Microstructural characterisation and corrosion studies of excimer laser-treated aluminium alloy AA2024-T351

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Abstract

Laser surface melting (LSM) of aluminium alloys with high power continuous wave (CW) CO\textsubscript{2} and Nd:YAG lasers has been shown to produce dendritic/cellular microstructures with refined second-phase particles distributed along the dendritic boundaries. Although refinement of the microstructure and extension of the solute solubility in the matrix can be achieved, the refined second-phase particles still act as preferential sites to initiate localized corrosion. In contrast to a CW laser, an excimer laser with a UV wavelength and pulses width in the range of nanoseconds, resulting in extremely high cooling rate up to $10^{11}$ K/s, is expected to generate a further refining of the near-surface microstructure and hence, improved corrosion performance.

In this project, a Lumonics IPEX 848 KrF excimer laser, with a wavelength of 248 nm and pulse width of 13 ns, has been used for surface melting of an AA2024-T351 alloy. The aim is to investigate the microstructure and the resultant corrosion behaviour of the laser treated surface, and its contribution to alloy performance. The laser fluence was fixed at 7 J/cm\textsuperscript{2} and the number of pulses per unit area was varied as 10, 25 and 50 pulses respectively. Microstructural characterisation and compositional analysis have been performed by SEM/EDX, TEM/EDX and XRD to disclose solidification phenomena and phase transformations. The results show that the melted layers, with a melt depth from 3 to 7 µm, have been achieved, that is far more chemically uniform than the bulk alloy. In particular, the relatively fine precipitates and dispersoids in the matrix have been dissolved, while large constituent intermetallic particles at the melted layer/matrix interface have been partially melted. In addition, solute-rich bands, containing particularly copper, were formed within the melted layers, especially at the melted layer/matrix interface. SKPFM also reveals that the laser-melted layers exhibit a uniform surface potential distribution.

The corrosion performance of AA2024-T351 alloy before and after LSM has been evaluated by anodic polarisation in deaerated and aerated 0.1 M NaCl solution, and
immersion tests in 0.1 NaCl solutions. Exfoliation corrosion immersion test ASTM G34-01 (EXCO test) was also carried out to evaluate the intergranular corrosion (IGC)/exfoliation resistance of the alloy. The results show that the untreated alloy exhibits severe pitting corrosion and IGC. After LSM, significant improvement of corrosion resistance has been achieved. However, delamination of the laser melted layer from the matrix was evident after an EXCO test for 6 hours. The absence of significant corrosion product may suggest a stress-related mechanism.

In order to investigate the effect of LSM on anodising of AA2024-T351 alloy and its influence on the corrosion resistance, excimer LSM has been applied as a pre-treatment method prior to anodising in 0.46 M H₂SO₄ solution. The results show that LSM significantly improved the corrosion performance following anodising compared with the alloy anodised without LSM and LSM alone.
Declaration

I hereby declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or any other institution of learning.

