still a precipitation of β'' in these samples. On the second one a meaningful change is displayed. In this stage of ageing, there is not any more the exothermic peak corresponding to the precipitation of β'' phase in any of the specimens. These have been replaced by an endothermic peak indicating that dissolution of some β'' has taken place. Also, a significant difference in the precipitation kinetics of the three materials studied is observed: whereas in the base material it is only observed a small dissolution peak, for the composites these peaks are greater. This is indicative of faster precipitation kinetics of the metastable precipitates of the aluminium alloy due to the presence reinforcement particles.

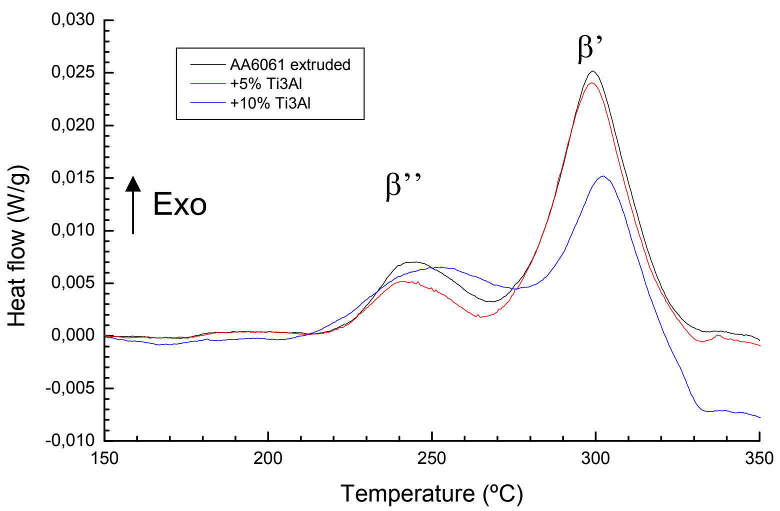

Figure 2. DSC runs of base alloy and related composite materials, after ageing 30 min. at 175ºC from the "as quenched" condition. Heating rate: 20ºC/min.

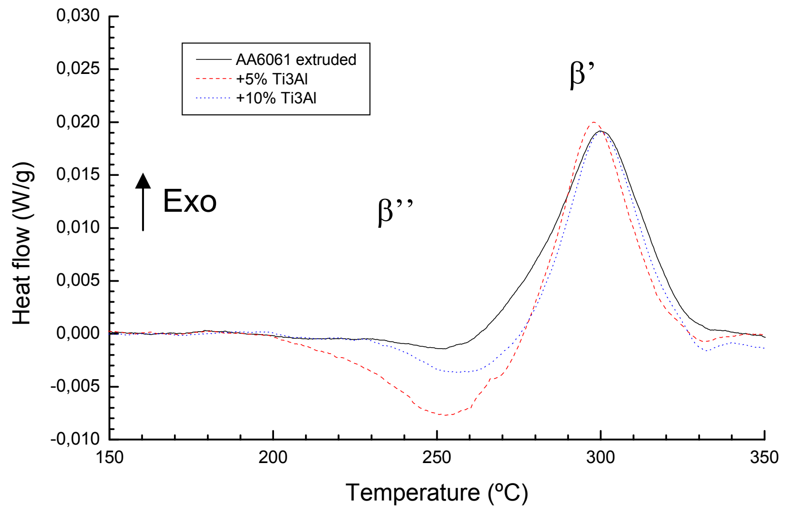

Figure 3. DSC runs of base alloy and related composite materials, after ageing 1 hour at 175ºC from the "as quenched" condition. Heating rate: 20ºC/min.

On the other hand, another interesting result that can be inferred after the observation of DSC curves after 1 hour of ageing is the fact that the dissolution peak for the composite with a 5% of reinforcement has a greater relative intensity than the reinforced with a 10%. This behaviour is unexpected for any kind of composites. In this case we have that the presence of a 5% of reinforcement increases the precipitation kinetics of phase β'' in a higher degree in comparison to the 10%. For the latter, it is still verified an acceleration of the precipitation with respect to the base alloy, but to a lesser extent when compared with the composite with less amount of Ti_3Al particles. The causes of this response could be attributed to the formation of precipitates or incipient reaction layers in the interface matrix-particle of reinforcement, being this effect amplified for greater amounts of reinforcement [17].

