Convergent Beam Electron Diffraction Analysis of the $\Gamma_1$ ($\text{Al}_2\text{CuLi}$) Phase in Al-Li-Cu Alloys

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Point and space group analysis of large $\Gamma_1$ ($\text{Al}_2\text{CuLi}$) crystals was performed by convergent beam electron diffraction. The structure of $\Gamma_1$ was determined to be hexagonal, possessing a 6/mmm point group and P6/mmm (No. 191) space group. The lattice constants were found to be $a \approx 0.497$ nm and $c \approx 0.93$ nm. This structure is in agreement with an existing model of $\Gamma_1$, although discrepancies between the observed and calculated intensities of certain reflections were evident. Electron probe X-ray microanalysis of these $\Gamma_1$ crystals indicates the composition is on the copper-rich side of stoichiometric $\text{Al}_2\text{CuLi}$. The slight deviation in the composition of $\Gamma_1$ from stoichiometry and the presence of planar defects in the microstructure may account for the discrepancy in the intensity of certain reflections.

I. INTRODUCTION

ALUMINUM-lithium based alloys have been studied extensively during the past few years as possible replacement alloys for the aircraft and aerospace industry. The importance of these alloys stems from the enhanced strength and decreased density that the addition of lithium produces in these alloys compared to conventional aluminum alloys. Of particular interest are the Al-Li-Cu based alloys (such as the 2090 series alloy introduced by ALCOA) due to their greater strength compared with binary Al-Li alloys.$^{[1,2]}$ In binary Al-Li alloys, strengthening occurs primarily as a result of coherent $\beta'$ ($\text{Al}_3\text{Li}$) precipitation. However, $\beta'$ is an ordered phase with a high degree of coherence which acts to promote planar slip during deformation (e.g., Reference 3). The addition of copper to Al-Li alloys results in the precipitation of $\Gamma_1$ ($\text{Al}_2\text{CuLi}$) and also $\Theta'$ ($\text{CuAl}_2$) within the Al matrix during aging treatments. The $\Gamma_1$ phase is a semi-coherent precipitate which aids in the dispersion of slip during deformation.$^{[3,4]}$ In order to develop a complete understanding of the role of $\Gamma_1$ in the mechanical properties of these alloys, a better understanding of the structure of $\Gamma_1$ is essential.

Hardy and Silcock$^{[5]}$ first studied the $\Gamma_1$ phase in Al-Li-Cu alloys by X-ray diffraction techniques and identified the structure of $\Gamma_1$ to be hexagonal, with $a \approx 0.496$ nm and $c \approx 0.935$ nm. Rotation X-ray photographs of $\Gamma_1$ showed that no glide planes or screw axes were present in the structure, which limits the space group to the four hexagonal groups P622, P6mm, P6m2, and P6/mmm; however, they were unable to distinguish among these four space groups. Hardy and Silcock proposed the orientation relationship between $\Gamma_1$ and the Al matrix to be (0001)$_{\Gamma_1} \parallel (111)$_{Al} and (10\overline{1}0)$_{\Gamma_1} \parallel (11\overline{0}0)$_{Al}. Later, Noble and Thompson$^{[6]}$ verified this orientation relationship using selected area electron diffraction (SAD) in the transmission electron microscope (TEM). The $\Gamma_1$ precipitates form as extremely thin (< 0.2 nm thick) hexagonal-shaped plates which makes detailed analysis of their structure using SAD difficult because the very thin precipitates cause alterations in the shape of reciprocal lattice points which result in streaking of diffraction spots in the SAD patterns. Finally, Noble and Thompson pointed out that strong (0001) reflections in the (10\overline{1}0) zone axis of $\Gamma_1$ could not be produced by double diffraction from the matrix and suggested that $\Gamma_1$ may be ordered along the $c$ direction. However, no further confirmation of an ordered $\Gamma_1$ structure was reported.

Recently, Suzuki et al.$^{[7]}$ and Rioja and Ludwiczak$^{[8]}$ have suggested that a phase $\Gamma_1'$ may form prior to the precipitation of $\Gamma_1$. In certain SAD patterns taken from $\Gamma_1$ precipitates, extra reflections occur which Rioja and Ludwiczak were unable to index in a manner consistent with the structure of $\Gamma_1$ proposed by Hardy and Silcock.$^{[5]}$ From this evidence they proposed $\Gamma_1'$ was orthorhombic, with $a \approx 0.2876$ nm, $b \approx 0.86$ nm, and $c \approx 0.406$ nm. Huang and Ardell$^{[9]}$ have argued that the existence of both $\Gamma_1$ and $\Gamma_1'$ is inconsistent with their dark-field TEM images. Furthermore, the extra reflections observed in their SAD patterns were rationalized as the result of the very thin nature of the $\Gamma_1$ plates, which produces streaking of reflections. Additional support for Huang and Ardell's results has been given by Cassada et al.$^{[10]}$ who demonstrated that the extension of reciprocal lattice points in the (0001) direction could account for the extra intensity observed in SAD patterns of $\Gamma_1$. In a more recent study by Huang and Ardell,$^{[11]}$ evidence was presented which demonstrates that these extra reflections can be rationalized solely by the $\Gamma_1$ structure. In addition, they proposed an "ideal" crystal structure for $\Gamma_1$ based on the space group P6/mmm. This model of $\Gamma_1$ was developed using the original X-ray data of Hardy and Silcock$^{[1]}$ and analyzing it with a computer program which matched experimentally-determined X-ray line intensities with those calculated for different structures. The measured and calculated intensities are in fair agreement, but the evidence presented does not clearly distinguish among the space groups P6/mmm, P622, and P6mm due to discrepancies between the measured and calculated intensities of certain reflections. In particular, Huang and Ardell pointed out that the calculated intensity of reflections (0005) and (1124) did not match the experimentally-measured intensities.$^{[5]}$ However, they also indicated that better matching between calculated and measured intensities could not be achieved by simply changing the atom po-

