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In-situ study of precipitate composition in 7000 series aluminium alloys by anomalous small-angle scattering

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1 Introduction

Nanoscale precipitates in Cu-containing 7000 series aluminium alloys can have a complex composition, with the presence of Al, Mg, Zn and Cu [1, 2]. The respective amounts of these elements in the precipitates are governed both by thermodynamic and kinetic effects, and may evolve during industrial heat treatments [3]. The precipitate composition, and the composition of the aluminium matrix associated to it, is a key parameter to control the properties of these alloys, whether mechanical (yield strength) or electrochemical (corrosion resistance) [4].

Small-angle X-ray scattering (SAXS) is a powerful technique to assess quantitatively the size and volume fraction of precipitates in a given microstructure. Measurements can be carried out in-situ during heat treatments, which can give a direct access to the kinetics of the precipitation process. In addition, SAXS measurements can be performed at different energies across the absorption edge of one of the elements present in the microstructure. Such measurements, called Anomalous SAXS or ASAXS, give access to information on the composition difference between the precipitate and matrix in this element [5].

In this study the precipitate composition has been studied by ASAXS experiments, performed at the European synchrotron light source (ESRF). Measurements have been carried out both at the Cu and Zn edges, continuously during a heat treatment, representative of an industrial T6 heat treatment, on three alloys of increasing Zn composition and decreasing Cu content.

2 Experimental procedure

The composition of the three studied materials is given in Table 1. They all have similar Mg contents, whereas the Zn content steadily increases from the 7150 to the PA alloy and the Cu follows an opposite tendency.

The three alloys were subjected to an identical heat treatment, consisting in a solution treatment of 6h at 470°C, followed by a cold water quench, 4 days of natural ageing and a two step heat treatment of 22h at 120°C (with a heating ramp of 30°C/h) followed by a heat treatment at 160°C (with a heating ramp of 15°C/h). In-situ ASAXS measurements were carried out during the 160°C heat treatment step, the three samples being placed together in the same furnace to ensure an identical thermal path. Samples were measured in transmission, with a thickness of ~ 80 µm. They were prepared by mechanical grinding down to 120 µm, followed by electropolishing in a nitric acid-methanol solution operating at -20°C.
ASAXS measurements were carried out on the D2AM-BM02 beamline of the European synchrotron radiation facility (ESRF) in Grenoble, France. A monochromatic beam of diameter ~200 µm was used, with an energy dispersion of $\delta E/E \sim 2 \times 10^{-4}$. Two absorption edges were used, namely the Zn and Cu Kα edges, with three to six different energies for each case. A series of these six to twelve measurements on the three materials lasted about 10 minutes, during which it was assumed that the microstructure did not change significantly. In between two successive measurements on the three studied samples, measurements were carried out in the same conditions on three reference samples (all containing precipitates), used to check for possible drifts in the beam energy calibration: a binary Al-Zn alloy, a binary Al-Cu alloy, and a binary Al-Li sample showing no anomalous effect.

The scattering curves were recorded by a CCD camera, and corrected for electronic noise, pixel efficiency, geometrical artefacts, and background noise. The data was then carefully normalized using the beam monitoring and the reference samples.

3 Results

3.1. Analysis of the precipitate composition from the ASAXS data

Figure 1 shows $Iq^2$ vs. $q$ plots (so-called Kratky plots, where $I$ is the scattered intensity and $q$ the scattering vector) for different energies of the X-ray beam at the two absorption edges, in the particular case of the 7150 alloy aged 6.5 h at 160°C. The variation of intensity with energy is related to the contrast variation between the precipitate and the matrix. More precisely, we have chosen to evaluate the contrast variation with energy in terms of integrated intensity $Q_o$. In a two-phase model (precipitate + matrix) this parameter is independent on the size and morphology of the precipitates, and depends only on the respective volume fractions and compositions of the two phases:

$$Q_o = \int_0^\infty Iq^2 dq = 2\pi^2(\rho_p - \rho_m)^2f_v(1-f_v)$$ (1)

where $\rho_p$ and $\rho_m$ are the apparent electronic densities of the precipitates and matrix (which depend on the chemical composition and on the X-ray energy), and $f_v$ is the precipitate volume fraction.

