

The measurement of lithium depletion in aluminium–lithium alloys using X-ray diffraction

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This paper examines the viability of using X-ray diffraction to monitor the loss of lithium from the surface of aluminium–lithium alloys during heat treatment in air at 530°C. It has been found that the amount of Li_2CO_3 , a major constituent of the surface film, can be related to the extent of lithium depletion as determined by microhardness measurements. The technique is very sensitive to the amount of lithium depletion, readily detecting the carbonate after only five minutes exposure at 530°C. Cooling rate, initial surface removal, surface finish and alloy composition were all found to influence results, but, provided these parameters are controlled, it is concluded that X-ray diffraction is a rapid and non-destructive method of monitoring lithium depletion in aluminium–lithium alloys.

1. Introduction

A number of studies [1–13] have shown that solution treatment of Al–Li based alloys at about 530°C leads to the formation of a lithium depletion layer at the alloy surface. Since the strengthening of these alloys is derived from precipitation of the δ' -phase (Al_3Li) during subsequent ageing, the presence of a lithium depletion layer results in a loss in strength at the surface [4]. This will have important consequences on the fabrication, heat-treatment and application of Al–Li based alloys, especially as thin sheet material [4, 9–11]. It is important, therefore, that techniques are available to monitor this lithium depletion, and there are recent reports of eddy current [5], nuclear reaction analysis [7, 8] and Auger and X-ray photoelectron spectroscopy [13], methods being applied to measure such depletion.

In the present paper, the use of X-ray diffraction as a method of monitoring lithium depletion in Al–Li based alloys, principally 8090, after solution-treatment at 530°C is reported. It will be shown that the intensities of Li_2CO_3 diffraction peaks, a major constituent of the surface film, can be related to the extent of the lithium depletion layer thickness as determined by microhardness measurements.

2. Experimental details

2.1. Alloys

Four Al–Li based alloys in the form of thin sheet were

used in the study. Their compositions are shown in Table I.

2.2. Specimen treatments

Samples, approximately 1 cm², were cut from each sheet and solution treated in air at 530°C for various times. This condition will be referred to as the as-received surface. Since there are a number of factors that could influence results, tests were carried out to check the following.

(i) The possibility of a lithium depletion layer existing on the as-received surface, and the effect of surface finish. This was studied on specimens which were ground to remove the initial surface layer and then solution treated either in this condition (800 grit finish) or after polishing with diamond paste (1 μm finish).

(ii) The effect of texture, where a comparison was made between specimens with $\{112\} \langle 111 \rangle$ and $\{110\} \langle 112 \rangle$ orientations exposed at the sheet surface. This was possible on 8090 sheet by polishing to $\frac{3}{4}t$ and $\frac{1}{2}t$ respectively (where t = original sheet thickness), because of the presence of a texture gradient [14].

(iii) Any differences in the rate of lithium depletion as a function of alloy composition.

(iv) The effect of cooling rate, by comparing data for water-quenched and air-cooled specimens.

(v) The effect of quench frequency, by comparing

TABLE I Composition of alloys used

| Identification | Composition (wt %) | | | | | | | Initial sheet thickness (mm) |
|----------------|--------------------|------|------|------|------|------|--------|------------------------------|
| | Li | Cu | Mg | Zr | Fe | Si | Na | |
| 8090 sheet 1 | 2.38 | 1.20 | 0.54 | 0.14 | 0.08 | 0.03 | <0.001 | 2.07 |
| 8090 sheet 2 | 2.38 | 1.20 | 0.54 | 0.14 | 0.08 | 0.03 | <0.001 | 1.6 |
| 8091 | 2.39 | 1.93 | 0.76 | 0.12 | 0.07 | 0.09 | 0.001 | 1.7 |
| 2090 | 2.09 | 2.68 | 0.05 | 0.11 | 0.12 | 0.03 | 0.0015 | 1.5 |
| 2091 | 2.10 | 2.11 | 1.40 | 0.08 | 0.05 | 0.05 | 0.001 | 1.5 |

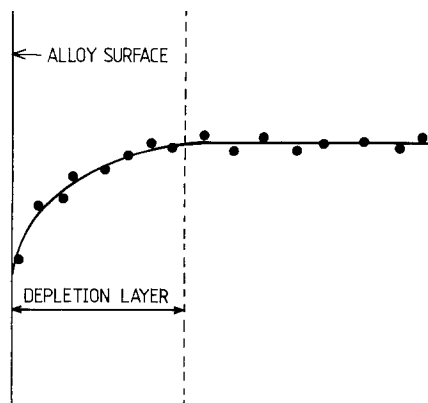


Figure 1 Schematic hardness plot showing the method used to define lithium depletion depth.

data from specimens given single and multiple solution treatments and quenches.

Note that (a) unless otherwise stated, specimens were water quenched from 530°C and (b) in all cases specimens were supported on aluminium foil with the sheet surface for X-ray examination exposed to the furnace atmosphere.

2.3. X-ray diffraction analysis

Specimens were examined in automated Philips and Siemens diffractometers using Cu K α radiation. Initial scans identified the surface film as consisting of Li₂CO₃ (JCPDS[†] card 22-1141) and γ -LiAlO₂ (JCPDS card 18-714). Since the peaks of Li₂CO₃ in the angular range 20 to 38° 2 θ were generally stronger and always present compared to those of γ -LiAlO₂, the four carbonate peaks at 21.4° (1 1 0), 29.5° (1 1 1), 30.6° ($\bar{2}$ 0 2) and 31.8° (0 0 2) were chosen to monitor lithium depletion.