With the purpose of obtaining a correlation between precipitation kinetics and hardening behaviour, a series of hardness tests were carried out simultaneously with the DSC runs. These tests were performed over similar samples (that is, in the same state of ageing) of those analysed in the DSC. On the other hand, ageing conditions were extended to higher times for some samples, in order to show in a clearer way the overaged stage. Figure 4 shows the Vickers microhardness evolution for the different materials studied. Microhardness indentations were located in the aluminium alloy matrix in every case, in order to separate the hardening effect due to the presence of the reinforcement particles from that of the acceleration in precipitation kinetics of hardening precipitates in the aluminium alloy.

Although maximum hardness values obtained in every material are lower compared with those achieved a wrought AA6061 alloy, this could be explained by the low contents in magnesium in the alloys base used for the composites (0.19%). This quite far from the optimum Mg/Si ratio (1.68) for the formation of the hardening phase Mg_2Si. In either the case, composites showed an accelerated hardening response in comparison with base alloy. Composite with a 5% of Ti_3Al show higher hardness for short treatment times in comparison with both base alloy and the composite reinforced with a 10%, as a direct correlation with the tendency observed in the DSC curves after 1 hour of ageing. In these, it could be observed that although the precipitation kinetics was accelerated for both composites, it was to a higher degree in the case of a 5% of reinforcement. The hardening peak in the base alloy encountered in a relatively long ageing time (32 hours) relates to precipitation of silicon [14].

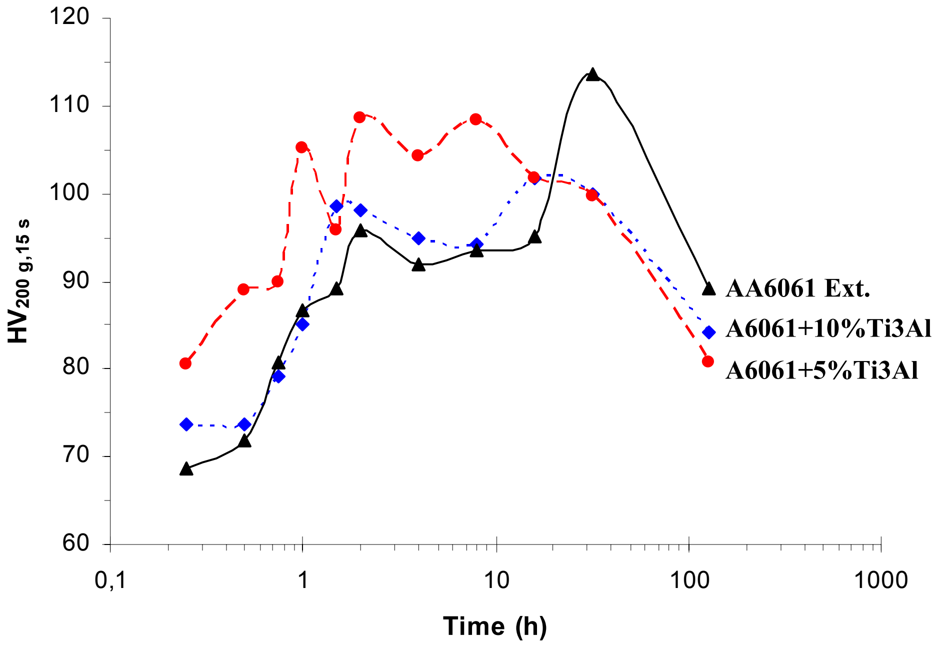

Figure 4. Vickers microhardness evolution for the different composites and the base alloy considered in this study. Solution heat treatment of 1 hour at 530ºC, quenching in water and ageing at 175ºC at different times.

Figure 5 shows TEM images of base alloy and composites reinforced with a 5 and a 10% of Ti_3Al respectively after ageing 2 hours at 175ºC. The presence of tiny precipitates distributed homogeneously all over the matrix is observed in every material. But the most important result that can be drawn from the comparison between the three micrographs is the marked difference between sizes of precipitates formed. It could be clearly observed that the level of growth of the precipitation distributed homogeneously all over the matrix is in an earlier stage of development in the case of the unreinforced alloy, when compared to the composites although its shape is not resolved neatly. This fact corroborates that the precipitation kinetics is faster in the composites, in accordance with the DSC results and microhardness measurements referred above and other research studies [10-12]. In those, the acceleration of the homogeneous precipitation in composites based in these kind of alloys, is explained by the enhanced diffusion of magnesium in the matrix, due to the presence of higher number of dislocations. These are formed by the differences in the coefficients of thermal expansion of the matrix and the reinforcements.