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Above all I am grateful and thankful to Allah, the creator of this universe.
### Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Absorptivity</td>
</tr>
<tr>
<td>A/cm²</td>
<td>Amper per centimetre square</td>
</tr>
<tr>
<td>a</td>
<td>Positive constant</td>
</tr>
<tr>
<td>at. %</td>
<td>Atomic weight percent</td>
</tr>
<tr>
<td>AEM</td>
<td>Analytical Electron Microscope</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-Scattered Electrons</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>C₀</td>
<td>Composition of alloy</td>
</tr>
<tr>
<td>C_L</td>
<td>Liquid concentration</td>
</tr>
<tr>
<td>C_p</td>
<td>Specific heat [J/kg K]</td>
</tr>
<tr>
<td>C_x</td>
<td>bulk solute concentration</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>d_A</td>
<td>Spacing between the planes in the atomic lattice</td>
</tr>
<tr>
<td>D_L</td>
<td>Liquid diffusion constant</td>
</tr>
<tr>
<td>e</td>
<td>Electron</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>E°</td>
<td>Standard potential</td>
</tr>
<tr>
<td>E_BSD</td>
<td>Electron Back Scattered Diffraction</td>
</tr>
<tr>
<td>E_corr</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>E_pit</td>
<td>Pitting potential</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>EXCO</td>
<td>Exfoliation corrosion</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>FEG-SEM</td>
<td>Field Emission Gun-Scanning Electron Microscope</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>G</td>
<td>Thermal gradient</td>
</tr>
<tr>
<td>$G_L$</td>
<td>Temperature gradient at the interface of the liquid</td>
</tr>
<tr>
<td>$G_S$</td>
<td>Temperature gradient at the interface of the solid</td>
</tr>
<tr>
<td>$\Delta G^\circ$</td>
<td>Standard Gibbs free energy change in reaction</td>
</tr>
<tr>
<td>g/cm$^2$</td>
<td>Gram per centimetre square</td>
</tr>
<tr>
<td>GP</td>
<td>Guinier-Preston</td>
</tr>
<tr>
<td>GPB</td>
<td>Guinier-Preston – Bagaratsky</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field</td>
</tr>
<tr>
<td>HB</td>
<td>Hardness Brinell</td>
</tr>
<tr>
<td>HV</td>
<td>Vickers hardness</td>
</tr>
<tr>
<td>I</td>
<td>Intensity of the laser beam</td>
</tr>
<tr>
<td>$I_a$</td>
<td>Anodic current</td>
</tr>
<tr>
<td>$I_c$</td>
<td>Cathodic current</td>
</tr>
<tr>
<td>$i_{corr}$</td>
<td>Corrosion current density</td>
</tr>
<tr>
<td>IGC</td>
<td>Intergranular corrosion</td>
</tr>
<tr>
<td>IMP</td>
<td>Intermetallic particle</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>$k$</td>
<td>Equilibrium partition</td>
</tr>
<tr>
<td>$k_a$</td>
<td>Attenuation index</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Equilibrium distribution coefficient</td>
</tr>
</tbody>
</table>
Abbreviations and Acronyms

\( k_d \) Medium refractive index
\( K_t \) Thermal conductivity
\( K_{L} \) Thermal conductivity for liquid
\( K_s \) Thermal conductivity for solid
kg Kilogram
kV Kilovolt
K/s Kelvin per second
l_d Diffusion distance
LSA Laser Surface Alloying
LSC Laser Surface Cladding
M Mole
\( m_L \) Slope of liquids vs concentration line
M^{n+} Metal cation
min Minutes
mm Millimetre
MPa Mega Pascal
\( \mu m \) Micro-meter
mV Milli volt
mm/s Millimetre per second
n Integer
Nd-YAG Neodymium yttrium-aluminium garnet laser
nm Nano-metre
OCP Open Circuit Potential
OM Optical Microscopy
\( P \) Peclet number
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Potential of Hydrogen</td>
<td></td>
</tr>
<tr>
<td>rb</td>
<td>Radius of laser beam</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Reflectivity</td>
<td></td>
</tr>
<tr>
<td>Sa</td>
<td>Mean height</td>
<td></td>
</tr>
<tr>
<td>Sq</td>
<td>Root mean square length surface</td>
<td></td>
</tr>
<tr>
<td>Sz</td>
<td>Maximum height of the scale surface</td>
<td></td>
</tr>
<tr>
<td>Sdr</td>
<td>Area increased percentage compared with a flat surface.</td>
<td></td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
<td></td>
</tr>
<tr>
<td>SCE</td>
<td>Calomel Saturated Electrod</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>SKPFM</td>
<td>Scanning Kelvin Probe Force Microscopy</td>
<td></td>
</tr>
<tr>
<td>SSS</td>
<td>Supersaturated Solid Solution</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>Temperature of liquid</td>
<td></td>
</tr>
<tr>
<td>T-351</td>
<td>Aluminium temper grade: Solution treated, stress relieved, stretched, cold worked and naturally aged</td>
<td></td>
</tr>
<tr>
<td>ΔT</td>
<td>Cooling rate</td>
<td></td>
</tr>
<tr>
<td>ΔT₀</td>
<td>Equilibrium freezing range</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
<td></td>
</tr>
<tr>
<td>Ts</td>
<td>Solidus temperature</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>Under cooling rate</td>
<td></td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
<td></td>
</tr>
<tr>
<td>v</td>
<td>Traverse velocity</td>
<td></td>
</tr>
<tr>
<td>v₀</td>
<td>Frequency</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Growth rate</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
<td></td>
</tr>
<tr>
<td>Va</td>
<td>Velocity at absolute stability</td>
<td></td>
</tr>
</tbody>
</table>
### Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_c$</td>
<td>Critical growth</td>
</tr>
<tr>
<td>$V_{Tmax}$</td>
<td>Growth rate of absolute stability</td>
</tr>
<tr>
<td>$x$</td>
<td>Distance</td>
</tr>
<tr>
<td>W</td>
<td>Watts</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_a$</td>
<td>Dendrite arm spacing</td>
</tr>
<tr>
<td>$\sigma_e$</td>
<td>Electric conductivity</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>Density of the material [kg/m$^3$]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>attenuation coefficient</td>
</tr>
<tr>
<td>$\alpha_t$</td>
<td>thermal diffusivity</td>
</tr>
<tr>
<td>$\alpha_{ss}$</td>
<td>Solid solution</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Gibbs-Thomson parameter</td>
</tr>
</tbody>
</table>
List of publications


