

Dispersoids in Al–Li AA8090 series alloys

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Chemical composition data of Al_3Zr -type dispersoids obtained using the EDAX attached to the transmission electron microscopes in three commercial AA8090 series Al–Li alloys demonstrated the incorporation of Ti in these dispersoids. The extrapolation technique led to the composition of dispersoids to be $\text{Al}_3(\text{Zr}_{0.92}\text{Ti}_{0.08})$. No dispersoids were found other than Al_3Zr -type in these alloys although one of the alloys contained Mn. Appearance of Mn-rich dispersoids in one of the re-cast alloys which contained Mn showed that the solubility of Mn in Al is significantly influenced by the Li concentration in Al–Li alloy systems.

1. Introduction

Al–Li alloys are of considerable interest for the aerospace industries. Lithium additions to aluminium provide the greatest reduction in density and offer the additional advantage of increasing the elastic modulus [1]. However, these improvements are accompanied by a significant decrease in ductility and fracture toughness. Attempts to improve the ductility and toughness of these alloys have been based on: (a) the introduction of ternary or quaternary additions such as Cu and Mg which can lead to the additional precipitation within the microstructure and (b) controlled additions of small amounts of transition elements such as Zr, Mn, Ti, V, and Cr. They form a fine dispersion of intermetallic phases which are usually called dispersoids. These dispersoids improve the mechanical properties by retarding recrystallization and suppressing grain growth and by reducing the inhomogeneous distribution of slip caused by the presence of shearable δ' precipitates [2]. The success of transition elements in the control of microstructure is mainly due to the retainment of these elements in supersaturated solution after relatively rapid solidification. The elements may then be precipitated as fine dispersoid particles, as small as 5 to 200 nm in diameter, by a suitable heat treatment. For heat treatable alloys of intermediate strength the standard procedure is to precipitate the transition elements by annealing the alloy at a relatively higher temperature before any working operation. Dispersoids occur in different forms depending on the alloying additions present and on the conditions of heat treatment. Information on specific dispersoid phases in commercial Al alloys are summarized in Table I.

In Al–Li alloy system, additions of Zr has received the greatest attention and is the most powerful recrystallization inhibitor [3, 4]. The behaviour is associated with the presence of fine (20–30 nm diameter) but uneven dispersion of coherent β' (Al_3Zr) particles

in a metastable cubic (LI2) form. These dispersoids are very stable as a result of low Zr solubility in Al, small misfit and sluggish Zr diffusion [5–8]. The aim of the present work is to study the chemical composition of dispersoid particles as a function of heat treatment in Al–Li alloys.

2. Experimental details

2.1. Materials

Three alloys coded P193, P194 and P263 were supplied by Alcan International Limited, Banbury Laboratories in the form of slabs. These slabs were sliced from the as-cast billets. The compositions of the alloys (Table II) are within the British Standard AA8090.

2.2. Heat treatment

To study the nucleation and composition of dispersoids as a function of soaking time, samples from each alloy, after ramp heating at 20°C h^{-1} , were solution treated at 550°C for different time intervals ranging from 0 to 100 h followed by water quenching.

2.3. Thin foil preparation

A standard jet polishing technique was employed by using a Struers Tenupol twin jet polishing machine for the thin foil preparation. A solution of 20% HNO_3 in analar-grade methanol was used as electrolyte at 30–40 V and temperature in the range -25 to -30°C .

2.4. Electron microscopy and microprobe analyses

Electron microscopy and microprobe analyses were carried out on Philips EM400 and EM430 electron microscopes equipped with EDAX energy dispersive

TABLE I Information about the specific dispersoid phases in commercial Al alloys

| Principal dispersoid-forming element | Formula | Crystal structure | Interface type | Lattice parameter(s) | Reference | |
|--|--|---------------------------------|----------------|---|-----------|--|
| Cr | $\text{Al}_{15}(\text{Cr},\text{Fe})_3\text{Si}$ | bcc | incoherent | 1.26 nm | 12 | |
| | $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ | fcc | | 1.47 nm | 13 | |
| | | | | | 12 | |
| | | | | | 14 | |
| Mn | $\text{Al}_{15}\text{Mn}_3\text{Si}_2$ | cubic | incoherent | 1.26 nm | 12 | |
| | $\text{Al}_{12}\text{Mn}_3\text{Si}$ | | | | 15 | |
| | | | | | 16 | |
| | | 17 | | | | |
| | $\text{Al}_6(\text{Fe},\text{Mn})$ | orthorhombic | | $a = 0.755$ nm $b = 0.65$ nm $b = 0.887$ nm | 18 | |
| $\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ | cubic | | | 18 | | |
| Zr | Al_3Zr | cubic | coherent | 0.405 nm | 12 | |
| | | | | 0.405 nm | 13 | |
| | | | | 0.408 nm | 14 | |
| | | | | (intermediate phase) | | |
| | | tetragonal (DO_{23}) | semi-coherent | $a = 0.401$ nm $c = 1.732$ nm | 19 | |
| | | (equilibrium phase) | | 20 | | |
| | | | | 21 | | |
| Ti | Al_3Ti | tetragonal (DO_{22}) | | $a = 0.385$ nm | 22 | |
| | | | | $c = 0.861$ nm | 23 | |
| Hf | Al_3Hf | tetragonal (DO_{23}) | coherent | $a = 0.3989$ nm | 19 | |
| | | | | $c = 1.7155$ nm | 21 | |
| | | | | | 23 | |
| V | Al_3V | tetragonal (DO_{22}) | | $a = 0.5345$ nm $c = 0.8322$ nm | 21 | |

