V. HIGH-RESOLUTION ELECTRON MICROSCOPY STUDY OF A HIGH Cu VARIANT OF WELDALITE™ 049 AND A HIGH STRENGTH Al-Cu-Ag-Mg-Zr ALLOY

R.A. Herring, F.W. Gayle, and J.R. Pickens
I. INTRODUCTION

Weldalite™ 049 is an Al-Cu-Li-Ag-Mg alloy that is strengthened in artificially-aged tempers primarily by very thin plate-like precipitates lying on \{111\} matrix planes [1,2]. This precipitate might be expected to be the T1 phase, Al2CuLi, which has been observed in Al-Cu-Li alloys. However, in several ways this precipitate is similar to the \(\Omega\) phase which also appears as \{111\} plates and is found in Al-Cu-Ag-Mg alloys. [3-5] The present study was undertaken to identify the \{111\} precipitate or precipitates in Weldalite™ 049 in the T8 (stretched and artificially aged) temper, and to determine whether T1, \(\Omega\), or some other phase is primarily responsible for the high strength (i.e. 700 MPa tensile strength) in this Al-Cu-Li-Ag-Mg alloy.

2. BACKGROUND METALLURGY

Polmear [4] developed a nominal Al-6.3Cu-0.5Ag-0.5Mg-0.5Mn-0.2Zr alloy that had exceptionally high ambient and warm temperature properties for an ingot metallurgy 2xxx (i.e. Al-Cu) alloy. He noted that the Ag+Mg addition stimulated precipitation of the \(\Omega\) phase, whose presence was apparently responsible for the significant strength increase (~25%) over that for conventional high strength Al-Cu alloys such as 2219 and 2618.

Langan and Pickens [2] performed transmission electron microscopy investigations of Weldalite™ 049 and a model Al-6Cu-0.4Ag-0.4Mg-0.14Zr alloy similar to that innovated by Polmear. Langan and Pickens identified the platelike phase in Weldalite™ 049 as T1, but a cursory investigation of the Al-Cu-Ag-Mg alloy underscored the similarities between T1 and \(\Omega\). Moreover, because of the similarity in the diffraction patterns for T1 and \(\Omega\), they [2] could not rule out the existence of \(\Omega\) in Weldalite™ 049 and, consequently, referred to the platelike precipitates as T1-type.

Additions of Ag have little or no effect on the strengthening or precipitation behavior of binary Al-Cu alloys but a marked increase in strength occurs if a small addition of Mg is also added [3, 4, 13]. The combined presence of Ag and Mg in Al-Cu alloys significantly enhances the formation of the \(\Omega\) phase [3, 13]. The mechanism by which these minor alloying additions jointly stimulate precipitation remains unclear although it is suggested that Ag and Mg may reduce the stacking fault energy in Al, which is quite high, resulting in enhanced fault
formation on matrix \{111\} planes which provide nucleation sites for the \(\Omega\) phase [14]. It has also been speculated that Ag and Mg form fine-scale particles on the \{111\} planes which serve to both nucleate \(\Omega\) and determine its morphology [15], although no evidence was presented to support this theory. More recently, Muddle and Polmear [16] found that Ag partitions to the \(\Omega\) phase in an Al-Cu-Ag-Mg alloy and concentrates at the precipitate/matrix interface in the overaged condition, perhaps to help accommodate the misfit strain that is present normal to the habit plane in the matrix. In that study [16], Mg was not detected and the role of Mg in \(\Omega\) phase formation is unknown. A recent study by Garg, et al. [18] has also shown that Ag is not required for \(\Omega\) phase formation in Al-Cu-Mg alloys.

3. ATOMIC STRUCTURE OF \(\Omega\) AND T1 PHASE

The structure of the \(\Omega\) phase in the Al-Cu-Mg alloy subsystem was proposed by Auld [6] and verified by Knowles and Stobbs [7] to be monoclinic with \(a = b = 0.496\) nm, \(c = 0.848\) nm and \(\gamma =120\) degrees (Figure 1). This structure is equivalent to and more appropriately described as orthorhombic with \(a = 0.496\), \(b = 0.859\), and \(c = 0.848\) nm and space group Fmmm [7,16]. Auld showed that this structure is best regarded as a slight distortion of the tetragonal \(\alpha\) (\(\text{Al}_2\text{Cu}\)) precipitate found in over-aged Al-Cu alloys [6].