2.4. Microhardness testing

Microhardness measurements were carried out on solution treated specimens that had been aged for 16 h at 170°C to precipitate the δ' -phase. Slices cut through the sheet were mounted, ground and polished with diamond paste. Microhardness traces across these vertical slices were taken using a load of 25 g, the final curve for each condition being calculated from the average of at least four traces.

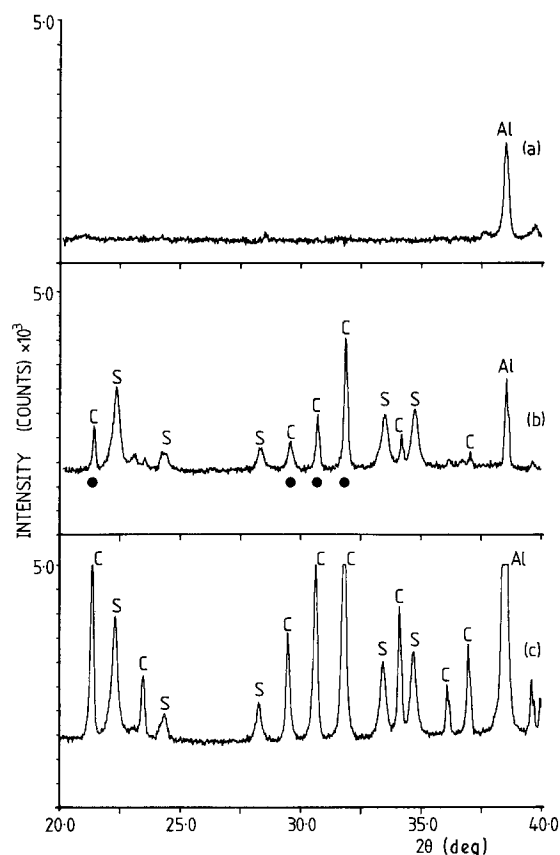


Figure 2 X-ray diffractograms from alloy 8090 (sheet 1) for (a) the as-received condition, and after solution treatment at 530°C for (b) 15 min and (c) 1 h. (C = Li₂CO₃, S = γ -LiAlO₂, ● measured peaks).

The lithium depletion layer thickness was determined by first calculating the average microhardness across the central region of the sheet thickness, and then measuring the depth at which a curve, drawn through the data, first deviated from the average value. A lithium depletion layer so defined is shown schematically in Fig. 1.

3. Results

3.1. Effect of solution treatment time at 530°C

Figs 2a to 2c show typical diffraction traces of the as-received 8090 (sheet 1) surface before solution treatment, and after 15 min and 1 h at 530°C. All of the additional

TABLE II Peak intensity for 8090 (sheet 1) as-received surface (individual specimens)

| Solution treatment time (min) | Li ₂ CO ₃ peak 2 θ | | | | | | | | Depletion depth (μ m) |
|-------------------------------|---|-------|---------------|-------|------------------------|------|---------------|-------|----------------------------|
| | 21.4° (1 1 0) | | 29.5° (1 1 1) | | 30.6° ($\bar{2}$ 0 2) | | 31.8° (0 0 2) | | |
| | AC | WQ | AC | WQ | AC | WQ | AC | WQ | |
| 0 | | | | | | | | | < 50 |
| 5 | 581 | * | 185 | * | 713 | * | 1498 | * | 50 \pm 10 |
| 15 | 2237 | 635 | 625 | 369 | 2079 | 708 | 3819 | 2333 | 110 \pm 20 |
| 30 | 3361 | 1482 | 1082 | 767 | 2237 | 1998 | 3576 | 3069 | 160 \pm 30 |
| 60 | 5491 | 5461 | 1592 | 2079 | 4122 | 4624 | 7157 | 7868 | 190 \pm 30 |
| 120 | 5914 | 4396 | 2500 | 2343 | 3807 | 3782 | 6241 | 7797 | 220 \pm 40 |
| 240 | | 10404 | | 3648 | | 6561 | | 10161 | 260 \pm 20 |
| 960 | | 15826 | | 5227 | | 7974 | | 14137 | 530 \pm 50 |
| 1440 | | 22983 | | 5883 | | 8372 | | 14544 | 600 \pm 50 |
| 3000 | | 24056 | | 10754 | | 6939 | | 12544 | 620 \pm 70 |

*Not measured AC = Air cooled WQ = Water quenched

[†]JCPDS - Joint Committee for Powder Diffraction Standards, 1603 Park Lane, Swarthmore, Pa, USA

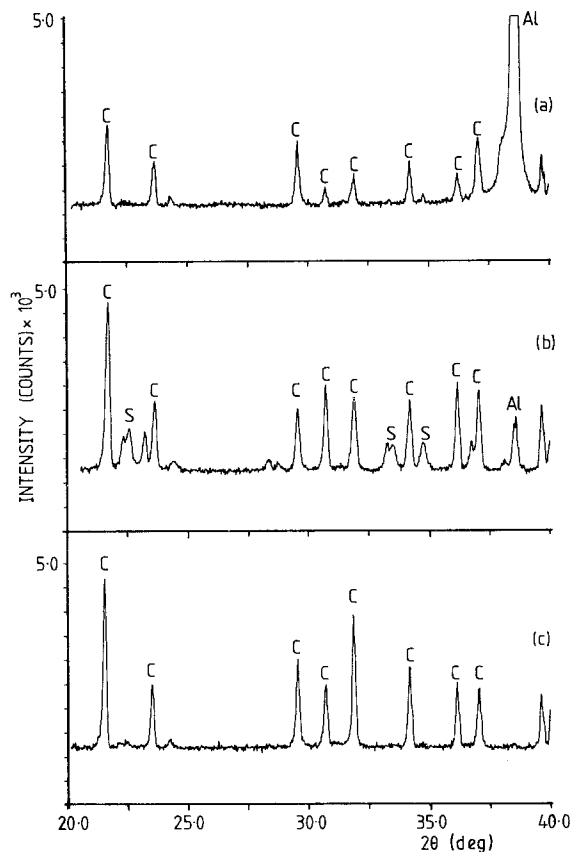


Figure 3 X-ray diffractograms from alloy 8090 after a solution treatment of 1 h at 530°C (a) sheet 2 as-received surface, (b) sheet 2 ($\frac{3}{4}t$ ground) and (c) sheet 1 ($\frac{1}{2}t$). (C = Li_2CO_3 , S = $\gamma\text{-LiAlO}_2$).