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Convergent beam electron diffraction (CBED) has become a well-established technique for determining the crystal structure, point group, and space group of micron and submicron crystalline phases. One limitation of CBED, however, is that the phase of interest must be obtained as a single, through-thickness constituent of the thin-foil sample. This is usually achieved by growing the phase sufficiently large that its size is greater than the foil thickness. When only very small particles are available for analysis, these particles are generally extracted from the bulk and analyzed. In the case of the very thin $T_1$ precipitates, neither of the above approaches works. Although $T_1$ precipitates can be grown to a fairly large size (>$0.5 \mu m$) in two dimensions, the thickness of these precipitates never exceeds more than a few atom layers (see Figure 1). As a result, CBED analysis of these thin precipitates in TEM foils has proved, so far, to be a fruitless endeavor. In addition, extraction of these very thin, lithium-rich particles from the bulk has proven impossible to date. Therefore, in this study we have chosen to conduct CBED analysis on large $T_1$ crystals prepared by melting an alloy with a bulk composition close to stoichiometric $A_12CuLi$. Cassada et al. attempted to use CBED on a similarly-prepared intermetallic $T_1$ specimen. They were unsuccessful in determining the space group of $T_1$, due to a large number of stacking faults present in the sample. Our sample had a much lower density of defects, and the CBED analysis discussed here allows us, for the first time, to determine directly the lattice type, point group, space group, and lattice constants of the $T_1$ phase. The results of this analysis are compared with the “ideal” structure of $T_1$ proposed by Huang and Ardell.

**II. EXPERIMENTAL PROCEDURE**

The $T_1$ alloy was prepared by using 99.99 pct pure starting materials of aluminum, copper, and lithium. The lithium metal was cut and weighed in a vacuum glove box, and all three materials were vacuum encapsulated in a tantalum tube sealed by welding the ends closed. The filled tantalum tube was then heated to 1150 °C in an argon-flushed furnace for ten minutes to melt the alloy, and subsequently transferred to another furnace at 500 °C for 7 days. The final bulk composition was determined by wet chemistry and atomic absorption to be $Al-53.48$ wt pct Cu-$5.04$ wt pct Li (49.53 at. pct $Al$-27.09 at. pct Cu-23.42 at. pct Li), slightly off-stoichiometric $T_1 (Al_{12}CuLi)$.

Specimens for electron probe microanalysis (EPMA) were prepared by grinding and polishing using a kerosene and paraffin solution as a lubricant, rather than water, which can etch the lithium-rich phases during preparation. Thin-foil specimens for TEM were prepared by electrodisharge machining 3 mm diameter rods from the alloy, and slicing disks from these rods for thinning. Thin-foil samples were produced by ion-beam milling in a Gatan Dual Ion Milling System with the samples cooled to liquid nitrogen temperature.

Quantitative wavelength-dispersive X-ray spectroscopy was conducted in a JEOL 733 Superprobe (EPMA) controlled by a Tracor Northern 2000 analysis system at an accelerating voltage of 20 kV and 15 nA beam current. Data acquisition and reduction was accomplished with Sandia Task using the $\phi(pZ)$ analysis procedure. Two high-purity (>$99.99$ pct) $Al$-Cu alloys (Al-33 wt pct Cu and Al-50 wt pct Cu) were used as calibration standards, and lithium compositions were determined by difference since Li is not detectable using X-ray microanalysis. The composition of each phase was determined as the average value of at least 40 analysis locations, with the Student-t errors for a 95 pct confidence level reported for $Al$ and Cu; the lithium errors are given as the sum of the errors in both the $Al$ and Cu values. TEM was carried out in a Philips EM430T analytical electron microscope operated at an accelerating voltage of 100 keV.

**III. RESULTS AND DISCUSSION**

Figure 2(a) shows the microstructure of the $T_1$ alloy used in this study. The large primary phase is $T_1$ and the interdendritic region consists of an $Al$ solid-solution region, $CuAl_2(\Theta)$ particles, and secondary $T_1$ particles. Figure 2(b) is a backscattered electron image of the central region of Figure 2(a), and Figures 2(c) and 2(d) are $Al$ and Cu X-ray maps of 2(b), respectively. The compositions of the phases present were determined by wavelength-dispersive X-ray spectroscopy and are given in Table I. The measured composition of $T_1$ is on the copper-rich side of stoichiometric $Al_{12}CuLi$, in good agreement with the original work of Hardy and Silcock, who proposed a composition for $T_1$ of $Al-52.8$ wt pct Cu-$5.4$ wt pct Li. In addition, the composition of the theta phase is close to the expected composi-