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AN IN SITU SMALL ANGLE X-RAY SCATTERING (SAXS) STUDY OF PRECIPITATION IN AN Al-Zn-Mg-Cu ALLOY.

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Abstract

The evolution of precipitates in an Al-Zn-Mg-Cu (7150) alloy during ageing has been followed using a combination of different experimental techniques. The distribution of hardening precipitates has been studied by *in situ* small angle X-ray scattering (S.A.X.S.) and transmission electron microscopy (T.E.M.). The effect of heat-treatment time and temperature, and stretching prior to ageing is discussed.

The S.A.X.S data show that prior deformation has no significant effect on precipitate size during ageing at 120°C. Ageing at higher temperature (160°C) leads to an increase in the average precipitate size in deformed specimens.

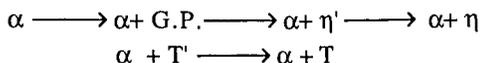
The integrated intensity has been obtained from S.A.X.S measurements. These results are compared with T.E.M. data. A small increase in integrated intensity is observed between specimens aged at 120°C and at 160°C. This may result from the co-precipitation of T' and η phases at the expense of η' .

Introduction

7XXX series (Al-Zn-Mg-Cu) alloys are used extensively in aerospace applications. Very high mechanical strengths can be obtained through control of the precipitation hardening process. The strength and corrosion resistance of these alloys depend on careful control of the time-temperature cycle during ageing. The composition and crystallography of the metastable precipitates evolve during low temperature ageing. As a result, overageing of Al-Zn-Mg-Cu alloys improves their resistance to stress corrosion cracking, but causes considerable loss of yield strength (10 to 20% of peak strength).

Much of the research effort to date has concentrated on analysing the size, morphology and

crystallography of the phases formed during ageing [1-5] and on understanding the effect of the microstructure on mechanical behaviour [6]. The decomposition of the solid solution has been studied extensively in ternary Al-Zn-Mg and quaternary Al-Zn-Mg-Cu alloys such as 7075; it may be summarized as follows [3]:



The G.P. zones [4] are spherical and coherent with the FCC aluminium lattice. The hexagonal η' phase is observed as very thin (20Å), coherent, plate-shaped particles lying in {111}Al planes. In the quaternary system, the equilibrium η -Mg(Zn, Al, Cu)₂ phase, which has a hexagonal crystal structure, can exhibit several orientation relationships [3]. The most commonly observed are η_1 platelets lying in {110}Al planes, η_2 thin platelets lying in {111}Al planes and η_4 laths parallel to <110>Al directions. Depending on the quench rate or the initial alloy composition, the cubic T' phase, a metastable form of the equilibrium T phase Mg₃₂(Al,Zn)₄₉, may appear during ageing [5].

Increasing interest in 7150 alloy has led us to make a careful study of the initial stages of structural hardening. The present study uses transmission electron microscopy (T.E.M.), electrical conductivity data and *in situ* small angle X-Ray scattering (S.A.X.S.) to obtain information about the evolution of precipitate crystal structure, size range and morphology during simple and duplex ageing.

Experimental procedure

Samples: Blocks were cut from a commercial 7150 alloy plate (37mm thickness) supplied by Pechiney Rhenalu. The chemical composition is given in table 1.

Table 1- Composition of the 7150 plate.

Alloy	Zn at% (wt%)	Mg at% (wt%)	Cu at% (wt%)	Zr at% (wt%)	Al
7150	2.5 (6.0)	2.8 (2.4)	0.9 (2.1)	0.03 (0.1)	Bal.

* The main impurities are Fe (0.04at%) and Si (0.05at%).

The thick plate exhibits a mixed recrystallized/pancake grain structure with 3 to 10 μm diameter subgrains. The substructure is related to the addition of Zr which precipitates as coherent, spherical Al₃Zr dispersoids (100-200Å in diameter) during solution heat-treatment.

The blocks were solution heat-treated at 478±2°C, water quenched and aged for about 4 months at room temperature. Natural ageing was followed by various isothermal ageing heat-treatments between 120°C and 160°C. The effect of 2% stretching on ageing was also studied.