TABLE II The chemical composition of the alloys used in the present investigation (wt %)

| Alloy code | Li | Cu | Mg | Mn | Fe | Ti | Zr |
|------------|------|------|------|------|------|-------|------|
| P193 | 2.32 | 1.05 | 0.82 | – | 0.07 | 0.023 | 0.06 |
| P194 | 2.52 | 1.06 | 0.89 | 0.26 | 0.11 | 0.026 | 0.07 |
| P263 | 2.3 | 1.14 | 0.87 | – | 0.08 | 0.02 | 0.12 |

detectors. The VG-HB501 STEM equipment was also used to analyse small particles. This equipment produced a very small electron beam (~ 2 nm in diameter) and was equipped with a LINK energy dispersive X-ray analysis system with a windowless detector.

Quantification of thin specimen microanalysis results was carried out using the ratio technique of Cliff and Lorimer [9, 10] and calculated k -factors. Analyses of embedded dispersoids were carried out using the extrapolation technique of Cliff *et al.* [11].

3. Results and discussion

3.1. Effect of artifacts on the analysis

Figs 1, 2 and 3 show the *in situ* analyses of several dispersoids analysed from the same specimen using different microscopes. The results which were obtained for Zr, Ti and Al were consistent for all three

instruments but the results for Cu showed large variations. The analyses done on the EM400T equipped with a LINK detector (in the Manchester Medical School) showed the incorporation of Cu in the dispersoids in large amounts (Fig. 1). The analyses done on the EM400T equipped with an EDAX X-ray detector (in Manchester Materials Science Centre) also showed the incorporation of Cu in the dispersoids but in relatively smaller amounts (Fig. 2). The analyses done on VG-HB501 STEM machine equipped with a LINK windowless detector demonstrated that Cu was not incorporating in the dispersoids (Fig. 3). These large variations in Cu concentration were assumed to be associated with effects which varied from instrument-to-instrument. The maximum Cu showed by the EM400T in the Medical School was due to the large hole count effect and/or the X-ray detector was not properly aligned and it detected excess Cu signal generated by the specimen holder, which was made of brass. The hole count is defined as the background counts when the electron beam passed through a hole in the specimen. Ideally there should not be any X-ray signal in this condition. A large hole count was observed in EM400T electron microscope when operated in the microprobe mode. In the nanoprobe mode the hole count was very low. The EM400T in the Medical School was not aligned properly to allow operation in the nanoprobe mode and it was necessary to operate it in the microprobe mode. At the time this

