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HYDROGEN EMBRITTLEMENT IN Al-Li-Cu-Mg ALLOYS (8090-T651)

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ABSTRACT

This paper describes the hydrogen embrittlement (HE) of an Al-Li alloy aged at 190°C and with different durations of ageing (10, 15, 20 and 30 hr). Two techniques were employed to measure HE: a) cathodic polarization in a molten salts bath with -3 V/Ag on tensile specimens; b) gaseous hydrogenation on disks. Hydrogen charging was achieved at 190°C. The results show that HE is important when the alloy is in the over-aged condition.

INTRODUCTION

Al-Li alloys have gathered strong interest especially in the aircraft industry. Compared to conventional high-strength aluminium alloys of the 2000 or 7000 series, it is known that Al-Li alloys offer a 10% increase in Young's modulus along with a 10% decrease in specific weight, thus making them rather competitive to new non-metallic materials like carbon fibre reinforced composites. Moreover, their mechanical properties are equivalent to those of conventional high-strength Al alloys.

In the binary Al-Li alloy system, the $\Gamma'$ (Al$_3$Li) particles which precipitate throughout the matrix are responsible for strengthening. In the Al-Li-Cu-Mg alloys apart from the $\Gamma'$, semi coherent, S' (Al$_2$CuMg) and T$_1$ (Al$_2$CuLi) phases precipitate during artificial ageing treatment. $\Gamma'$ is a metastable phase which forms as spherical particles which remain coherent with the matrix (1). During plastic deformation, these particles may be cut by moving dislocations such that further deformation along the same slip plane is favoured; slip becomes coplanar (2, 3) and leads to poor toughness and ductility. The slip coplanarity gives rise to stress concentrations at grain boundaries inducing intergranular failures (4). The growth rate of $\Gamma'$ depends...
on vacancy concentration which in turn is affected by high solution treatment temperature followed by cold water quenched (5). The strength enhancement during room temperature ageing appears to be due to the precipitation of $\delta'$ phase. Subsequent artificial ageing gives rise to a grain boundary P.F.Z. (Precipitation Free Zone) indicating that $\delta'$ precipitation is dependent upon the presence of excess vacancies (5). The P.F.Z. grows according to $t^{1/3}$ law, where $t$ is the ageing time at a given ageing temperature (6). Attempts to improve toughness of Al-Li alloys have been based on the change in grain structure to influence the fracture process. Addition of manganese is known as a grain-refiner but as an improvement to gross intergranular failure (7). Zirconium addition of less than 0.2% forms $\beta'$ ($\text{Al}_3\text{Zr}$) precipitation which gives rise to grain-refinement, inhibition of recrystallisation and decreasing sheared $\delta'$ particles by the moving dislocations (8). However, zirconium gives highly textured structures (5) in Al-Li alloys.

The Cu and Mg precipitate heterogeneously during artificial ageing as $S'$ ($\text{Al}_2\text{CuMg}$) and $T_1$ ($\text{Al}_2\text{CuLi}$). The nucleation sites of these precipitates are dislocations formed during quenching, dislocations introduced during stretching and low-angle subgrain boundaries. Grain boundary precipitation of $\delta$($\text{AlLi}$) and complex Al-Cu-Mg phases occur during artificial ageing (9). A stretch before artificial ageing increases the rate of ageing and then increases the yield strength and the ultimate tensile strength but reduces the elongation to fracture. For each chemical composition of Al-Li alloy, there is a specific ageing heat treatment condition (peak aged condition) at which the mechanical properties are optimum. In the under-aged condition, the deformation is localized within slip bands while at the peak condition the deformation is homogeneous and due to the increased volume fraction of $S'$ throughout the matrix. In the overaged condition, the precipitation of $'S'$ is at once within the matrix and in the sub-grain boundaries (9).

On the other hand, conventional high-strength aluminium alloys such as Al-Zn-Mg, Al-Zn-Mg-Cu and Al-Mg suffer a reversible hydrogen embrittlement whereas Al-Cu and al-Cu-Mg appear to be resistant to hydrogen introduced either by cathodic charging or by exposure to water containing environments (10).

To the best of our knowledge, Al-Li-Mg-Cu-Zr (8090 alloy) has not been studied so far. In this paper, hydrogen embrittlement of 8090 - T651 was then investigated.
The chemical composition and the thickness t of the alloys studied in this investigation are given in Table I.

Table I: Chemical composition and thickness of the alloys studied (wt%).

