Liqation Mechanisms in Multicomponent Aluminum Alloys during Welding

Three mechanisms cover most, if not all, wrought aluminum alloys and, for a given alloy and temper, the mechanism can vary from heat to heat

BY C. HUANG AND S. KOU

ABSTRACT. The mechanisms by which liqation is initiated in the partially melted zone of wrought, multicomponent aluminum alloys during welding were studied using three representative liqation-susceptible alloys 2024, 6061 and 7075 as examples. Three different liqation mechanisms were identified. In Mechanism I, which is for alloys beyond the solid solubility limit, liqation-inducing particles are always present and liqation can occur at any heating rate. In Mechanism II, for alloys within the limit but with the particles, liqation requires high heating rates. In Mechanism III, for alloys within the limit and without the particles, liqation occurs when the matrix starts to melt. These three mechanisms cover most, if not all, wrought aluminum alloys since an alloy is either beyond or within the limit. Termary phase diagrams were found a useful approximation for checking if the alloys were within or beyond the limit. Alloy 7075, which contained liqation-inducing CuMgAl2 particles and Cu2FeAl7 coatings on Fe-rich particles, was well within the limit and it liquated by Mechanism II. Alloy 6061 was also within the limit, but the mechanism depended on whether the solution heat treatment of the heat was thorough enough to dissolve liqation-inducing Si-rich particles. If so, it liquated by Mechanism III; if not, by Mechanism II. Alloy 2024, which contained liqation-inducing CuAl2 particles, was near the limit and it liquated by Mechanism I if the heat was beyond the limit and by Mechanism II if within. The liqation reactions caused by these particles or coatings were identified. Liqation-induced grain boundary segregation was severe, suggesting severe degradation of mechanical properties, as demonstrated in binary alloy 2219.

Introduction

The partially melted zone (PMZ) is a region immediately outside the weld metal where liqation can occur during welding and lead to hot cracking and degradation of mechanical properties. The partially melted zone (PMZ) is a region immediately outside the weld metal where liqation can occur during welding and lead to hot cracking and degradation of mechanical properties. The partially melted zone (PMZ) is a region immediately outside the weld metal where liqation can occur during welding and lead to hot cracking and degradation of mechanical properties. The partially melted zone (PMZ) is a region immediately outside the weld metal where liqation can occur during welding and lead to hot cracking and degradation of mechanical properties.

KEY WORDS

Aluminum Alloys
Grain Boundaries
Hot Cracking
Liqation
Solidification

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multicomponent and it is essential their li-
quation mechanisms be understood. Un-
fortunately, this has not been done so far
because multicomponent aluminum alloys
are much more difficult to understand.

The purpose of the present study is to
extend understanding of liquation in alloy
2219 to wrought multicomponent alu-
mínium alloys. The three representative li-
quation-susceptible alloys, 2024, 6061,
and 7075, are selected. To help understand
the liquation mechanisms in these alloys,
relevant heat treating literature is cited
and ternary phase diagrams are used as an
approximation. To identify the liquation-
inducing particles and the liquation reac-
tions involved, compositions of both parti-
cles in the base metal and particles and
grain boundaries in the PMZ are deter-
dined. Liquation-induced grain boundary
segregation is also determined.

**Experimental Procedure**

The three commercial aluminum alloys
studied were alloys 2024-T351, 6061-T651,
and 7075-T651. T3 stands for solution heat
treating and cold working followed by nat-
ural aging. T6 stands for solution heat treat-
ing and then artificial aging. T51 stands for
stress relieving by stretching (Ref. 18). Ac-
tual compositions of the alloys are listed in
Table 1 with nominal compositions included
for reference (Ref. 18).

Bead-on-plate welding was conducted by
gas metal arc welding (GMAW) per-
pendicular to the rolling direction of the
workpiece. The dimensions of the work-
piece were 20 cm long, 10 cm wide, and 9.5
mm thick. It was welded in the length di-
rection in the as-received condition.

The welding parameters were 7.41
mm/s (17.5 in./min) welding speed, 30 V
arc voltage, 245 A average current, and Ar
shielding. The filler metal was an alloy
4043 wire of 1.2-mm diameter. Its nominal
composition is Al-5.2 wt-% Si. The wire
feeding speed was 18.6 cm/s (440 in./min).

After welding, the base metal and the
PMZ were examined. For optical mi-
croscopy, alloys 2024 and 7075 were
etched by a solution of 0.5 vol-% HF in
water, and alloy 6061 was etched by
Keller’s reagent. Composition measure-
ments were conducted both in the base
metal and PMZ by energy dispersive spec-
troscopy (EDS) at 15 KV. In order to min-
imize the possible effect of etching on the
accuracy of composition measurements,
samples were lightly etched with 10 vol-%
phosphoric acid for 15 s. However, light
etching made the GBs in the base metal
difficult to observe. One 6061 sample was
etched with Keller’s reagent for 30 s to
better reveal the PMZ microstructure in
SEM images. All SEM images were taken
with backscattered electrons at 15 KV and
a 9-mm working distance.