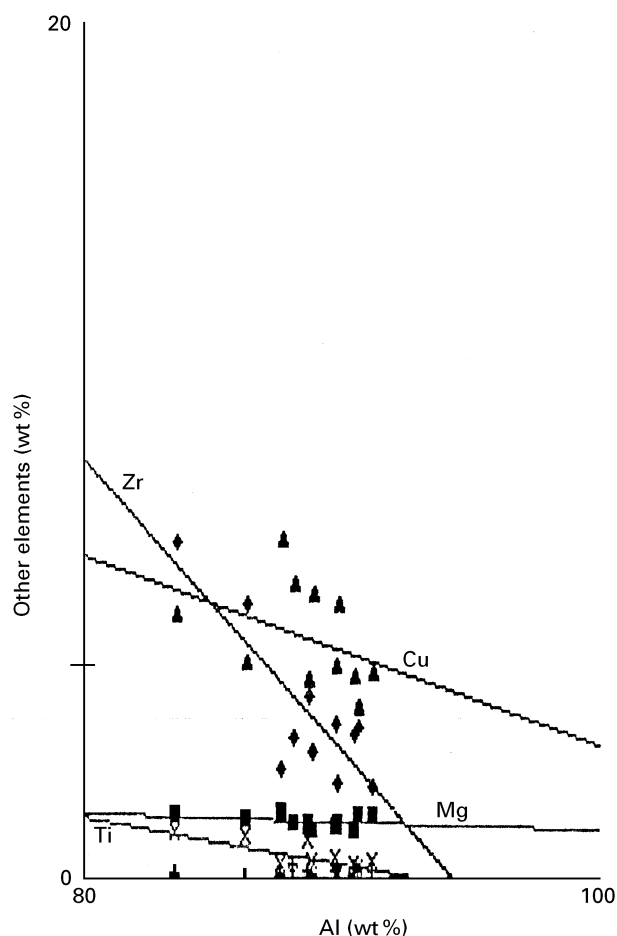


Figure 1 Chemical analyses data for dispersoids in alloy P194 after soaking at 550 °C for 96 h, water quenched. The analyses were done on a Philips EM400T operating in the microprobe mode installed at the Manchester Medical School. Key: ■ Mg; □ Al; XTi; + Mn; ▲ Cu; ◆ Zr.

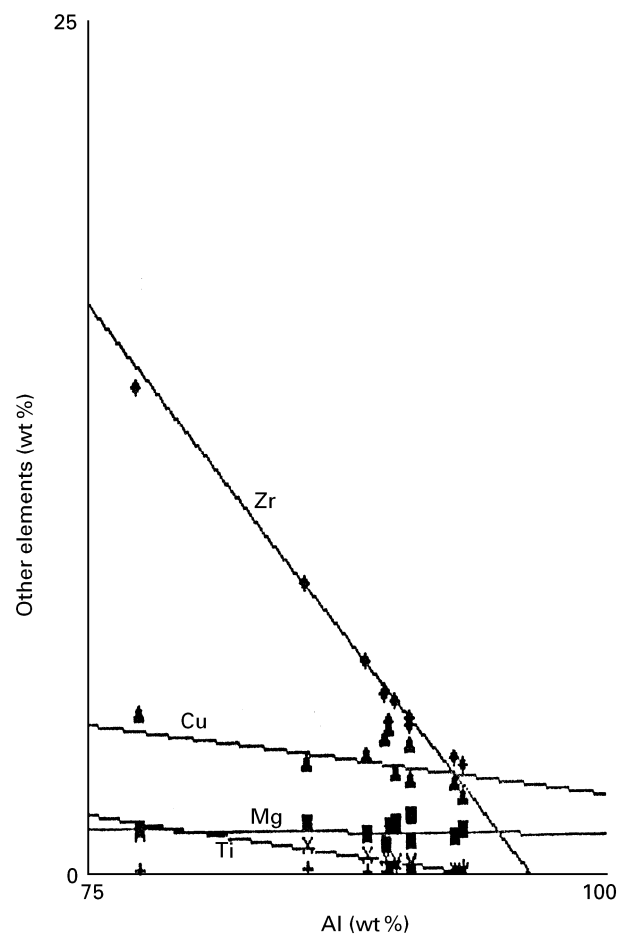


Figure 2 The analyses data of the same specimen as in Fig. 1 but the analyses were done on a Philips EM400T operating in the nanoprobe mode installed at the Manchester Materials Science Centre. Key: as Fig. 1.

work was carried out it was not fully appreciated that there was a problem with the hole count in the microprobe mode on EM400T. The EM400T in the Materials Science Centre was used in the nanoprobe mode where the Cu contribution due to hole count was minimized. Furthermore, the detector was carefully aligned so that spurious X-rays scattered by the specimen holder could not enter the detector. The trend of Cu concentration to increase with Zr was due to the large scattering of the incident beam from the high atomic number of Al_3Zr dispersoids. The true composition of dispersoids was obtained using the VG-HB501 STEM machine at Liverpool University. The hole count was almost negligible in this instrument. The analyses done on this microscope demonstrated that Cu was not incorporated in the dispersoids (Fig. 3).

The X-ray analysis fingerprint of a single dispersoid particle in alloy P194 which was taken using an EM430 electron microscope is shown in Fig. 4. The X-ray analysis fingerprint from the nearby matrix region is also overlapped for reference. The Cu contributions in both the analysis were similar while the fingerprint of the dispersoid particle demonstrated the incorporation of Zr and Ti. This comparison showed that in the analyses of dispersoids all the contribution of Cu was coming from the matrix region.

EDAX fingerprint from a single dispersoid particle in one of the alloys (P193) is shown in Fig. 5. The analysis showed that the dispersoid primarily consisted of Al and Zr. Some Ti was also incorporated in the dispersoid. EDAX analysis of dispersoids in the other two alloys also showed the incorporation of Ti in dispersoids.

