Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 395-400

Effect of Natural Ageing on the Artificial Ageing Response of an Al-Mg-Si-Cu Alloy

Lingfei Cao[1], Paul A. Rometsch[1], Hao Zhong[1,2], Yagnesh Mulji[3], Sam X. Gao[1] and Barry C. Muddle[1]

[1]ARC Centre of Excellence for Design in Light Metals, Monash University, VIC 3800, Australia
[2]Suzhou Nonferrous Metals Research Institute, CHALCO, Suzhou 215026, China
[3]Polytech Nantes, F-44306 Nantes, Cedex 3, France

The mechanism of natural ageing and its effect on the subsequent artificial ageing response of an Al-Mg-Si-Cu alloy has been investigated by hardness and electrical conductivity testing, along with nanostructural characterisation using transmission electron microscopy (TEM) and 3-D atom probe (3DAP) analysis. The alloy is based on the AA6022 specification, with an additional 0.3 wt% Cu. The initial hardening behaviour of the alloy is influenced significantly by the degree of clustering of solute Mg, Si and Cu atoms. The artificial ageing response is greatest in samples aged immediately after quenching, but decreases very rapidly if samples are allowed several hours of prior natural ageing. The combined hardening effect of natural ageing and short artificial ageing continues to decrease with longer-term natural ageing and, after several days of natural ageing, results in a lower hardness than that achieved by natural ageing alone. The hardening behaviour during natural ageing and subsequent artificial ageing is discussed in relation to various distributions of clusters, zones and/or precipitates.

Keywords: *6xxx; natural ageing; ageing response; 3DAP; clustering.*

1. Introduction

Al-Mg-Si-Cu heat treatable alloys show a significant hardening response during artificial ageing, but this hardening response is also strongly influenced by the degree of natural ageing after solution treatment [1-4]. Since storage at room temperature can not be easily avoided in practical processing, an understanding of how natural ageing affects the artificial ageing response is of great interest from both fundamental scientific and industrial perspectives.

In studying this phenomenon, Pashley *et al* [1, 2] first proposed a model of solute clustering to explain the two-step ageing behaviour of an Al-Mg-Si alloy, and concluded that the solute/vacancy supersaturation in the matrix during the early stages of artificial ageing is most important. It was suggested that the deleterious effect was accompanied by a coarser precipitate structure, and could be reduced by slowing down the ageing during storage, e.g. by adding Cu or lowering the storage temperature. Edwards *et al* [4] applied atom probe field ion microscopy to examine the precipitation sequence in alloy 6061. They found separate Si- and Mg- clusters and Mg-Si co-clusters, and proposed that the nature of clusters (i.e. co-cluster or individual clusters), rather than their size, was critical for the formation of subsequent intermediate phases. The Mg/Si ratios in the intermediate precipitates and co-clusters were all close to unity. Murayama *et al* [5] also found Mg-Si co-clusters in addition to separate Si and Mg atom clusters after long-term natural ageing. They found the chemical compositions of zones and β" precipitates to change with the alloy composition. Serizawa *et al* [6] reported two types of nanoclusters: cluster (1) formed near room temperature and cluster (2) formed at 100 °C. The distribution of both the size and Mg/Si ratio of cluster (1) did not change during prolonged natural ageing, while cluster (2) grew by a diffusion-controlled mechanism and had a Mg/Si ratio similar to that of the β" phase. Only cluster (2) could easily transform continuously into the β" phase during early stage artificial ageing. Despite their successes, there is still some uncertainty

about the nature of clustering, the precipitation sequence and the corresponding influences on alloy properties under different ageing conditions.

In order to better understand the mechanism of natural ageing and its effect on the subsequent artificial ageing response of Al-Mg-Si-Cu alloys, therefore, the current study examines the above aspects by combining hardness and electrical conductivity testing, along with nanostructural characterisation using transmission electron microscopy (TEM) and 3-dimensional atom probe (3DAP) analysis. An Al-Mg-Si-Cu alloy based on the AA6022 specification with an additional 0.3 wt% Cu was chosen for this work.

