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# Ageing characteristics of rapidly solidified Al–Li–Ti alloys at 473 K

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The influence of titanium on the $\delta'$ precipitate free zones (PFZs) and on the stable $\delta$ phase is investigated in four melt-spun Al–Li–Ti alloys with ~2 mass% lithium and 0.10–0.35 mass% titanium. Rapid solidification gives rise to a homogeneous distribution of titanium on the wheel side of the ribbons, and to a cellular distribution of solute atoms in intermediate regions and on the gas side. Heat treatments of up to 1000 h at 473 K do not modify titanium distribution, which remains in solid solution. During ageing, preferential coarsening of $\delta'$particles occurs on cell walls. The growth rate of the $\delta'$ PFZs is lower than in other Al–Li alloys and is mainly controlled by the titanium concentration of the alloys. The nucleation and growth of the stable $\delta$ phase is also delayed by the presence of titanium. These results indicate that the effect of titanium in solid solution is to retain vacancies thus reducing lithium diffusion rate.

## 1. Introduction

Aluminium–lithium alloys are very attractive to the aerospace industry because of their low density and high Young's modulus and tensile strength [1, 2]. Lithium acts as a hardening agent through the precipitation of the coherent meta-stable $L1_2$-type $\delta'$ ($Al_3Li$) phase. Homogeneous precipitation of spherical $\delta'$ particles occurs when an Al–Li alloy is heat treated at a temperature below the $\delta'$ solvus line. Simultaneous to $\delta'$ coarsening, $\delta'$ precipitate free zones appear adjacent to grain boundaries, with growth rates proportional to the square root of the ageing time [3]. In addition, heterogeneous precipitation of the stable $\delta$ (AlLi) phase occurs generally on grain boundaries [4]. Technological application of the Al–Li alloys is limited by their low ductility and toughness, caused by the shear of the $\delta'$ particles, and the presence of $\delta'$ PFZs and $\delta$ precipitates [5]. In order to improve Al–Li mechanical properties, various methods, such as addition of other elements and application of rapid solidification technology, have been used [6].

In a previous work [7], the evolution of the meta-stable $\delta'$ phase was studied in four melt-spun Al–Li–Ti alloys. A microcellular structure was observed, and preferential coarsening of $\delta'$ particles took place on cell walls, caused by a heterogeneous distribution of titanium atoms in the aluminium matrix. The current study deals with the effect of rapid solidification and titanium on the evolution of the $\delta'$ PFZs, and the stable $\delta$ phase.

## 2. Experimental procedure

Four melt-spun Al–Li–Ti alloys, aged at 473 K up to 1000 h were studied. Compositions are summarized in Table I. Preparation details are described elsewhere [7]. Ribbons were ~ 2 mm wide and 20–60 μm thick.

Heat treatments were carried out in argon-filled glass capsules. $CuK_\alpha$ radiation was used for X-ray diffraction (XRD) analyses, in order to evaluate the volume fraction of the stable $\delta$ phase. Microstructures of the ribbons were characterized by analytical transmission electron microscopy (TEM). TEM foils were double jet electrothinned in a 33% $HNO_3$–67% methanol electrolyte at 243 K. PFZ half widths were measured with an image analyser. Care was taken to align the grain boundaries parallel to the electron beam direction, so that the true width of the PFZ was measured.

## 3. Results and discussion

As has been previously reported [7], the presence of titanium in solid solution in the melt-spun Al–Li–Ti alloys greatly alters $\delta'$ coarsening rate, in comparison with other Al–Li alloys of similar lithium contents. Due to rapid solidification, while on the wheel side of the ribbons titanium distribution is homogeneous, in intermediate regions and on the gas side, a cellular distribution of solute atoms appears. Furthermore, as the partition coefficient of titanium is $> 1$ in the aluminium-rich side of the Al–Ti phase diagram [8], titanium content is higher within the cells than on the cell walls. Heat treatments at 473 K produce the precipitation of the meta-stable $\delta'$ phase. Depending on ageing time and ribbon section, different microstructures can be observed. For short ageing times $\delta'$ distribution is homogeneous, regardless of ribbon section. As ageing time increases, while $\delta'$ distribution remains homogeneous on the wheel side of the ribbons (Fig. 1), in intermediate regions and on the gas side, a

