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SIMS DETERMINATION OF THE SURFACE LITHIUM DEPLETION ZONE IN Al-Li ALLOYS BY QUANTITATIVE IMAGE ANALYSIS

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ABSTRACT

The heat treatment of Al-Li alloys induces a Li depletion zone of up to 100 μm beneath the metal surface. Characterisation of the Li concentration profile is not possible using conventional Energy Dispersive X-Ray (EDX) based techniques as they are limited to "heavy elements" (At. N° > 5). Secondary Ion Mass Spectrometry (SIMS) has no such limit and "long range" quantitative Li depth profiles may be obtained from polished cross-sections. The advent of direct ion imaging allied with quantitative image analysis provides two major improvements over traditional "line-scans": optimised lateral (depth) resolution of 1 μm and acquisition times reduced by a factor of about 100.

1. INTRODUCTION

During the heat treatment of Al-Li alloys, especially solution heat treatment at temperatures > 500°C, the strong reactivity of Li creates a relatively thick surface layer composed primarily of Li_2CO_3 . This reaction product does not provide a protective barrier film. The bulk of the alloy acts as a Li reservoir for the continuing reaction, resulting in a Li depletion zone extending up to as much as 100 μm beneath the metal surface. Heat treatment parameters (temperature, duration and atmosphere) may be altered so as to control or limit the extent of the depletion zone which may otherwise have consequences on the mechanical properties of thin semi-products < 3 mm in section.

From the analytical point of view the determination of Li depth profiles and hence characterisation of the Li depletion zone presents a problem, as conventional techniques relying on Energy Dispersive X-ray (EDX) analysis cannot detect light elements such as Li (atomic N° < 5). Indirect methods of measuring the depletion zone have been attempted, and include microhardness profiles and precipitation/etch techniques. Apart from being only indirect, these methods are also rather long, alloy dependent, and difficult to quantify. Secondary Ion Mass Spectrometry (SIMS), increasingly used in material science, is not limited to "heavy" elements and may be used to investigate the entire periodic table (H $\rightarrow$ U) with excellent sensitivity of 10^{-6} to 10^{-9} g/g ⁽¹⁾⁽²⁾. In the following, the methodology used for obtaining quantitative Li depth profiles between the surface and bulk of Al-Li samples is detailed. The use of direct ion microscopy and quantitative image analysis techniques to improve the rapidity and ease of analysis are also described.

2. EXPERIMENTAL PROCEDURE

SIMS analysis was performed using a CAMECA IMS 3f direct imaging ion microscope. The samples were bombarded by a mass filtered primary beam of Ar^+ ions with an energy of 12.5 keV. The sample surface was flooded with oxygen to obtain the maximum sensitivity and stability of the secondary ion signals.

The general method of quantitative SIMS analysis used relies on the fact that the intensity of the secondary ion X^+ , normalised with respect to the intensity of the matrix ion M^+ (to eliminate instrument parameters), is proportional to the concentration of element X in the matrix M. Comparison with carefully prepared standard samples of similar composition therefore allows the quantitation of SIMS results ⁽³⁾.

Basically, three choices are available for SIMS depth profile analysis: conventional bombardment perpendicular to the sample surface or, using polished cross-sections prepared perpendicular to the sample surface, line-scan analysis or direct ion imaging. These techniques are illustrated in the schematic diagram of Figure 1 and their respective characteristics compared in Table 1.

Conventional SIMS depth profiles are obtained with excellent depth resolution (about 60 Å) by gradual sputtering (about 1 Å/s) of the sample perpendicular to the specimen surface. However,

Table 1 : Comparison of the characteristics associated with the three depth profile modes illustrated in Figure 1.

operating mode	depth resolution	max. depth	acquisition time
Conventional bombardement perpendicular to the sample surface	50 Å - 100 Å	≈ 5 μm	up to several hours
Line scan on cross-section perpendicular to the sample surface	analysis zone diameter (1 to 8 μm)	8000 μm	≈ 1 hour / 200 data points
direct ion images of cross-section perpendicular to the sample surface	same as lateral image resolution (about 1 μm)	150 or 400 μm	1 minute / image + 5 minutes image analysis

this is only valid for the first few microns of material and cannot be used for "long-range" concentration profiles. This may be overcome by the lateral analysis of polished cross-sections prepared perpendicular to the sample surface. Considerable attention must be paid to the polishing quality at the sample edge (corresponding to the surface) so as to avoid bevelling. A lateral SIMS "line-scan" analysis is performed by displacing a variable analysis zone (1 to 8 μm diameter) across the section and obtaining the ratio ${}^7\text{Li}^+ / {}^{27}\text{Al}^+$ at each point. Considering typical sputter etch rates and the analysis time at each step, each data point corresponds to a sputtered depth of up to 500 Å (a volume corresponding to about 1×10^{-14} g of aluminium). The "depth" resolution of the resultant profile is directly proportional to the diameter of the chosen analysis zone (ie, 1 to 8 μm).

In the ion microscope, secondary ion images of the sample are produced by stigmatic ion optics and as such the entire image of up to 400 x 400 μm is quasi-instantaneously projected onto a multi-channel plate detector. The image resolution of about 1 μm is independent of the primary ion beam diameter. An improved version of the standard image acquisition system has been used, and comprises an ultra-sensitive video camera (individual ion sensitivity) connected to a real-time image processor allowing image averaging/integration routines. The final image is then transferred to a Kontron image analyser for storage in digital form ⁽⁴⁾.