2. Experimental Procedures

The alloy, of composition shown in Table 1, was cast, homogenised, and hot and cold rolled to 1.0 mm thick sheets. Small pieces were solution treated at 550 °C for 0.5 h and quenched into water at room temperature. Samples were analysed before and after artificial ageing (AA) in an oil bath at 170 °C, following natural ageing intervals of 0.03, 0.1, 0.3, 1, 3, 12, 24, 72, 168 and 504 h.

Natural ageing curves were determined by measuring the Vickers hardness and electrical conductivity of the samples at room temperature with a 5 kg load and a Foerster Sigmatest 2.068 eddy current tester, respectively. Microstructural observations were carried out both with conventional TEM using a Philips CM20 (200kV) and high-resolution transmission electron microscopy (HRTEM) using a JEOL 2011 (200kV). An Oxford NanoScience 3D atom probe field ion microscope was used for 3DAP analysis. The tip was prepared by using a standard two-step electro polishing technique. The analysis proceeded under an ultrahigh vacuum of ~3.4×10^{-11}mbar, with a pulse fraction of 20%, a temperature of 25 K, and a detection efficiency of 45%. Analysis of the 3DAP data was carried out using POSAP software, with the particle analysis function used to select and quantify the precipitates. The parameters (N, D, L and S) of the particle selection were determined both from the literature and atomic reconstruction results. Values for D (minimum distance between atoms), L (the surround distance) and S (the erosion distance) were all selected to be 0.5 nm. The minimum number of solute atoms (N) was first set to 10, as in previous work [7], but was then set to 2 in order to obtain more atom distribution and size information related to smaller solute aggregates.

Table 1: Alloy Composition (wt%)

Si	Mg	Cu	Fe	Mn	Cr	Zn	Ti
1.07	0.48	0.29	0.12	0.06	0.08	0.19	0.01

3. Results and Discussion

3.1 Hardness and Electrical Conductivity

The variation in hardness and electrical conductivity with natural ageing time of the Al-Mg-Si-Cu alloy after solution treating for 0.5 h at 550 ºC and water quenching (T4 treatment) is presented in Fig. 1 and Fig. 2. In the T4 condition, considerable hardening occurs within several hours of natural ageing, coinciding with a decrease in electrical conductivity. It is postulated that during natural ageing, the solute atoms form clusters or co-clusters of Mg, Si and Cu, which are not large enough to be detectable by conventional TEM. Such clusters are believed to obstruct the free movement of dislocations and electrons and therefore cause an increase in hardness and a decrease in electrical conductivity with increasing natural ageing time [8-10].

Figure 1 shows the effect of prior natural ageing (from 0.03 to 504h) on the hardness after artificial ageing at 170 ºC for 0, 0.13, 0.5, 2 and 8 h after different natural ageing times. At all artificial ageing times, the hardness is greatest when the prior natural ageing time is shortest (0.03 h). It is clear that after natural ageing for a given time, longer artificial ageing times (from 0.13 h to 8 h) result in a higher hardness. For a given artificial condition, however, a longer natural ageing time (0.03 h up to 504 h) generally results in a 15-40 HV_5 lower artificially aged hardness.

When considering the hardening response during the early stages of artificial ageing, i.e. 0.5 h in the current work, it is evident that for short natural ageing times of up to about 3 h, the hardness after 0.5 h at 170 ºC is clearly higher than the naturally aged hardness. For natural ageing times of greater than about 24-72 h, however, the hardness after 0.5 h at 170 ºC is lower than the naturally aged hardness. As a result, the early-stage artificial age hardening response is greatest at very short natural ageing times and then decreases very rapidly to zero within about 12 h of natural ageing and to less than zero after longer natural ageing times.