peaks shown in Figs 2b and 2c could be indexed as either Li_2CO_3 or $\gamma\text{-LiAlO}_2$. The Li_2CO_3 peaks chosen to monitor lithium depletion, labelled in Fig. 2b, increased in intensity with solution treatment time (Table II).

No diffraction peaks due to Li_2O , LiAl_5O_8 or Li_5AlO_4 , which have been previously reported to form on Al-Li based alloys [13, 15–17], were found in the present study.

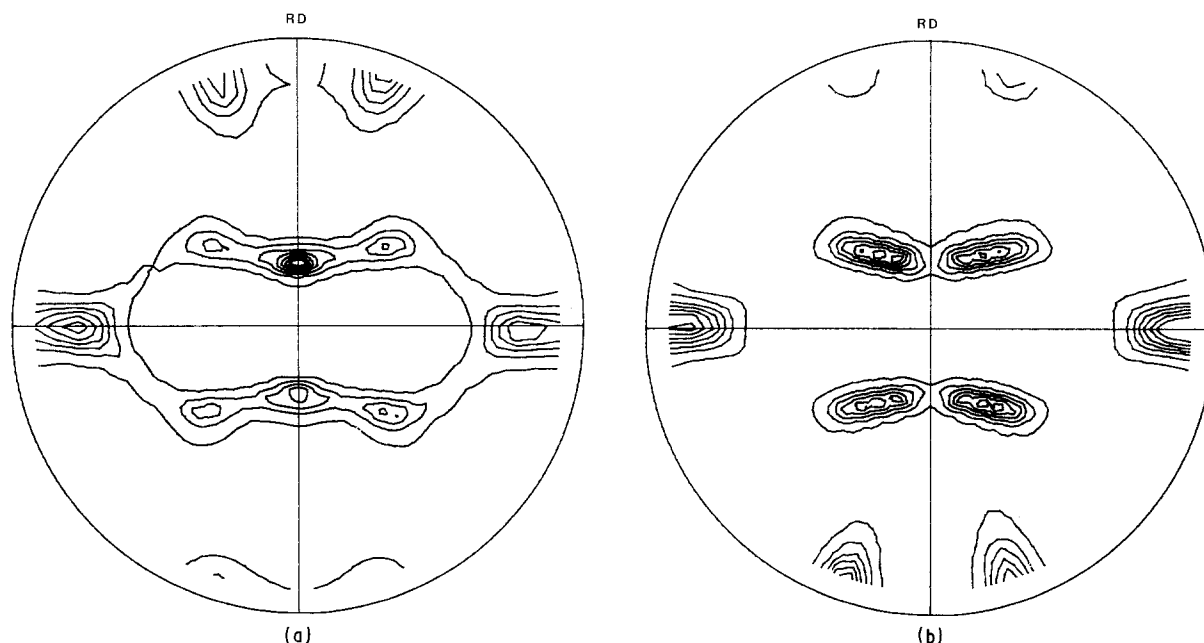


Figure 4 (111) Pole figures for alloy 8090 at (a) $\frac{3}{4}t$ and (b) $\frac{1}{2}t$. Contour levels: 1, 3, 5, 7, 9, 11, 13 x random. RD is the rolling direction.

3.2. Effect of initial surface removal

In specimens of alloy 8090 (sheet 1), where the initial surface layer had been removed, the intensities of the Li_2CO_3 peaks were usually greater than those from the as-received surface, irrespective of surface finish. This was observed for specimens where only $40\ \mu\text{m}$ was removed, as well as those reduced to $\frac{3}{4}t$ and $\frac{1}{2}t$. These results indicate that a lithium depletion layer already existed in the as-received sheet, and this was confirmed by subsequent microhardness testing (see Section 3.7). Figs 3a and 3b show the increase in intensities for the Li_2CO_3 peaks at $\frac{3}{4}t$ compared to the as-received surin 8090 (sheet 2) after 1 h exposure at 530°C. Fig. 3c shows the analysis for polished 8090 (sheet 1) at $\frac{1}{2}t$. This trace cannot be compared directly with Fig. 2c due to different measuring conditions. However, from a comparison of Figs 2 and 3 it is clear that the $\gamma\text{-LiAlO}_2$ phase is not a suitable phase for monitoring lithium depletion because of variable intensities.

3.3. Effect of texture

Texture gradients exist in unrecrystallized Al-Li based alloy sheets e.g. [14], with $\frac{3}{4}t$ regions possessing a $\{112\} \langle 111 \rangle$ texture (Fig. 4a) and $\frac{1}{2}t$ regions a $\{110\} \langle 112 \rangle$ texture (Fig. 4b). Typical diffraction traces representing these two conditions are shown in Figs 2c and 3c, from which it would appear that there is little effect of texture on the intensities of the Li_2CO_3 peaks.