3.2. Effect of homogenization on the chemistry of dispersoids

The chemical composition data of dispersoids, after homogenizing the alloys for 3, 10 and 96 h at 550 °C, (Figs 6–8) confirm the presence of Al_3Zr -type dispersoids. Besides Al_3Zr , there was no evidence for the presence of any other type of dispersoids in all three alloys during the entire homogenization. Although one of the alloys (P194) contained some Mn (Table II) which is also known as a dispersoid forming element in conventional Al-alloy systems [18] yet no evidence was found for the presence of any Mn-rich dispersoids.

In order to study the nucleation of dispersoids and to determine whether the dispersoid distributions in the original alloys had coarsened extensively during cooling following casting, the alloys were re-melted and chill-cast in the laboratory. These alloys were then

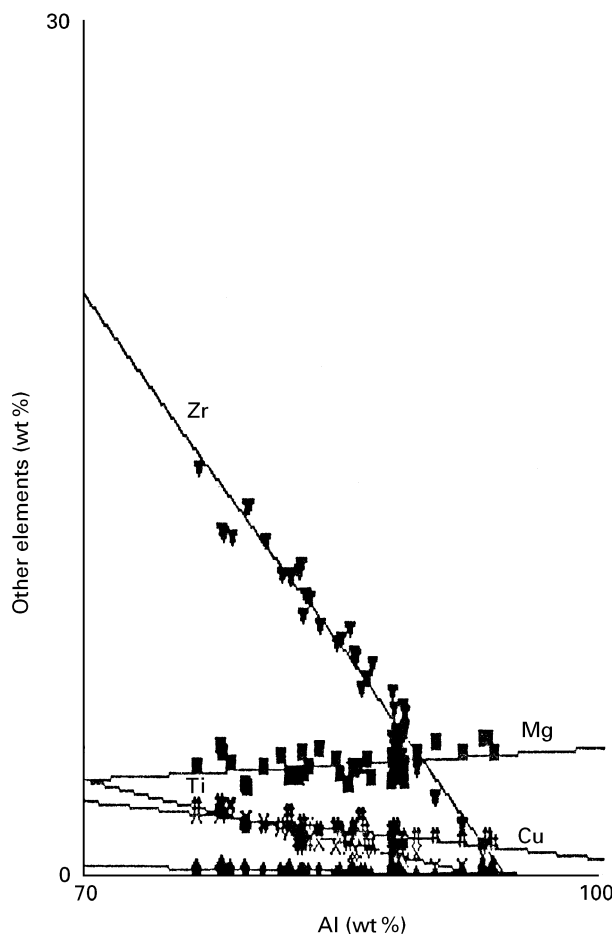


Figure 3 The analyses data of the same specimen as in Fig. 1 but the analyses were done on VG-HB501 STEM equipment installed at the Liverpool University. Key: ■ Mg; □ Al; X Ti; + V; ▲ Mn; ◆ Fe; # Cu; ▼ Zr.

ramp heated to the homogenization temperature and their microstructures were studied during heat treatment. Although alloys were re-melted and re-cast in an argon atmosphere, it appeared that the concentration of Li decreased during re-casting. Re-cast sections of the alloys were analysed by Alcan International Banbury Laboratories and the compositions are given in Table III. From the analyses it is evident that significant Li loss occurred during re-casting.

During ramp heating of the re-cast alloys, Al_3Zr dispersoids nucleated during ramp heating to the homogenization temperature. In alloy P194 some Mn-rich dispersoids were also observed following ramp heating to 510°C . An EDAX microanalysis fingerprint obtained from a single Mn-rich dispersoid is shown in Fig. 9. These particles appeared identical to Al_6Mn -type dispersoids which were reported to form in conventional Al alloys containing Mn [18]. The reason that these dispersoids were not seen in the original alloy P194 was possibly because the solubility of Mn in Al was significantly decreased in the presence of Li, with the result that most of the Mn was incorporated into the coarse grain boundary phases during the later stages of solidification. Lithium was lost during re-casting (Table III) and it appears that this allowed significant retention of Mn in solid solution to form Mn-rich dispersoids during ramp heating. It is possible that the rapid cooling rate which was obtained during re-casting also assisted the retention of Mn.