In addition, the variation of electrical conductivity with natural ageing time after artificial ageing for 0.5 h at 170 ºC (termed as T6) is plotted in Fig. 2. The next sections will show that the decrease in T6 conductivity with increasing prior natural ageing time can be explained in terms of an increase in the concentration of solute in solution.

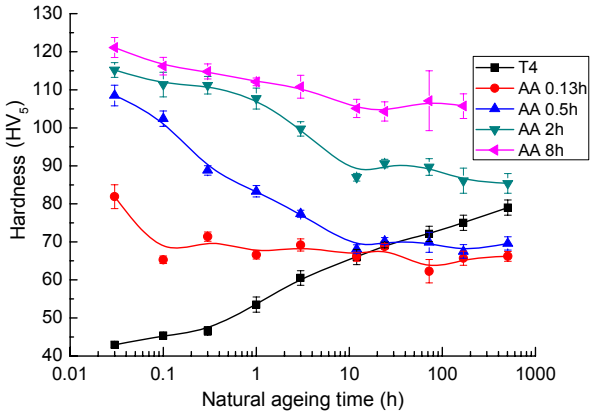

Fig. 1: Effect of natural ageing time on the hardness before and after ageing at 170 ºC.

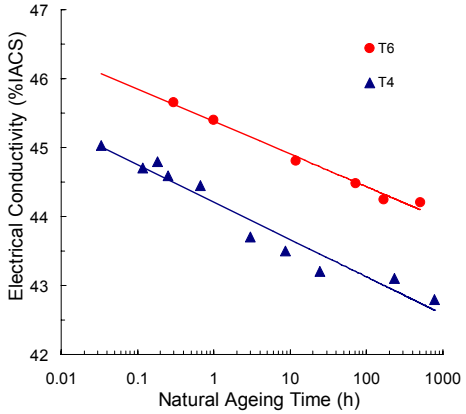

Fig. 2: Effect of natural ageing on the electrical conductivity.

3.2 Transmission Electron Microscopy

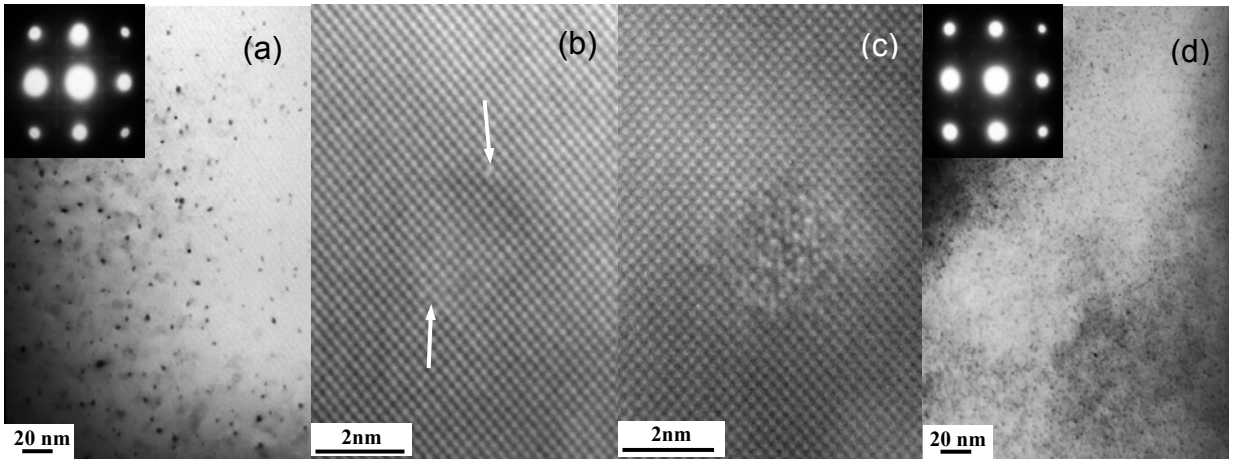

Fig. 3: Bright-field TEM and HRTEM micrographs along the $[001]_{Al}$ direction in different ageing conditions: (a) Quenched + 0.03 h@20 ºC + 0.5 h@170 ºC, (b) HRTEM of (a) showing a coherent zone, (c) HRTEM of (a) showing a β" precipitate, (d) Quenched + 168 h@20 ºC + 0.5 h@170 ºC.