Table 1. Composition of the studied materials in the main elements

<table>
<thead>
<tr>
<th>Composition in wt%</th>
<th>Zn</th>
<th>Cu</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>7150</td>
<td>6.4</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>7449</td>
<td>8.6</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>PA</td>
<td>10.3</td>
<td>1.6</td>
<td>2</td>
</tr>
</tbody>
</table>
In the approximation that the average atomic volumes are the same in the precipitate and matrix, the apparent electronic density contrast writes:

$$\Delta \rho = \rho_p - \rho_m = \frac{\sum f_i C_i^p - \sum f_i C_i^m}{V_{at}}$$  \hfill (2)

where $V_{at}$ is the average atomic volume, and $f_i$, $C_i^p$ and $C_i^m$ are respectively the X-ray diffusion factor, the precipitate composition and the matrix composition of element $i$ (=Al, Zn, Cu, Mg).

In the quaternary system Al-Zn-Mg-Cu, probed at the Zn and Cu absorption edges, it can be considered that $f_{Al}/f_{Mg}$ is constant and equal to 1. Thus the equation 2 above becomes:

$$V_{at} \Delta \rho = (f_{Zn} - f_{Al}) (C_{Zn}^p - C_{Zn}^m) + (f_{Cu} - f_{Zn}) (C_{Cu}^p - C_{Cu}^m) - (C_{Mg}^p - C_{Mg}^m)$$ \hfill (3)

which can be written in a simpler manner:

$$V_{at} \Delta \rho = \Delta f_{Zn/Al} \cdot \Delta C_{Zn} + \Delta f_{Cu/Al} \cdot \Delta C_{Cu} - \Delta C_{Mg}$$ \hfill (4)

Figure 1. $Iq^2$ vs $q$ plots of the scattered intensity at the different energies (a) close to the Cu edge and (b) close to the Zn edge, showing the anomalous effect.

Figure 2. (a) changes in relative scattering factors $\Delta f_{Cu/Al}$ and $\Delta f_{Zn/Al}$ as a function of the X-ray energy; (b) plot of equation (4) in one particular case (7150, 6.5 h at 160°C), whose slope and origin provides a measurement of the precipitate composition in Cu and Zn.
It can actually be shown that the term \( \Delta C_{\text{Mg}} \) is always very small as compared to the other terms, and that it can be neglected. If we do so, and include equation (4) in equation (1), a relationship between the integrated intensity and the volume fraction is obtained, which depends on the values of the contrast terms \( \Delta f_{\text{Cu/Al}} \) and \( \Delta f_{\text{Zn/Al}} \), that are varied during the anomalous experiments:

\[
\frac{1}{\Delta f_{\text{Zn/Al}}} \frac{\Delta C_{\text{Zn}}}{Q_0} = \left( \frac{\Delta f_{\text{Cu/Al}}}{\Delta f_{\text{Zn/Al}}} \right) \left( \frac{\Delta C_{\text{Zn}}}{\Delta C_{\text{Cu}}} \right)
\]

The variation of diffusion factors with energy across the two edges is shown in Figure 2(a). The arrows indicate the range of energy used in the present experiments. It is apparent that the apparent atomic number of the Zn and Cu elements has been changed of approximately 3 units over the studied range.

Thus, a graph representing the (presumably) linear relationship between \( \sqrt{Q_0}/\Delta f_{\text{Zn/Al}} \) and \( \Delta f_{\text{Cu/Al}}/\Delta f_{\text{Zn/Al}} \) provides two sets of equations, linked to the slope \( A \) and the ordinate at the origin \( B \), to which we can add the balance of solute species in the precipitates:

\[
C_{\text{Zn}}^p = C_{\text{Zn}}^m + \frac{B V_{\text{at}}}{\sqrt{2\pi^2 f_V (1-f_V)}}, \quad C_{\text{Cu}}^p = C_{\text{Cu}}^m + \frac{A V_{\text{at}}}{\sqrt{2\pi^2 f_V (1-f_V)}}, \quad \sum_i C_i^p = 1
\]

The matrix compositions in Zn and Cu are generally small as compared to the precipitate ones, and we can make reasonable estimates of their values. However the two above equations still have three unknowns, namely \( C_{\text{Zn}}^p, C_{\text{Cu}}^p \) and \( f_v \). Some additional assumptions have thus been made, based on tomographic atom probe analysis (which will be published elsewhere) of selected samples, and on the data available in the literature (e.g.[2]):

- the composition in Mg has been taken as constant and equal to 0.33; this is equivalent to state that the \( \eta' \) phase has a composition of Mg(Zn,Al,Cu)\(_2\).
- the composition in Al has been taken as constant and equal to 0.15.

