Ultramicroscopy 111 (2011) 690–694

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Atom probe analysis of early-stage strengthening behaviour in an Al–Mg–Si–Cu alloy

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ARTICLE INFO

Available online 19 November 2010

Keywords:
Atom probe
Natural ageing
Cluster
Aluminium

ABSTRACT

The strengthening of an Al–Mg–Si–Cu alloy during natural ageing and subsequent short artificial ageing was investigated using three-dimensional atom probe (3DAP) analysis and tensile testing. The contingency table and Markov chain analyses confirmed that non-random arrangements of atoms already exist after a natural ageing time of only 3.5 h. Extensive use of particle analysis tools in the IVAS and PoSAP software packages revealed that whilst the commonly used minimum aggregate size (N_{min}) of 10 is a reasonable choice, much more useful information about the system can be gained by additionally employing a wide range of larger and smaller N_{min} values. In particular, it was found that the density and volume fraction of solute aggregates increased with increasing natural ageing time in the T4 condition. After a 0.5 h artificial ageing treatment at 170 °C (designated as T6), the size, volume fraction and Mg/Si ratio of the aggregates were all found to decrease with increasing prior natural ageing time. These findings are used to discuss the detrimental effect of natural ageing, where the T6 strength has been observed to decrease rapidly with increasing prior natural ageing time before stabilising after several hours of natural ageing.

1. Introduction

The enormous amount of quantitative data generated by modern three-dimensional atom probe (3DAP) tomography poses a significant data analysis challenge. Software packages like PoSAP or IVAS are typically used to process raw data of millions of detected atoms. This includes the visualisation of atoms in three dimensions, the determination of various local compositions and the use of a range of inbuilt algorithms to detect and quantify any deviations from purely random arrangements of atoms in the lattice. Of particular interest for the current work are the various cluster detection and analysis tools.

The purpose of this work is to study the clustering behaviour of solute atoms during the natural ageing and subsequent artificial ageing of an Al–Mg–Si–Cu alloy. Although this alloy system has been studied extensively [1–5], some long-standing issues such as the so-called detrimental effect of natural ageing that plagues many such 6xxx series aluminium alloys are not yet well understood. This detrimental effect of natural ageing is the phenomenon whereby the artificially aged strength (T6 temper) is reduced when the material is held at room temperature prior to artificial ageing. Due to difficulties in resolving atomic scale clusters with transmission electron microscopy, the use of 3DAP tomography is vital for gaining deeper insights into the solute clustering behaviour to help resolve these issues.

Even though 3DAP analysis techniques have by now been widely applied to study clustering in a range of aluminium alloys, some significant questions remain both in the realm of data analysis techniques and in the interpretation of the results to understand material behaviour in relation to early stage clustering effects. The current work will therefore explore how the choice of values for commonly used cluster analysis parameters can affect the results. The use of contingency tables and Markov chains [6] is also explored to evaluate deviations from random arrangements of atoms. Special attention is given to outputs that are most useful for explaining variations in strength. To avoid confusion over what may be considered a cluster, a coherent zone or a precipitate, all such 'particles' will simply be referred to as variously sized solute aggregates.

2. Materials and methods

The chemical composition of the 6xxx series alloy investigated in this work is given in Table 1. The alloy was DC-cast, homogenised and hot and cold rolled to 1 mm thick sheets. All samples were solution treated for 0.5 h in a salt bath at 550 °C, quenched in room temperature water and then either naturally aged only (designated as T4) or artificially aged for 0.5 h in an oil bath at 170 °C after various times of prior natural ageing. To distinguish them from the T4 condition, the artificially aged samples are designated here as

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doi:10.1016/j.ultramic.2010.11.009

being in the T6 temper (in the broad sense of the term), even though they are clearly in the under-aged condition. Tensile testing was carried out on samples with a cross-sectional area of 5 mm^2 and a gauge length of 20 mm using an Instron 4505 tensile machine at an extension rate of 1.0 mm/min.