3.4. Effect of cooling rate

Quenching specimens into water after solution treatment resulted in some loss of surface film and hence lower Li_2CO_3 peak intensities compared to those of air-cooled specimens given an identical treatment (Table II). This was only noticeable for short solution treatment times of up to ~ 1 h. In addition, Table III shows that for specimens with polished surfaces the

TABLE III The effect of quench rate and surface finish on the Li_2CO_3 peak intensity in alloy 8090 (sheet 2)

| Solution treatment time (min) | Specimen condition | | | | | |
|-------------------------------|---|-------------|---|-------------|---|-------------|
| | $\frac{3}{4}t$ Polished 1 sample per test 1 quench per test | | $\frac{3}{4}t$ Polished 1 sample multiple quenches | | $\frac{3}{4}t$ Ground 1 sample per test 1 quench per test | |
| | 21.4° (110) | 29.5° (111) | 21.4° (110) | 29.5° (111) | 21.4° (110) | 29.5° (111) |
| 15 | 5700 | 216 | 2673 | 906 | 524 | 243 |
| 30 | 2981 | 812 | 1211 | 256 | 1980 | 686 |
| 60 | 2401 | 1414 | 50 | 376 | 4449 | 1024 |

(110) Li_2CO_3 peak intensities showed a decrease with solution treatment time compared to the more usual increase with ground surfaces. The results shown in Table III also indicate that multiple solution treatments on a single polished specimen resulted in a greater reduction in Li_2CO_3 peak intensities compared to polished specimens given only one solution treatment. As this effect was consistent for this alloy, it should not affect the measurement of the Li_2CO_3 peak intensities unless they fall to values too low to measure accurately. However, this problem can be overcome by using data from other Li_2CO_3 diffraction peaks, and Table III lists some results from the 29.5° peak, (111), which shows an increase with solution treatment time.

3.5. Alloy composition

Table IV lists the Li_2CO_3 peak intensities for four different Al-Li based alloys after solution treatment times of up to 1 h at 530°C. Data are shown for the as-received and $\frac{3}{4}t$ (ground + polished) conditions. The measurements were carried out on single specimens given a series of solution treatments and quenches. The results obtained for the alloys 8091, 2090 and 2091 were similar to those of 8090 and can be summarized as follows.

(i) For the same solution treatment, Li_2CO_3 peak intensities for $\frac{3}{4}t$ specimens were generally higher than those for the as-received surface; again suggest-

ing that lithium depletion existed in the as-received sheets.

(ii) The surface film was predominantly Li_2CO_3 and $\gamma\text{-LiAlO}_2$, although very little $\gamma\text{-LiAlO}_2$ was detected on the surface of $\frac{3}{4}t$ specimens of 2091 (see Fig. 5a), and very little Li_2CO_3 or $\gamma\text{-LiAlO}_2$ on the as-received surface of the same alloy (see Fig. 5b).

(iii) For the same solution treatment, surface finish and cooling rate, Li_2CO_3 peak intensities were generally greater in 8090 and 8091 compared to 2090 and 2091.

(iv) Water quenching resulted in some loss of surface film.

(v) For a 1 h solution treatment, the depth of lithium depletion, as measured by microhardness tests, was the same in all four alloys (see Section 3.7).

3.6. Lattice parameter measurements

Table V compares the lattice parameters for Li_2CO_3 and $\gamma\text{-LiAlO}_2$ calculated from the reflections in the angular range 20 to 50° 2 θ and shows, with increasing solution treatment times, a shift towards the values quoted by JCPDS, particularly for $\gamma\text{-LiAlO}_2$. The lattice parameter of the aluminium matrix was found not to be a sensitive guide to lithium depletion.

3.7. Microhardness measurements and lithium depletion

Fig. 6 shows optical micrographs of microhardness

TABLE IV Maximum intensity for three Li_2CO_3 peaks in four Al-Li alloys solution treated and water quenched from 530°C

| Li_2CO_3 peak | Alloy | Solution treatment time (min) | | | | | |
|-------------------------------|-------|-------------------------------|-----------------------------|-------------|-----------------------------|-------------|-----------------------------|
| | | 15 | | 30 | | 60 | |
| | | As-received | Polished ($\frac{3}{4}t$) | As-received | Polished ($\frac{3}{4}t$) | As-received | Polished ($\frac{3}{4}t$) |
| 21.4° (110) | 8090* | 202 | 12365 | 671 | 12321 | 2200 | 11990 |
| | 8091 | 1616 | 2034 | 2663 | 2440 | 2938 | 3434 |
| | 2090 | 114 | 289 | 106 | 310 | 740 | 625 |
| | 2091† | 61 | 686 | 188 | 1318 | 228 | 1656 |
| 29.5° (111) | 8090 | 213 | 471 | 353 | 369 | 2470 | 882 |
| | 8091 | 534 | 376 | 734 | 686 | 986 | 1050 |
| | 2090 | 88 | 188 | 1274 | 210 | 1592 | 317 |
| | 2091 | 88 | 404 | 121 | 433 | 256 | 615 |
| 31.8° (002) | 8090 | 222 | 2070 | 1043 | 1043 | 1739 | 1739 |
| | 8091 | 1656 | 3758 | 2333 | 3376 | 2209 | 3660 |
| | 2090 | 117 | 234 | 85 | 259 | 566 | 543 |
| | 2091 | 92 | 566 | 71 | 404 | 166 | 615 |

