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# 3D Atom Probe study of solute-atoms clustering during natural ageing and pre-ageing of an Al-Mg-Si alloy

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## Abstract

The pair-correlation function applied to 3D Atom Probe reconstructed volumes has been used to study the influence of a pre-ageing treatment (363K) on the early stages of precipitation at 458K in an Al-Mg-Si 6016 alloy. Mg-Si short-range positive pair correlation (clustering) is shown to form after a pre-ageing treatment. The hetero-atomic clusters are thought to act as preferential nucleation sites and lead to a finer dispersion of precipitates after ageing.

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## 1 Introduction

The Al-Mg-Si-(Cu) alloys from the 6xxx series are often used for closure panels in the automotive industry because of their high strength after paint baking and their high quality surface finish after stamping and painting. Depending on the composition, several metastable phases form before precipitation of the  $\beta$  phase  $\text{Mg}_2\text{Si}$  [1,2]. In the ternary alloys, the precipitation sequence is:



Although very important, the transition between the supersaturated solid solution and the  $\beta''$  phase is extremely difficult to study experimentally because of the size of atomic clusters which are already present after a few days storage at room temperature. These clusters greatly influence the mechanical properties before and after the subsequent ageing at paint-bake temperature [3]. It is of great industrial interest to understand how the properties of the alloy after paint baking (typically around 458K) are influenced by fine-scale clustering during room-temperature ageing or low-temperature pre-ageing. Edwards *et al* [1] and Murayama *et al* [4,5] have used Atom Probe to study the early stages of clustering. Both studies are based on concentration profiles given by 1D Atom Probe. The solute clustering tendency is detected by concentration peaks that represent unique objects and can be difficult to dissociate from sampling statistical fluctuations. In order to solve this problem, the authors used statistical methods that only test the randomness of the solid solution.

If Edwards *et al* [1] and Murayama *et al* [4,5] agreed on the existence of homo-atomic clusters of Mg and Si independently, they concluded oppositely on the chronology of their appearance. Only the presence of Mg-Si clusters after a pre-ageing at a temperature below 370K is clear from both studies. More recently, Vaumousse *et al* [6] came to the same conclusion using a cluster-identification procedure [7]. However, the choice of a minimum number of solute atoms to define a cluster seems to limit the efficiency of the method to pre-aged and aged states,

where the clustering tendency is strong. The authors claimed that clusters were present at the as-quenched state only in Cu-containing alloys, but could not be precise about the nature of the clusters (homo- or hetero-atomic clusters).

In the last decade, the Atom Probe technique has been improved continuously [8,9,10]. In particular, the analysed volumes have been multiplied by a few orders of magnitude with the advent of the 3D Atom Probe. Some new data interpretation tools were developed to study clustering effects and follow their evolution during heat treatments in a statistically more robust way. In this paper the pair-correlation function derived from 3D images is used as a powerful tool to characterize the presence of solute atoms clusters in the early stages of decomposition of the solid solution of an Al-Mg-Si 6016 alloy. In particular, the influence of a pre-ageing treatment on clustering and subsequent precipitation during ageing will be discussed. The presence of Mg-Si co-clusters will be particularly investigated.

## **2 Experimental**

The alloy is an industrial 6016. Its composition in the two main alloying elements Mg and Si is 0.4 wt.% and 1 wt.%, respectively. It also contains secondary addition elements, mainly Cu. The samples were solution-treated as 1.2mm thick sheets for 30 minutes at 800K under an Ar atmosphere. They were then water quenched and some were pre-aged at 363K for 8 hours whereas some were not.

Rods of 0.3mm were then mechanically cut and Atom Probe samples were prepared by a standard electropolishing method using 5% perchloric acid (70%) in 2-butoxyethanol at room temperature. The 3D Atom Probe analyses were performed on the Energy Compensated Tomographic Atom Probe (ECoTAP) [11] in a temperature range between 40K and 80K. The effective pulse fraction was 20% and the pulse repetition rate was 1.7kHz. The data processing was done with the data-treatment software developed in our laboratory and with specific routines written

in the C language.

### 3 Pair-correlation function computation from 3DAP data set

The estimation of the randomness of a solid solution in 3DAP is usually made by statistical methods based on a frequency distribution of concentrations. The main drawback of these methods is the influence of the spacing of the sampling grid. Furthermore, it is difficult to derive more than simply a probability of non-randomness from these methods.

