# Precipitation in stretched Al-Cu-Mg alloys with reduced alloying content studied by DSC, TEM and atom probe

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**Abstract.** The hardening and microstructural evolution during ageing of a Al-1.2Cu-0.5Mg and a Al-1.2Cu-1.2Mg (at.%) alloy has been investigated. Artificial ageing at 150°C of stretched and naturally aged samples initially (up to about 48 h) leads to very limited further strengthening, but ageing at 190°C results a quick increase in strength. Detailed microstructural investigation using differential scanning calorimetry, transmission electron microscopy and three-dimensional atom probe demonstrated that hardening at 150°C is mostly dominated by the formation of solute clusters with varying compositions and plate-like zones rich in copper at early stages of ageing (t<24h) and by the formation of S phase at the later stages of ageing. At higher 190°C no zones or clusters form and the ageing is dominated by the formation of S precipitates.

#### Introduction

The Al-Cu-Mg alloys are capable of developing medium-high strength and retaining their strength at relatively high temperatures. It has been found that hardening occurs in two distinct stages in Al-Cu-Mg alloys [1]. For a long time, it has been generally accepted that the origin of the first stage of rapid hardening is related to GPB zone formation and the second stage is attributed to the precipitation of the S' / S phase [2]. However controversy exists, especially relating to the existence of a S" phase and the nature of the precipitation responsible for the first stage of hardening [3,4,5].

It has been noted that the majority of research on early-stage precipitation in Al-Cu-Mg alloys so far has been focused on alloys either at T4 (solution treated and naturally aged) or at T6 (solution treated and artificially aged) condition. However, stretching after quenching, which is common for commercial applications, will have a profound influence on the precipitation and properties of the alloys. Little detailed work on precipitation in these stretched and aged materials has been reported. This paper combines the use of hardness measurement (HV), differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and 3-dimensional atom probe (3DAP) techniques to provide a comprehensive insight into the precipitation behaviour of two Al-Cu-Mg alloys with reduced alloying content (compared to standard 2024 and 2018 type alloys), which have been quenched, stretched and subsequently artificially aged. The aim is to explain the relation between precipitation and strength for these alloys.

#### **Experimental Procedures**

Two Al-Cu-Mg alloys with a Cu/Mg ratio of 2.3 and 1.0 (at% ratio) have been manufactured and studied (Table 1). Details on production route for the alloys are given in the companion paper [6]. After solution treatment (Alloy 1 at 525°C and Alloy 2 at 495°C), water quenching and stretching by 2.5%, the alloys have been left at room temperature for a few months before further ageing for 12-72 h at 150°C and for 6-48 h at 190°C respectively. Vickers hardness values were obtained from surfaces ground with #1200 grade SiC paper. Four indentations were made on each specimen with a 20 kg load and a mean HV is given. The DSC experiments were conducted using a Perkin-Elmer

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Pyris 1 in nitrogen atmosphere at a constant heating rate of 10°C/min, using disc-shaped DSC samples with a thickness about 0.9 mm and diameter 5mm. All runs were corrected by subtracting the baseline of the DSC, which was obtained from a run with an empty pan as reference. Experimental details of the TEM work are given elsewhere [7]. All observations were performed in the <100> matrix orientation. The 3DAP analyses were conducted on an energy-compensated optical position sensitive atom probe [4]. The specimens (in the shape of sharp needles with an end radius less than 100 nm) were prepared by a two-stage electropolishing method. Analyses were carried out

at 15 K with a pulse fraction (ratio of the pulse voltage to the direct current standing voltage) of 20% and a pulse repetition rate of 1500 Hz. The voltage was between 4.5 and 9.5 kV depending on the analysis.

Alloy	Cu	Mg	Mn
Alloy 1	1.18	0.51	0.21
Alloy 2	1.21	1.19	0.20

Table 1: Compositions of the alloys

# **Experimental Results**

Vickers hardness and DSC analysis
In quenched state hardness values are
63 for Alloy 1 and 72 for Alloy 2 [8].
Fig. 1 shows the hardness for stretched
and stretched and aged conditions for
both alloys. At 150°C hardness
increases slowly with ageing time and
only shows an obvious increase after
48 hrs. At 190°C the hardness rapidly
increases at first and then gradually
decreases.