*Sheet 1

†Pre-existing lacquer removed by light grinding

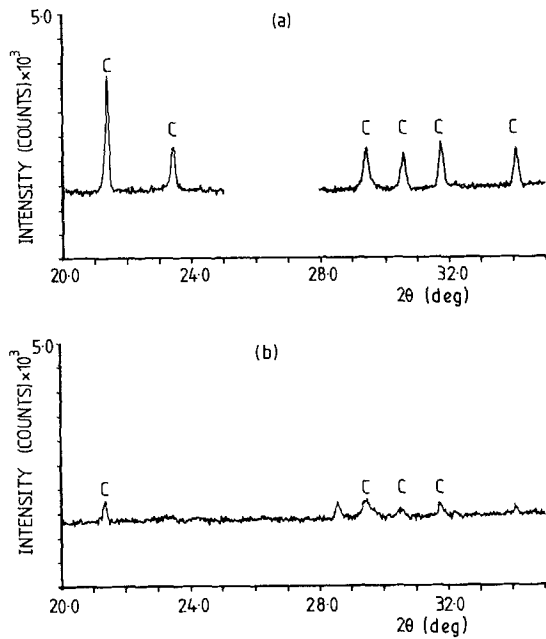


Figure 5 X-ray diffractograms showing the effect of surface removal in alloy 2091, after a solution treatment for 1 h at 530°C (a) $\frac{3}{4}t$ (polished) and (b) as-received surface. (C = Li_2CO_3).

traces across 8090 (sheet 1) after solution treatment times of 5, 30 and 60 min at 530°C, followed by ageing for 16 h at 170°C. After 5 min there was no measurable size difference between the indents near the alloy sur-

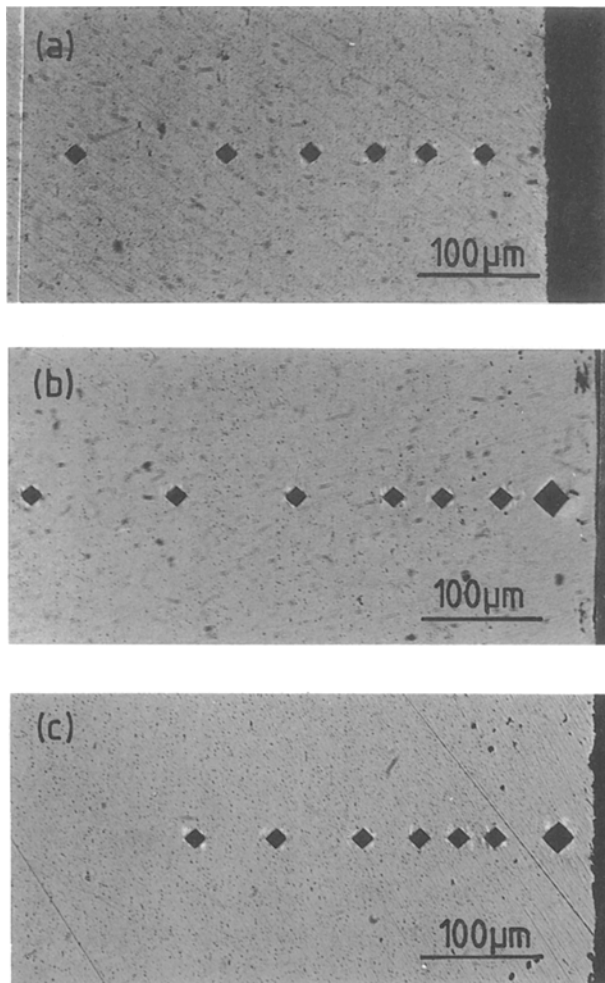


Figure 6 Optical micrographs showing microhardness indents on cross-sections of alloy 8090 (sheet 1) after solution treatment at 530°C for (a) 5 min, (b) 30 min and (c) 1 h.

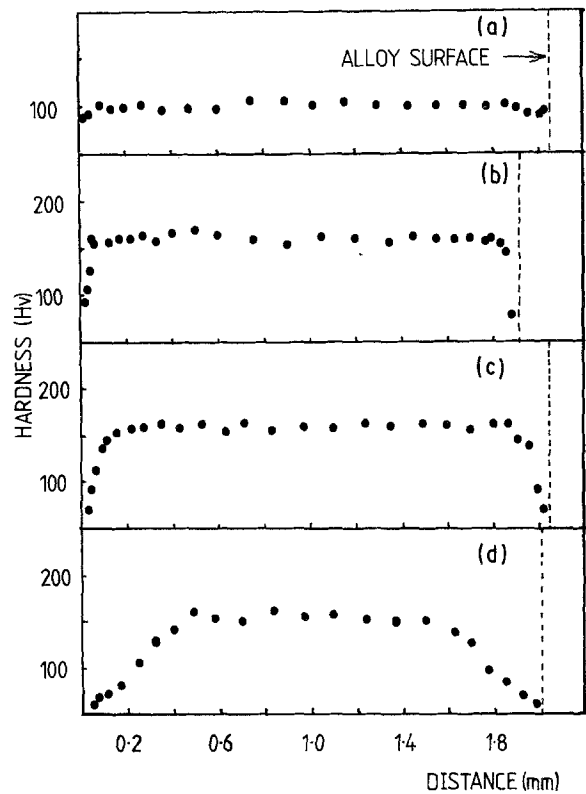


Figure 7 Microhardness traces across a vertical cross-section of alloy 8090 (sheet 1) after solution treatment at 530°C. (a) as-received, (b) 15 min (c) 1 h (d) 24 h.

face and those at the centre of the specimen. However, for longer times the indents can clearly be seen to be larger at the specimen surface i.e. the alloy has a softer surface layer.

Transmission-electron microscopy studies [1,2] and measurements of lithium depletion using nuclear reaction analysis [7, 8] have confirmed that microhardness measurements correlate well with the lithium concentration in Al-Li based alloys. Fig. 7 shows a series of microhardness traces obtained from specimens given various solution treatments. These show clearly that the lithium depletion layer increases with time. The slight drop in microhardness at the surface of the as-received condition supports the X-ray results, suggesting that some lithium depletion exists in the as-received alloys. Fig. 8 shows similar microhardness traces for the four different Al-Li based alloys after 1 h exposure at 530°C for the as-received condition. The lithium depletion depth of $\sim 200 \mu\text{m}$ appears to be similar in all four alloys, indicating similar lithium loss, in contrast to the X-ray intensity measurements presented in Section 3.5.