The analyses of Zr-type precipitates demonstrated the incorporation of Ti in Al_3Zr dispersoids. The amount of Ti concentration, incorporated in the dispersoids, as a function of homogenization time remained the same in all three alloys. While

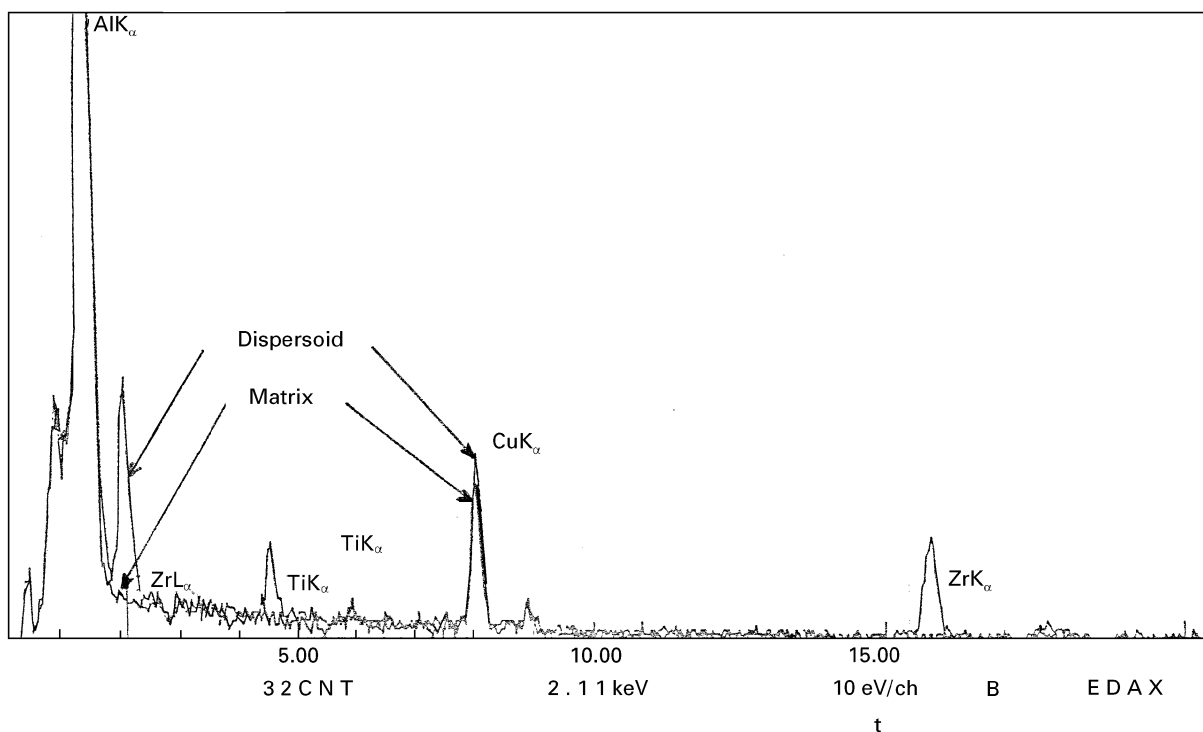


Figure 4 Energy dispersive X-ray microanalysis fingerprint from a single dispersoid particle in alloy P194. The microanalysis fingerprint from the matrix region is overlapped over the fingerprint from that of dispersoid.