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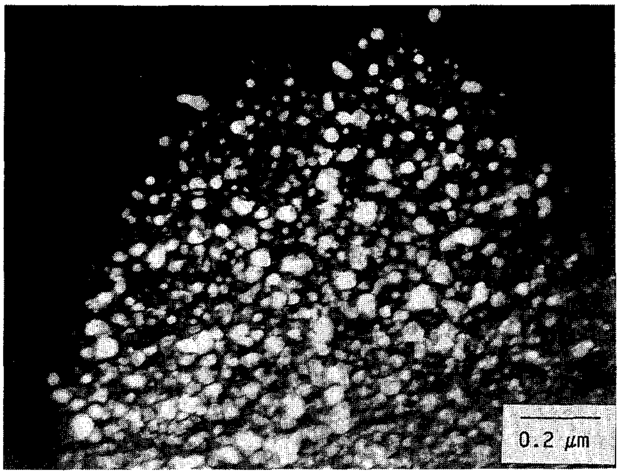

*Figure 1* Dark-field image of the homogeneous distribution of δ′ on the wheel side. Alloy B (Al–2.33%Li–0.20%Ti) aged at 473 K for 500 h.

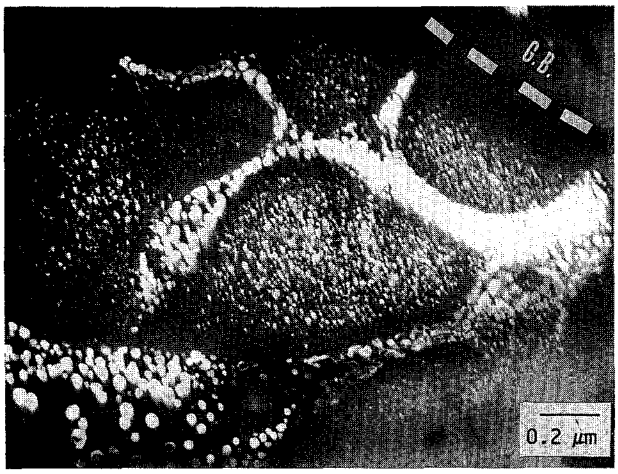

*Figure 3* Dark-field image of δ′ delineating circular cells on the gas side. Alloy A (Al–1.88%Li–0.35%Ti) aged at 473 K for 24 h.

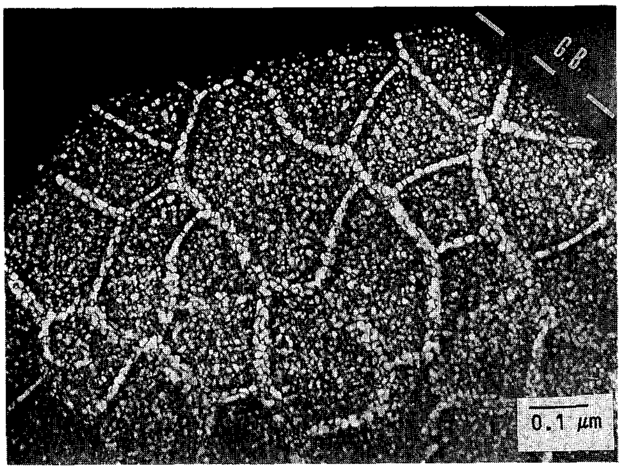

*Figure 2* Dark-field image of δ′ delineating narrow-walled cells in intermediate regions. Alloy C (Al–2.26%Li–0.15%Ti) aged at 473 K for 48 h.

TABLE I Composition of the Al–Li–Ti alloys, mass % (at %)

| Alloy | Li | Ti | Al |
|---|---|---|---|
| A | 1.88 (6.92) | 0.35 (0.18) | Balance |
| B | 2.33 (8.48) | 0.20 (0.10) | Balance |
| C | 2.26 (8.29) | 0.15 (0.08) | Balance |
| D | 2.02 (7.47) | 0.10 (0.05) | Balance |

preferential coarsening of δ′ particles takes place on the cell walls. In intermediate regions, δ′ delineates narrow-walled cells (Fig. 2), and on the gas side, it delineates circular cells (Fig. 3). On the other hand, the preferential coarsening of δ′ has been shown to start first, and to be faster, in the alloy with the higher titanium concentration.