For 3DAP analysis, an Oxford nanoScience energy-compensated three-dimensional atom probe field ion microscope was used under ultrahigh vacuum conditions ($<10^{-10}$ mbar) with a pulse fraction of 20%, at a specimen temperature of 25 K, and with a detector efficiency of 45%. Samples sized $0.5\times0.5\times10$ mm^3 were wire cut from the cold-rolled sheet with the needle axis aligned along the rolling direction. These samples were wrapped in aluminium foil for heat treatment in salt and/or oil baths. Sharp tips were prepared with a standard two-stage electro-polishing technique using a 33% nitric acid–67% methanol solution for stage one and a 2% perchloric acid–98% butoxyethanol solution for stage two.

Data analyses were carried out using both PoSAP 1.76.1 (2008) and IVAS^{TM} 3.4.1 (2009) software. Various values were tested for the commonly used particle analysis parameters—maximum distance between solute atoms (D_{max}), surround distance (L), erosion distance (S) and the minimum number of detected solute atoms comprising an aggregate (N_{min}). The IVAS integrated cluster finding and analysis tool was used to determine optimum values for D_{max} and N_{min} by maximising the ratio of actual to random signals based on the nearest neighbour, cluster size and cluster count distribution plots of actual and randomised data (see Table 2). These results were then compared to the PoSAP results obtained for N_{min} values ranging from 2 to as high as possible, with D_{max}, L and S all set to 0.5 nm. The choice of 0.5 nm for D_{max}, L and S is comparable with the values used by other authors [1,2,7], but may be considered to be a little more stringent. It was found, for example, that it was not desirable to increase L to above the value of D_{max}, as proposed by Vaumousse et al. [7], because this was found to unnecessarily increase the amount of solvent Al atoms included in the aggregates. For D_{max}, a value of between one and two times the lattice parameter is reasonable for detecting nearest neighbours. Furthermore, the choice of $D_{max}=L=S=0.5$ nm is in keeping with the IVAS requirements of $D_{max}/2\le L\le D_{max}$ and $0\le S\le L$. The contingency tables and Markov chains were calculated using PoSAP and IVAS, respectively.

Table 1
Chemical composition of the Al–Mg–Si–Cu alloy.

	Si	Mg	Cu	Fe	Mn	Cr	Zn	Ti
wt%	1.07	0.48	0.29	0.12	0.06	0.08	0.19	0.01
at%	1.03	0.54	0.12	0.06	0.03	0.04	0.08	0.01

3. Results and discussion

The current work was motivated by a desire to understand the significant detrimental effect of natural ageing observed in this alloy, whereby the T6 yield strength (after 0.5 h of artificial ageing at 170 °C) decreases from almost 250 to less than 150 MPa when the delay at room temperature (before artificial ageing) is increased from 0.03 to $\ge$ 3 h. The yield strength results are presented in Fig. 1. The corresponding 3DAP atom maps and results determined with the IVAS optimised values are presented in Fig. 2 and Table 2, respectively. There is a significant amount of scatter in these results (e.g. unexpected variations in average size and volume fraction of solute aggregates for different T6 conditions), making it difficult to ascertain whether the solute aggregate number density, average size, volume fraction and Mg/Si ratio all really do decrease with increase in prior natural ageing time in the T6 condition. It is believed that this scatter results primarily from the use of different IVAS optimised values of N_{min}, D_{max}, L and S for different data sets. In order to clarify these results, PoSAP was also used to systematically investigate the effect of varying N_{min} (as discussed later). The PoSAP results using $N_{min}=10$ and $D_{max}=L=S=0.5$ nm are

