Stress Corrosion Cracking Behaviour of Excimer Laser Treated Aluminium Alloy 6013

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The effect of excimer laser surface melting on the stress corrosion cracking behaviour of aluminium alloy 6013 has been investigated by means of a slow strain rate test at the open circuit potential, and at a constant anodic potential. After the laser treatment, a relatively thin non-dendritic re-solidified layer, of the order of a few micrometres, and largely free of coarse constituent particles, has been produced. At the top surface of the re-solidified layer, an oxide-nitride bearing film, having a thickness of a couple of hundred nanometres, is present. The results of the slow strain rate test in a 3.5% NaCl solution showed that, in terms of total displacement to failure and corrosion current density, the stress corrosion resistance of the alloy was greatly increased by excimer laser melting. The superior stress corrosion resistance of the laser-treated material is attributed to the laser-formed oxide-nitride top film acting as a barrier and retarding the initiation of cracks.

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1. Introduction

High strength aluminium alloys (HSAL) are widely used in aircraft and other heavy stress-bearing engineering structures due to their high specific mechanical properties. However, these alloys are susceptible to stress-related corrosion, such as stress corrosion cracking (SCC), particularly in the presence of chloride-containing media. This is primarily caused by the grain boundary structure and chemistry. Moreover, these alloys usually contain significant amounts of constituent particles, which could act as corrosion sites allowing pits to develop. Thus, in service, the combined effect of corrosion and loading on a high strength aluminium alloy structure can dramatically decrease its service life. Regarding the problem of SCC, the application of HSAL has long been limited by the susceptibility to serious SCC when used in their peak-aged condition and especially when stressed in the short-transverse direction. It has been reported that the threshold stress below which SCC would not occur could be as low as one-tenth of the yield strength of the alloys. Such a low stress threshold for SCC to occur has limited the application of these alloys in some harsh corrosive environments.

Currently, the corrosion of HSAL is mainly prevented by the application of corrosion protective systems including inhibitors, anodizing, conversion coatings, primers and paint finishes. However, these remedial methods are not without penalties and have their own limitations. For example, as far as chromate coatings are concerned, current environmental legislation is moving towards the total exclusion of chromium (VI), and many attempts are being made to develop alternative non-toxic methods of corrosion protection. Moreover, although the overaging treatment, which was developed in late 1970’s, can improve the SCC resistance of some HSAL, this was associated with a strength penalty. Thus, based on the results of previous work, it is clear that not withstanding the excellent achievements that scientists and engineers have made in combating the problems of SCC in HSAL, further solutions must be continuously sought.

In the search for alternative methods to combat the various corrosion problems of HSAL, laser surface melting (LSM) has attracted growing interest in recent years. Laser surface modification is a versatile technique that can be used to modify the surface properties of a material without significantly affecting its bulk properties. Indeed, much attention has been given to the study of the effect of LSM on the electrochemical behaviour of aluminium alloys when tested under the condition of no external loads. However, knowledge on the ability of LSM for improving the resistance of HSAL to SCC is still limited. Recognising this lacking, this research concentrates on studying the benefits that LSM may provide in increasing the resistance of HSAL to SCC.

2. Experimental Details

Aluminium alloy 6013 is used in this investigation, and is a material widely used in aircraft fuselages. Al-alloy 6013 is a high-strength aluminium alloy developed by Alcoa to replace the traditional alloy 2024-T3. Although it is claimed that the alloy is virtually immune to exfoliation cracking, this alloy is susceptible to pitting and intergranular corrosion. The materials used in this investigation were supplied by Alcoa in the form of 40 mm thick plate and were produced by rolling to a cold finished surface. The chemical composition of 6013-T651 is given in Table 1. The T651 condition involved heat treatment at a solution temperature of 475°C for 1 hour, quenching in water, followed by a 2% stretch, and an aging treatment of 24 hours at 120°C. Prior to laser treatment and corrosion testing, all the specimens were finely ground in successive steps using silicon carbide abrasive papers of 240, 400, 800, 1200, and 2400 grit and

Table 1 Chemical composition (mass%) of aluminium alloy 6013.