Figure 3 shows microstructures typical of the current Al-Mg-Si-Cu alloy under selected ageing conditions. When the alloy was artificially aged at 170 ºC for 0.5 h with only 0.03 h of prior natural ageing, its hardness was 108±3 HV_5, and both zones and β" precipitates were observed in this condition. When it was artificially aged with a prior natural ageing time of 7 days, the hardness dropped obviously by about 41 HV_5. Fig. 3 (d) shows the corresponding bright-field TEM image and the $[001]_{Al}$ selected-area electron diffraction (SAED) pattern. The shape of the fine solute aggregates

appears largely spherical, and unlike in Fig. 3 (a), the SAED pattern shows little diffraction intensity corresponding to β". This suggests that when the alloy was naturally aged for 7 days and then artificially aged at 170 ºC for 30 min, the visible solute aggregates in Fig. 3 (d) are mainly coherent zones. In addition, the corresponding hardness is low (67±3 HV_5). Based on these comparisons, it may be deduced that β" precipitates are the main hardening phase for such Al-Mg-Si-Cu alloys after artificial ageing at 170 ºC.

3.3 Atom Probe Analysis

Table 2: Selected results of solute aggregate analysis for different ageing conditions (N = 10)

Ageing condition	(a)	(b)	(c)
Density (aggregates/m^3)	2.4x 10^{24}	1.4x 10^{24}	3.2x 10^{24}
Average size$^{(min\text{-}max\ size)}$ (atoms/aggregate)	$111^{(15\text{-}464)}$	$31^{(22\text{-}41)}$	$50^{(12\text{-}166)}$
Mg/Si atom ratio in aggregates	1.1	0.8	0.9

Note: (a) Quenched + 0.03 h @20 ºC + 0.5 h @170 ºC;
(b) Quenched + 168 h @20 ºC;
(c) Quenched + 168 h @20 ºC + 0.5 h @170 ºC