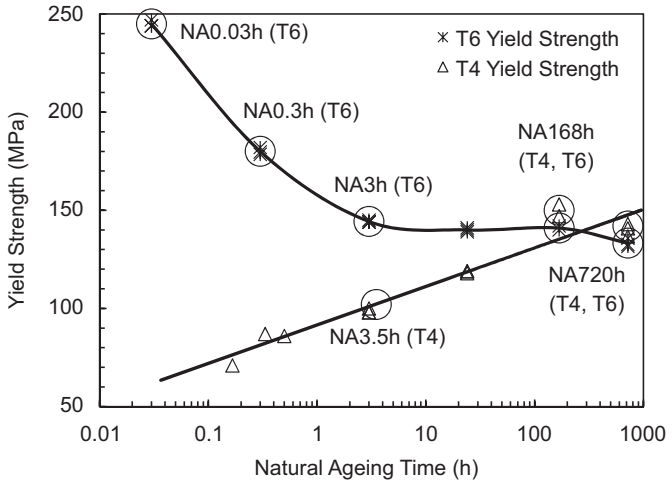

Fig. 1. Effect of natural ageing on yield strength in both the T4 condition and after subsequent artificial ageing for 0.5 h at 170 °C (T6). Circles show conditions chosen for 3DAP analysis.

Table 2
Solute aggregate details are listed for various 3DAP reconstruction volumes. Optimum values for N_{min}, D_{max}, L and S (with Mg, Si and Cu as solute elements) were determined using the IVAS integrated cluster finding and analysis tool. Results from PoSAP using $N_{min}=10$ and $D_{max}=L=S=0.5$ nm are shown for comparison in brackets using bold typeface. Aggregate sizes and volume fractions include Al (i.e. all detected atoms).

Condition designation	NA0.03h (T6)		NA0.3h (T6)		NA3h (T6)		NA168h (T6)		NA720h (T6)		NA3.5h (T4)		NA168h (T4)		NA720h (T4)	
Natural ageing time (h)	0.03		0.3		3		168		720		3.5		168		720	
Artificial ageing time at 170 °C (h)	0.5		0.5		0.5		0.5		0.5		0		0		0	
Reconstruction volume (nm^3)	$10\times11\times150$		$12\times13\times225$		$6\times6\times160$		$9\times9\times70$		$6.5\times10.5\times150$		$12.5\times12.5\times240$		$7.8\times8.1\times70$		$11\times5\times100$	
N_{min} (number of solute atoms)	7	**(10)**	10	**(10)**	8	**(10)**	10	**(10)**	12	**(10)**	14	**(10)**	10	**(10)**	11	**(10)**
$D_{max}=L=S$ (nm)	0.49	**(0.5)**	0.55	**(0.5)**	0.48	**(0.5)**	0.52	**(0.5)**	0.51	**(0.5)**	0.52	**(0.5)**	0.53	**(0.5)**	0.57	**(0.5)**
Average aggregate size (atoms)[a]	34	**(100)**	54	**(85)**	22	**(46)**	45	**(51)**	27	**(22)**	31	**(17)**	25	**(31)**	35	**(32)**
Volume fraction aggregates (%)[b]	0.33	**(0.38)**	0.30	**(0.16)**	0.20	**(0.26)**	0.28	**(0.27)**	0.04	**(0.09)**	0.01	**(0.01)**	0.10	**(0.07)**	0.24	**(0.05)**
Aggregate number density ($\times10^{24}$ m^{-3})[c]	5.6	**(2.2)**	3.4	**(1.2)**	5.6	**(3.5)**	3.7	**(3.2)**	1.0	**(2.6)**	0.2	**(0.4)**	2.5	**(1.4)**	4.4	**(1.1)**
Aggregate Mg/Si ratio[d]	1.2	**(1.2)**	1.0	**(1.0)**	1.2	**(1.4)**	1.0	**(0.9)**	0.6	**(0.8)**	1.0	**(1.1)**	0.7	**(0.8)**	0.7	**(0.6)**

[a] Sum of atoms in all aggregates divided by number of aggregates.
[b] Sum of atoms in all aggregates divided by number of atoms in reconstruction volume.
[c] Number of aggregates divided by reconstruction volume.
[d] Sum of Mg atoms in all aggregates divided by sum of Si atoms in all aggregates.