<table>
<thead>
<tr>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Other</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6–1.0</td>
<td>0.5</td>
<td>0.6–1.1</td>
<td>0.2–0.8</td>
<td>0.8–1.2</td>
<td>0.1</td>
<td>0.25</td>
<td>0.1</td>
<td>0.15</td>
<td>balance</td>
</tr>
</tbody>
</table>
subsequently cleaned with distilled water and alcohol to standardize the condition of the surface.

Excimer laser surface treatment was conducted using a Lambda Physik LPX315i laser, which operates with a wavelength of 248 nm (laser active medium KrF), having a maximum pulse energy and a repetition rate of 800 mJ and 150 Hz, respectively. Laser surface treatment was performed under 99% pure N\textsubscript{2}, at a flow rate of 25 L/min. The laser pulse frequency and the table feed rate were fixed at 10 Hz and 2 mm s\textsuperscript{-1}, respectively, while the laser energy density was kept at 5.5 J/cm\textsuperscript{2}. A 70% laser track overlapping condition was used, and the laser energy was measured by an energy meter at a position below the final focussing lens. The employment of these parameters for laser treatment has taken into consideration some related previous work\textsuperscript{10,11})

A slow strain rate tensile (SSRT) test was employed in this study for investigating the SCC behaviour of the laser-treated materials. In fact this method has been widely accepted for studying the SCC behaviour of aluminium alloys\textsuperscript{12}) The SSRT test was performed in a 3.5 mass\% NaCl solution. A cross-head speed of 0.00001 mm s\textsuperscript{-1} was used in the test. In the test, a 20 mm length of the middle section of the specimen was exposed to the testing solution, while the rest of the specimen was coated with epoxy resin. To accelerate corrosion attack and promote pitting to occur, the test was conducted not only at the open circuit potential (OCP) but also at an anodic potential of +50 mV above OCP. The SCC resistance of the untreated and laser-treated specimens was evaluated based on the value of total displacement to failure.

3. Results and Discussion

3.1 Microstructure

After laser melting, a re-solidified layer about 8 \mu m thick was formed at the surface (Fig. 1). An examination of the re-solidified microstructure showed that no dendritic structures were observed, and solidification is considered to proceed under planar growth. In fact, it has been shown elsewhere that for the conditions of the present study, both the temperature gradient and the solidification velocity satisfy the criterion for planar growth\textsuperscript{13}) With the absence of dendritic structures in the re-solidified layer, the problem of composition gradient would be much reduced, and as such a relatively homogenised structure can be obtained. Forsyth\textsuperscript{14}) in a study of the initiation of intergranular cracking in high strength wrought aluminium alloy 7010, showed that when the alloy was corrosion tested in seawater, intergranular corrosion cracks were concentrated at interdendritic regions. This is likely to be due to the segregation of solute elements in interdendritic regions and the coring in dendrites. In the case of LSM, the formation of a re-solidified planar layer without dendrites would eliminate such inhomogeneities in the structure. As a result, the susceptibility of pitting corrosion and intergranular cracking in 6013 would be reduced.

An examination of the TEM specimen together with the analysis of the diffraction patterns showed that a couple of hundred nanometres thick Al\textsubscript{2}O\textsubscript{3}-AlN film formed at the outmost surface of the re-solidified layer (Fig. 2). The calculated Miller indices were (110) and (101) for the AlN phase, and (202), (018) and (300) for the \alpha-Al\textsubscript{2}O\textsubscript{3} phase. During LSM, due to the high photon energy of the KrF excimer laser, which has energy of 5 eV, nitrogen and oxygen gases in the environment could be excited, resulting in the formation of active O\textsuperscript{-2} and N\textsuperscript{-3} ions. Moreover, when the aluminium alloy was melted by excimer laser, a plasma plume was instantaneously formed just above the melting pool. Previous studies have shown that the excimer laser induced plasma plume could generate a high pressure in the GPa range at the specimen surface, which could enhance the adsorption of the ionised gases at the melt surface\textsuperscript{15}) During the following solidification process, the adsorbed ions reacted with Al atoms and consequently formed the corresponding oxide and nitride at the surface of the aluminium alloy.