It is possible to plot the partial-pair-correlation function  $g(r)_{ij}$  from a 3D atom probe data set (a slightly different approach from that described here can be found in [12]). It represents the probability function of having two atoms of given natures  $(i, j)$  at a distance  $r$ , reduced to a unit density. It can be derived from the radial distribution function  $G(r)_{ij}$  by the following relation:

$$g(r)_{ij} = \frac{G(r)_{ij}}{\rho 4\pi r^2 dr} \quad (1)$$

where  $\rho$  is the atomic density. The radial distribution function is the probability density of finding an atom  $j$  at  $r$  when an atom  $i$  is at the origin. It can be noticed that  $\rho 4\pi r^2 dr$  is the radial distribution function of a random distribution in the ideal case of an infinite volume. In the case of a finite 3D atom probe analysis volume, there are two ways of computing the pair-correlation function. First, one can compute the mean concentration in spherical shells around each atom of a selected element, and then divide this concentration by the overall concentration of the alloy. This method implicitly assumes that the radial distribution of all the atoms around the selected element is random. The alternative method described below makes no assumption of this kind and treats the distribution of the considered element on itself, independently of the other chemical elements.

Let us consider a volume  $V$  in which we find  $N_A$  atoms of A and  $N_B$  atoms of B.

In order to take the effect of a finite volume into account, periodic conditions are applied. For computing the A – B pair correlation function, we count the number  $n(r)_{AB}$  of B atoms situated between a distance  $r$  and a distance  $r + dr$  of any A atom. It will be given by the expression:

$$n(r)_{AB} = N_A G(r)_{AB} \quad (2)$$

Thus :

$$g(r)_{AB} = \frac{n(r)_{AB}}{N_A \rho_B 4\pi r^2 dr} \quad (3)$$

where  $\rho_B = N_B/V$  is the volume density of B in the volume  $V$ . As the computation step  $\Delta r$  is not infinitely small, the practical relation becomes :

$$g(r)_{AB} = \frac{n(r)_{AB}}{\frac{N_A N_B}{V} \frac{4}{3}\pi \left( (r + \Delta r)^3 - r^3 \right)} \quad (4)$$

This pair correlation function is equal to unity if there is no correlation between A and B and is superior to unity in the case of a positive correlation. The main restriction of our method comes from the periodic conditions applied to the computation. They limit the validity of the result to the minimum dimension of the volume (typically a few nm). It is thus well adapted to very first stages of decomposition where the observed objects represents only a few atoms. The main source of uncertainties comes from statistical sampling errors and will be represented on the profiles by error bars of twice the standard deviation (i.e. 95% confidence interval). An important advantage of using the pair-correlation function is the possibility to increase the statistical significance of results by summing the radial distribution related to all the analysed volumes obtained. Similar treatments have been applied to the computation of binding energies [13] and to the study of ordering processes [14].

Note that for the sake of simplicity, positive pair correlation will be referred as clustering. However, it is not ascertained that this terminology can be rigorously

applied : pair correlation can either be the signature of isolated homo-atomic or hetero-atomic pairs ( $\approx$  short-range ordering) or solute clusters with a certain spatial extent (i.e. containing several pairs).

#### 4 Results and discussion

A pair-correlation function analysis was applied to three different states of the alloy. The first sample was solution heat treated and RT water quenched. An Atom Probe sample was immediately prepared. For clarity, although the sample preparation time (approximately 1 hour) has an influence on clustering, this sample will be referred as "as quenched". The second sample was stored at room temperature for 1 week after solution heat treatment and RT water quenched. It will be referred as "quenched and stored for one week". The third sample was solution treated, water quenched, pre-aged at 363K for 8 hours and stored at room temperature for 1 week. It will be referred as "pre-aged and stored for one week".

3D Atom Probe reconstructed volumes of the "quenched and stored for one week" and the "pre-aged and stored for one week" samples are shown on Fig. 1. For both samples, the solute elements seem randomly distributed in the volumes. Three different pair-correlation functions were computed for all samples: the two autocorrelations Mg-Mg and Si-Si and the cross correlation Si-Mg (Fig. 2, 3 and 4).

[Fig. 1 about here.]

[Fig. 2 about here.]

[Fig. 3 about here.]

[Fig. 4 about here.]

In the "as quenched" sample, both Mg and Si show positive autocorrelation. The absence of significant Si-Mg cross-correlation demonstrates that Mg and Si form

two distinct population of clusters. The maximum intensity of the correlation and the correlation distance (i.e. the distance above which the correlation tends to unity) for Mg-Mg compared to the Si-Si correlation show that a large proportion of the Mg atoms are involved in the clusters, whereas the proportion of randomly distributed Si atoms is larger.

The presence of Mg clusters had already been suggested by Murayama *et al* [4] and the formation of Si clusters during the quench had been proposed on the basis of the Al-Si behaviour by Edwards *et al* [1]. However, it was unclear whether the Si pairs formed before or after the Mg pairs during room-temperature ageing. The present study demonstrates that the only significant pair correlation in the "quenched and stored for one week" state is the Si-Si correlation. The Mg-Mg correlation is compatible with a random solid solution of Mg atoms within the error bars. A small clustering tendency seems visible, though. No Si-Mg cross correlation is detected in the non pre-aged state. This indicates that the Mg clusters that were formed during or immediately after the quench have dissolved without forming any Si-Mg pair during the 1 week RT ageing.