<table>
<thead>
<tr>
<th>Li</th>
<th>Mg</th>
<th>Cu</th>
<th>Zr</th>
<th>Si</th>
<th>Ti</th>
<th>Fe</th>
<th>Na, ppm</th>
<th>t, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>1.1</td>
<td>1.3</td>
<td>0.09</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>2.9</td>
<td>1.1</td>
<td>1.3</td>
<td>0.09</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The experimental material was supplied by CEGEDUR PECHINEY in the form of 0.8 and 1.6 mm rolled plate in the solution treated (535°C during 1 hr and then cold water quenched) and 3% stretched, condition T-351. Hydrogen charging was achieved by two methods:

1) Cathodically on tensile specimens having 1.6 mm thickness in a molten salts bath (11) at 190°C during 10, 15, 20 and 30 hr and at different cathodic potentials: -1.5, -2.0, -2.5 and -3.0 V/Ag. After hydrogenation, outgasing was achieved, and $Q_H$ was measured at 520°C and 1000°C. Uncharged and hydrogen cathodically charged specimens were tensile tested at room temperature, using a strain rate of $2.7 \times 10^{-4}$ s$^{-1}$ to study the effect of hydrogen charging on tensile properties. Reference specimens were those aged at 190°C in furnace during 10, 15, 20 and 30 hr.

2) Gaseous hydrogen on disks having 0.8 mm thickness. The details of this method were described elsewhere (12). The reference gas was helium. The following procedures were achieved:

a) increasing the rate of hydrogen pressure $\Delta P/\Delta t$ from 0.007 to 188 MPa/min (external hydrogen). The alloy was in T651 condition;
b) thermal hydrogen or helium charging on both sides at 190°C, during 20 hr. Gas pressure was 400 Pa (internal hydrogen);
c) cathodically hydrogen charging at 190°C during 20 hr and with $-3$ V/Ag (internal hydrogen).

In the two last conditions either helium (b) or/and hydrogen gas (c) were used to achieve failure.

All the failures were carried out at 20°C. Fracture surfaces were examined using a scanning electron microscope.
EXPERIMENTAL RESULTS

1) Cathodically hydrogen charging

Figure 1 shows that the outgased QH is an increasing function as the applied cathodic potential level and the time of hydrogen charging are increased whatever the outgasing temperature is 520°C or is 1000°C. However, QH measured at 1000°C is higher than that obtained at 520°C showing that molecular hydrogen trapping occurs and increases with the severity of hydrogen charging condition. QH prior to hydrogen charging is measured at 520°C to be about 5 ppm for \( t = 1.6 \) mm and about 10 ppm for \( t = 0.8 \) mm, and is due to quenching the alloy from 535°C in cold water.

Figure 2 shows the variation of the yield strength Re as a function of hydrogen charging time in the molten salts bath at free potential and at -3V/Ag, and as a function of ageing time when the ageing treatment is achieved in the furnace with or without vacuum. The yield strength is independent on the ageing time and on the cathodic potential level and exceeds those due to ageing heat treatment in furnace during various times; their Re achieves a maximum for 15 hr ageing.

Maximum tensile strength Rm variation as a function of ageing time is very sensitive to the ageing heat treatment condition, figure 3. However, Rm values measured in the molten salts bath are higher than that obtained when using the furnace to achieve the ageing heat treatment. Independently of the heat treatment condition, the maximum stress Rm is also maximum for 15 hr ageing.

Ductility loss \( F \% \) due to hydrogen charging is about 20% for ageing time varying from 10 to 20 hr, figure 4. \( F \% \) drastically increases up to 75% for a 30 hr ageing time.

2) Gaseous hydrogen charging

For all test conditions, the disks central part (under pressure) breaks into numerous little pieces, figure 5, indicating the material brittle condition. we have to remember that the retained QH prior gaseous hydrogen charging was measured to be about 10 ppm. Partly for this reason and certainly due to the effectiveness of surface oxides, no significant embrittling effect of hydrogen could be evidenced, figure 6.
DISCUSSION

The results show that we have introduced high concentrations of hydrogen in A1-Li alloy by using the molten salts bath technique at the optimum ageing temperature. To the best of our knowledge, no attempt has been done to measure the hydrogen diffusion coefficient $D_H$ in A1-Li alloys at 190°C. However, NAKASHIMA and coll. (13) have measured $D_H$ in binary A1-Li system as a function of Li percentage and of temperature. Their results show great scattering and $D_H$ is estimated as about $10^{-9}$ cm$^2$.s$^{-1}$ in the temperature range 180 to 480°C, independently of Li%. In our conditions, hydrogen may diffuse at a distance $d$ from the surface of the metal equal to about 85 to 150 μm for charging time varying from 10 to 30 hr respectively and according to the relation: $d \approx \sqrt{2D_Ht}$. That is to say hydrogen may diffuse up to or behind lithium depletion zone (14) (≈100 μm), which is far beyond the oxide thickness (≈2 μm) (14).

As mentionned above, $S'$ phase is initiated on dislocations sites. Knowing that internal hydrogen promotes dislocations density (15, 16), the probability of $S'$ formation is then more important in the presence of hydrogen than without hydrogen. Tensile stresses are increased when the A1-Li alloy is cathodically hydrogen charged. This increase does depend on hydrogen concentration, namely the polarisation time at 190°C. Table II gives the percentage increase in tensile properties due to hydrogen charging for two durations 15 and 30 hr. The reference alloy is taken as that heat treated in furnace under vacuum.