In the Al-Cu-Li alloy subsystem, controversy exists as to the structure of the T1 phase -- nominally \(\text{Al}_2\text{CuLi}\). Hardy and Silcock [8] determined that the T1 structure belonged to one of the hexagonal space groups P622, P6mm, P6m2, or P6/mmm with \(a = 0.4965\) and \(c = 0.9345\) nm, based on a cast, stoichiometric \(\text{Al}_2\text{CuLi}\) alloy. Vecchio and Williams [9] further determined, using convergent beam electron diffraction, that a cast \(\text{Al}_2\text{CuLi}\) phase had P6/mmm symmetry. Huang and Ardell [10] proposed the space-group symmetry P6/mmm (Figure 2a) from calculated X-ray intensities which compared with "fair agreement" with the Debye-Scherrer X-ray intensity measurements reported by Hardy and Silcock [8]. Huang and Ardell [10] suggested the positional stacking of planes to be ABAB..., where the A planes are close-packed with ordered arrangements of Li and Al in 2:1 and 1:2 ratios for alternate A planes, and the B planes having a disordered arrangement of Cu and Al atoms which are not close packed. Cassada et al. [11] performed a high-resolution electron microscopy study of T1.
Figure 1. Monoclinic structure of the $\Omega$ phase showing the corrugated planes in the $Z$ direction where the small balls are Al at $Z = 0, 1/6, 1/3, 1/2, 2/3, 5/6,$ and $1,$ and the large balls are Cu at $Z = 1/4$ and $3/4.$
They proposed a modification of Huang and Ardell's structure which consists of four close packed layers. (Fig. 2b).

A model for T1 was recently proposed by Howe, Lee and Vasudevan [12] based on high-resolution electron microscopy image calculation. They reported a space group of P6mm. Their favored structure consists of four close-packed basal planes within the unit cell, as shown in Figure 2c, having a stacking sequence of ABAC...

Alternate A planes consist of pure Al or pure Li atoms. The B and C planes consist of 50% Al plus 50% Cu which are randomly mixed. Evidence was also given that the B and C planes may vary from the 50/50 Al/Cu mixture.

Thus, several models for T1 have been proposed and none is completely satisfactory with respect to matching experimental X-ray intensities or HREM images. The various T1 structures are listed by space group and atomic positions in Table 1 along with the structure of Ω as given by Knowles and Stobbs [7]. In the course of the present work it was found that Howe et al.'s structure was not P6mm (this is most easily seen by a lack of the required 2-fold rotation axes for this space group). Indeed, the structure is not hexagonal but is a closely related trigonal space group P3m1. Lattice parameters of the trigonal lattice are a = 0.286 and c = 0.935 nm, giving coherent matching with [111]Al planes. Though this trigonal structure does not agree with the space groups given by Hardy and Silcock [8], it is possible that the latter, being from a stoichiometric Al2CuLi cast structure, is not the same as the T1 that precipitates within the aluminum matrix.