The lithium depletion layer depth is plotted against $t^{1/2}$ in Fig. 9. The resultant straight-line plot indicates that the lithium depletion layer growth rate is parabolic.

3.7.1. Calibration curves for lithium depletion in 8090 (sheet 1)

The lithium depletion values obtained from microhardness measurements and the corresponding Li_2CO_3 diffraction peak intensities are listed in Table II. Although fluctuations occurred for some Li_2CO_3 peaks, intensities increased with time of exposure at 530°C, and hence lithium depletion depth. A set of

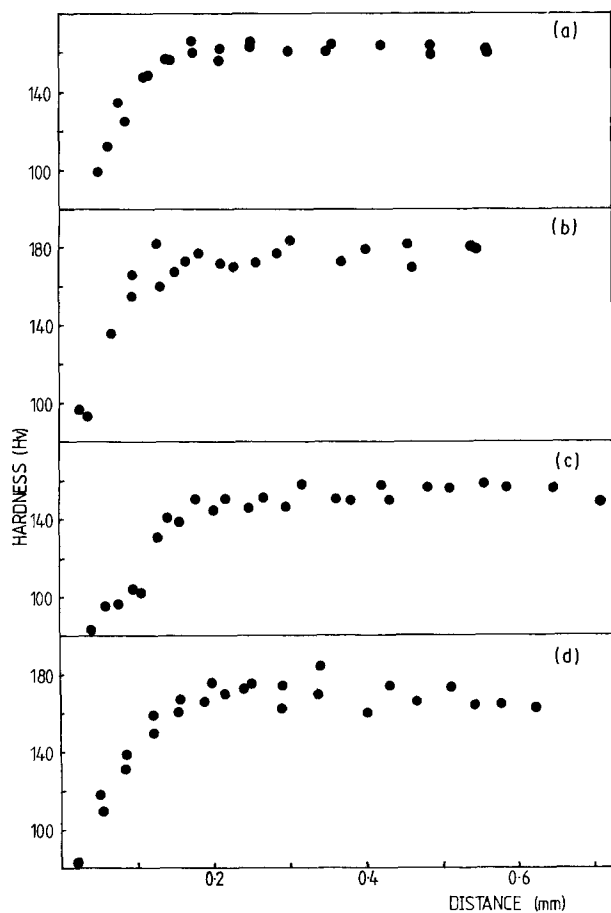


Figure 8 Microhardness traces across vertical cross-sections of four Al-Li alloys after solution treatment for 1 h at 530°C. (a) 8090, (b) 8091, (c) 2090, (d) 2091.

three results for 8090 (sheet 1) are shown in Fig. 10 for solution treatment times up to ~4 h. These types of plots can be used to estimate the lithium depletion depth from X-ray intensity data, provided identical experimental conditions are used in obtaining the calibration curves and in measuring unknown specimens.

3.8. The use of integrated intensity measurements

Table VI lists a set of results using the integrated peak intensities instead of the previously used maximum intensities. These results show that both the maximum and integrated intensity values show increases with increasing solution treatment times since errors due to differences in peak widths do not occur.

3.9. Effect of repeated tests

Table VII shows the effect of repeated measurements on different specimens of 8090 (sheet 2) which had been given identical preparations. The Li_2CO_3 diffraction peak at $21.4^\circ 2\theta$ again showed more variation in intensity compared to the other Li_2CO_3 peaks monitored. A comparison of these results also shows how water quenching causes some loss of surface film, and hence a lower X-ray intensity. The loss in intensity, especially of the 21.4° peak, suggests that polishing should be avoided if possible.

4. Discussion

Experiments have shown that X-ray diffraction is a viable, non-destructive technique for monitoring lithium depletion in Al-Li based alloys. The technique is also rapid since peak intensities can be measured in a few minutes once a calibration curve (lithium depletion plotted against Li_2CO_3 peak intensities) has been established. In addition, it is a sensitive method in that, in most cases, measurable peak intensities for solution treatment times as short as five minutes can be obtained readily; although the problems of surface film loss due to water quenching and variations between alloys need to be considered. However, the limiting accuracy in this, and in other indirect methods, is likely to be in the microhardness measurements since it is difficult to determine accurately small changes in microhardness very close to the alloy surface. The technique would appear to be quicker and cheaper

TABLE V Lattice parameter measurements of Li_2CO_3 and $\gamma\text{-LiAlO}_2$ formed on alloy 8090 after various solution treatment times

| | JCPDS Card no | Crystal structure | Lattice parameters (nm) | Solution treatment time (min) | | |
|--------------------------|---------------|--------------------|-------------------------|-------------------------------|---------|---------|
| | | | | 15 | 30 | 60 |
| Li_2CO_3 | 22-1141 | Monoclinic SG (15) | $a = 0.83590$ | 0.83986 | 0.83869 | 0.83829 |
| | | | $b = 0.49767$ | 0.49643 | 0.49673 | 0.49637 |
| | | | $c = 0.61940$ | 0.61890 | 0.61973 | 0.61929 |
| | | | $\beta = 114.72^\circ$ | 114.83 | 115.01 | 114.9 |
| $\gamma\text{-LiAlO}_2$ | 18-0714 | Tetragonal SG (92) | $a = 0.5169$ | 0.52065 | 0.51817 | 0.51756 |
| | | | $c = 0.62668$ | 0.62354 | 0.62687 | 0.62684 |