Chapter 1

General Introduction

This chapter presents the research motivation and rationale, and defines the overall aim of the project along with objectives. The structure of the thesis is also provided.

1.1 Research motivation and rationale

AA2024-T351 aluminium alloy belongs to the 2xxx aluminium alloy series. Due to its high strength, damage tolerance and low density, it has been widely used in the aerospace and aircraft industry as a constructural material, such as fuselage, door skin, trailing edge panel and dorsal fin. However, the main alloying elements of AA2024-T351 alloy such as copper along with magnesium, iron, manganese and silicon, promote the formation of various intermetallic particles with dimensions up to tens of microns and population densities ranging from $3 \times 10^5$ to $1 \times 10^6$/cm$^2$.[1, 2]. Such intermetallic particles provide driving forces for microgalvanic activities, particularly when the alloy is exposed to an environment containing chloride[3]. Such microstructure and local chemistry normally results in increased susceptibility to localized corrosion of the alloy including pitting, intergranular and sever exfoliation corrosion damage.

In order to improve localised corrosion resistance of AA2024 alloy, its surface often requires protection against corrosion. This is usually accomplished by anodising, followed by application of organic coatings[4]. However, it is worth pointing out that the presence of intermetallic particles within aluminium matrix has been well-recognised causing a reduction in efficiency of the anodising process, modifying the film morphology and generating flaws in the anodic film[5], therefore, leading to degradation of the corrosion protection.

In addition to anodising, recently, laser surface melting (LSM) has been recognised as an approach that offers potential for improving the corrosion resistance of aluminium alloys by modifying microstructures. Characterized by its high cooling
rates, LSM uses a laser beam to melt a thin surface layer, with the underlying substrate acting as an effective heat sink to draw energy rapidly away from the surface. The rapid heating and cooling cycles can modify both the microstructure and chemical homogenisation by refinement, dissolution of precipitates and inclusions, as well as redistribution of the alloying elements in the melted layer, and thus affect surface related properties such as corrosion resistance.

It has been reported that AA2024-T3/T351 aluminium alloy treated with LSM using high power continuous wave (CW) CO₂ and CW or long pulses Nd:YAG lasers have shown to produce dendritic / cellular microstructures with refined second phase particles distributed along the dendritic boundaries [6-17]. Although refinement of the microstructure and extension of the solubility, particularly like copper, in the α-Al matrix can be achieved, the refined structure is still susceptible to localized corrosion, resulting in negligible improvement of corrosion resistance [6, 9, 16, 18-20].

In contrast to a CW laser, an excimer laser, with a UV wavelength and nanosecond pulses width for LSM is capable of producing much faster cooling rates, up to 10¹¹ K/s. As a result, it has been expected that a more uniform near-surface structure without precipitation of intermetallics could be achieved for aluminium alloys, thereby giving a significantly improved corrosion performance. On the other hand, since LSM removes intermetallic particles that cause thin film defects on the surface, it is also expected that LSM prior to anodising may provide significant benefits in terms of improved anodising behaviour and hence corrosion performance.