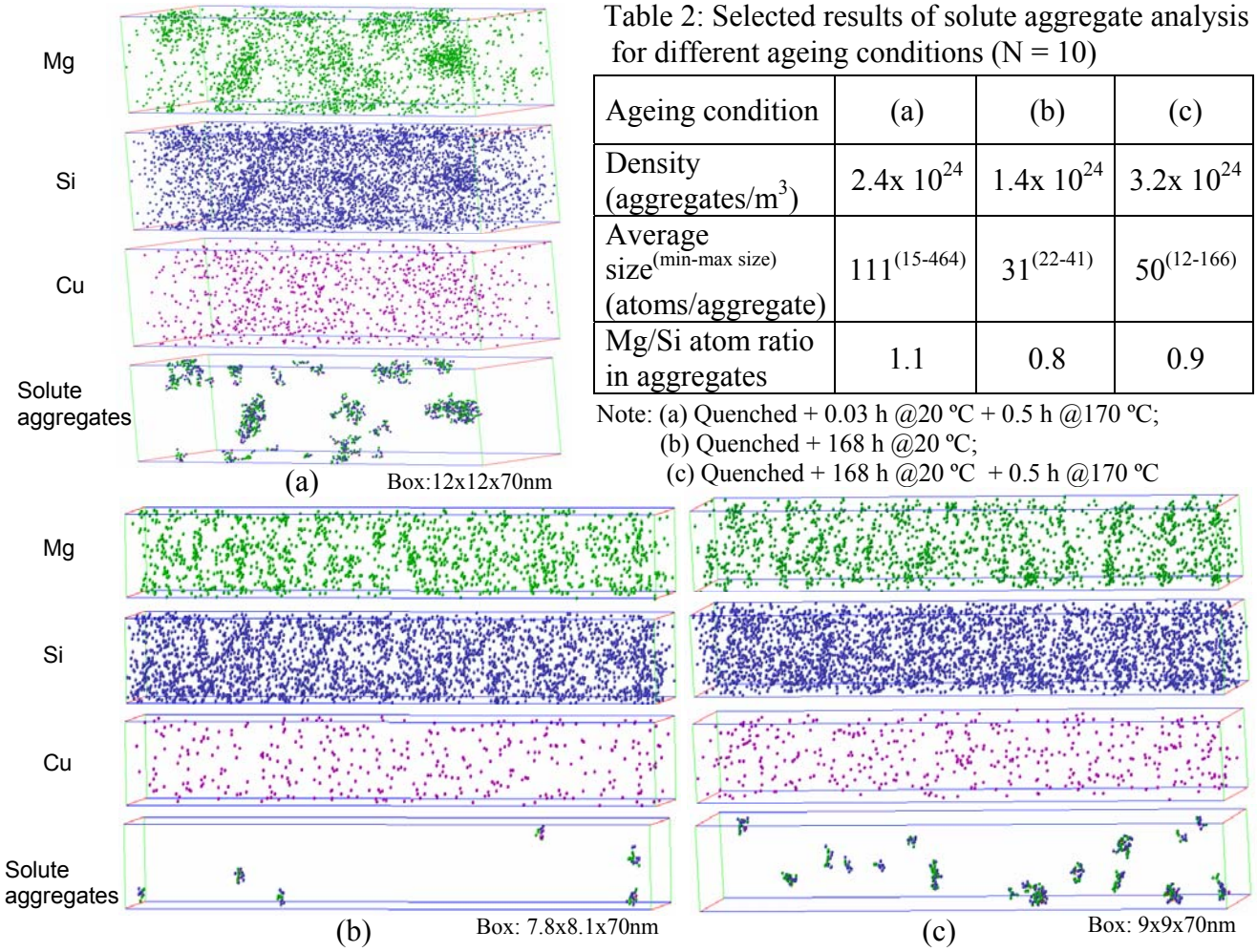

Fig. 4: 3DAP elemental maps in different conditions , showing Mg, Si and Cu atom distributions, and corresponding maps of solute aggregates resolved using particle analysis parameters of D = 0.5 nm, L = 0.5 nm, S = 0.5 nm and N = 10 atoms. Heat treatments for (a) (b) and (c) are specified in Table 2.

Figure 4 shows typical elemental maps recorded using 3DAP from samples in different ageing conditions. Both Mg and Si atoms show certain aggregations while Cu is relatively randomly distributed. Using the particle analysis function in the POSAP software, solute aggregates were resolved, with analysis results listed in Table 2. It is clear that there are significant changes in the density, average size and distribution of solute aggregates after different natural ageing and artificial ageing treatments. When the alloy was artificially aged at 170 ºC for 0.5 h with only 0.03 h of prior natural ageing, large solute aggregates were formed with an average and maximum size 2-3 times larger than when aged after 168 h of natural ageing. Ageing for 0.5 h at 170 ºC after natural ageing for 7 days caused both the aggregate density and the average aggregate size to double compared to the T4 condition. Further work is required to understand this. It is possible that N = 10 does not give sufficient information about the smaller aggregates occurring in the T4 conditions.