Preferential coarsening of δ′ on the cell walls in the Al–Li–Ti alloys has been attributed to the ability of titanium to retain vacancies: as the titanium content is higher within the cells than on the cell walls, a lithium atom released from a δ′ particle within the cells would diffuse to the walls, while an atom released from a δ′ particle on the walls would not diffuse towards the cell centres, and the cellular distribution of δ′ takes place.

### 3.1. Grain boundary δ′precipitate free zones (PFZs)

In Al-Li alloys, growth of PFZs is due to the progressive dissolution of δ′ particles in the vicinity of grain boundaries during ageing. PFZ growth kinetics has been shown to depend on several factors, such as ageing time, temperature and lithium content [3, 9–11]. According to Jha *et al.* [3], PFZ half width, $h$, can be assumed to be proportional to the square root of ageing time, $t$

$$h = Kt^{1/2} \qquad (1)$$

$K$ being a parameter which increases with ageing temperature and lithium content.

In the Al–Li–Ti alloys, grain boundary δ′ PFZs can be observed in all microstructures. Figs 2 and 3 show examples of PFZs corresponding to grains with narrow-walled cells and circular cells, respectively (in Fig. 1 the PFZ is out of contrast). It is noteworthy that in the cellular microstructures, as ageing time increases, the number and size of δ′ particles within the cells become smaller or even disappears (Fig. 4). Therefore, the line which delimitates the PFZ becomes more imprecise (compare Fig. 3 with Fig. 4). This means, in practice, that the data dispersion would be greater for longer ageing times. Moreover, alloy A would exhibit the highest data dispersion because, having the highest titanium content, the dissolution of δ′ within the cells is faster than in the remaining alloys.

Fig. 5 shows the PFZ half widths of the melt-spun Al–Li–Ti alloys plotted against $t^{1/2}$. According to Equation 1, growth data can be fitted to a $t^{1/2}$ law in alloy D only, which has the lowest titanium content. In alloys A–C, PFZ growth rate decreases as $t^{1/2}$ increases and it is not possible to fit the data to a single straight line. In these three alloys, PFZ growth could be assumed to be two stage, the first one (stage I) up to 24–48 h (294–416 $s^{1/2}$) of ageing time and the second

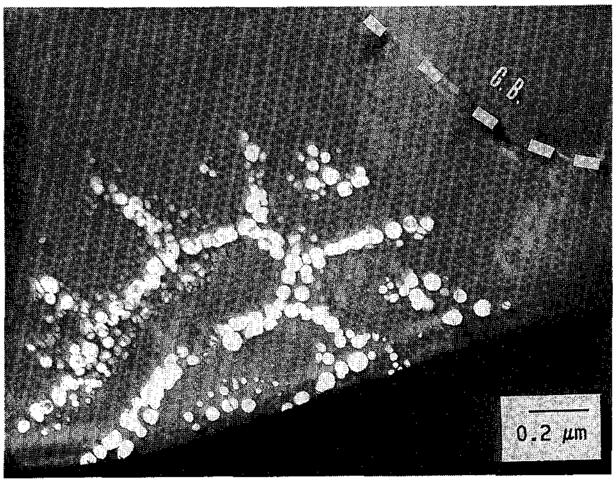

*Figure 4* Dark-field image showing a cellular microstructure in alloy A (Al–1.88%Li–0.35%Ti) heat treated at 473 K for 500 h.

one (stage II) from then on. Following this assumption, the curves in Fig. 5 can be replaced by two straight lines, as shown in Fig. 6, and the growth parameters $K_{\rm I}$ and $K_{\rm II}$ of both stages can be calculated for every alloy (Table II).

Comparison of $K_{\rm I}$ and $K_{\rm II}$ with data available in the literature indicates that PFZ growth rates are lower than those found by other authors. For example, Jha *et al.* [3] calculated a $K$ value of $\sim 1.4 \times 10^{-3}\ \mu{\rm m\,s}^{-1/2}$ for an Al–2.4 mass % Li alloy aged at 473 K. This result indicates that titanium must play a main role in PFZ kinetics reducing $\delta'$ dissolution rate to some extent in the vicinity of the grain boundaries, and thus, decreasing PFZ growth rate.