SG - Space Group

TABLE VI Variation of maximum and integrated peak intensities with solution treatment time in alloy 8090 (sheet 1)

| Solution treatment time (min) | Li_2CO_3 Peak Intensity | | | | | |
|-------------------------------|---|-------|--------------------|-------|--------------------|--------|
| | $21.4^\circ (110)$ | | $29.5^\circ (111)$ | | $31.8^\circ (002)$ | |
| | Max | Int | Max | Int | Max | Int |
| 15 | 247 | 3738 | 371 | 11356 | 367 | 5681 |
| 30 | 919 | 9491 | 511 | 9611 | 727 | 7589 |
| 60 | 2221 | 19329 | 873 | 13742 | 1789 | 20653 |
| 360 | 3530 | 36668 | 1447 | 19028 | 4570 | 52675 |
| 720 | 8676 | 96322 | 3426 | 42410 | 10774 | 125113 |

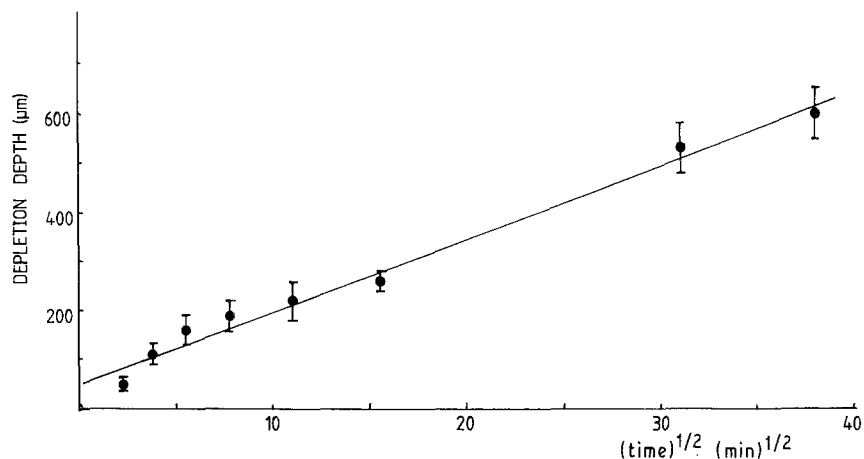


Figure 9 Depletion depth plotted against $\text{time}^{1/2}$ for alloy 8090 (sheet 1).

than nuclear reaction analysis [7, 8], Auger and X-ray photoelectron spectroscopy [13] methods, and also more sensitive than eddy currents [5].

The X-ray diffraction technique relies on the ability to measure Li_2CO_3 peak intensities. In this study, a number of variables were found to affect these intensities, but provided these variables are carefully controlled, it should be possible to make useful measurements of lithium depletion using X-ray diffraction.

The observation that Li_2CO_3 was found to be the stable compound formed after solution treatment at 530°C is in agreement with recent work by Ahmad [13], who used free-energy calculations to show that Li_2CO_3 would be stable at 530°C . This is in contrast to earlier X-ray diffraction results of Field *et al.* [15, 16] on binary and ternary Al–Li based alloys. From their observations they suggested that at 530°C , Li_2CO_3 would gradually be replaced by $\gamma\text{-LiAlO}_2$ in dry air, and that it would not be stable in wet air; being replaced by a mixture of LiAl_5O_8 and $\gamma\text{-LiAlO}_2$. Both of these suggestions do not appear to hold for the present study: for instance, with increasing solution treatment time any decrease in Li_2CO_3 peak intensity did not lead to a corresponding increase in $\gamma\text{-LiAlO}_2$ peak intensity. Also, no evidence for LiAl_5O_8 was found by X-ray diffraction. One possible explanation for these differences could be the presence of copper and magnesium in the present alloys. For example, the presence of copper may explain the absence of detectable quantities of MgO or MgO -containing compounds

in a manner similar to that found in Al–Zn–Mg–Cu alloys [18]. The lithium concentration at the alloy surface can explain the effect of initial surface removal on the Li_2CO_3 peak intensities. In the four alloys investigated, a pre-existing lithium depletion layer meant that less lithium was initially available to form Li_2CO_3 , than at either $\frac{3}{4}t$ or $\frac{1}{2}t$. The lower bulk lithium to 8090 and 8091; although other factors such as alloying element ratios and cooling rate may be important. For instance, the lithium to copper ratio is 0.78 and 1.0 for 2090 and 2091, compared to 1.98 and 1.24 for 8090 and 8091. Any variability in Li_2CO_3 peak intensity due to surface finish or cooling rate can be controlled by using a fine-ground surface finish and, if possible, air cooling. Where quenching is necessary, single solution treatments on each specimen are preferable to multiple treatments. The use of a ground surface finish is thought to provide better adherence of the surface film and is therefore less likely to be affected by quenching.

Table VIII lists some recent measurements of lithium depletion depth in a number of Al–Li based alloys. Due to variations in solution treatment temperatures, it is not possible to compare all of the results with those obtained in the present study. However, the value of $190 \pm 30 \mu\text{m}$ for a 1 h solution treatment is in good agreement with the value found by Wert and Ward [5], but is somewhat larger than the $120 \mu\text{m}$ quoted by Fox *et al.* [1, 2] and the value of $80 \mu\text{m}$ by Ahmad [13]. It is probable that the different results obtained arise from the methods used to determine the