**Results and Discussion**

**Liquation Mechanisms**

To help understand liquation in the
PMZ, liquation mechanisms for wrought
binary aluminum alloys will be discussed
first. Three liquation mechanisms are pro-
posed in Fig. 1. The binary phase diagram
in Fig. 1A is similar to the Al-rich side of
the binary Al-Cu phase diagram. The solid
solubility limit refers to the maximum sol-
ubility of the solute B in the solid phase α.
Alloys 1 and 2 are within and beyond the
solid solubility limit, respectively. Alloy 2
is similar to wrought aluminum alloy 2219
(essentially Al-6.3 w-% Cu), which is be-
Yond the maximum solid solubility of 5.65
wt-% Cu. In Alloy 2, AlB2 particles are
stable up to the eutectic temperature Te
because the alloy is in the two-phase re-
gion of α + AlB2. In Alloy 1, on the other
hand, AlB2 particles are stable up to the
solvus temperature only. Alloy 1 (an Al-
4.5%Cu alloy, for instance) contains no
such particles before welding if it is solu-
tion heat treated in the α-phase region
and quenched (Ref. 19).

Liquation in Alloy 2 is initiated by
Mechanism I, as shown in Fig. 1B. The
PMZ of Alloy 2 covers the area where the
peak temperature during welding is be-
tween the liquidus temperature TL and
the eutectic temperature TE. Upon heat-
ing to TL, liquation begins by the eutectic
reaction AlB2 + α → L. Since AlB2 is
thermodynamically stable up to TL, liqua-
tion occurs at TE regardless of the heating
rate during welding.

Before proceeding further, it is worth
mentioning the eutectic reaction at the eu-
At the fusion boundary, the fraction of liquid becomes, as dictated by the phase diagram, and the greater the fraction liquid becomes, the higher the local peak temperature is. PMZ. The closer to the fusion boundary, the higher the local peak temperature is between the liquidus temperature TL1 and the eutectic temperature TE. Consequently, the resultant PMZ covers the area where the peak temperature during welding is between the liquidus temperature TL1 and the eutectic temperature TE. Mechanism II is the same as the constitutional liquation mechanism proposed by Pepe and Savage (Refs. 16, 17), which is well recognized in some steels and Ni-based superalloys but not in aluminum alloys.

Liquation can also be initiated in Alloy 1 by Mechanism III if no AlxBy particles are present and if the heating rate is high enough to keep AlxBy from dissolving completely in α before reaching TE. The residual AlxBy, if there is still any at TE, will initiate liquation at TE by the eutectic reaction AlxBy (+α) → L. The resultant PMZ covers the area where the peak temperature during welding is between the liquidus temperature TL1 and the eutectic temperature TE. Mechanism II is the same as the constitutional liquation mechanism proposed by Pepe and Savage (Refs. 16, 17), which is well recognized in some steels and Ni-based superalloys but not in aluminum alloys.

Liquation can also be initiated in Alloy 1 by Mechanism III if no AlxBy particles are present at TE to cause liquation. This happens when Alloy 1 is heated slowly during welding and AlxBy particles dissolve in α before reaching TE or when Alloy 1 is solutionized and quenched before welding (Ref. 19). Liquation occurs by melting of the α phase, α → L, at the solvus temperature TSα, rather than by the eutectic reaction at TE. Consequently, the resultant PMZ covers the area where the peak temperature during welding is between the liquidus temperature TL1 and the solvus temperature TSα.

For wrought ternary aluminum alloys, the three liquation mechanisms shown in Fig. 2 are proposed. These mechanisms correspond to those for wrought binary alloys shown in Fig. 1. In a ternary phase diagram, the solid solubility limit is represented by a nonisothermal curve, while in a binary one, it is represented by a point of fixed composition and temperature (Fig. 1A). Again, Alloy 2 is beyond the solid solubility limit, and particles AlxByCz can react with the Al-rich phase α to initiate liquation by Mechanism I. Alloy 1 is within the limit, and liquation can be initiated by either Mechanism II or III, depending on whether the liquation-inducing particles AlxByCz are present at the reaction temperature or not.

According to Hatch (Ref. 20), both alloys 7075 and 6061 are within the solid solubility limit. Therefore, their liquation mechanisms can be expected to be either Mechanism II or III — Fig. 2. Also according to Hatch (Ref. 20), alloy 2024 is near the limit, and it can be either beyond or within the solid solubility limit, depending on the actual composition of the heat. If it is beyond the limit, the liquation mechanism can be expected to be Mechanism I. If it is within the limit, on the other hand, the liquation mechanism can be expected to be either Mechanism II or III.

Multicomponent phase diagrams, if they can be constructed, are rather complicated and difficult to understand. Therefore, it will be convenient if ternary phase diagrams can be used as an approximation to check if an alloy is within or beyond the limit. Figure 3 shows the solid solubility limits in the ternary phase diagrams of Al-Zn-Mg, Al-Si-Mg, and Al-Cu-Mg near the Al corner (Ref. 21). According to the workpiece compositions shown in Table 1, alloy 7075 is close to ternary Al-5.7Zn-2.6Mg by wt-%, which is well within the solid solubility limit as shown in Fig. 3A. Likewise, alloy 6061 is close to ternary Al-0.9Mg-0.6Si by wt-%, which is also within the solid solubility limit as shown in Fig. 3B. Alloy 2024 is close to Al-4.2Cu-1.3Mg by wt-%, which is near the solid solubility limit as shown in Fig. 3C. Therefore, it appears that ternary phase diagrams can be used as an approximation to determine the location of a multicomponent alloy with respect to the solid solubility limit.

Since an alloy is either within or beyond the solid solubility limit, Mechanisms I, II, and III cover the liquation mechanisms in most, if not all, wrought aluminum alloys.