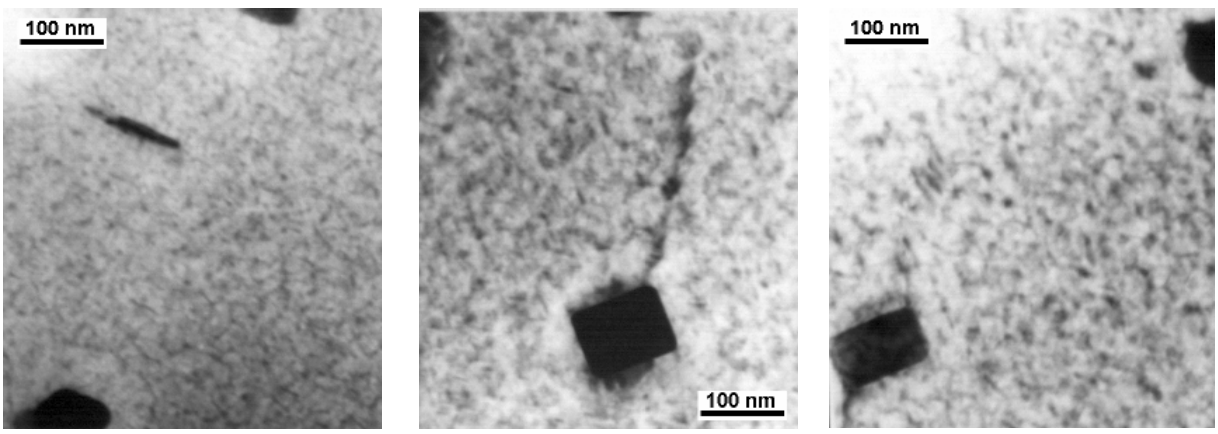

Figure 5. TEM Image of precipitates on AA6061 base alloy and related composites after 2 hours ageing at 175°C: a) extruded base alloy b) composite with 5% Ti_3Al c) composite with 10% Ti_3Al.

Composite AA7015-Ti_3Al

Activation energies of formation of metastable precipitates where again obtained by the Ozawa method for composites based on the AA7015 alloy. In this case starting conditions for the DSC runs were that of quenching in water at 20ºC, after a solution treatment at 480ºC for 1 hour. Again special care was taken in order to ensure that every sample was in the conditions of sobre-saturated solution (s.s.s.) to avoid any possible precipitation of GP zones at ambient temperature that occurs in the alloys of this series (7XXX).

Figure 6 shows the DSC runs obtained for the three materials considered (base alloy and composites with 5 and 10% of Ti_3Al). Heating rate represented is 20ºC/min, and the curves have been shifted vertically for a better comparison (so heat flow values have to be considered only in a relative sense and individually for each curve).

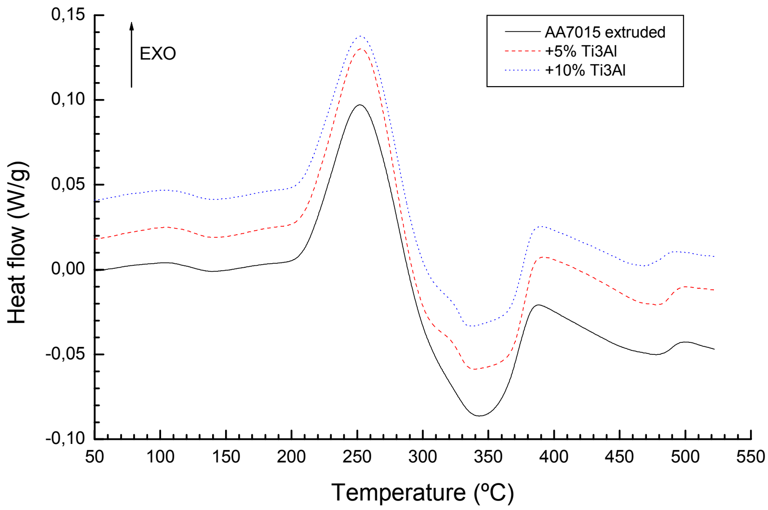

Figure 6. DSC runs of extruded AA7015 base alloy and composites reinforced with 5 and 10% of Ti_3Al particles, after solution treatment at 480ºC for one hour and quenched in water. Heating rate 20ºC/min.