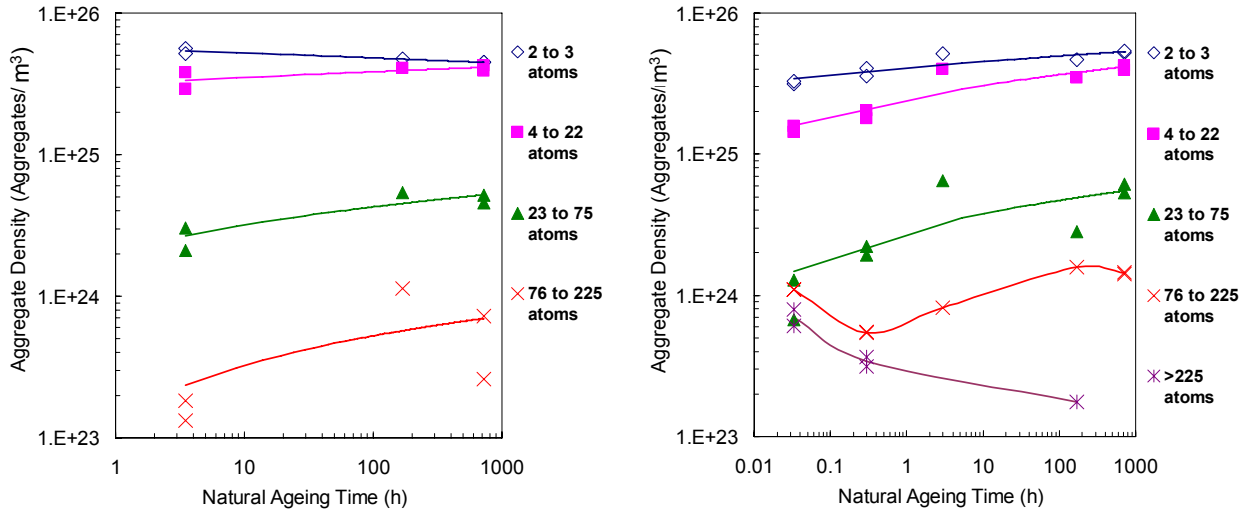

Fig. 5: Effect of natural ageing on the density of differently sized solute aggregates in (a) T4 and (b) T6 conditions, based on the number of aggregates per box divided by the box volume (N = 2).

In the above analysis, the minimum number of solute atoms (N) is set to 10, which is quite common in 3DAP work for Al alloys [7]. However, in order to investigate the various distributions of clusters, zones and/or precipitates, N= 2 can give more information. Accordingly, in the following analysis, solute aggregates were categorised into five size groupings, as represented in Fig. 5; the classification method is described in greater detail elsewhere [11]. According to this classification, aggregates with ⩽75 detected atoms were designated as clusters, aggregates with 76-225 atoms as coherent zones and aggregates with more than 225 detected atoms as precipitates.

The statistical results for the alloy in the T4 condition show that the density of clusters increases with natural ageing time, except for the smallest clusters (⩽3 detected atoms). Combined with the T4 hardness results in Fig. 1, these results suggest that the higher hardness after longer natural ageing times is caused by the increasing density of solute aggregates in the larger size categories (4-225 detected atoms).

In the T6 condition, the quantity of small clusters increases with increasing prior natural ageing time, while for the larger aggregates with no less than 76 detected atoms, the tendency has certain variations. For the aggregates containing more than 225 detected atoms (classified as precipitates), the density of these precipitates decreases as the prior natural ageing time increasing from 0.03 h to 504 h. As discussed in Section 3.2, the β" precipitates should be the main hardening phase for such Al-Mg-Si-Cu alloys in the T6 condition. Therefore, these 3DAP results can provide an explanation for the decrease in T6 hardness with increasing natural ageing time, as illustrated in Fig. 1.

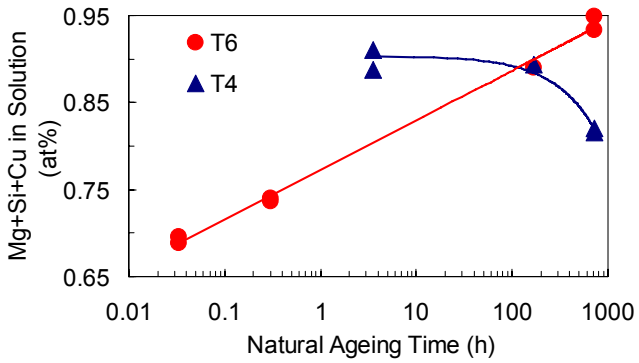

Fig. 6: Effect of natural ageing on amount of solute in solution as determined by using N = 2.