**Liquation-Inducing Particles and Liquation Reactions**

The compositions of the predominant particles in the base metal were determined to help understand the liquation re-
actions in each alloy. Compositions of similar particles at different locations were compared to check the consistency of EDS analyses. Iron-rich particles existed in the base metal of each alloy. Iron (Fe) is an ever-present impurity in Al and particles form because the solubility of Fe in solid Al is very low.

### Alloy 2024

The EDS results for the particles in the base metal (and the PMZ) of alloy 2024 are listed in Table 2 in at.-%. Referring to Fig. 4, the compositions (in at.-%) of the particles in the base metal were essentially:

#### Cu-rich particles

- Al-34Cu at $a_1$, Al-36Cu at $a_2$, and Al-34Cu at $a_3$

#### Fe-rich particles

- Al-9Fe-7Cu-6Si-6Mn at $b_1$
- Al-10Fe-9Cu-6Si-6Mn at $b_2$
- Al-11Fe-7Mn-6Si-6Cu at $b_3$

The Cu-rich particles appeared to be CuAl$_2$ (that is, Al-33Cu in at.-%). CuAl$_2$ (and CuMgAl$_2$) particles have been observed in alloys 2219, 2024, and 2014.

### Table 2 — Compositions (in at.-%) of Particles and a Grain Boundary in Alloy 2024

<table>
<thead>
<tr>
<th>Position</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Metal (Fig. 4)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_1$</td>
<td>0.04</td>
<td>33.52</td>
<td>0.00</td>
<td>0.32</td>
<td>0.17</td>
<td>0.39</td>
<td>0.33</td>
<td>65.22</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.07</td>
<td>35.81</td>
<td>0.05</td>
<td>0.36</td>
<td>0.04</td>
<td>0.12</td>
<td>0.19</td>
<td>63.35</td>
</tr>
<tr>
<td>$a_3$</td>
<td>0.06</td>
<td>34.30</td>
<td>0.02</td>
<td>0.54</td>
<td>0.10</td>
<td>0.05</td>
<td>0.09</td>
<td>64.85</td>
</tr>
<tr>
<td>$b_1$</td>
<td>6.33</td>
<td>7.02</td>
<td>5.76</td>
<td>0.00</td>
<td>0.00</td>
<td>0.32</td>
<td>9.45</td>
<td>71.11</td>
</tr>
<tr>
<td>$b_2$</td>
<td>6.19</td>
<td>8.66</td>
<td>6.01</td>
<td>0.07</td>
<td>0.01</td>
<td>0.00</td>
<td>10.31</td>
<td>68.75</td>
</tr>
<tr>
<td>$b_3$</td>
<td>5.91</td>
<td>5.94</td>
<td>6.95</td>
<td>0.10</td>
<td>0.16</td>
<td>0.31</td>
<td>10.65</td>
<td>69.98</td>
</tr>
</tbody>
</table>

| **Partially Melted Zone (Fig. 8A)** |     |     |     |     |     |     |     |     |
| $p_1$    | 6.56| 5.80| 4.95| 0.00| 0.05| 0.08| 9.81| 72.75|
| $p_2$    | 6.74| 2.77| 6.98| 0.00| 0.08| 0.10| 7.99| 75.34|
| $p_3$    | 0.62| 23.60| 0.08| 8.36| 0.02| 0.00| 0.12| 67.20|
| $g_1$    | 2.64| 15.14| 0.02| 2.26| 0.05| 0.00| 0.12| 79.88|

**Fig. 4** — SEM images of alloy 2024 at two different locations in the base metal.  
**Fig. 5** — SEM images of alloy 7075 at two different locations in the base metal.
CuAl₂ particles can cause liquation by the following eutectic reaction (Ref. 23):

\[
\alpha + \text{CuAl}_2 \rightarrow \text{L at 548°C. (1)}
\]

Above the eutectic temperature the surrounding Al matrix melts into the eutectic liquid and dilutes it to a hypoeutectic liquid. Upon subsequent cooling, the hypoeutectic liquid solidified first as \(\alpha\) and last as eutectic (\(\alpha + \text{CuAl}_2\)). Small CuAl₂ particles were present along the GBs in the base metal (though too small for composition analysis) and they can cause GB liquation, as observed in alloy 2219 (Ref. 13).

The presence of many large CuAl₂ particles in the base metal and a composition near the solid solubility limit together suggested the as-received alloy 2024 was either beyond the solid solubility limit or was within the limit but had not been solution heat-treated thoroughly to dissolve CuAl₂. In the former case, Mechanism I can occur regardless of the heating rate during welding. In the latter, however, Mechanism II (constitutonal liquation) can occur under rapid heating. CuMgAl₂ particles, though not shown in Fig. 4, are likely to be present to cause similar liquation (Reaction 2).

The Fe-rich particles were similar to those insoluble by heat treating. Examples of such particles include (Fe,Cu,Mn)_3SiAl₁₂ (19 at.-% for Fe, Cu, and Mn together) and 6 at.-% for Si alone) or (Fe,Cu,Mn)_3SiAl₁₅ (15 at.-% for Fe, Cu, and Mn together, and 10 at.-% for Si alone) (Refs. 20, 22, 23). No liquation-causing reactions between Fe-rich particles and the Al matrix were found in the numerous reactions listed by Mondolfo (Ref. 23).