1.2 Aims and objectives

The aim of the project is to investigate the possibility of improving the localised corrosion resistance of AA2024-T351 alloy using a KrF excimer laser with a wavelength of 248 nm and pulses width of 15 ns. The specific objectives are as follows.

- Optimization of laser operating conditions with respect to both surface condition and microstructure characterisation of AA2024-T351 alloy.
1. Introduction

- Characterisation of the microstructure of AA2024-T351, before and after excimer laser surface melting, in terms of morphology, grain orientation, particle distribution and crystallographic directions, as well as potential distribution of various intermetallic particles with respect to aluminium matrix, using SEM/EDX, TEM/EDX, XRD and SKPFM.
- Evaluation of corrosion behaviours of AA2024-T351 alloy before and after excimer laser surface melting, using electrochemical tests and 24 hours immersion tests in 0.1 M NaCl solution as well as EXCO solution immersion test for 6 hours.
- Investigation of corrosion mechanisms involved in various tests for the alloy with and without excimer laser surface melting.
- Exploration of excimer laser surface melting as a pre-treatment method prior to anodising in sulphuric acid at fixed voltage of 12 V to enhance further improvement of the corrosion resistance compared with the anodised alloy without laser treatment.

1.3 Outline of the thesis

This thesis contains nine chapters.

Chapter 1: provides a general introduction on the motivation and rationales of the research, and defines the aims and objectives of the project.

Chapter 2: covers the fundamental aspects of corrosion, particularly pitting and intergranular corrosion involved in AA2024-T351 alloy. Previous work on corrosion mechanisms of this alloy has been reported.

Chapter 3: briefly introduces lasers and laser beam interaction with materials, and gives a brief introduction to laser surface engineering, with an emphasis on laser surface melting. It also presents a literature review on the previous work regarding laser surface melting of various aluminium alloys for improvement in corrosion resistance. The factors affecting the corrosion properties of laser-melted surfaces have been discussed in the consideration with types of lasers applied and the types of aluminium alloys treated.
Chapter 4: gives details of the experimental equipment and procedures used in this thesis, including materials, laser experimental setup, and preparation of the samples for laser treatment and for different characterisation techniques adopted in this work before and after laser treatment.

Chapter 5: presents the microstructural characterisation of the as-received AA2024-T351 alloy, in terms of phases, grain orientations, potential mapping of various intermetallics.

Chapter 6: presents the microstructural characterisation of the laser-melted AA2024-T351 alloy with different laser treatment conditions, in terms of intermetallics, grain orientations, potential mapping of the laser-melted layer.

Chapter 7: presents the results and discussion obtained from different corrosion techniques used to evaluate corrosion performance of AA2024-T351 alloy before and after laser treatment.

Chapter 8: presents the results and discussion obtained from anodised AA2024-T351 alloy with and without LSM as a pre-treatment, in terms of microstructures, and corrosion performance.

Chapter 9: provides general conclusions achieved from this work. Recommendations for future work are also suggested.
1.4 References


Chapter 2

Literature Review Part I

Aluminium Alloys and their Corrosion Properties

2.1 Introduction

Aluminium alloys are recognised to have their highly heterogeneous microstructures as a result of the additions of other elements and impurities, which produce a microstructure with desired mechanical properties, but also undesired comparatively large, constituent particles, which greatly affect the corrosion resistance of alloys such as those of the 2xxx series. The inhomogeneous distribution of copper in the microstructure of 2xxx series alloys is a major cause of the low resistance to different form of corrosion such as pitting, intergranular and stress corrosion cracking. In this Chapter a review of aluminium alloys in terms of microstructure and fundamental aspects of corrosion is presented.

2.2 Aluminium and aluminium alloys

In nature, aluminium exists as the mineral bauxite, rich in alumina. Because of its high reactivity with oxygen, aluminium requires a large amount of energy to be extracted from its ore. In 1885 aluminium was isolated as a pure element by Hans Christian Oersted and its commercial production started in 1886 [1]. Nowadays bauxite production has reached 200 million tonnes worldwide; where Australia and China are the largest producers. To produce one tonne of aluminium requires four tonnes of bauxite [2].