We have checked that changing this assumption did not change significantly the results in terms of precipitate composition.

Figure 2(b) shows one example of such linear plot. A high sensitivity of the composition in Cu and Zn in the precipitates can be obtained, and the linearity of the plot for the two absorption edges (Cu and Zn) is an indirect validation of the assumptions made.

### 3.2. Microstructural evolution in the three alloys during the heat treatment

In a previous paper [6], we have presented the evolution of the precipitate microstructure in the three alloys during the two step heat treatment. It was notably shown that the growth and coarsening kinetics were different in the three alloys, namely faster in the alloy most concentrated in Zn and least concentrated in Cu. We will here concentrate on what happens during the 160°C heat treatment step.

Figure 3 (a) and (b) show the evolution of the precipitate compositions in Cu and Zn in the three alloys during the heat treatment. Figures 3(c) and (d) show the size and volume fraction evolutions in the same conditions, along with an evaluation of the precipitate number density made by \( N = 3f_v/(4\pi R^3) \).
Figure 3. (a) Evolution of the measured Cu concentration in the precipitates; (b) evolution of the Zn concentration in the precipitates; (c) evolution of precipitate volume fraction and (d) evolution of precipitate radius and number density during the heat treatment at 160°C.

It is striking that at the beginning of the measurement (namely at the end of the 120°C heat treatment step) the precipitates contain almost no Cu; this is true for the three alloys. The Zn concentration, under the hypothesis made of an Al concentration of 15%, is slightly higher than 45%, consistently with a concentration of 33% in Mg.

During the heat treatment, the copper concentration in the precipitates evolves quickly, and reaches 6 to 10% after more than 15h at 160°C. Initially, during the ramp leading from 120 to 160°C, the three alloys show a comparable evolution of precipitate composition. Later on during the heat treatment, the Cu content is highest in the 7150 alloy, followed by the 7449 and the PA alloy, which is in the same order as the alloy Cu content. The evolution of the Zn composition is exactly complementary from the Cu composition.

In terms of precipitate size, volume fraction and precipitate number density, the evolution is the result, both of the general composition of the alloy, and of the differences in diffusion coefficients of the atomic species present.

The PA alloy, having the largest solute content, also has the largest precipitate volume fraction at the end of the heat treatment. However, this difference is even larger at the end of the first step of the heat treatment at 120°C, and reduces somewhat at the end of the 160°C heat treatment. This is certainly due in part to the faster diffusion of Zn: since the PA alloy is richer in Zn its precipitation at lower temperature is faster as compared to the other alloys, which have a higher Cu concentration, thereby leading to a much higher volume fraction. At the end of the 160°C heat treatment, the Cu has been incorporated to the precipitates and
therefore the difference in volume fraction corresponds to the total difference in solute content and not only to the difference in Zn content as after the 120°C heat treatment.

We can observe as well that the evolution of precipitate radius with ageing time is faster, as the Zn/Cu ratio increases. Again, this can be related to the increased equivalent diffusion coefficient when the slow-diffusing Cu is replaced by the fast-diffusing Zn.

The resulting precipitate number density comes out to be strongly dependent on the solute content at the beginning of the heat treatment, and then to converge with time to a constant value, which is the result of a compensation between volume fraction and size evolutions.

4 Conclusion

Using anomalous small-angle scattering, we have evaluated the evolution of the composition in Zn and Cu in the precipitates of three 7000 series aluminium alloys, during a 160°C heat treatment. We have shown that the prominent feature is the increase of the Cu concentration from ~0 to 6 to 10% along the heat treatment, the final value depending on the alloy composition. This Cu content evolution has been shown to have consequences on the precipitation kinetics.

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References