Figs. 2 and 3 present the DSC results for both alloys aged at 150°C. Four effects (two exothermic and two endothermic) are evident. In line with results from literature [9,10], the dissolution of GPB zones and/or clusters occurs at 100-230°C and S

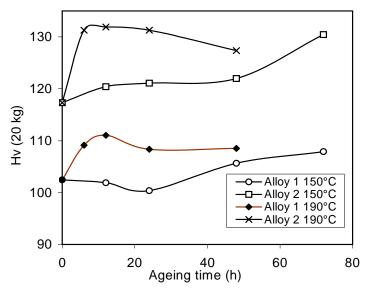


Fig. 1: Vickers hardness for both alloys aged at 150 and 190°C.

formation occurs at 230-320°C with a peak at about 270°C. The S dissolution is in the range of 330-470°C. The DSC curves reveal that the magnitude of the S precipitation effect in Alloy 1 is less than half that of Alloy 2. This is due to the limited Mg content in Alloy 1. Alloy 2 with a low Cu/Mg ratio only precipitates S phase; but Alloy 1 with a high Cu/Mg ratio appears to show a second precipitation effect (at about 390°C) which thought to be caused by  $\theta$  or  $\Omega$  formation. For ageing at 150°C, the heat content of S formation peaks decreases with increase of ageing time from 12 to 72 hours. From the reductions it is clear that substantial S precipitation occurs especially after 24 h ageing. Figs. 2 and 3 further show that at 150°C initially zones form, which are later gradually replaced by S phase. During 190°C ageing for Alloys 1 and 2, no zones form (effect at 100-230°C vanishes) and only S formation occurs (Figs. 4). At 6 h ageing there is still a small S formation peak, but with further ageing, the S precipitation peak completely disappears. This means that on isothermal ageing at 190°C most of the S formation is completed within about 6 h. For the solution-treated and natural aged Alloy 1, the zones/clusters dissolution effect occurs in two stages with the first stage being completed at about 160°C (Fig. 2). Ageing at 150°C causes this first stage to disappear.

# TEM analysis

At 150°C/12 h, TEM reveals many dislocation lines and loops for both alloys. The dislocations result from the stretching after solution treatment and the loops generally caused are condensation of quenched in vacancies. No precipitates were observed in bright field (BF) and no extra diffraction spots except the aluminium matrix could be resolved from the [001]<sub>Al</sub> zone. When the ageing time was increased to 24 h, dislocations still dominate the structure. Only from 150°C/48 h or longer ageing, could S precipitation be found, initially by dark field (DF) images and selected-area diffraction patterns (SADP). Zones/clusters could not be detected probably due to their sizes being below detection limit of the conventional TEM. 190°C/12 h, there are many S precipitates in the form of needles or laths in the matrix (Fig. 5), as well as some coarse ones located on grain boundaries. Analysis patterns diffraction indicates that there only S phase is present in Allov 2. precipitates are S phase in Alloy 1, but a few diffraction patterns evidence reveal of precipitates (Fig. 5(b)). No  $\theta$ was found by SADP in either alloy. Some S phase precipitates form as loop-like structures, which were apparently inherited from the shapes of original dislocation loops.

#### 3DAP analysis

Analyses have been performed by 3DAP on both alloys aged at 150°C/12 h. Fig 6a shows an example of atom map from the

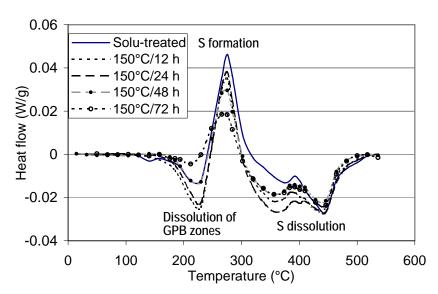


Fig. 2 DSC curves of Alloy 1 aged at 150°C.

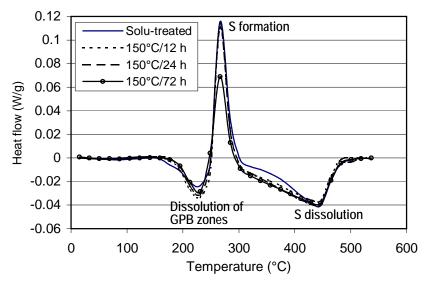


Fig. 3 DSC curves of Alloy 2 aged at 150°C.