3.2 Stress corrosion crack behaviour

Typical stress-displacement curves of the untreated and laser-treated specimens are presented in Fig. 3. The results show that for the untreated specimens, the elongation to failure was much reduced when they were tested in the 3.5% NaCl solution, especially for the condition when an anodic
The employment of the anodic potential was to accelerate the development of corrosion pits. For the laser-treated specimens, when comparing the result of the test in a 3.5% NaCl solution to that in air at open circuit potential, the reduction in elongation was only about 11% (Table 2). When tested under the anodic potential, the reduction in elongation to failure for the untreated and laser-treated specimens were 44% and 25%, respectively. The results thus confirmed that laser treatment in nitrogen gas can improve the resistance to SCC. In addition, the results show that after laser treatment, the tensile strength of the specimen tested in a 3.5% NaCl solution at 50 mV above OCP was not significantly reduced; this is different from the results of the untreated specimen, where a loss of over 40% in tensile strength was experienced.

In addition to the measurement of elongation, the corrosion current densities of the untreated and laser-treated specimens during SSRT were recorded, and the results are given in Fig. 4. The untreated specimen experienced a relatively high current density (about 5 mA) right from the very beginning till the end of the test (Fig. 4(a)). The current density experienced by the laser-treated specimen was kept at an extremely low value up to a displacement of 0.8 mm (see Fig. 4(b)), beyond which, though, the current increased till the end of the test, the ultimate value was still less than half that of the untreated specimen.

The fracture surfaces of the untreated and laser-treated specimens were examined by SEM, and typical examples are shown in Figs. 5 and 6 respectively. The fracture surface of the untreated specimen was dominated by intergranular cracking (Figs. 5(a), 5(b)); only at the central area was there evidence of transgranular cracking (Fig. 5(c)). On the contrary, the fracture of the laser-treated specimen was dominated by transgranular cracking (Fig. 6(a)), and a large portion of the fracture surface was covered by ductile dimples (Fig. 6(b)). An examination of the longitudinal surface of the fracture specimens shows that severe corrosion attacks had occurred in the untreated specimen, while much less damage was found in the laser-treated specimen, with some secondary cracks present (Fig. 7).

### 3.3 Corrosion resistance of the surface film

The improvement in SCC resistance is considered to be mainly a result of the formation of the aluminium oxide-nitride film at the surface. Previous studies\(^\text{16}\) have shown that...
Fig. 5 Fracture surface of an untreated specimen after the SSRT: (a) an overall view; (b) a large portion of the surface showing intergranular cracking [marked I]; (c) an enlargement of region [T] in (b) showing transgranular cracking near the central region.
one of the mechanisms of corrosion in Al-alloys involves the absorption of Cl\textsuperscript{−} in the oxide layer, the penetration of Cl\textsuperscript{−} through the oxide, and the localised dissolution of the interface between the aluminium alloy substrate and the surface oxide film. The corrosion behaviour of aluminium alloys is, therefore, very much governed by the nature and the integrity of the surface film, which often consists of oxides. For the untreated specimen, corrosion pits were often found to have developed at or around coarse second phase particles\textsuperscript{17}) indicating that the oxide film was probably disrupted at the location of these particles. However, after laser melting, the chemical heterogeneities at the surface of the specimen were largely removed which permits the formation of a more uniform and a continuous protective oxide film at the surface of the specimen. Moreover, for the laser-treated specimens, a compact oxide-nitride film of thickness of the order of 200 nm, some twenty times thicker than the naturally formed oxide film, was obtained at the surface. This would provide a strong corrosion protection to the alloy.