**Alloy 7075**

The EDS results for the particles in the base metal (and the PMZ) of alloy 7075 are listed in Table 3 in at.-%. Referring to Fig. 5, the compositions (in at.-%) of the particles in the base metal were

- **Cu-rich particles**
  - Al-26Cu-23Mg at \(a_1\)

- **Fe-rich particles**
  - Al-14Fe-4Cu-2Zn at \(b_1\),
  - Al-13Fe-4Cu-2Zn at \(b_2\),
  - Al-15Fe-4Cu-2Zn at \(b_3\), and
  - Al-14Fe-4Cu-2Zn at \(b_4\).

- **Cu-rich coatings**
  - Al-19Cu-9Fe at \(b_3\) and
  - Al-21Cu-10Fe at \(b_4\).

![Fig. 6 — SEM images of alloy 6061 at two different locations in the base metal.](image)

### Table 3 — Compositions (in at.-%) of Particles and a Grain Boundary in Alloy 7075

<table>
<thead>
<tr>
<th>Position</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
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<tr>
<td><strong>Base Metal (Fig. 5)</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_1)</td>
<td>0.03</td>
<td>26.08</td>
<td>0.00</td>
<td>22.99</td>
<td>0.07</td>
<td>1.86</td>
<td>0.16</td>
<td>48.81</td>
</tr>
<tr>
<td>(b_1)</td>
<td>0.00</td>
<td>4.38</td>
<td>0.37</td>
<td>0.13</td>
<td>0.17</td>
<td>1.97</td>
<td>13.68</td>
<td>79.30</td>
</tr>
<tr>
<td>(b_2)</td>
<td>0.00</td>
<td>3.78</td>
<td>0.40</td>
<td>0.28</td>
<td>0.25</td>
<td>2.19</td>
<td>13.16</td>
<td>79.94</td>
</tr>
<tr>
<td>(b_3)</td>
<td>0.00</td>
<td>4.28</td>
<td>0.24</td>
<td>0.19</td>
<td>0.25</td>
<td>2.27</td>
<td>14.58</td>
<td>78.19</td>
</tr>
<tr>
<td>(b_4)</td>
<td>0.71</td>
<td>3.96</td>
<td>0.47</td>
<td>0.06</td>
<td>0.15</td>
<td>1.88</td>
<td>14.31</td>
<td>78.47</td>
</tr>
<tr>
<td>(b_3)</td>
<td>0.00</td>
<td>18.87</td>
<td>0.11</td>
<td>0.23</td>
<td>0.26</td>
<td>0.84</td>
<td>9.04</td>
<td>70.65</td>
</tr>
<tr>
<td>(b_4)</td>
<td>0.50</td>
<td>20.77</td>
<td>0.13</td>
<td>0.14</td>
<td>0.17</td>
<td>0.56</td>
<td>9.81</td>
<td>67.91</td>
</tr>
</tbody>
</table>

| **Partially Melted Zone (Fig. 8B)** |     |     |     |     |     |     |     |     |
| \(p_1\)  | 0.00| 3.16 | 0.39| 0.09 | 0.18| 1.77| 14.57| 79.85|
| \(p_2\)  | 0.11| 9.51 | 0.03| 14.54| 0.04| 11.82| 0.00 | 63.95|
| \(p_3\)  | 0.48| 3.77 | 0.67| 1.65 | 1.89| 2.90| 11.88| 76.76|
| \(g_1\)  | 0.00| 6.75 | 0.09| 12.07| 0.44| 9.45| 0.00 | 71.20|

### Table 4 — Compositions (in at.-%) of Particles and a Grain Boundary in Alloy 6061

<table>
<thead>
<tr>
<th>Position</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Metal (Fig. 6)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(b_1)</td>
<td>8.26</td>
<td>0.75</td>
<td>1.00</td>
<td>0.02</td>
<td>1.70</td>
<td>0.00</td>
<td>15.53</td>
<td>72.74</td>
</tr>
<tr>
<td>(b_2)</td>
<td>7.85</td>
<td>0.82</td>
<td>0.84</td>
<td>0.00</td>
<td>1.25</td>
<td>0.18</td>
<td>16.48</td>
<td>72.58</td>
</tr>
<tr>
<td>(b_3)</td>
<td>8.60</td>
<td>0.58</td>
<td>1.04</td>
<td>0.01</td>
<td>2.49</td>
<td>0.02</td>
<td>14.77</td>
<td>72.50</td>
</tr>
</tbody>
</table>

| **Partially Melted Zone (Fig. 8C)** |     |     |     |     |     |     |     |     |
| \(p_1\)  | 8.21| 1.39| 0.79| 0.09| 1.97| 0.00| 15.70| 71.85|
| \(p_2\)  | 5.66| 1.00| 1.12| 0.11| 1.82| 0.00| 17.46| 72.63|
| \(g_1\)  | 19.68| 3.88| 0.00| 9.96| 0.04| 0.00| 0.14 | 66.30|
Fig. 8 — SEM images of the partially melted zone. A — Alloy 2024; B — alloy 7075; C — alloy 6061 in Fig. 6. In alloy 6061, the thick grain boundary liquid and the little grain interior liquid suggest the liquid from the weld pool penetrated deep into the partially melted zone along the grain boundary.
The Cu-rich particles appeared to be CuMgAl\(_2\) (that is, Al-25Cu-25Mg in at.-%) (Refs. 20, 23). The presence of some CuMgAl\(_2\) particles in the base metal suggested the solution heat treatment of the as-received alloy 7075 was not thorough enough. CuMgAl\(_2\) particles can cause liquation by the following eutectic reaction (Ref. 23):

$$\alpha + \text{CuMgAl}_2 \rightarrow L \text{ at } 518^\circ\text{C}. \quad (2)$$

As shown in Fig. 3A, alloy 7075 is considered an Al-Zn-Mg ternary alloy just for determining the approximate location of the alloy relative to the solid solubility limit. This does not contradict the presence of Cu-rich particles or coatings in the alloy.