3.1 Experimental Procedure

Two alloys were fabricated: a relatively high Cu variant of Weldalite™ 049, and a nominal Al-6Cu-0.4Ag-0.4Mg-0.1Zr alloy. These alloys are the same materials used by Langan and Pickens [2] and will be referred to as Weldalite™ 049 and alloy 2 respectively, with measured compositions given in Table 2. Each alloy was cast into a 16.5-cm diameter permanent mold and was homogenized by the practices developed by Pickens et al [1]. Each alloy was extruded at a ratio of 21:1 into 10.2 x 0.95-cm bar at a nominal preheat temperature of 370°C. The Weldalite™ 049 extrusion was solutionized at 504°C and Alloy 2 was solutionized at 530°C, each for 1 h. Each extrusion was
Figure 2. Various models proposed for the T\textsubscript{1} structure showing (a) Huang and Ardell's [10] having space group P6/mmm, (b) Cassada et al's [11] sites at $z = 0$ are occupied by an average of 0.67 Al and 0.33 Li, whereas at $z = 1/2$ the occupancy is 0.33 Al and 0.67 Li (c) Howe et al's [12] having space group P3\textsubscript{1}m1. The structure in (a) has 12 atoms/unit cell and (b) and (c) have 4 atoms/unit cell.
Table 1.
Space groups and atom positions of $\Omega$ and $T_1$ structures reported in the literature.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ref.</th>
<th>Structure</th>
<th>Group</th>
<th>Wyckoff Letter</th>
<th>Positions</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$</td>
<td>Knowles &amp; Stobbs [7]</td>
<td>Orthorhombic</td>
<td>Fmmm</td>
<td>8h</td>
<td>0 1/3 0</td>
<td>8Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(#69)</td>
<td></td>
<td>8i</td>
<td>0 0 1/6</td>
<td>8Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8l</td>
<td>1/4 1/4 1/4</td>
<td>8Cu</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Howe et al. [12]*</td>
<td>Trigonal</td>
<td>P3m1</td>
<td>1a</td>
<td>0 0 0</td>
<td>1Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(#164)</td>
<td></td>
<td>2d</td>
<td>1/3 2/3 1/4</td>
<td>1Al/1Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1b</td>
<td>0 0 1/2</td>
<td>1Li</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Cassada et al. [11]</td>
<td>Hexagonal</td>
<td>P6m2</td>
<td>1a</td>
<td>0 0 0</td>
<td>0.67Al/0.33Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(#187)</td>
<td></td>
<td>1b</td>
<td>0 0 1/2</td>
<td>0.33Al/0.67Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2i</td>
<td>2/3 1/3 1/4</td>
<td>1Al/1Cu</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Huang &amp; Ardell [10]</td>
<td>Hexagonal</td>
<td>P6/mmm</td>
<td>1a</td>
<td>0 0 0</td>
<td>1Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(#191)</td>
<td></td>
<td>1b</td>
<td>0 0 1/2</td>
<td>1Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2c</td>
<td>1/3 2/3 0</td>
<td>2Li</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2d</td>
<td>1/3 2/3 1/2</td>
<td>2Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6i</td>
<td>1/2 0 1/4</td>
<td>3Al/3Cu</td>
</tr>
</tbody>
</table>

*This is the Howe et al. [12] structure rewritten as trigonal.
water quenched to about 20°C, stretched 3%, and artificially aged at 160°C for 24 h to the near-peak strength, T8 temper.

Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>Li</th>
<th>Ag</th>
<th>Mg</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weldalite™ 049</td>
<td>5.83</td>
<td>1.25</td>
<td>0.38</td>
<td>0.42</td>
<td>0.13</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>6.16</td>
<td>-----</td>
<td>0.41</td>
<td>0.42</td>
<td>0.16</td>
</tr>
</tbody>
</table>

4. RESULTS

High-resolution images of the Ω phase in alloy 2 and the {111} strengthening phase (i.e., "T1-like") in Weldalite™ 049 were obtained in the [112] and [110] matrix orientations. The low symmetry of the Ω phase leads to the presence of three variants of Ω lying on each {111} matrix plane. Alloy 2 at the [110] matrix orientation, which is equivalent to the [010] and [310] orthorhombic variants of the Ω phase, shows {111} precipitates with thin Cu-rich (dark) and thick Al-rich (light) layers (Figure 3a) for a multi-unit-cell-thick precipitate. Lattice images of the Ω phase show the two variants that exist at the [112] matrix orientation (equivalent to the [100] and [110] orthorhombic orientations of the phase) which produce a square array of dark and light spots in one image (Figure 3b) and a wavy pattern in another (Figure 3c).