TEM experiments : Disks of 3mm diameter were cut from blocks of the 2% stretched alloy and ground to a thickness of about 50 μm . The disks were subsequently electropolished to perforation in a Fischione twin-jet electropolishing unit using a methanol-10% perchloric acid solution held at about -40°C . The thin foils were examined in a 120 kV Philips 420 microscope.

SAXS experiments : Diffracted intensity from a $\text{CuK}\alpha$ source ($\lambda=1.541 \text{ \AA}$) was recorded *in situ* using a position sensitive detector ($q=4\pi/\lambda\sin\theta$) in the range 0.015 and 0.5 \AA^{-1} . A point focus geometry was used. The experimental rig was held under vacuum in order to reduce background scattering. The experiment has been described in detail in [6]. The *in situ* method, which gives a better estimation of small modifications in scattered intensities, was used to follow microstructural evolution during duplex ageing. The experimental spectra were corrected for background, dead time, Cu and Fe fluorescence and absorption effects, and were calibrated using the $\text{el.}^2 \text{ \AA}^{-3}$ units described in [6]. A background intensity of about $0.2 \text{ el.}^2 \text{ \AA}^{-3}$ was subtracted from the experimental data in order to obtain the integrated intensity. In the low q region, the particle dimensions were estimated using the Guinier gyration radius R_g [7].

Results and interpretation

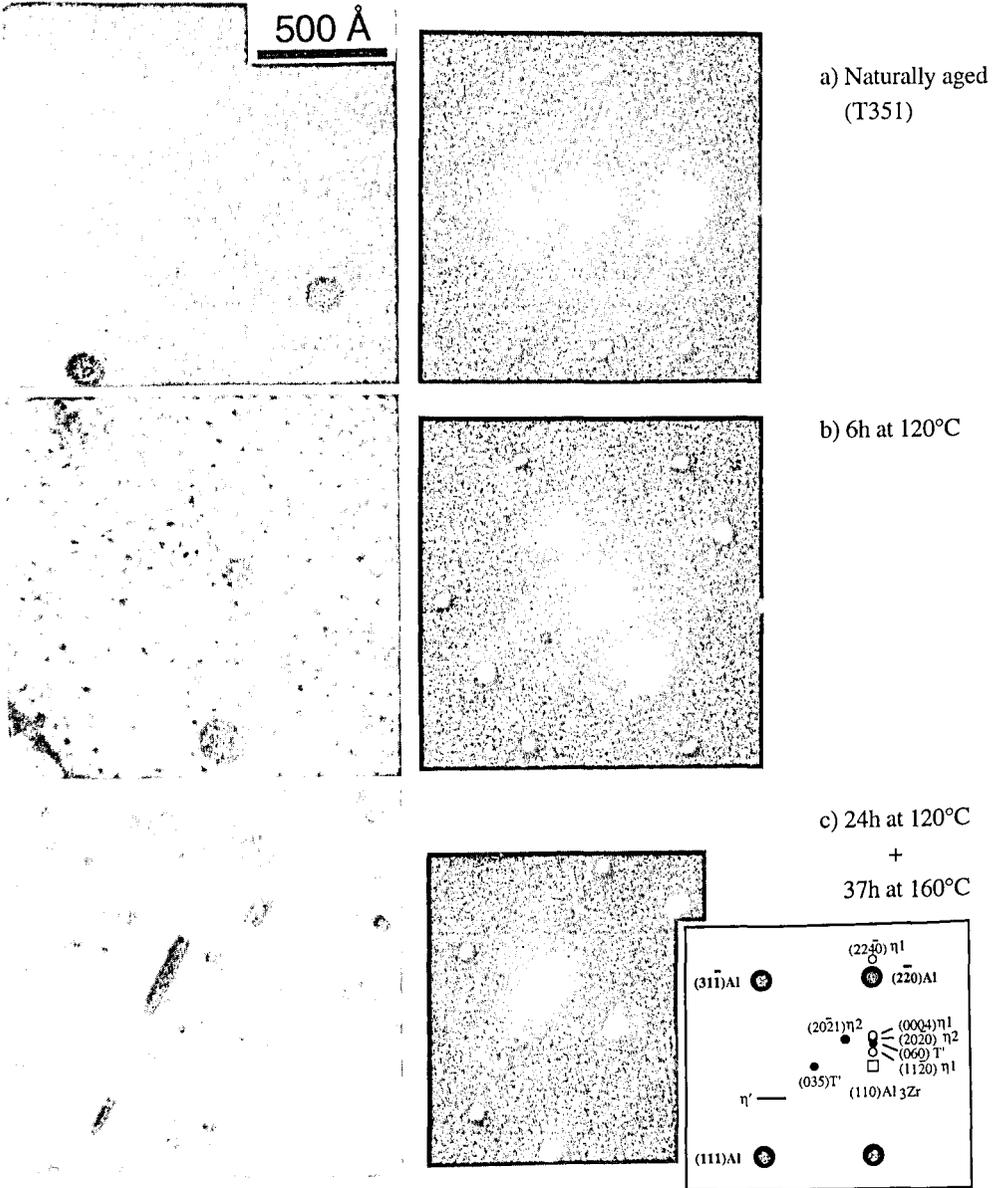
TEM investigations: The microstructures of 2% stretched specimens aged for 4 months at room temperature, 6 hours at 120°C and 24 hours at 120°C followed by 37 hours at 160°C are compared in fig.1. Each bright-field image is accompanied by the corresponding [112]Al zone axis diffraction pattern. The structure, morphology and size range of the precipitates are detailed in table 2.