These Fe-rich particles (in Fig. 5) differed from those in the base metal of alloy 2024 (Fig. 4) because they had some Zn but little Si and Mn due to the composition of alloy 7075. Liquation-causing reactions between such Fe-rich particles and the Al matrix were not found (Ref. 23).

The Cu-rich coatings appeared to be Cu\(_2\)FeAl\(_7\) (that is, Al-20Cu-10Fe in at.-%)
Fig. 12 — Grain boundary segregation in the partially melted zone of alloy 2024. A — SEM image; B — Cu; C — Si; D — Mg. The overall composition of the workpiece (Table 1) is included for reference (from ~2 to 0 µm).

Fig. 13 — Grain boundary segregation in the partially melted zone of alloy 7075. A — SEM image; B — Zn; C — Cu; D — Mg.
Fe-rich particles are known to transform to Cu$_2$FeAl$_7$ during heat treating of alloy 7075 ingots (Ref. 20). The following reaction is known to exist (Ref. 23):

\[
\alpha + \text{Cu}_2\text{FeAl}_7 \rightarrow L + (\text{Cu,Fe})\text{Al}, \text{ at } 590^\circ\text{C.} \quad (3)
\]

Therefore, Cu$_2$FeAl$_7$ on the surface of Fe-rich particles was likely to cause liquation by reacting with the surrounding Al matrix.

**Alloy 6061**

The EDS results for the particles in the base metal (and the PMZ) of alloy 6061 are listed in Table 4 in at.-%. Referring to Fig. 6, the compositions (in at.-%) of the particles in the base metal were essentially:

**Fe-rich particles**

- Al-16Fe-8Si-2Cr-1Mn at $b_1$
- Al-16Fe-8Si-1Cr-1Mn at $b_2$, and
- Al-15Fe-9Si-2Cr-1Mn at $b_3$

The Fe-rich particles were often thin and, when oriented normal to the polishing surface, appear as short line segments. Liquidation-causing reactions between such Fe-rich particles and the Al matrix were not found (Ref. 23).

No liquidation-causing particles were found in this alloy 6061. Since the Fe-rich particles did not cause liquation and there were no liquidation-causing particles present, liquation occurred by Mechanism III in this alloy 6061.

However, coarse Mg$_2$Si particles were reported to be present and cause liquation in alloy 6061 (Refs. 20, 22, 23). To resolve this discrepancy, an alloy 6061 from a different supplier was also welded, as will be discussed later.

**PMZ Microstructure**

The PMZ optical micrographs are shown in Fig. 7. As shown, the liquated and resolidified GB material consisted of a light etching $\alpha$ band that solidified first and a dark etching eutectic GB that solidified last. GB solidification was directional, that is, upward (indicated by the thick arrows) and toward the weld (Ref. 13). The latter was clearer in alloy 2024 because of more GBs facing the weld (to the upper right of the micrograph). The SEM images of the PMZ are shown in Figure 8. It is interesting to note the $\alpha$ band appeared as dark etching while the eutectic GB appeared as light etching.

**Alloy 2024**

The EDS results for the particles in the PMZ of alloy 2024 are listed in Table 2 in at.-%. Referring to Fig. 8A, the compositions (in at.-%) of the particles were essentially:

**Fe-rich particles**

- Al-10Fe-7Si-6Cu-5Mn at $p_1$
- Al-8Fe-7Si-7Mn-3Cu at $p_2$

**Cu-rich particle**

- Al-24Cu-8Mg-1Si at $p_3$

**Grain boundary**

- Al-15Cu-3Si-2Mg at $g_1$.

The compositions of Fe-rich particles were close to those of the Fe-rich particles at $b_1$ through $b_3$ in the base metal — Fig. 4. As evident in SEM images of higher magnifications (not shown here because of space limitations), these Fe-rich particles looked similar in microstructure to the Fe-rich particles in the base metal.
Therefore, it appeared Fe-rich particles did not react with the Al matrix to cause liquation. Otherwise, their composition and microstructure would have changed.

The Cu-rich particle at p3 had a composite-like structure of a normal eutectic and a particle-free α ring surrounding it as shown in the inserted micrograph in Fig. 8A. It appeared a large CuAl2 particle reacted with the Al matrix and caused liquation here, and the eutectic particle formed during subsequent solidification. Since the Al matrix contained Mg (Table 1), it brought Mg into the liquid hence the resultant eutectic particle at p3. It was also possible some CuMgAl2 particles were present in the base metal, and they reacted with the Al matrix to cause liquation and formed the particle at position p3 upon solidification.

The GB at g1 had a composite-like eutectic structure, as evident from SEM images of higher magnifications (not shown), and it had a particle-free α band below it. These were typical signs of a liquated GB (Refs. 13–15). Its Cu and Mg contents were lower than those of the eutectic particle at p3, possibly because the GB was relatively thin and the electron beam in EDS included the surrounding Al matrix of lower Cu and Mg contents.