Fig. 6 shows that the amount of solute atoms in solution decreases with increasing natural ageing time in the T4 condition, which implies that a higher volume fraction of aggregates (with 4-225 detected atoms as shown in Fig. 5 (a)) was formed at longer natural ageing times. These aggregates are within the range of clusters or zones, which are normally coherent with the matrix, and will tend to obstruct the free movement of electrons. A similar tendency of small aggregates can be found in the T6 condition (Fig. 5 (b)) as well, causing the electrical conductivity in both the T4 and T6 condition to decrease as shown in Fig. 2. In the T6 condition, the concentration of Mg+Si+Cu solute atoms in solution increases with increasing prior natural ageing time. This means that natural ageing inhibits the growth in volume fraction of solute aggregates during artificial ageing, particularly the larger solute aggregates with more than 225 detected atoms, as shown in Fig. 5 (b). Consequently, the formation of the main hardening precipitate is restrained and the hardness decreases with increasing prior natural ageing time, as shown in Fig. 1. This might be explained in terms of a decrease in vacancy supersaturation during natural ageing, as suggested by Pashley *et al* [1,2].

4. Summary

The effect of natural ageing on the subsequent artificial ageing response of an Al-Mg-Si-Cu alloy was investigated. The results show that the initial hardening behaviour of the alloy is influenced significantly by the degree of clustering of Mg, Si and Cu solute atoms. The artificial ageing response is greatest in samples aged immediately after quenching, but decreases very rapidly with increasing prior natural ageing time from 0 to 3 hours.

Transmission electron microscopy results show both coherent zones and β" precipitates to exist in the T6 condition after 0.5 h at 170 ºC with 0.03 h of prior natural ageing. The main hardening precipitates were identified as β". These precipitates can increase the hardness significantly, but natural ageing before artificial ageing inhibits their formation. Atom probe results also show that the density of large solute aggregates (designated as precipitates with more than 225 detected atoms) in the T6 condition decreases with longer prior natural ageing times, while the density of small aggregates (4-75 detected atoms) increases.

Acknowledgements

The authors would like to thank the Aluminium Corporation of China (CHALCO) for supporting this work financially and providing materials as part of the Australia-China International Centre for Light Alloys Research (ICLAR). The assistance of Dr. X.Y. Xiong with 3DAP analysis at the Monash Centre for Electron Microscopy (MCEM) is also gratefully acknowledged.

References

[1] D. W. Pashley, J. W. Rhodes and A. Sendorek: J. Inst. Metals. 94 (1966) 41-49.
[2] D. W. Pashley, M. H. Jacobs and J. T. Vietz: Phil. Mag. 15 (1967) 51-76.
[3] S. Esmaeili, X. Wang, D. J. Lloyd and W. J. Poole: Metal. Mater. Trans. A. 34 (2003) 751-763.
[4] G. A. Edwards, K. Stiller, G. L. Dunlop and M. J. Couper: Acta Mater. 46 (1998) 3893-3904.
[5] M. Murayama and K. Hono: Acta Mater. 47 (1999) 1537-1548.
[6] A. Serizawa, S. Hirosawa and T. Sato: Meta. Mater. Trans. A. 39 (2008) 243-251.
[7] J. Buha, R. N. Lumley and A. G. Crosky: Phil. Mag. 88 (2008) 373-390.
[8] I. Kovacs, J. Lendvai and E. Nagy: Acta Metall. 20 (1972) 975-983.
[9] S. Esmaeili, D. Vaumousse, M.W. Zandbergen, W.J. Poole, A. Cerezo and D.J. Lloyd: Phil.Mag. 87 (2007) 3797-3816.
[10] Y. Birol: Mat. Sci. Eng. A. 391 (2005) 175-180.
[11] P. A. Rometsch, L. Cao and B. C. Muddle: The 12th International Conference on Aluminium Alloys (2010) in press.