It is well known that oxide films on aluminium and aluminium alloys exhibit $n$-type semiconductive properties.\textsuperscript{18}) The corrosion property of passivated metals was often determined by the electrical parameters, such as flat band potential and donor/acceptor density of the passive film. In order to understand the extent of protection provided by the laser-formed surface films, the relationship between corrosion resistance and electrical properties should be established. The donor density of the film can be characterised by the Mott-Schottky measurements. Figure 8 shows the Mott-Schottky plots for the different surface films, \textit{i.e.} naturally formed oxide and N\textsubscript{2} treat formed oxide-nitride. The passive films on most metals and alloys exhibit semiconduction behaviour, which can be examined by the Mott–Schottky analysis. The Mott–Schottky equation is given by:

\begin{equation}
\frac{1}{C^2_{SC}} = \frac{2}{n_{EE}eN_d} \left( E - E_{fb} - \frac{kT}{e} \right) \tag{1}
\end{equation}

\begin{equation}
\frac{1}{C^2_{SC}} = \frac{2}{n_{EE}eN_a} \left( E - E_{fb} - \frac{kT}{e} \right) \tag{2}
\end{equation}

Fig. 6 Fracture surface of a laser-treated specimen: (a) an overall view; (b) an enlargement of the marked region in (a) showing ductile dimples.
where $C_{SC}$ is the space charge capacitance, $N_d$ is the donor density in the passive film, $N_a$ is the acceptor density in the passive film, $\varepsilon$ is the dielectric constant of the film (8.6 for $\text{Al}_2\text{O}_3$), $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-14} \text{ F cm}^{-1}$), $e$ the electron charge, $E$ the electrode potential, $k$ is the Boltzmann constant, $T$ the absolute temperature, $A$ the area and $E_{fb}$ the flat band potential. For a $p$-type semiconductor, $C_{SC}^{-2}$ versus $E$ should be linear with a negative slope that is inversely proportional to the acceptor density. On the other hand, an $n$-type semiconductor yields a positive slope, which is inversely proportional to the donor density. According to this principle and based on the measured results for the untreated and laser-treated materials (Fig. 8), it is clear that for both materials, the surface films formed exhibit the nature of $n$-type semiconductors. The donor density was calculated using eq. (1) based on the results of Fig. 8, for the untreated and laser-treated materials, and the results are presented in Table 3.

Among the many models that explain the pitting corrosion of metals with passive films, the point defect model developed by Macdonald\textsuperscript{19} is probably the most widely accepted one. It suggests that the donors are the defects in the passive film, and can be determined by the Mott-Schottky analysis.\textsuperscript{20} In aluminium alloys, such donors are oxygen vacancies. It is well known that corrosion reaction
of aluminium is controlled by the mass transfer of oxygen to the active bare metal. Thus, a high density of oxygen vacancies (i.e., donor density) will result in a high rate of migration of oxygen, and consequently a high rate corrosion reaction. In the present study, the untreated aluminium alloy 6013 would readily experience localized corrosion caused by the migrated oxygen as they were covered by the oxide film having a high donor density. However, for the excimer laser-treated specimens, the laser formed film was over 200 nm thick and contained a low level of donor density. Hence, the film was less defective and a slow mass transportation of oxygen could be expected. This explains the observed high SCC resistance of the laser-formed surface film on aluminium alloy 6013. The results of the Mott–Schottky analysis are also in agreement with the results of the corrosion current density measurements.

3.4 Resistance to the initiation of stress corrosion cracking

The development of cracks in aluminium alloys, under stress, in an aggressive environment, whether containing Cl ions or not, has often been found to nucleate and initiate at some pits on the surface of the material. Corrosion pits can not only act as stress concentration sites and increase the stress intensity factor at the bottom, but can also provide an appropriate environment where a concentration of ions and a change in pH value occurs. Connolly and Puiggali have shown that under SCC conditions, cracks were prone to nucleate at the bottom of corrosion pits of aluminium alloys. With aluminium alloy 6013, pitting readily occurred in solutions containing Cl−, which was most likely related to the active dissolution of the coarse intermetallics. It is expected that crack initiation would also be accelerated due to the formed pits. In the present study, the corrosion-resisting oxide-nitride top film acts as a barrier layer and retards the crack initiation.