Alloy 7075

The EDS results for the particles in the PMZ of alloy 7075 are listed in Table 3 in at.-%. Referring to Fig. 8B, the compositions (in at.-%) of the particles and grain boundary were essentially:

Fe-rich particles
Al-15Fe-3Cu-22Zn at p1, Al-12Fe-4Cu-32Zn-2Cr-2Mg at p3a
Mg,Zn,Cu-rich particles
Al-15Mg-12Zn-10Cu at p2, Al-15Mg-13Zn-9Cu at p3b, and
Grain boundary
Al-12Mg-9Zn-7Cu at g1.

The composition of the particle at p1 was close to those of the Fe-rich particles in the base metal (b1 and b2 in Fig. 5). This particle was, therefore, a bare Fe-rich particle that did not dissolve.

The particle at p2 had a composite-like structure of a normal eutectic (shown later in Fig. 13A at a higher magnification). The eutectic reaction involving a eutectic liquid of this composition was not found (Ref. 23). The high Mg and Cu contents of this particle suggested it was likely a large CuMgAl2 particle liquated here, incorporated Zn from the surrounding matrix, and solidified into a eutectic particle rich in Mg, Zn, and Cu.

The GB at g1 has a composite-like structure (as observed under higher magnifications) and a Mg/Zn/Cu-rich composition like the particle at p2. Its Mg, Zn, and Cu contents appeared lower than those of the particle at p2, possibly because of the background effect of this thin GB in the EDS composition analysis.

Consider the particle at position, p3, which was labeled at two positions, p3a and p3b (shown later in Fig. 13A at a higher magnification). It was interesting to note the liquated material at p3 (its lower left corner) penetrated into the GB. It was also interesting to note the particle at position p3 was on the average brighter on the outside and somewhat darker inside. This particle is discussed further as follows.

As mentioned previously, the base metal contained Fe-rich particles with Cu2FeAl7 on the surface. One possibility was Cu2FeAl7, liquated but the Fe-rich portion did not dissolve in the liquid produced by the liquidation process. However, the material at position p3b was essentially Al-15Mg-13Zn-9Cu by at.-% and contained little Fe. This suggested it did not come from the liquation of Cu2FeAl7. Furthermore, the material at position p3a was essentially Al-12Fe-4Cu-3Zn-2Cr-2Mg by at.-% and had more Cr and less Fe than those at positions b3a and b4a in Fig. 5. This suggested it did not come from the undissolved Fe-rich portion of a particle like b3 and b4 in the base metal.

The other possibility was that Cu2FeAl7, liquated, for instance, through Reaction 3 and formed (Cu,Fe)Al6. During subsequent solidification of the resultant liquid, the Fe-rich portion of the particle at p3 formed first and then the Cu-containing portion. It was interesting to note the composition of the material at p3b was close to that of the normal eutectic at position p2. It is possible the Fe-rich solid precipitated from the liquid and grew and became the Fe-rich portion and, upon further cooling, the eutectic nucleated heterogeneously on the Fe-rich portion and formed the Cu-containing portion.

Alloy 6061

The EDS results for the particles in the PMZ of alloy 6061 are listed in Table 4 in at.-%. Referring to Fig. 8C, the compositions of the particles (in at.-%) and grain boundary were essentially:

Fe-rich particles
Al-16Fe-8Si-2Cr-1Mn-1Cu at p1, Al-17Fe-6Si-2Cr-1Mn-1Cu at p2
Grain boundary
Al-20Si-10Mg-4Cu at g1.

The sample in Fig. 8C was etched with Keller’s regent for 30 s to reveal the PMZ microstructure more clearly in the SEM image. Otherwise, only Fe-rich particles would have been visible (Fig. 6). As shown previously, the base metal of alloy 6061 contained angular Fe-rich particles (Fig. 6) but no liquation-causing reactions between these Fe-rich particles and the Al matrix were found (Ref. 23). Figure 8C is further discussed as follows.

The composition of the particle at p1 was similar to the compositions of the Fe-rich particles in the base metal (b1 through b3 in Fig. 6). Its microstructure was also similar to that of the Fe-rich particles, that is, without a composite-like eutectic. The groove around the particle was caused by etching. These similarities suggested Fe-rich particles do not cause liquation in alloy 6061. The small particle at p2 was a similar Fe-rich particle that happened to be close to the GB, and was caught in the GB liquid.

The GB at g1 had a composite-like structure of a normal eutectic and a particle-free α band below it, typical of a liquated GB.

It was interesting to note in Fig. 8 that the amount of liquid along one GB was much greater in alloy 6061 than in alloy 2024 or 7075, even though alloy 6061 was much less alloyed and thus can be expected to liquate less. It was not likely liquation alone could produce so much GB liquid in alloy 6061, especially when there was little liquation in the grain interior. Therefore, most of the GB liquid could have come from the weld pool.

As mentioned previously, coarse Mg2Si particles were reported to be present in alloy 6061 (Refs. 20, 22, 23), and Al-Mg2Si eutectic particles were reported to be present in the PMZ of such an alloy 6061 (Ref. 22). However, no coarse Mg2Si particles were observed in the 6061 base metal in Fig. 6, and no Al-Mg2Si eutectic particles were observed in the 6061 PMZ in Fig. 8C, either.