Aluminium is silver-white with an atomic number of 13, an atomic weight of 27 and a melting point 683°C. It is a soft, ductile, non-toxic and paramagnetic material, with a high electric and thermal conductivity and has an excellent resistance to corrosion.
Aluminium reacts with oxygen to produce coherent thin oxide aluminium (Al₂O₃) layer of 1-5 nm on its surface that protects the metal from further corrosion. It can be easily extruded to form bars and tubes and rolled to foils, sheets and plates and is suitable for low cost recycling processing [1, 3]. These properties make it irreplaceable for food and pharmaceutical packaging. Additionally, it can be cast, mainly by sand and/or die casting, and machined. It is widely used in both mechanical and electrical conducting applications in modern industry.

2.2.1 Effect of additional elements on aluminium properties

Pure aluminium has limited engineering applications due to its poor mechanical properties, e.g. the tensile strength of pure aluminium is less than 90 MN/m² [06, 07]. An addition of other elements to aluminium is required to enhance its mechanical properties. The desired mechanical and chemical properties depend on both the elemental composition and microstructure of an alloy. Elements are added in the liquid state and the liquid solution needs to be cooled down in order for a solid solution to be achieved. Therefore, the temperature at which the solution solidifies depends on the concentrations of the alloying elements in the solution.

In general, additions of these alloying elements make aluminium an essential and important material with a wide range of applications in today’s modern life. However, there is a maximum concentration of solute atoms that can be dissolved in the matrix of the aluminium to form a solid solution, this limit is usually called solubility limit. Only a small number of metal elements have sufficient solubility to act as a major alloying element, for example copper, magnesium, silicon and zinc [8]. Other elements, for example boron, chromium, manganese, titanium and zirconium are added in amounts of less than 1% because of their very low solubility, for instance to enhance alloy properties such as grain refinement [9].

2.2.1.1 Aluminium-copper alloys

Because of the low solid solubility of copper in aluminium solid solution, copper is added with less than 5 weight %. The addition of copper along with magnesium in 2xxx series alloys has a great effect on the strength and toughness of the alloy, but conversely decreases the alloy weldability and corrosion resistance [5, 6, 10]. Hence,
Aluminium-copper alloys are widely used in the aerospace industry, for example as pistons, rivets and fuselage skin in aircraft construction.

2.2.1.2 Aluminium -manganese alloys

Manganese (Mn) addition accelerates the response to precipitation hardening, providing a medium range of strength with an acceptable level of ductility through solid solution strengthening. The maximum solubility of manganese in $\alpha$ solution is 1.82 weight % at the eutectic temperature of 657.8°C [11]. A minor addition of Manganese to Al-Cu series alloys can modify the precipitation process, forming fine precipitates that restrict grain boundary movements resulting in greater age hardening and an increased cathodic polarization, providing higher corrosion resistance [12]. Al-Mn series alloys are not heat treatable and have high formability and weldability. These alloys are applied in construction; beverage cans industries, pressure vessels and gasoline and oil tanks [6,11,13].

2.2.1.3 Aluminium and silicon alloys

Addition of silicon to aluminium can significantly increase the formability of the material for forming complex shapes by forging. Silicon reduces the melting point of aluminium with an increase in fluidity making this group of alloys excellent for gap-filling during welding with other alloys [10].

2.2.1.4 Aluminium-magnesium alloys

Aluminium-magnesium alloys are widely used in construction, chemical storage tanks as well as in automotive and marine industries [6], because of their weldability and relatively high corrosion resistance. Magnesium intensifies precipitation, which considerably improves the alloy strength. The improvement in performance is highly dependent on the amount of added magnesium [11]. However, additions of magnesium as an alloying element are known to reduce solid solubility of copper in Al-Cu-Mg alloys [14,15].
2.2.1.5 Aluminium-zinc alloys

Addition of zinc provides both high strength and high toughness with average corrosion resistance. These alloys normally require coatings for corrosion protection, and their applications are mainly limited to aerospace [3].

2.2.1.6 Miscellaneous aluminium alloys

Elements that are used in small quantities in these alloys, such as chromium (Cr), titanium (Ti), boron (B) and zirconium (Zr), work as grain refiners, improving the corrosion resistance, particularly stress corrosion cracking in high strength alloys. Iron and nickel increase the strength of aluminium without affecting the electrical conductivity. Lithium increases both stiffness and strength properties. These aluminium alloys are characterized by high corrosion resistance at high temperature and pressure and deep drawing, making them suitable for applications in nuclear energy installations, bottle caps and soft bears [3, 6, 9, 10].