On the other hand, some studies realised by Mukhopadhyay et al. [18] have shown that in 7XXX series alloys with Cr additions, DSC curves are very similar to those obtained in this investigation. The formation of GP zones is clearly seen (exothermic peak at about 100ºC), and another peak of higher magnitude, identified in the above mentioned work as corresponding to the precipitation of metastable phase η' and equilibrium phase η. However, in other studies [19], this peak has been considered to be the energy released during precipitation of the metastable phase η' only. Is important to emphasise the great similarities encountered in all three curves, regarding number, morphology, intensity of peaks present and the temperature at which the peaks reach the maximum. This fact gives us a first approximation on precipitation behaviour, in the sense that no important differences would be expected.

After performing every DSC run, activation energies of formation of metastable phase η' were determined through the so-called Ozawa method. Results are showed in table 2. It is observed that activation energy values for the three materials match quite well, taking into account that this is only an approximate method. It could be concluded that the addition up to a 10% of reinforcement of the type Ti_3Al in this alloy has not an appreciable effect on the activation energy of formation of metastable phase η', and therefore the precipitation kinetics is not affected either.

Table 2. Activation Energies of formation of metastable phase η'.

Material	AE η' (kJ/mol)
AA7015 Extruded	59.5±2
AA7015+5%Ti_3Al	58±3
AA7015+10%Ti_3Al	59±3

Due to the fact that the previous experiences showed that the presence of reinforcement has not an effect on precipitation phenomena for the base alloy used, no further DSC runs at different stages of ageing were carried out.

In order to corroborate the observed behaviour by the DSC analysis, a series of hardness measurements for different ageing times at 150ºC were carried out. Again, hardness evolution is plotted against ageing time, and it could be verified that precipitation kinetics (and therefore ageing response) is not affected by the presence of reinforcement particles.

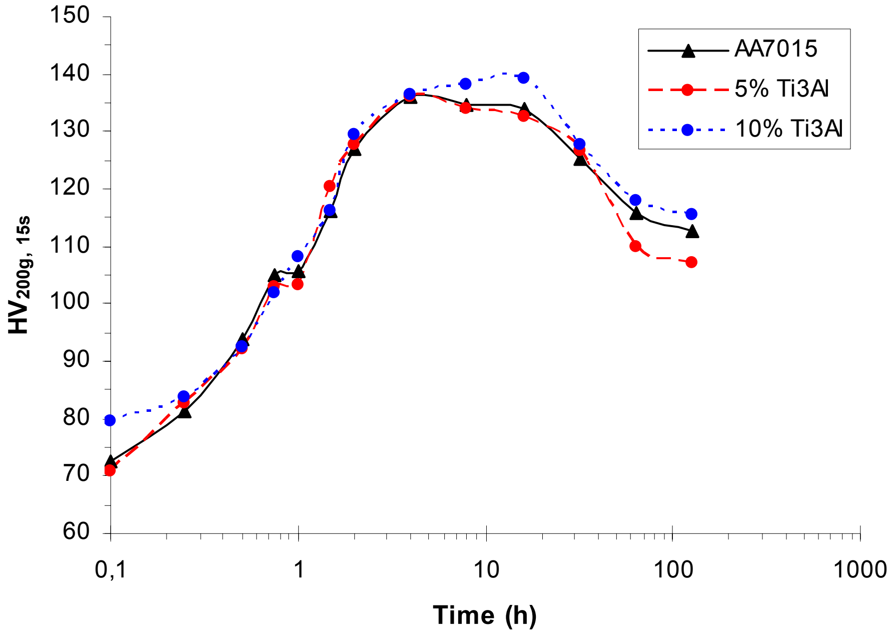

Figure 7. Vickers hardness evolution against ageing time at 150ºC for the extruded base alloy AA7015 and composites with 5 and 10% of reinforcement.