To resolve the discrepancy between the present study and previous studies regarding the presence of coarse Mg2Si particles in alloy 6061, additional welding experiments were conducted on similar 6061 plates from a supplier different from that of the alloy 6061 shown in Fig. 6. Figure 9A shows the SEM image of the base metal of a 6061-T651 plate from one such supplier. Unlike the alloy 6061 shown in Fig. 6, many dark particles were present in the base metal. One such particle was enlarged for closer examination. The sample was not etched at all in order not to dis-
solve the dark particles, which disappeared quickly even just briefly etched. Results of EDS analysis showed these particles had different compositions. Examples of the compositions in (at.-%) included Al-47Si-1Cu (the dark particle shown in the enlarged SEM image in Fig. 9A), Al-41Si-1Fe, Al-34Si, Al-49Si-20Mg-3Cu, Al-41Si-14Mg-5Cu-3Zn, Al-36Si-22Zn-1Mg, and Al-29Si-19Zn-1Cu. As such, these dark particles in the base metal were Si-rich particles with various concentrations of Mg, Cu, and Zn. These particles may have come from the eutectic particles formed during the terminal stage of casting. However, since alloy 6061 is within the solubility limit, the presence of the Si-rich particles in the base metal suggests the solution heat treatment was not thorough enough to dissolve these particles completely. Most of these particles looked similar to that shown in the enlarged SEM image in Fig. 9A. They did not look like composites but had some light Fe/Cu-rich particles embedded in them. Apparently, these dark, Si-rich particles were much more complicated in composition and had less Mg than the previously reported MgSi particles (Refs. 20, 22, 23). No composition analysis was shown to back up the claim of MgSi. As shown in Fig. 9A, there appeared to be some light angular Fe-rich particles scattered in the base metal as well.

In the PMZ these dark, Si-rich particles caused liquation by reacting with the surrounding Al matrix and formed eutectic particles, such as those shown in Figs. 9B and 9C. Results of EDS analysis showed that the dark areas in the eutectic were mostly Si-rich with various concentrations (in at.-%) of Mg, Cu, Zn, and Fe. For instance, Al-38Si-10Mg-3Cu (p1 in Fig. 9C), Al-20Si-8Zn-4Mg-5Cu, Al-12Si-4Mg-4Fe-5Cu, Al-29Mg-16Si-7Zn-2Cu (p2 in Fig. 9C), and Al-18Zn-16Si-3Cu. The light spots in the eutectic, on the other hand, were Fe-rich particles with Cu, Mg, Zn, and Si, for instance, Al-18Fe-12Cu-6Zn-3Si (p3 in Fig. 9C), and Al-15Fe-9Cu-8Mg-4Si-3Zn. Apparently these eutectic particles had more complicated compositions than the Al-Mg-Si eutectic composition previously reported (Ref. 22). No EDS results were shown to substantiate the claim of the Al-Mg-Si eutectic composition.

Figure 10 shows an optical micrograph of the PMZ in this 6061 plate. A portion of the PMZ was enlarged for clarity. As shown, a light etching α phase surrounds the dark etching eutectic particle. The dark etching eutectic particles are the eutectic particles shown previously in Fig. 9B, though the light etching α phase was not light under SEM. This is clear evidence of liquation caused by dark particles in the base metal shown in Fig. 9A. In the PMZ of alloy 2219, a light etching α phase surrounds the dark etching eutectic particle of Al-CuAl2 as a result of liquation caused by coarse CuAl2 particles (Ref. 13–15). The α phase is light in optical micrographs, but not the SEM images.

According to the compositions of the dark, Si-rich particles in the matrix, they can cause liquation by the following and other eutectic reactions (Ref. 23):

\[
\alpha + \text{Si} \rightarrow L \text{ at } 577^\circ \text{C} \tag{4}
\]

\[
\alpha + \text{MgSi} + \text{Si} \rightarrow L \text{ at } 555^\circ \text{C} \tag{5}
\]

Grain Boundary Segregation

Figure 11 provides a mechanism for the GB segregation that develops during solidification of the GB liquid in the PMZ. Allowing Cα to be the concentration of a given alloying element in the base metal, theoretically, the concentration of the GB eutectic, Cg, is the composition of the eutectic if the GB eutectic is normal, and of AlBg if the GB eutectic is divorced. In practice, the value of Cg can be affected by the GB thickness if it is not significantly greater than the interaction volume of electrons in the EDS analysis. In the absence of solute back diffusion into the solidified material, the concentration of the element at the starting edge of the α band should be kCα, where k is the equilibrium partition ratio of the element. The dash line shows the resultant GB segregation of the element. However, if back diffusion is significant, the concentration of the element at the starting edge of the α band will be greater than kCα, as the solid line indicates.

In the case of alloy 2219 (Al-6.3 wt-% Cu with k = 0.17), back diffusion was evident. The Cu concentration at the starting edge of the α strip was essentially 3 wt-%, which was significantly higher than the 1.07 wt-% Cu based on kCα (Ref. 14). For the aluminum alloys studied here, back diffusion of alloying elements is expected to be significant. However, this cannot be verified because k is not readily available in multicomponent alloys.

The SEM micrograph in Fig. 12A shows an α band in the PMZ of alloy 2024 and path XY along which solute segregation (in wt-%) across the α band was measured. As shown in Fig. 12 B through D, Cu, Si, and Mg segregated to the GB and the α band became depleted in these elements. For reference, the workpiece composition taken from Table 1 was superimposed on the segregation curve from –2 to 0 µm. As compared to the GB at g1 in Fig. 8A, this GB had much more Cu and a different microstructure. It should be pointed out that in the PMZ, the GB composition can vary from GB to GB or even within one GB. It can be affected by a large particle nearby (such a Cu-rich particle) if the particle liquates and joins the local GB liquid.