As for the "pre-aged and stored for one week" sample, both solute elements auto-correlations are positive, showing a strong Mg-Mg and Si-Si clustering tendency, whereas it was not clear in the direct space (Fig. 1). The Si-Si correlation distance is longer than in non pre-aged states. More important, a strong Si-Mg cross correlation has appeared. The three correlation lengths of the pre-aged specimen are roughly the same (approx. 1.5nm), indicating either that only co-clusters exists or that co-clusters are the same size as homo-atomic clusters.

In order to clarify the role of the pre-ageing treatment on the microstructure of the alloy after ageing, we performed 3DAP analyses on samples "pre-aged and stored for one week" and "quenched and stored for one week" aged for 2h at 458K. In the 3D image from the sample without preageing ("quenched and stored for one week" Fig. 5a), Mg- and Si-rich needles in the three [001] directions can clearly be

distinguished. They can be identified as the three [001] variants of  $\beta''$  precipitates. In the pre-aged alloy ("pre-aged and stored for one week" Fig. 5b), the number density of objects is much larger. There are also many solute atoms remaining in the solid solution. Furthermore, some Mg- and Si-rich particles are not needle shaped but seem more spheroidally shaped. There is co-existence of both the  $\beta''$  phase and Mg- and Si- rich hetero-atomic clusters. These latter clusters are larger and much more solute enriched compared to the very diffuse objects revealed by pair-correlation functions in the non-aged samples. These clusters are possibly the GP zones as described in the literature. They are known to be coherent with the matrix and contribute significantly to the material hardness.

[Fig. 5 about here.]

Both in the pre-aged sample and in the non-preaged sample, the  $\beta''$  phase was found to contain aluminium (20-30% in the particle core) as already reported by some authors [15,16,17]. The Mg/Si ratio is around 0.8. This latter ratio is not altered by local magnification effects [18] ( $\beta''$  are brightly imaged in FIM and lead to a higher magnification compared to the surrounding matrix). In contrast, Al concentration measurements must be carried out with care. Whereas Al concentration at the  $\beta''$ -matrix interface is expected to be over-estimated because of the trajectory overlaps (defocusing effect), the core concentration is not thought to be biased in a large extent. More detailed information on the influence of ageing in the phase composition will be published elsewhere.

## 5 Conclusions

The Mg and Si clustering in an Al-Mg-Si 6016 alloy was investigated with 3D atom probe with the help of the pair-correlation function. It was shown that:

- Mg-Mg and Si-Si clusters are formed during or immediately after quenching.

- The Mg clusters tend to dissolve during room temperature ageing (1 week) whereas Si clusters remain.
- A pre-ageing treatment at 363K leads to a Mg-Si short range correlation interpreted as the formation of Mg-Si mixed clusters.
- These Mg-Si co-clusters may act as preferential nucleation sites that lead to a higher density of hardening particles in the aged state and improve the paint-bake hardening response of the material.

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## List of Figures

- 1 Parts of reconstructed volumes in a) the non-pre-aged sample and b) the pre-aged sample. Both volumes dimensions are  $5 \times 5 \times 20nm^3$ . Only Mg (gray) and Si (black) atoms are represented. Clusters of atoms are not visible at a glance. 12
- 2 Mg-Mg pair correlation functions for non-pre-aged (as quenched and after 1 week storage) and pre-aged samples. 13
- 3 Si-Si pair correlation functions for non-pre-aged (as quenched and after 1 week storage) and pre-aged samples. 14
- 4 Si-Mg pair correlation functions for non-pre-aged (as quenched and after 1 week storage) and pre-aged samples. 15
- 5 Comparison of the microstructures of the samples aged for 2 hours at 458K a) without pre-ageing and b) with preageing. The dimensions of both volumes are  $14 \times 14 \times 230nm^3$ . For the sake of clarity, Al atoms are omitted. 16