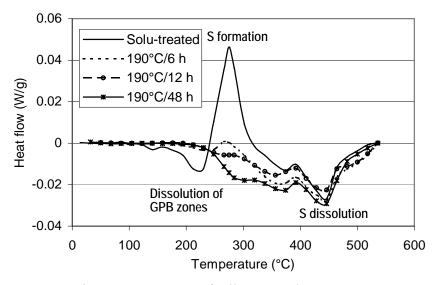
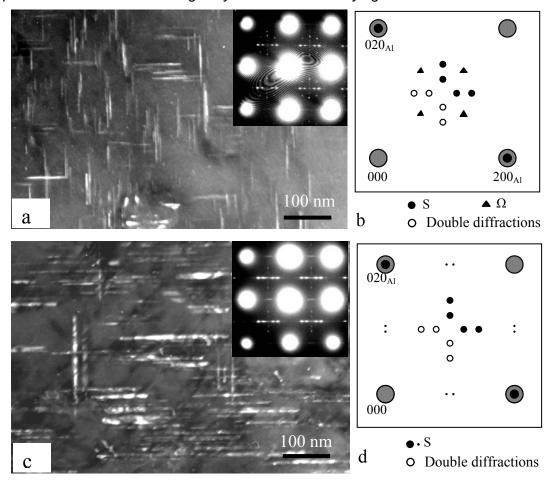


Fig. 4 DSC curves of Alloy 1 aged at 190°C.

Fig. 5 TEM micrographs of precipitation. (a-b) S and Ω precipitates in Alloy 1; (c-d) S phase in Alloy 2, all aged for 12 h at 190°C (dark field, B=[001]).



3DAP analysis of alloy 1 showing the distribution of the alloying elements. Analytical software developed by Vaumousse et al [11] has been employed to analyse the clusters in the alloys. The selection of solute-rich regions is performed by connecting solute atoms (in our case Cu and Mg), which lie within a fixed distance (d), and eliminating clusters containing less than a minimum of solute atoms ( $N_{min}$ ). Other atoms within some distance L greater than d are then taken to belong to the same cluster. The value of d and L have been selected as 0.6 and 0.8. The value of  $N_{min}$  varies from 8 to 14 atoms of Mg and Cu. Fig 6b shows all the microstructural features (clusters and different types of precipitates) detected on the 3DAP analysis of fig 6a using this software. 3DAP analysis of a number of specimens show that there are more Mg/Cu clusters in Alloy 2 than in Alloy 1. Table 2 shows the compositions of six of the largest clusters containing more than 10 (in Alloy 1) and 14 (in Alloy 2) atoms of Mg and Cu, in which the A stands for the total composition of the clusters and B stands for the solute atom composition of the clusters. From this Table, it can be seen that most of the clusters contain more than 90% of aluminium. The contents of Mg and Cu are in the range of 0.9-4.2 and 1.7-5.2. The Mg/Cu ratio is found to vary from one cluster to another and in most cases they are richer in Cu than Mg.

	Alloy 1					Alloy 2							
	Clus	ter 1	Cluster 2		Cluster 3		Cluster 1		Cluster 2		Cluster 3		
No of atoms	1280		404		24	240		260		631		601	
	Α	В	Α	В	Α	В	Α	В	Α	В	Α	В	
AI %	96.4	-	93.6	-	93.3	-	93	-	96.5	-	94	-	
Mg %	0.9	26.1	1.2	19.2	4.2	62.5	1.9	28	1.3	37	2.5	43	
Cu %	2.5	69.6	5.2	80.8	1.7	25	4.6	67	2.2	63	3	51	
Mn %	0.16	4.4	0	0	8.0	12.5	0.4	5	0	0	0.3	0	

Table 2: The composition of Mg/Cu clusters in both alloys

3DAP further revealed small plate-like precipitates/zones rich in copper in both alloys. Their diameter is about 6 nm, and compositions are about 90.7%Al, 1.3%Mg, 8%Cu. Charai et al. [12]

referred to similarly shaped (pre-)precipitates of similar size in T6 type material as GPB zones. However our plates appear larger than a monolayer in thickness and pure copper whereas Charai et al observed a significant Mg level. Some small rod like Cu/Mg rich precipitates have also been found . From their analysed compositions (95%Al, 2.6Cu, 2.2Mg for Alloy 1 and 94%Al, 2.5Cu, 3.3Mg for Alloy 2), it is expected that they are probably S phase (Al<sub>2</sub>CuMg) since the Cu and Mg contents are approximately equal.