For untreated specimens, pits would nucleate and initiate in the substrate material right after the breakdown of the natural oxide film at the surface, and this could lead to the development of SCC. As is evident in Fig. 4(a), the natural oxide film did not provide an enduring corrosion protection to the material underneath, and a rapid rise in current density to a high value was obtained soon after the test began. Perhaps what is more important is the development of intergranular cracks at the grain boundaries. The second phase particles at the grain boundaries, such as the Al-Cu-Si-Mg particles, could function as local cathodes and cause dissolution of the grain boundaries. For the laser-treated specimens, no apparent grain boundaries were observed in the TEM study of these specimens, and the laser-melted layer was largely free from second phase particles. Such a modification in structure would help to deter intergranular stress corrosion cracks from developing. This is evident by a comparison of the fracture surfaces of the SSRT specimens (Fig. 5(a) and Fig. 6(a)), where the degree of intergranular corrosion attack found close to the circumference surface of the laser-treated specimen was much less than in the untreated specimen.

Obviously, the life endurance of a laser-formed oxide-nitride film will depend on how well it remains intact when the specimen is tested at a slow strain rate condition. Previous work has shown that the passive film of chromate treated aluminium alloys would break right after the yielding of the materials. In the case of the laser-formed surface film, the film is thicker than those of the naturally formed passive films. If the relatively thick laser-formed film can not accommodate any strain, it will rapture, even within the elastic region. Should this happen, corrosion attacks will start soon after the test begins, and this will be reflected by an upsurge in corrosion current. A measurement of the corrosion density of the laser N2-treated specimen, under the condition of SSRT, shows that, practically, the current remained constantly low until the displacement reached 0.6 mm (Fig. 9). At this point, according to the stress-displacement curve (Fig. 3(b)), the laser-formed oxide-nitride films had survived up to the point of yielding. After the film was damaged, corrosion will set in rapidly. This is reflected by an abrupt increase of current density at a displacement of 0.6 mm (Fig. 9), but the current measured between the displacements of 0.6 mm and 0.8 mm was still relatively low when considering the entire test period (Fig. 4(b)). Within this range, a period of transient current was observed, and this is considered to be due to the development of metastable pits at the surface of the re-formed layer. Such a current transient has also been suggested to be a characteristic feature of the formation of the metastable pits in Trueman’s study. Once corrosion has penetrated the re-melted layer, it is anticipated that intergranular cracks would develop.

4. Conclusions

Under the conditions of this study, laser treatment using a KrF excimer laser produced a non-dendritic planar growth modified surface. This consisted of a distinct laser-melted...
layer with a thickness of the order of a few micrometers, within which the coarse constituent particles and grain boundaries that were present in the untreated material were largely eliminated. As a result, a more homogeneous microstructure was obtained. In addition, the results of the TEM study showed that a compact layer of a couple hundred nanometers thick, composed of Al₂O₃-AlN, had formed at the outmost surface. The resistance to SCC of the alloy increased significantly after laser treatment. The laser-formed oxide-nitride top film acted as a barrier and retarded the initiation of the cracks. Comparing the result of the test in a 3.5% NaCl solution to that in air, the reduction in elongation of the laser-treated specimens was found to be much less than that of the untreated specimens. Moreover, due to the relatively small thickness of the laser-modified layer, the tensile strength of the alloy was not affected.

The effect of the outer surface oxide and nitride bearing film, per se, on pitting corrosion resistance was evaluated. The results of the Mott–Schottky analysis suggest that the top surface film, which exhibited an n-type semiconductor nature, is responsible for the significant improvement of the SCC resistance of the laser-treated material. The improvement in SCC resistance is considered to be mainly a result of an increase in the resistance to the initiation of stress corrosion cracks.

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