2.2.2 Alloying classification

Since additions of alloying elements have great effect on the performance of aluminium alloys, an international designation system was required. The American aluminium association developed a designation system for wrought and casting alloys [16]. A four-digit numerical system was adopted; XXXX for wrought and XXX.X for cast aluminium alloys, respectively, where the latter incorporate three digits followed by a decimal. The first digit indicates the aluminium alloy series, representing its main alloying element. For example, 2XXX is for the aluminium-copper alloy series where the main alloying element is copper. In the 3XXX series; manganese is the main alloying element. The second digit indicates the modification or level of impurities, if the second digit is zero it means an original alloy. The last two digits identify different aluminium alloys in a group of aluminium alloys [3, 4, 6, 16-18]. Table 2.1 summarises the aluminium alloy series, according to their microstructure precipitates, reactivity towards the aluminium matrix as well as the applications of these series.
### Table 2.1: Designation, precipitates and applications of wrought and cast aluminium alloys [18].

<table>
<thead>
<tr>
<th>Wrought alloys</th>
<th>Cast alloys</th>
<th>Descriptions</th>
<th>Typical precipitates and their reactivity</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1XXX</td>
<td>1XX.X</td>
<td>Aluminium of 99% minimum purity.</td>
<td>$\text{Al} - \text{Fe} \text{[Cathodic]}, \text{Al} - \text{Mn}_2 \text{[Cathodic]}, \alpha - (\text{Fe-Mn})\text{Si} \text{[Cathodic]}$</td>
<td>Electrical conductors, chemical process equipment foils, decorative finishes, food &amp; pharmaceutical, packaging.</td>
</tr>
<tr>
<td>2XXX</td>
<td>2XX.X</td>
<td>Aluminium-copper alloys</td>
<td>$\text{Al}_6\text{Cu} \text{[Cathodic]}, \text{Al}_6\text{Cu}_2\text{Mg} \text{[Anodic]}, \text{Al}(\text{Cu-Fe-Mn}) \text{[Cathodic]}, \text{Mg}_2\text{Si}$</td>
<td>Pistons, rivets, fuselage for aircraft constructions, fuel tanks</td>
</tr>
<tr>
<td>3XXX</td>
<td>3XX.X</td>
<td>Aluminium-manganese alloys. Silicon and copper and/or magnesium alloys.</td>
<td>$\text{Al}_6\text{Mn}[\text{Cathodic}], \text{Al}_6\text{Mn}[\text{anodic}], \text{Al}_6(\text{Fe-Mn})[\text{Cathodic}], \text{Al}_6(\text{Fe-Mn})[\text{Cathodic}]$</td>
<td>Foil, roofing sheets, manufacturing beverage cans</td>
</tr>
<tr>
<td>4XXX</td>
<td>4XX.X</td>
<td>Aluminium-silicon alloys</td>
<td>$\text{Si}[\text{Cathodic}], \alpha - \text{AlFeSi}$</td>
<td></td>
</tr>
<tr>
<td>5XXX</td>
<td>5XX.X</td>
<td>Aluminium-magnesium alloys</td>
<td>$\beta - \text{Al}_6\text{Mg}_2[\text{Anodic}], \text{Al}_6(\text{Fe-Mn})[\text{Cathodic}]$</td>
<td>Transportation structural plates, large tanks for petrol, milk, grain, pressure vessels, architectural components.</td>
</tr>
<tr>
<td>6XXX</td>
<td>unused</td>
<td>Aluminium-magnesium-silicon alloys</td>
<td>$\beta - \text{Mg}_2\text{Si}[\text{Anodic}], \text{Al}_6\text{Cu}_6\text{Mg}_3\text{Si}_3[\text{Cathodic}]$</td>
<td></td>
</tr>
<tr>
<td>7XXX</td>
<td>7XX.X</td>
<td>Aluminium-zinc - magnesium alloys. Aluminium and zinc alloys.</td>
<td>$\eta - \text{MgZn}_3[\text{Anodic}], \text{Al}_6\text{Cu}_6[\text{Cathodic}]$</td>
<td></td>
</tr>
<tr>
<td>8XXX</td>
<td>8XX.X</td>
<td>Miscellaneous alloys, e.g. Aluminium-lithium alloys. Aluminium-tin alloys.</td>
<td></td>
<td>Nuclear energy installation, Bottle caps and soft bearing</td>
</tr>
</tbody>
</table>