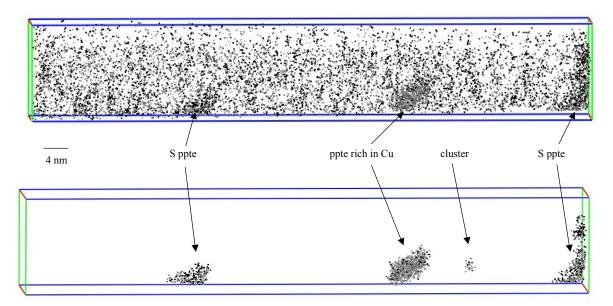


Fig. 6. Atom maps of the alloy 1 heat treated at 150°C for 12h: complete map (a) before extraction of cluster/precipitates (ppte) formed by more than 10 atoms of Copper and Magnesium (b)

### **Discussion**

Altogether, the experimental results have allowed the precipitation sequence to be defined in both alloys 1 and 2 heat treated at 150°C. In alloy 1, clusters, zones and S phase were found, the latter existing only in late stages. In alloy 2, clusters, zones and S phases were also found. However the density of S phase is greater in alloy 2 compared to alloy 1. DSC indicates that at 190°C clusters and zones have disappeared for both alloys and TEM also shows that S phase forms in both alloys with some limited  $\Omega$  precipitation only in Alloy 1. Equilibrium phase diagrams indicate that in Alloy 1 aged at 150-190°C the tetragonal  $\theta$  phase is one of the equilibrium phases, but this phase was not detected in the present experiments. It is believed that  $\Omega$  forms in preference to  $\theta$  because it is partially coherent with the Al rich phase, and hence has a lower nucleation barrier.

Inhomogeneities in solute atom and vacancy concentrations may favour the appearance of two sorts of pre-precipitates, Mg-rich clusters containing Cu atoms and vacancies, and Cu-rich GPB zones containing some Mg atoms [12]. It is well established that the binding energy between Mg atoms and vacancies is higher than that between Cu atoms and vacancies [13]; the activation energy for Mg diffusion in aluminium is also lower than for Cu diffusion [14]. This suggests that Mg-Mg clusters are the first to appear followed by Cu-Cu and Cu-Mg co-clusters. Lattice parameter measurements performed on a similar alloy during natural ageing also suggest that up to 1 h, Mg atom clustering prevails and that at longer times mainly Cu atom clustering occurs [12]. Therefore, it is not surprising that in our specimens (aged 12 hrs at  $150^{\circ}$ C), most of clusters are Cu-rich (Table 2). Silcock [2] proposed that these zones formed along the  $<100>\alpha$  directions as small cylinders estimated to be 1-2 nm in diameter, and with lengths ranging from 4 to more than 8 nm. Charai et al.

[12] have found the Cu-rich GPB zones at 200°C with a width about 5 nm, which contains some Mg atoms in similar alloys. These descriptions fit with the small plate-like precipitates/zones rich in copper observed by 3DAP in both alloys.

In terms of microstructure-strength relations the present results indicate that peak strength during artificial ageing is due to S precipitation. Strengthening during the early stages (less than 24h) of ageing at 150°C is mainly caused by clusters and zones. On continued ageing at 150°C strengthening due to S phases becomes progressively more important, whilst clusters and zones dissolve.

#### **Conclusions**

Extensive experimental work by HV, DSC, TEM and 3DAP analysis has been conducted on a Al-1.2Cu-0.5Mg and a Al-1.2Cu-1.2Mg (at.%) alloy at 150 and 190°C after solution treatment and stretching. During ageing at 150°C both alloys contain clusters, zones and S phase, but more S phase forms in the alloy with higher Mg content. For both alloys the precipitation hardening at 150°C is mostly dominated by the formation of these solute clusters and zones at early stages of ageing (less than 24h) and by the formation of S phase at the later stage of ageing. DSC indicates that for both alloys at 190°C clusters and zones have disappeared and TEM shows that S phase forms, which dominates the hardening response. In the alloy with the lower Mg content also some limited  $\Omega$  precipitation occurs at 190°C.

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