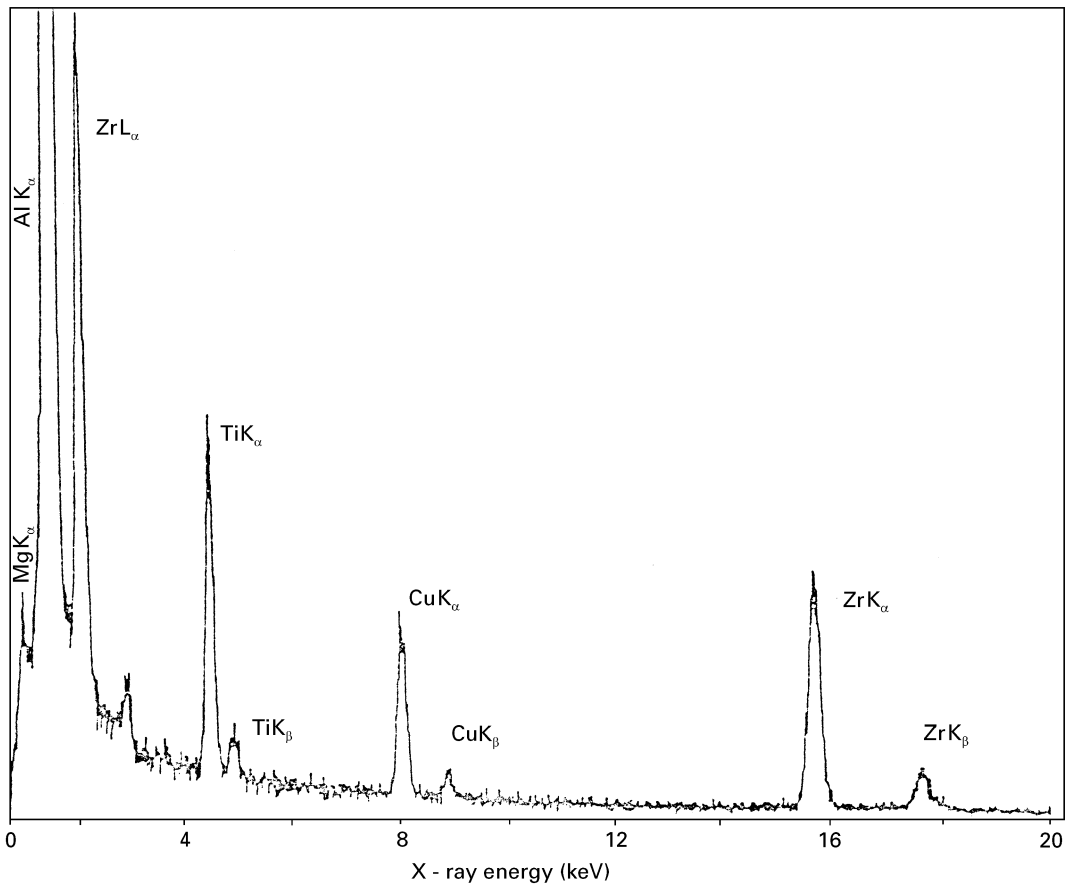


Figure 5 Energy dispersive X-ray microanalysis fingerprint from a single dispersoid particle in alloy P139 after soaking at 550 °C for 96 h, water quenched (EM400 nanoprobe).

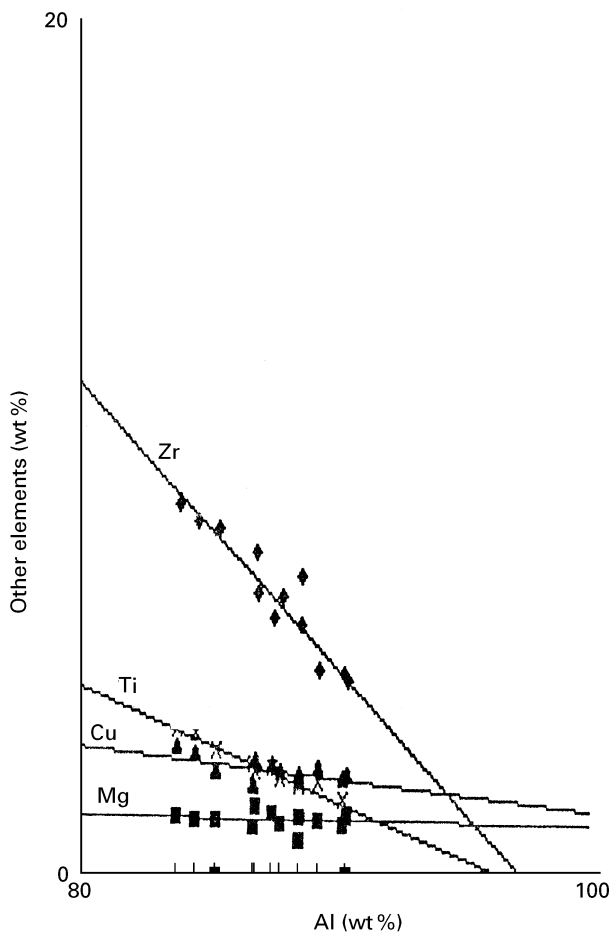


Figure 6 Chemical analyses data from dispersoids in alloy P139 after soaking at 550 °C for 10 h, water quenched. Key: as Fig. 1.