Table II: Relative variation in the mechanical properties due to time of hydrogen charging (ageing time) at -3.0 V/Ag.

<table>
<thead>
<tr>
<th>$t$, hr</th>
<th>$\Delta Re%$</th>
<th>$\Delta Rm%$</th>
<th>$F%^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>6</td>
<td>5</td>
<td>23</td>
</tr>
<tr>
<td>30</td>
<td>115</td>
<td>19</td>
<td>75</td>
</tr>
</tbody>
</table>

$F\% = [\frac{(\varepsilon_{max,air} - \varepsilon_{max,hydrogen})}{\varepsilon_{max,air}}] \times 100$

The effect of internal hydrogen on the mechanical properties is very important when the alloy is in an overaged condition (190°C, 30 hr). Without internal hydrogen and ageing heat treatment, the failure surfaces show ductile rupture with flat surfaces containing slip lines, figure 7a. Figure 7b shows that when the alloy is aged heat treatment at 190°C during 30 hr in the
furnace under vacuum, a mixed rupture type occurs. Deep cracks in the sub-grain boundaries and many tearings throughout the matrix are observed. This result points out that coarsed $\delta'$ particles (8) and $S'$ phase within the matrix (9) and also, $S'$ ($A_{12}CuMg$) (9), $T_2$ ($A_{12}CuLi$) (17) and $A_{16}(Fe, Cu)$ (18) particles may be present in the sub-grain boundaries. With internal hydrogen and at 500 $\mu$m from the surface, the rupture type changes from intergranular (10 hr) to mixed (inter + transcristalline) (15 and 20 hr) and finally becomes intergranular (30 hr), figure 8. However, at 100 $\mu$m from the surface, the failure has an intergranular feature, independently of time of ageing. The last results prove that hydrogen has diffused and embrittled the metal at a distance equal to or greater than 100 $\mu$m from the metallic surface. The surface oxides is then overcome during cathodic charging in molten salts bath. This is not the case while gaseous hydrogen charging. However the restricted number of disks left available did not allow the necessary investigation of the pressure increase rate influence. Therefore, the scarce tests on disks hydrogen charged by this technique are inconclusive but ought to be resumed more consistently, especially with thicker disks.

CONCLUSION

In this work we have investigated the hydrogen embrittlement of an Al-Li alloy (8090). The results obtained lead to the following conclusions:

1) Using the molten salts bath technique and cathodically hydrogen charged the 8090 - T351 alloy at the peak temperature (190°C). The outgased quantity of hydrogen is an increasing function as the time of charging (ageing time) and cathodic potential level increase. Molecular hydrogen trapping is pointed out.

2) Hydrogen may promote dislocations density which are the initiation sites of $S'$ phase. Tensile stresses and ductility loss are then increased. The effect of hydrogen is important when the alloy is in the overaged condition.

3) Hydrogen promotes also intergranular failure, especially in the overaged condition. Precipitation of $S'$, $T_2$ and $A_{16}(Fe, Cu)$ particles in the sub-grain boundaries may interact with hydrogen atoms and the embrittlement is favoured.

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(18) N.J. OWEN, D.J. FIELD, E.P. BUTLER - Ibid. 4, p. 1217.
Figure 1: Variation of $Q_d$ desorbed at $520^\circ C$ and $1000^\circ C$ as a function of cathodic potential level and of hydrogen charging (ageing time); hydrogen charging temperature = $190^\circ C$.

Figure 2: Variation of yield strength as a function of either the hydrogen charging time (with and without cathodic polarization) or ageing time; peak temperature = $190^\circ C$.

Figure 3: Variation of maximum true stress as a function of either the hydrogen charging time (with and without cathodic polarization) or ageing time; peak temperature = $190^\circ C$.

Figure 4: Variation of maximum strain as a function of either the hydrogen charging time (with and without cathodic polarization) or ageing time; peak temperature = $190^\circ C$. 
Figure 5: View of a disk failure by increasing hydrogen gas pressure at 0.1 MPa.min⁻¹.

Figure 6: Disk failure pressure of hydrogen or helium gas versus the rate of increasing of the gas and of prior internal hydrogen charging: 1st series corresponds to natural ageing until 1985, 2nd series corresponds to natural ageing until 1986.

Figure 7a: Surface failure by tensile test at room temperature of 8090-T351 alloy.

Figure 7b: Surface failure by tensile test at room temperature of 8090 alloy aged at 190°C during 30 hr.
Figure 8: Variation of the type of rupture in 8090 alloy cathodically hydrogenated (-3V/Ag) as a function of time of hydrogenation and the depth from the specimen surface; peak temperature = 190°C.