Figure 13 shows GB segregation in the PMZ of alloy 7075. As shown, Zn, Cu, and Mg all segregated heavily to the GB, leaving the α band solute depleted. GB segregation in the PMZ of alloy 6061 in Fig. 6 is shown in Fig. 14. Segregation of Si and Mg to the GB was clear. Like all other liquated GBs in alloy 6061, this GB was connected to the fusion boundary. The location of the segregation measurement is 205 µm from the fusion boundary. It is interesting to note that along the same GB but at 568 µm away from the fusion boundary, the measured segregation shows Si rose from below 1 wt-% in the α band to 25 wt-% at the GB, and Mg rose from below 1 to 1.6 wt-%. As such, much more Si than Mg was present here, even though alloy 6061 had more Mg than Si (Table 1). Based on the diffusion distance d = 568 µm, a typical diffusion coefficient of D = 5 x 10^{-3} cm²/s in the liquid and the approximation of d² = Dt, the required time for Si to diffuse from the fusion boundary to this location was t = 65 s. This long diffusion time suggests the high Si content here is not likely to be caused by Si diffusion from the weld pool. Therefore, it appeared the Si-rich liquid from the weld pool backfilled the GB. The liquid was enriched in Si because of the 4043 filler metal (Al-5.2 wt-% Si).

Summary and Conclusions

In summary, since liquation can cause hot cracking and/or severe loss of strength and ductility and since most aluminum alloys are multicomponent, a fundamental study was conducted on the mechanisms by which liquation is initiated in the PMZ of wrought multicomponent aluminum alloys during welding. Three representative liquation-susceptible alloys 2024, 6061, and 7075 were studied. Three liquation mechanisms were identified. The compositions and morphologies of the particles in the base metal were examined in order to help identify the liquation-inducing particles and the corresponding liquation reactions. The compositions and morphologies of both the particles and grain boundary phases in the PMZ were also examined to help further understand the liquation mechanisms. Liquation-induced grain boundary segregation was determined.

Conclusions are as follows:

1) Three different liquation mechanisms have been identified, and they cover most, if not all, of the wrought multicomponent aluminum alloys. For alloys
beyond the solid solubility limit, liquation-inducing particles react with the α matrix and liquation can occur at any heating rate (Mechanism I). For alloys within the limit but with such particles, liquation requires high heating rates (Mechanism II). For alloys within the limit and without such particles, liquation occurs when the aluminum matrix starts to melt (Mechanism III).

2) For a given alloy and temper, for instance, alloy 6061-T651 and alloy 2024-T351, the liquation mechanism can vary from heat to heat, depending on the exact alloy composition and the heat treatment history.

3) Alloy 2024 contains CuAl2 and likely CuMgAl2 particles and is near the solid solubility limit. Therefore, the liquation mechanism depends on the composition of the heat welded. An alloy 2024 can liquate by Mechanism I if it is beyond the solid solubility limit and by Mechanism II if within the limit. In either case, liquation can occur by the following reactions:

\[ \alpha + \text{CuAl}_2 \rightarrow L \text{ at 548°C, and} \]
\[ \alpha + \text{CuMgAl}_2 \rightarrow L \text{ at 548°C.} \]

4) Alloy 7075 contains both CuMgAl2 particles and Fe-rich particles coated with CuFeAl2. It is well within the solid solubility limit and thus liquates by Mechanism I. Liquation can occur by the following reactions:

\[ \alpha + \text{CuMgAl}_2 \rightarrow L \text{ at 518°C,} \]
\[ \alpha + \text{CuFeAl}_2 \rightarrow L \text{ + (Cu,Fe)Al}_4 \text{ at 590°C.} \]

5) Alloy 6061 is also within the solid solubility limit. Depending on how thorough the solution heat treatment, it may or may not contain Si-rich particles. Liquation is initiated by Mechanism III when Fe-rich particles alone are present, and by Mechanism II when Si-rich particles are also present. Si-rich particles can cause liquation through, for example, the following reactions:

\[ \alpha + \text{Si} \rightarrow L \text{ at 577°C} \]
\[ \alpha + \text{MgSi} + \text{Si} \rightarrow L \text{ at 555°C.} \]

6) Ternary phase diagrams can be a useful approximation for determining the location of a multicomponent alloy with respect to the solid solubility limit, at least in the cases of alloys 2024, 6061, and 7075. The liquation-causing particles in alloy 6061, at least in the one studied here, are not Mg2Si particles as suggested in the literature but Si-rich particles with varying Mg, Cu, and Zn contents. The eutectic particles in the PMZ are not the Al-Mg2Si eutectic particles as suggested in the literature either, but eutectic particles consisting of Si-rich and Fe-rich phases.

8) Numerous bare Fe-rich particles are present in wrought aluminum alloys, but they do not appear to cause liquation.

9) GB segregation can be rather severe in the PMZ of multicomponent aluminum alloys. Severe GB segregation can dramatically degrade the PMZ mechanical properties, as demonstrated in binary alloy 2219.

Acknowledgments

The authors thank the National Science Foundation (Grant Numbers DMR-9803589 and -0098776) for financial support and Miller Electric Manufacturing Co., Appleton, Wis. for donating the welding equipment used in the present study.

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