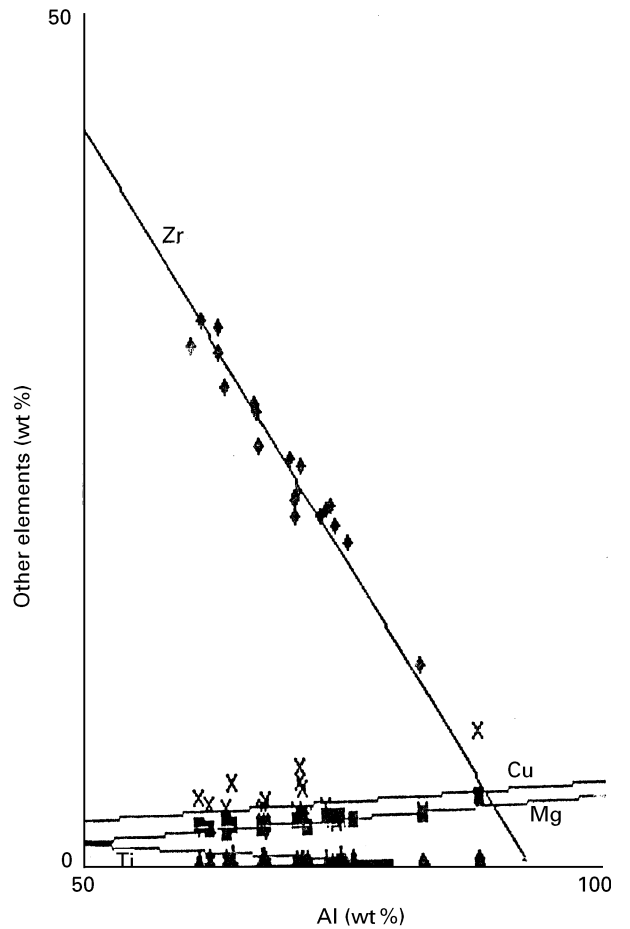


Figure 7 Chemical analyses data from dispersoids in alloy P139 after soaking at 550 °C for 96 h, water quenched. Key: ■ Mg; □ Al; X Cu; + Ti; ▲ Fe; ◆ Zr.

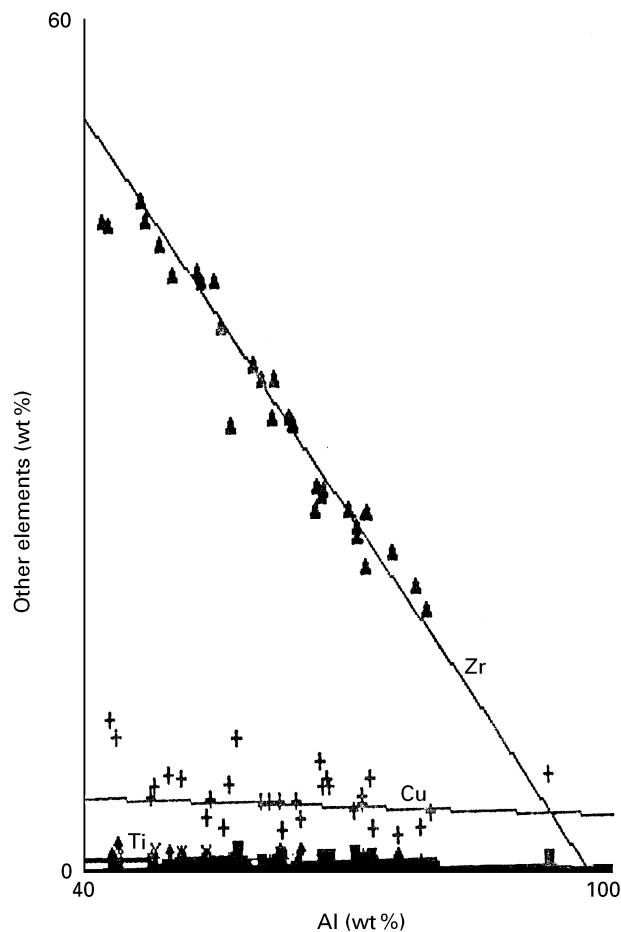


Figure 8 Chemical analyses data from dispersoids in alloy P263 after soaking at 550 °C for 96 h, water quenched. Key: ■ Mg; □ Al; X Ti; + Cu; ▲ Zr; ◆ Fe.

TABLE III The chemical composition of the alloys after re-casting as determined by Alcan International Ltd (wt %)

| Alloy code | Li | Cu | Mg | Mn | Fe | Ti | Zr |
|------------|------|------|------|-------|------|-------|------|
| P193 | 0.96 | 1.05 | 0.65 | 0.003 | 0.10 | 0.36 | 0.07 |
| P194 | 1.45 | 0.97 | 0.68 | 0.30 | 0.16 | 0.04 | 0.07 |
| P263 | 0.67 | 0.99 | 0.63 | 0.01 | 0.09 | 0.015 | 0.15 |

extrapolating the composition of dispersoids in these analyses the concentration of Cu in dispersoids was assumed 0 and the rest of the elements were normalized accordingly. The extrapolation of Al composition between the range 40–75 wt % led to the composition of the dispersoids to $\text{Al}_3(\text{Zr}_{0.92}\text{Ti}_{0.08})$ which remained constant during the entire homogenization. A 13:1 ratio of Zr and Ti in dispersoids demonstrates that out of every 14 atoms of Zr, 1 is being replaced by Ti atom. The incorporation of Ti in Al_3Zr -type dispersoids has not been documented previously.