On the other hand, as shown in Table II, at the first stage $K_{\rm I}$ is higher the lower the lithium content

$$K_{\rm I}({\rm B}) \leqslant K_{\rm I}({\rm C}) < K_{\rm I}({\rm D}) < K_{\rm I}({\rm A})$$

indicating that for short ageing times growth kinetics is mainly controlled by the lithium concentration in the alloy.

The increase in growth rate with the decrease of lithium concentration seems to contradict the results of Jha *et al.* [3]. However, as these authors point out, their conclusions are obtained for alloys containing more than 2.4 mass % lithium and should not be extrapolated to more dilute alloys, as in the present case. Nevertheless, it is possible to use their theoretical results to try to explain the dependence of $K_{\rm I}$ on lithium content. According to Jha *et al.* [3], the growth parameter, $K$, can be related to the diffusion coefficient of lithium in aluminium, $D$, and to a parameter $S$ which depends on the lithium concentration in the alloy, and decreases as lithium content increases

$$K = SD^{1/2} \qquad (2)$$

In concentrated alloys, the diffusion coefficient would increase enough with lithium content to counteract the decrease of the parameter $S$. In Al–Li–Ti alloys, where the relationship between $K$ and the concentration of lithium is the opposite, the diffusion

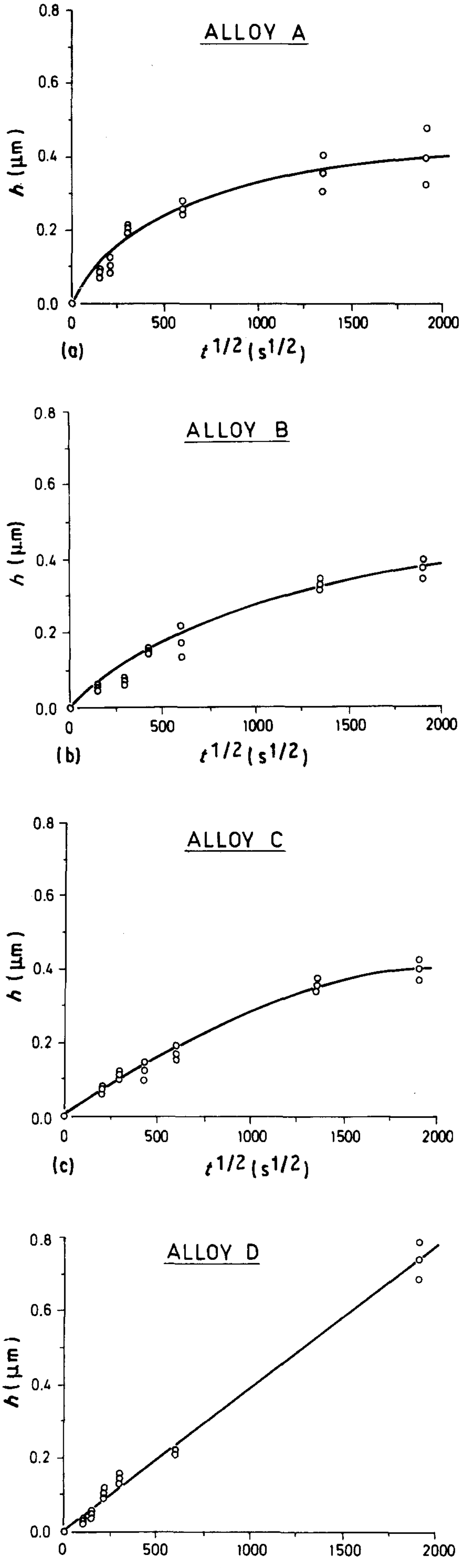

*Figure 5* PFZ half width $h$ versus $t^{1/2}$ of the Al–Li–Ti alloys aged at 473 K.