It is interesting to emphasise the high level of correlation encountered between DSC results and hardness measurements. In the former section it was revealed that activation energies of formation of metastable precipitates η' were similar for base alloy and composites. As this phase is the responsible of hardening of this alloy for artificial ageing, this result will suggest that ageing kinetics for these treatments is not affected by the reinforcement. This last point has been corroborated by hardness tests.

In a similar way as done for the AA6061 alloy, a microscopic study of precipitates developed during ageing was carried out with the help of the transmission electron microscope (TEM). The ageing stage chosen for observation was the one that gave the highest degree of hardening, that is, 8 hours at 150ºC.

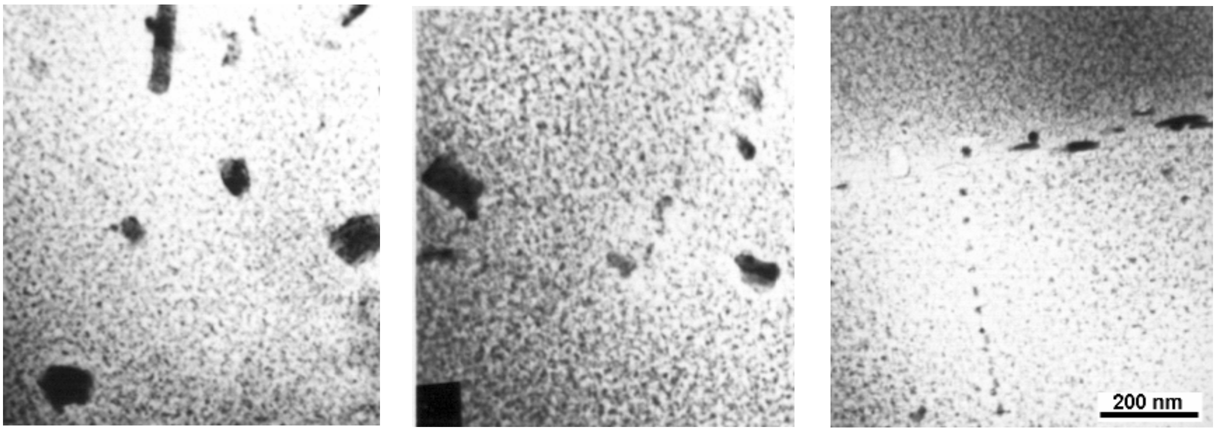

Figure 8. TEM Image of precipitates on A7015 base alloy and related composites after 8 hours ageing at 150°C: a) extruded base alloy b) composite with 5% Ti_3Al c) composite with 10% Ti_3Al

Figure 8 show the micrographs obtained from the three materials studied (base alloy and composites with 5 and 10% of Ti_3Al) at the same magnification. All three micrographs result very similar, from a general point of view. Every one has a very fine and homogeneously distributed precipitation all over the aluminium grains. Quantity, size and distribution of precipitates appear almost identical. These observations corroborate the results obtained above, regarding the statement made that precipitation kinetics is not affected by reinforcement for this alloy.

After extensive observation of different samples, three ways have been observed in which heterogeneous precipitation takes place in this alloy. In the first one, and most important regarding hardening potential, the precipitation is very fine and homogeneously distributed all over the matrix. Precipitate growth was improved by the solute rich zones (Zn and Mg) produced in the reversion of GP zones. In the second and third ones, precipitation took place in grain boundary and dislocations, although the non-extensive nature of this behaviour did not influence hardening response in a significant way.

CONCLUSIONS

The presence of particles of reinforcement in AA6061 based composites modifies the activation energy of formation of metastable precipitate β''. On the other hand, for the β' precipitate, there is not a significant difference for the different composites.

Precipitation kinetics of AA6061 based composites is accelerated in comparison to unreinforced alloy, and so a faster hardening response is observed during ageing

In composites based on AA7015 alloy, the presence of Ti_3Al reinforcement particles (up to the 10% vol. used in this study) do not modify the activation energy of formation of η' precipitates, having a value of about 59 kJ/mol in either case. In this case, precipitation kinetics and hardening response are similar in both composites and base material.

Finally, as a general conclusion, it has been shown that the presence of Ti_3Al reinforcement produces a very different precipitation behaviour in relation to the matrix to which is added. Whereas for the AA6061 alloy there is a remarkable effect on modification of precipitation kinetics for the composites, for the alloy A7015 there is not modification at all, for the percentages used and the conditions of the tests.

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