4. Conclusions

1. EDAX analysis of Al_3Zr -type dispersoids in commercial Al–Li alloys demonstrated the incorporation of Ti in these dispersoids. The extrapolation technique revealed the chemical composition of dispersoids to be $\text{Al}_3(\text{Zr}_{0.92}\text{Ti}_{0.08})$.
2. Appearance of Mn-rich dispersoids in alloy P194 after re-casting showed that the solubility of Mn in Al

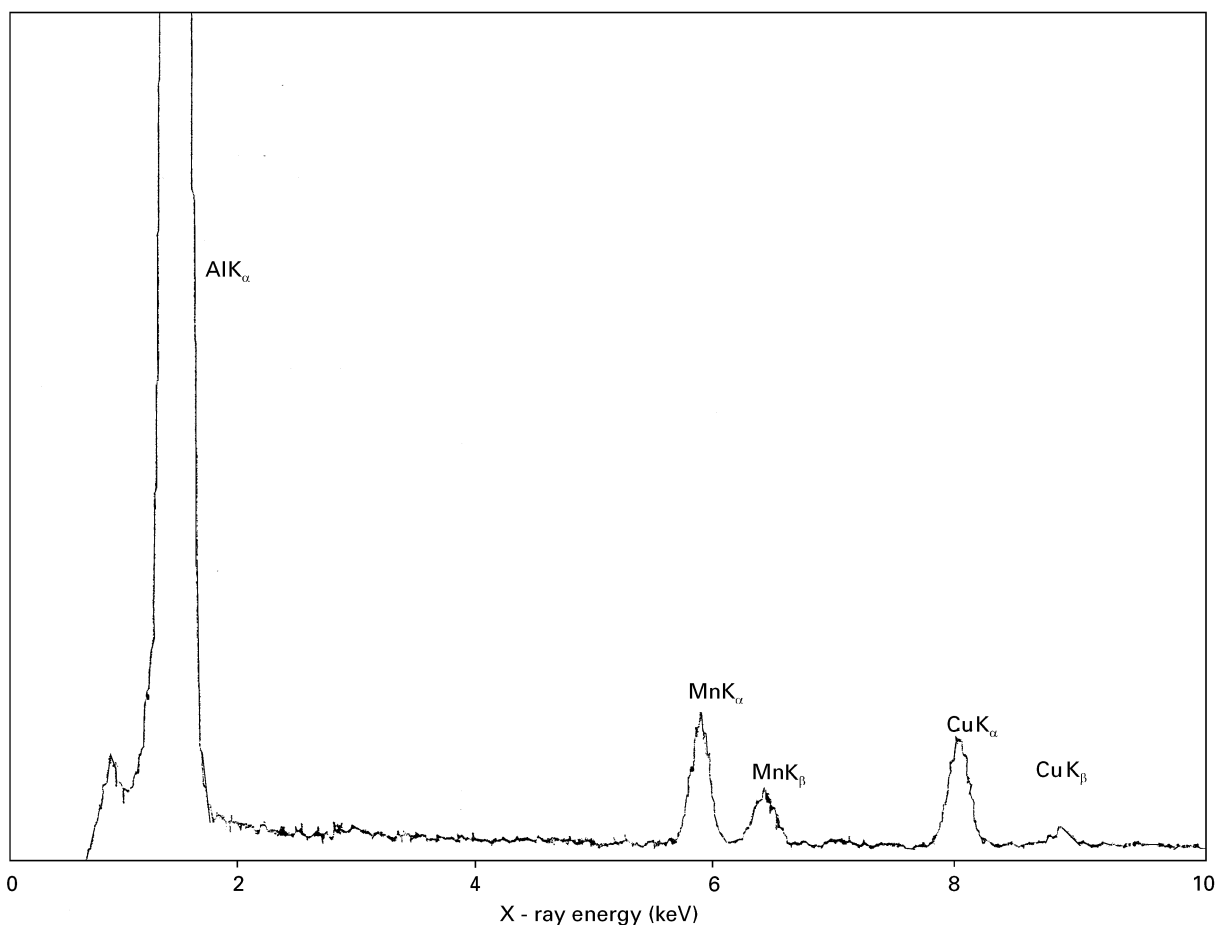


Figure 9 Energy dispersive X-ray microanalysis fingerprint from a Mn-rich dispersoid particle seen in re-cast alloy P194, ramp heated to 510 °C, water quenched.

is significantly influenced by the concentration of Li in Al–Li alloy systems.

3. While doing the energy dispersive X-ray analysis of any specimen using the EM400T-type electron microscopes, care must be taken in the quantification of Cu concentration for which the detector can pick the spurious X-ray signal generated by the specimen holder which is usually made of brass. Excess Cu can also be picked by TEM with large hole counts.

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