TABLE II Calculated values of the PFZ growth parameters $K_{\text{I}}$ and $K_{\text{II}}$

| Alloy (mass%) | $K_{\text{I}}$ (up to 24–48 h) ($\times 10^{-4}$ μm s$^{-1/2}$) | $K_{\text{II}}$ (from 24–48 h) ($\times 10^{-4}$ μm s$^{-1/2}$) |
|---|---|---|
| A (Al-1.88Li-0.35Ti) | 4.9 | 1.2 |
| B (Al-2.33Li-0.20Ti) | 3.5 | 1.9 |
| C (Al-2.26Li-0.15Ti) | 3.5 | 2.4 |
| D (Al-2.02Li-0.10Ti) | 3.9 | 3.9 |

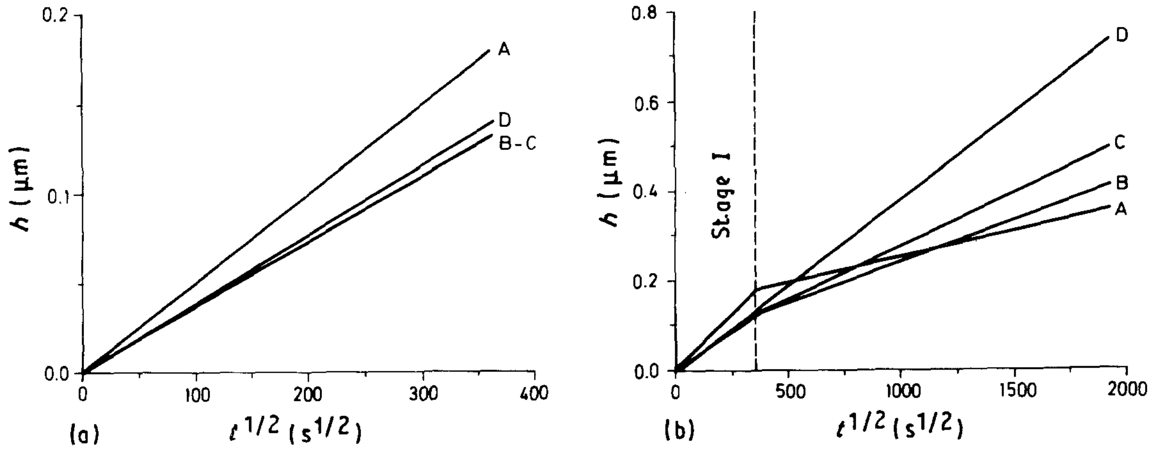

*Figure 6* Growth kinetics of PFZs in Al–Li–Ti alloys aged at 473 K: (a) stage I: up to 24–48 h; (b) stage II: from 24–48 h.

coefficient does not counteract the parameter $S$, indicating that for short ageing times the presence of titanium in solid solution reduces lithium mobility.

At stage II (Table II), $K_{\text{II}}$ is higher the lower the titanium content

$$K_{\text{II}}(\text{A}) < K_{\text{II}}(\text{B}) < K_{\text{II}}(\text{C}) < K_{\text{II}}(\text{D})$$

which indicates that, with increasing ageing time, PFZ growth kinetics, and the diffusion coefficient of lithium, according to Equation 2, are mainly controlled by the titanium concentration of the alloy. Therefore, titanium would act retaining either lithium atoms or vacancies [7]. As no phase containing both lithium and titanium has been found in these alloys, titanium in solid solution would retain vacancies, diminishing lithium mobility and decreasing $\delta'$ dissolution rate as compared to other Al–Li alloys.

For short ageing times, the number of quenched-in vacancies is very high and titanium would slightly alter PFZ growth kinetics. For long ageing times, the amount of free vacancies diminishes and the effect of titanium would prevail, retarding even more $\delta'$ dissolution, and therefore, decreasing more the PFZ growth rate the higher the titanium concentration of the alloy. In alloy D, with the lowest titanium content, titanium influence on PFZ growth is not very pronounced and PFZ half width data can be fitted to a single straight line.