For the {111} precipitates in Weldalite™ 049, the lattice image (Figure 4) at the [110] matrix orientation gives an image similar to the T1 lattice images reported by others in Ag- and Mg- free alloys [11, 12]. The [112] matrix orientation produced only one distinct type of lattice image of the precipitates with examples being given in Figure 5. These images always have three rows of bright spots per unit cell. Two adjacent rows of spots form a rectangular pattern and the third row of spots, of decreased intensity, are positioned at a (sometimes variable) distance between the rectangular pattern, i.e., they are slightly offset to one side. This pattern of spots is different from previously reported T1 lattice images at the [112] matrix orientation which also have three rows of bright spots but which do not form a rectangular array for adjacent rows of spots [11, 17].
Figure 3. Lattice images of the \( \Omega \) phase in Li-free alloy-2 showing a) then, Cu-rich and thick Al-rich layers at the [110] matrix orientation, b) and c) square array of black and white spots, and wavy light and dark pattern at the [112] matrix orientation (see text).
Figure 4 Lattice images of the primary strengthening phase in Weldalite\textsuperscript{TM} 049 at the [110] matrix orientation showing the "classic" T\textsubscript{1} structure in (a) where the layers A, B, and C have been designated as being Li rich, Cu rich and Al rich, respectively (see text).
Figure 5  Lattice images of Weldalite™ 049 showing the 'non-classic' structure at the [112] matrix orientation (see text) where in (b) faulting appears to be occurring in between the arrows and in (c) the rectangular array of white spots changes from the top two rows to bottom two rows when scanning from left to right.
distance between the spots along the precipitate length were measured for both Weldalite™ 049 and the T₁ images of references 11 and 17, using the {111} matrix planes for a reference length in each case, and the white spots in Weldalite™ 049 were found to have the same separation as those in previously reported T₁ images. The platelike precipitates in Weldalite™ 049 thus have a different structure from that of the Ω precipitates in alloy 2. Furthermore, the structure is similar to that of T₁ reported in other Al-Cu-Li alloys, although the pattern viewed along the [112] matrix orientation is different.

5. DISCUSSION

The lattice images of the Ω phase in alloy 2 fit well with those produced by Knowles and Stobbs in an Al-Cu-Ag-Mg alloy [7]. Figure 3a has the thick-light layers and thin-dark layers equivalent to the [310] orthorhombic orientation image of Knowles and Stobbs. The square array of Figure 3b is equivalent to the [100]₀ and the wavy array of Figure 3c is equivalent to the [110]₀ orientation.

The presence of only one type of lattice image at the [110] and [112] orientations for alloy Weldalite™ 049, which is different from that seen in alloy 2, indicates that the Ω phase is not present in Weldalite™ 049 in the condition investigated. The primary strengthening phase in Weldalite™ 049 has the previously reported T₁ image at the [110] matrix orientation. However, at the [112] matrix orientation, they have a consistently different lattice image from the T₁ images reported by Cassada et al. [11] and Blackburn and Starke [17] in the same matrix orientation. It is significant that every {111} precipitate in Weldalite™ 049 T8 investigated (dozens) shows this distinct structure.

6. CONCLUSIONS

High-resolution micrographs of the primary strengthening phase in the T8 temper in each of the two alloys listed in Table 1 have been obtained. By comparing these experimental images to those images published by Knowles and Stobbs [7] it was found that the Ω phase exists in alloy 2, i.e., the Al-6Cu-0.4Mg-0.4Ag -0.1Zr alloy. By comparing the lattice images of the Ω phase to those of Weldalite™ 049, it was found that the Ω phase is not present in the Weldalite™
049 alloy under the conditions investigated. In this alloy, the lattice images have the "classic" T₁ lattice image at the [110] but not at the [112] matrix orientations. Thus, the primary strengthening phase in Weldalite™ 049 in the T8 temper examined appears to be T₁ or a closely related variation. This structure may be a faulted (with respect to that seen in Ag-free Al-Cu-Li alloys) version of the T₁ phase.

7. ACKNOWLEDGEMENTS

Part of Dr. Gayle's time spent in preparing this section was supported by the National Institute of Standards and Technology. The authors are grateful to T.J. Langan for providing the experimental materials in the appropriate tempers and to S. Mannan for his technical assistance.
8. REFERENCES


Weldalite™ 049 is an Al-Cu-Li-Ag-Mg alloy designed to have ultrahigh strength and to serve in Aerospace Applications. The alloy displays significantly higher strength than competitive alloys in both naturally aged and artificially aged tempers. The strengthening phases in such tempers have been identified to, in part, explain the mechanical properties attained. In general, the alloy is strengthened by \( \delta' \) (Al\(_3\)Li) and GP zones in the naturally aged tempers. In artificially aged tempers in slightly underaged conditions, strengthening is provided by several phases including GP zones, \( \Theta' \) (Al\(_2\)Cu), \( S' \) (Al\(_2\)CuMg), \( T_1 \) (Al\(_2\)CuLi) and possibly a new phase. In the peak strength artificially aged tempers, \( T_1 \) is the predominant strengthening phase.