2D quantitative elemental maps are produced in much the same way as for a line-scan. In a given zone the ${}^7\text{Li}^+$ and ${}^{27}\text{Al}^+$ images are obtained and stored in digital form by the image analyser (up to 500Å of material is generally required to achieve statistically correct ion images). At each image point (pixel) the ratio ${}^7\text{Li}^+ / {}^{27}\text{Al}^+$ is then calculated and compared to a standard for quantification. By retrospective image analysis the Li concentration at any pixel can be obtained so as to produce, for example, a 1D line profile. Two major advantages are inherent in this procedure: the lateral resolution is optimised (about 1 μm) and each image point or pixel of about 1 μm^2 is simultaneously analysed, resulting in a gain of $>10^2$ in acquisition time.

3. RESULTS AND DISCUSSION

3.1 Verification

The stigmatic ion optics of the ion microscope are susceptible to variation of the field lines extending between the sample surface and the extraction lens. In the case of polished cross-sections where the specimen edge is of importance, edge effects due to sample bevelling may well introduce an experimental error. The validity of the SIMS line scans was therefore verified by making use of a second reference technique, the Nuclear Microprobe (NM), which does not rely on an extraction field. In this technique the Li concentration was obtained by the nuclear reaction ${}^7\text{Li} (p,\alpha) {}^8\text{Be}$ induced by bombarding the specimen with a proton beam of 1.2 MeV. A lateral line scan was performed by scanning a focused primary beam of 5 x 5 μm^2 across the cross-section⁽⁵⁾. The SIMS and NM results obtained on the same specimen are shown in Figure 2. The two curves are identical within experimental error and confirm the validity of the SIMS approach.

In fact, ion images of the matrix element obtained near the edge of the cross-section show that minor edge effects are present and affect the intensity of secondary ion signals within the first few microns from the surface. However, as the edge effects are the same for each secondary ion, normalisation with the matrix ion allows a satisfactory correction.

3.2 Li depth profiles as a function of heat treatment conditions

The above methodology is demonstrated in Figure 3 for the case of an Al-Li alloy (8090 CP271) which was chemically milled (reference condition without Li depletion) and then solution heat-treated under furnace conditions designed to produce controlled samples with a wide range of Li depletion zones. This enabled the evaluation of both the heat treatment conditions on the extent of Li depletion, and the resultant changes in the mechanical properties. Results obtained from two of the specimens are presented:

- 1) specimen heat treated at 535°C for 30 minutes in a molten salt bath
- 2) specimen heat treated at 535°C for 60 minutes in an air furnace

Figures 3a,b and 3d,e present the "raw" images of ${}^7\text{Li}^+$ and ${}^{27}\text{Al}^+$ obtained on the specimen treated in the salt bath and air furnace respectively. Before normalisation the ${}^7\text{Li}^+$ images are difficult

Figure 2: Quantitative Li line-scan depth profiles obtained on the same heat treated Al-Li specimen, using SIMS and the Nuclear Microprobe techniques. The similarity of the two profiles show that edge effects in SIMS do not constitute a source of experimental error, and confirms the use of the NM as a reference technique.

to visually interpret and little difference between the two specimens can be detected. Figures 3c and 3f respectively show the resultant quantitative SIMS Li elemental map obtained by pixel normalisation and calibration. The concentration scale has been split into 6 discrete grey levels to aid visual interpretation. It is evident from these quantitative images that the specimen heat treated in an air furnace has undergone significantly greater Li depletion.

The individual pixel intensities (corresponding to about $1\mu\text{m} \times 1\mu\text{m}$ of the specimen surface) may be output by the image analyser; a 1D line scan from such an image (in any chosen direction) is therefore a simple matter. Figure 4 presents such profiles obtained for the two specimens from their respective quantitative images along the line A->B. If the Li depletion zone is defined as the depth below the surface at which the Li concentration is 90 % of the bulk concentration, Figure 4 suggests a depth of approximately $30\mu\text{m}$ and $60\mu\text{m}$ respectively for the specimen heat treated in a salt bath and in an air furnace respectively.

4. CONCLUSION

The Li depletion zone created beneath the metal surface during the solution heat-treatment of Al-Li alloys may be of considerable importance for the mechanical properties of thin sheet products. Conventional analysis techniques are not capable of detecting light elements and hence qualitative indirect techniques have been tried. SIMS provides an ideal technique allowing the quantitative determination of Li depth profiles. Recent advances in quantitative SIMS ion microscopy and image analysis allow an extremely rapid method of directly observing the extent of Li depletion, ie. as a function of heat-treatment parameters.

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Figure 3: Quantitative ion image analysis demonstrated for the case of two Al-Li alloys, one heat treated in a molten salt bath at 535°C for 30' (3a,b and c), the other in an air furnace at 535°C for 60' (3d,e and f):

- a,b,d and e) "raw" ion images of $^7\text{Li}^+$ and $^{27}\text{Al}^+$
- c and f) quantitative Li maps produced by normalising the $^7\text{Li}^+$ images with their respective matrix $^{27}\text{Al}^+$ image. The Li concentration scale, split into 6 discrete grey levels for ease of visual interpretation, was produced by calibration with respect to the known bulk Li concentration. The lines A→B correspond to the 1D line profiles of Figure 4

Figure 4: The pixel intensities along the lines A→B of Figures 3c and f were used to calculate 1D quantitative Li depth profiles for each specimen. It is evident that the specimen heat treated in the air furnace has suffered significantly more Li depletion than the specimen heat treated in the molten salt bath.

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