### 3.2. Stable $\delta$ phase

According to the most accepted precipitation sequence [12], as ageing time increases, part of the lithium atoms released during dissolution of $\delta'$, instead of contributing to the coarsening of other $\delta'$ particles, diffuse towards the grain boundaries to contribute to the heterogeneous nucleation and growth of the stable $\delta$ phase. In general, in Al–Li alloys it has been determined that $\delta$ growth rate increases with lithium content and ageing temperature [2, 10].

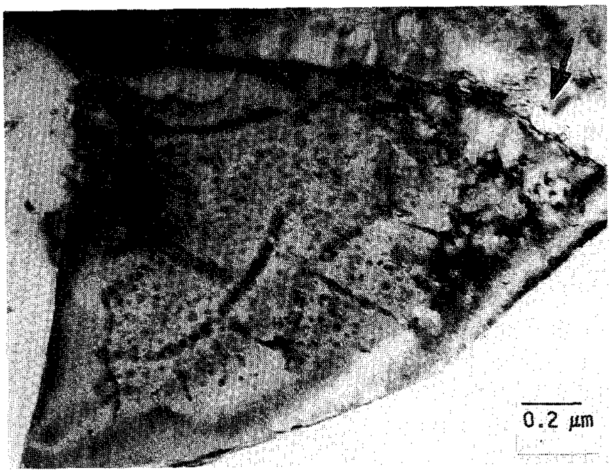

*Figure 7* Bright-field image showing a stable $\delta$ particle on grain boundary. Alloy B (Al–2.33%Li–0.20%Ti) aged at 473 K for 100 h.

In the Al–Li–Ti alloys, growth of $\delta$ phase greatly depends on the titanium concentration of the alloy. By TEM, plate-shaped $\delta$ particles are first visible on grain boundaries in the alloy with lower titanium content (starting from ~ 12 h of heat treatment in alloys D and C, ~ 48 h in alloy B and ~ 500 h in alloy A). Fig. 7 shows a stable $\delta$ particle of ~ $80 \times 120$ nm$^2$ in size precipitated on a grain boundary in alloy B aged for 100 h. The grain corresponds to an intermediate region of the ribbon, having a microstructure of narrow-walled cells. A PFZ half width of ~ 0.15 μm around the grain boundary can also be observed.

The relationship between titanium concentration and the amount of stable phase is also revealed by X-ray diffraction. Measuring the area under the diffraction peaks at 1000 h of ageing time, a lower volume fraction of δ has been determined, the higher the titanium content. Furthermore, in alloy A, which has the highest titanium concentration, at 1000 h of ageing it is possible to find grains with only a few δ′ particles [7]. In this condition, a high volume fraction of δ is expected. However this does not happen.

The fact that the precipitation of the stable phase is retarded in rapidly solidified Al–Li–Ti alloys, and that this effect is more pronounced for higher titanium concentration of the alloy indicate once more that this element reduces lithium mobility, delaying solute arrival to the grain boundaries. In the particular case of the cellular microstructures, the predominant mechanism would be as follows: within the cells, due to the higher concentration of titanium, the amount of free vacancies is lower than on the cell walls. Thus, to form the δ phase a lithium atom released by a δ′ particle has to diffuse towards the grain boundaries crossing or surrounding vacancy-depleted zones, where its diffusion rate is lower the higher the titanium concentration of the alloy.

Obviously, it should be expected that for ageing times long enough to transform all δ′ in δ, the volume fraction of the stable phase would only be related to the lithium content.

## 4. Conclusion

Titanium in solid solution greatly modifies the ageing characteristics of the Al–Li alloys. PFZ growth rate is lower in rapidly solidified Al–Li–Ti alloys than in other Al–Li alloys. Moreover, PFZ growth rate can be assumed to have two different stages. At the first one, up to 24–48 h, kinetics is mainly controlled by the lithium concentration of the alloy, whilst for longer ageing times, kinetics is mainly titanium controlled, the growth rate being higher at lower titanium contents. On the other hand, it has been determined that the stable δ phase precipitates later at higher titanium contents.

Both results lead to the conclusion that titanium in solid solution would retain vacancies, reducing lithium diffusion rate. Therefore, δ′ dissolution would be retarded, and so would the PFZ growth rate. On the other hand, the time required for lithium atoms to diffuse to grain boundaries would be increased, and thus, precipitation of the stable δ phase would also be retarded.

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