Table 2 - Results of the T.E.M. investigation of 2% stretched 7150 alloy specimens.

Specimen	Intragranular precipitation	Morphology & Size Range
R.T. Aged	<u>G.P.</u> Zones (coherent)	Spherical (5-10 \AA diameter)
6h 120°C	<u>η'</u> $\text{Mg}(\text{Al,Cu,Zn})_2$ (coherent) η_2 $\text{Mg}(\text{Al,Cu,Zn})_2$ (dislocations) T'	Plates (10-35 \AA by 5-10 \AA) Plates (50-150 \AA by 10-20 \AA) Equiaxed (10-30 \AA)
24h 120°C +	<u>η_1</u> $\text{Mg}(\text{Al,Cu,Zn})_2$ (semi-coherent) <u>T'</u> (semi-coherent)	Equiaxed (60-100 \AA diameter) Equiaxed (60-120 \AA diameter)
37h 160°C	η_2 $\text{Mg}(\text{Al,Cu,Zn})_2$ (dislocations) <u>η'</u> $\text{Mg}(\text{Al,Cu,Zn})_2$ (coherent)	Plates (150-350 \AA by 45-55 \AA) Plates (20-45 \AA by 10-15 \AA)

* The majority phase is underlined.

Figure 1 - T.E.M. micrographs showing the microstructures of the three 2% stretched 7150 alloy specimens. The dark, spherical particles (1-200 Å diameter) in figures 1a and b are Al₃Zr dispersoids. Each image is accompanied by the corresponding [112]Al diffraction pattern.



SAXS experiments: In SAXS experiments, given types of atom can be labelled according to their atomic scattering factor. In the case of Al-Zn-Mg-Cu alloys, the Al and Mg atoms and Cu and Zn atoms are mutually indistinguishable. The assumption of a two phase system was therefore applied to the analyses. In this case, the integrated intensity Q (in $\text{el.}^2 \text{\AA}^{-6}$) can be expressed as follows:

$$Q = \int_0^{+\infty} I(q) q^2 dq = \frac{2\pi^2 \Delta Z^2}{V_{at}^2} Q_0 \dots \dots \dots (1)$$

where $Q_0 = (C_p - C_o)(C_o - C_m) = F_v(1 - F_v)(C_p - C_m)^2 \dots \dots \dots (2)$

C_o , C_m , C_p are respectively the atomic concentrations of Zn+Cu in the alloy, in the matrix and in the precipitates (at%). ΔZ is the difference between the atomic numbers of Al and a given solute element (el.), and V_{at} is the atomic volume (in \AA^3) of Al (the lattice misfit is negligible). Q therefore gives an indication of the quantity of Cu and Zn atoms involved in the precipitation.

• Effect of ageing on precipitates evolution.