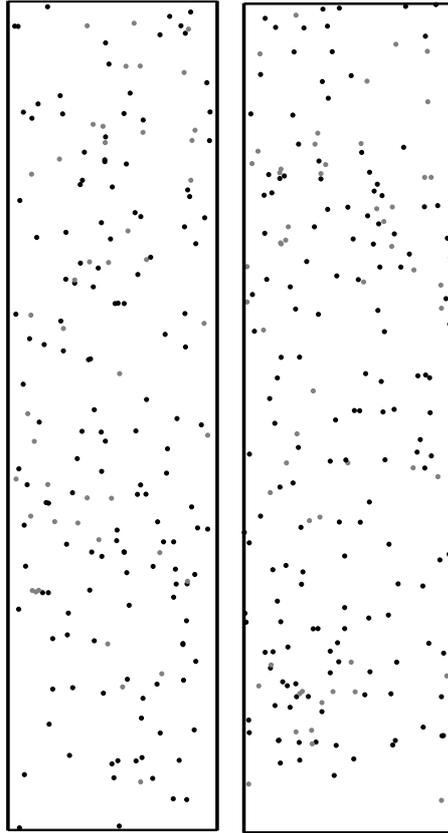


Fig. 1. Parts of reconstructed volumes in a) the non-pre-aged sample and b) the pre-aged sample. Both volumes dimensions are  $5 \times 5 \times 20nm^3$ . Only Mg (gray) and Si (black) atoms are represented. Clusters of atoms are not visible at a glance.

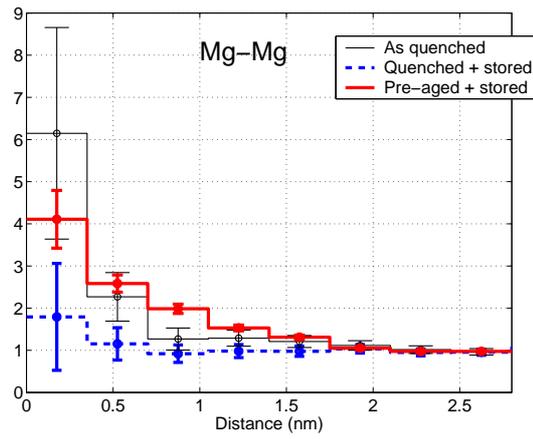


Fig. 2. Mg-Mg pair correlation functions for non-pre-aged (as quenched and after 1 week storage) and pre-aged samples.

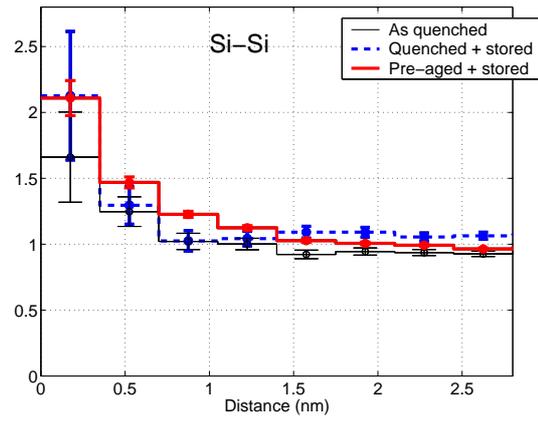


Fig. 3. Si-Si pair correlation functions for non-pre-aged (as quenched and after 1 week storage) and pre-aged samples.

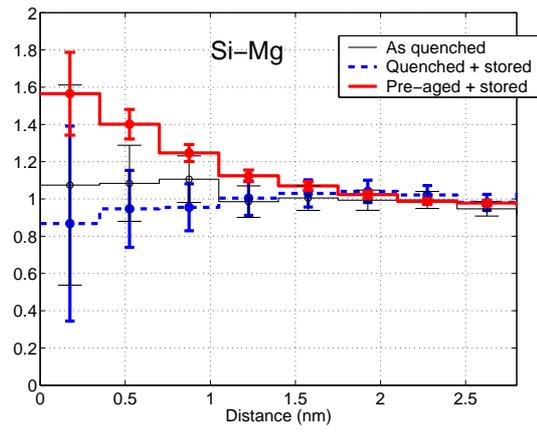


Fig. 4. Si-Mg pair correlation functions for non-pre-aged (as quenched and after 1 week storage) and pre-aged samples.

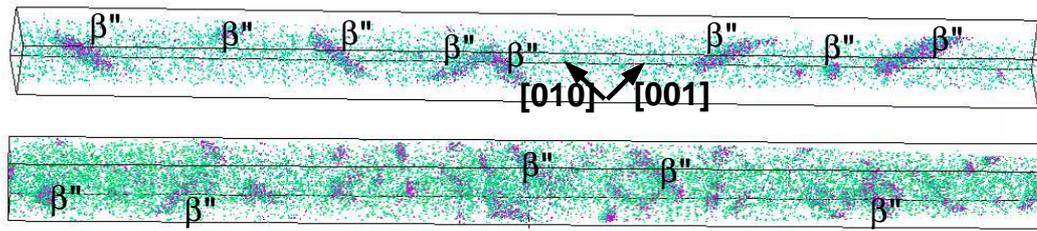


Fig. 5. Comparison of the microstructures of the samples aged for 2 hours at 458K a) without pre-ageing and b) with preageing. The dimensions of both volumes are  $14 \times 14 \times 230\text{nm}^3$ . For the sake of clarity, Al atoms are omitted.