TABLE VII Reproducibility of Li_2CO_3 peak intensities in alloy 8090 (sheet 2)

| Solution treatment time (min) | Alloy condition | Test No | Li_2CO_3 peak intensity (total counts) | | | |
|-------------------------------|-------------------------|---------|--|--------------------|------------------------------|--------------------|
| | | | 21.4° (110) | 29.5° (111) | 30.6° ($\bar{2}$ 02) | 31.8° (002) |
| 15 | $\frac{3}{4}t$ Polished | 1 | 51166 | 812 | 1584 | 3204 |
| 15 | air cooled | 2 | 24087 | 1116 | 1505 | 5098 |
| 15 | | 3 | 35382 | 437 | 1399 | 2510 |
| 15 | | 4 | 87379 | 620 | 1122 | 3080 |
| 60 | $\frac{3}{4}t$ Polished | 1 | 1806 | 1176 | 801 | 1024 |
| 60 | water quenched | 2 | 3994 | 3069 | 949 | 3091 |
| 60 | | 3 | 3832 | 2642 | 480 | 2134 |

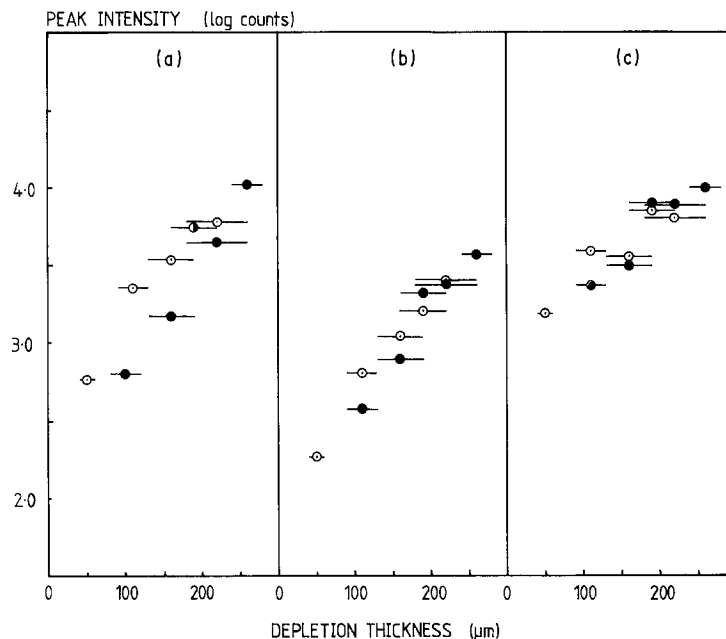


Figure 10 Calibration plots of peak intensity plotted against depletion depth for three Li_2CO_3 peaks (alloy 8090 (sheet 1)). (a) 21.4° (b) 29.5° (c) 31.8° (O air cooled, ● quenched).

lithium depletion depth from microhardness measurements, and from the different definitions of the lithium depletion depth used by different workers. Other factors that may affect microhardness measurements are the presence of the pre-existing depletion layer and the observation in the present study of varying amounts of large recrystallized grains at the sheet surface.

From data accumulated during this investigation, it is possible to suggest the following experimental procedure for using X-ray diffraction to monitor lithium depletion.

(i) Treat all specimens, both for calibration and subsequent measurement, consistently i.e. specimens must be similar in size, ground to the same depth with the same surface finish (polishing not recommended) and cooled at the same rate.

(ii) Scan Li_2CO_3 diffraction peaks in the angular range 20 to $33^\circ 2\theta$ (Cu $K\alpha$).

(iii) Measure the maximum or integrated peak intensities.

(iv) Build up a series of calibration curves using microhardness measurements to obtain the lithium depletion depth. It is suggested that a number of specimens given the same solution treatment are used, to allow for any variability and to reduce problems due to surface film lost during multiple-quenches.

(v) Check calibration curves from time-to-time, to take into account any changes in set-up, for example, a deterioration in X-ray tube intensity.

5. Conclusions

The conclusions are as follows.

(1) The surface film formed on four Al-Li based alloys heat treated in air at 530°C consists predominantly of Li_2CO_3 and $\gamma\text{-LiAlO}_2$.

(2) The intensity of Li_2CO_3 peaks in X-ray diffractograms can be related to the extent of lithium depletion as measured by microhardness measurements.

(3) Water-quenching results in some loss of surface film, compared to air cooling, with multiple-treated specimens showing a larger effect than single-treated specimens.

(4) All specimens showed some evidence of a pre-existing lithium depletion layer at the alloy surface.

(5) There was no apparent effect of texture on the extent of lithium depletion.

(6) X-ray diffraction can be used to monitor lithium depletion in Al-Li based alloys heat-treated in air at 530°C , provided that all specimens are treated in the same way. Moreover, the technique is economic, rapid and non-destructive.

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TABLE VIII Summary of recent literature values of Lithium depletion in Al-Li-Cu-Mg-Zr alloys

| Solution treatment temperature ($^\circ\text{C}$) | Time (h) | Lithium depletion depth (μm) | Reference |
|---|----------|---|----------------------------|
| 500 | 1 | 60 | [4] |
| 510 | 2 | 60 | [3] |
| 510 | 5 | ~350 | [3] |
| 510 | 10 | ~420 | [3] |
| 510 | 24 | 800 | [3] |
| 525 | 1 | 200 | [5] |
| 525 | 512 | 1500 | [5] |
| 530 | 1 | 190 | Present work (Table II) |
| 530 | 4 | 260 | |
| 530 | 24 | 600 | |
| 530 | 0.3 | 125 | [1, 2] |
| 530 | 1 | 120 | [1, 2] |
| 530 | 4 | 215 | [1, 2] |
| 530 | 1 | 80 | [13] |
| 543 | 12 | 381 | [12] |
| 543 | 48 | 889 | [12] |
| 550 | 1 | ~350 | [6] |
| 550 | 3 | ~450 | [6] |
| 550 | 10 | ~750 | [6] |

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