Figs.2 and 3 show the evolution of the Guinier radius R_g and Q as a function of ageing time at 120°C . A sharp decrease in Q is observed during heating from 20°C to 120°C . This corresponds to the reversion of the G.P. zones formed during room-temperature maturation. The subsequent increase of Q is attributed to the precipitation of the η' phase.

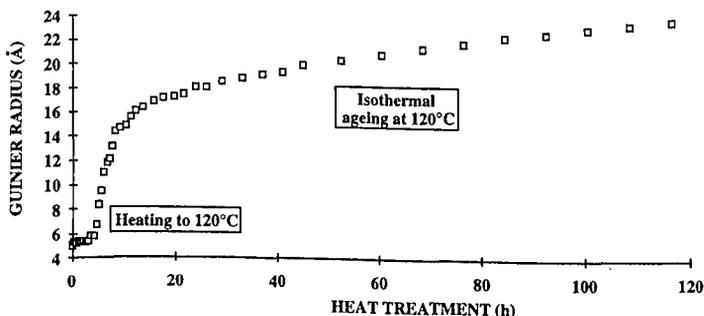


Figure 2 - Variation of the Guinier radius R_g as a function of ageing time at 120°C .

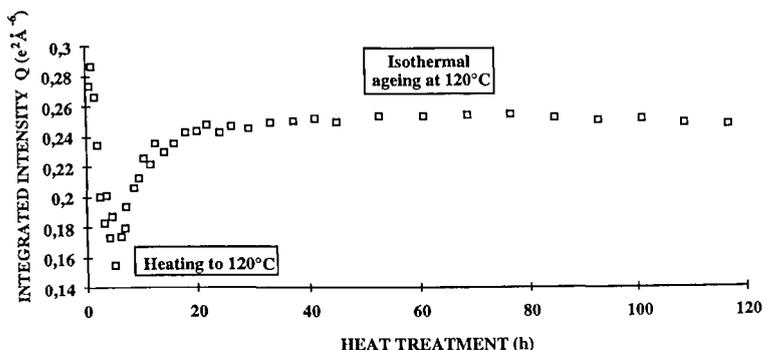


Figure 3 - Variation of the integrated intensity Q as a function of ageing time at 120°C .

After about 20 hours at 120°C , Q becomes constant, which suggests that the $(\text{Zn}+\text{Cu})$ content of the precipitates becomes constant. According to T.E.M. observations, η' is the majority phase at 120°C (see fig.1b and table 2). Assuming a constant composition for the η' precipitates during isothermal ageing at 120°C , it follows that their volume fraction must become constant. These assumptions are supported by the plot of R_g^3 versus ageing time (fig.4), which shows a linear relationship after 20 hours at 120°C , suggesting that the η' precipitation is undergoing a Lifschitz-Slyosov-Wagner coarsening process [8].

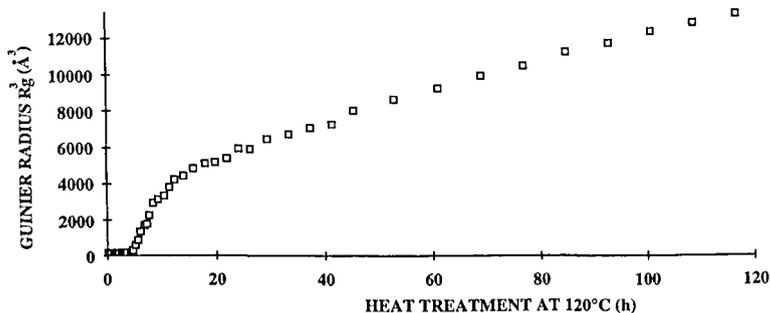


Figure 4 - Variation of the Guinier radius R_g^3 as a function of ageing time at 120°C .

As shown in figure 5, the plot of electrical conductivity as a function of isothermal ageing at 120°C shows a continuous increase during ageing. Various parameters can affect the electrical conductivity [9]: cluster compactness, cluster size, interference between clusters, residual solute atoms in solid solution. As the integrated intensity is observed to be stationary and assuming a constant composition of η' precipitates, the residual solid solution reaches rapidly a roughly constant level. As explained in [9], the main contribution to increase of electrical conductivity may therefore result from the evolution of the precipitate size during ageing.