### 2.3 Metallurgy of aluminium alloys

Behind the required properties for high performance aluminium alloys, lie a microstructure that has undergone thermal, chemical and mechanical processing. Alloying elements are added with regard to their solubility in aluminium to form intermediate particles, responsible for strengthening of the alloys, such as in 2xxx and 7xxx series. The most efficient increase in strength is achieved, or age hardening, which can result in strength as high as 800 MPa [102].

#### 2.3.1 Phase diagram of Al-Cu alloys

During the fabrication process, the temperature of the alloy is varied and hence, the equilibrium conditions of a material are continually changed, resulting in phase transformations. These transformations determine the final phases and their distribution in the microstructure. The use of Al-Cu phase diagram in Figure 2.1 illustrates important information that can predict the final microstructure of Al-Cu alloys that underwent heat treatment.
2. Literature Review Part I

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Figure 2.1: Al-Cu phase diagram showing the presence of various phases with respect to temperature and solid solubility [19].

2.3.2. Heat treatment

Heat treatment refers to heating and cooling operations where desirable properties such as softening, hardening and a homogeneous microstructure can be achieved. Homogenization of an ingot is done at high temperatures around 550°C, where compositional variation and the presence of soluble eutectic phases are reduced. Fast cooling of the ingot leads to the formation of precipitation sites, producing precipitation hardening that is responsible for the strength of the alloys. When the billet is formed, it can be rolled to sheets or plates and forged or extruded to the required shapes. Wrought materials are categorized as heat-treatable and non-heat-treatable alloys. Alloys subject to heat treatments are called “heat-treatable” alloys such as Al-Cu-Mg and Al-Zn-Mg based alloys. When heat treatment is applied to AA2024 alloy, it alters the microstructure by the displacement of the precipitated particles [18, 20]. On the other hand, non-heat-treatable such as Al-Mg and Al-Mn based alloys are dependent on cold work hardening to increase the strength [4, 7]. Heat treatment is based on three process steps:

**Step 1 - Solution heat treatment**: alloying elements are dissolved at temperatures ranging from 450 to 548°C, as indicated by the phase diagram in Figure 2.1, between the solvus and solidus temperatures and soaked there until all of the solute dissolves into the α phase where a uniform solid-solution structure is formed [21]. By dissolving, a maximum amount of
soluble precipitate hardening elements, such as copper, magnesium, manganese either a substitutional or an interstitial (a nearly homogeneous) solid solution is achieved.

**Step 2 – Quenching:** to keep or preserve the maximum amounts of dissolved soluble precipitate hardening elements in solid solution quenching is applied. It is a rapid cooling process, without interruption, to room temperature. During quenching, the solutes are not immediately able to diffuse out of the phase. As a result a supersaturated solution solid solution (SSSS) is formed [6, 22].

**Step 3 – Ageing:** because of quenching the SSSS is in a non-equilibrium state. As time elapses (ageing), it starts to decompose, forming finely dispersed precipitates. Ageing at room temperature is called natural ageing, with the duration ranging from a few days to many years, depending on the alloy compositions. Ageing at elevated temperatures (from 100 to 200°C) is called artificial ageing [6, 20, 23]. Figure 2.2 demonstrates the 3 stages of age or precipitation hardening, with related microstructures.

Figure 2.2: The left part of the Al-Cu phase diagram illustrates the three steps of solution-heat-treatment, quenching and ageing. On the right, sketches of the microstructure that result from the three steps we shown [19].
2.3.3 Microstructure of 2xxx series aluminium alloys

Throughout the heat treatment, transformation of phases leads to the generation of different particles, with different compositions, shapes and sizes at different times and temperatures of the process. The resulting microstructure, which can be predicted from the phase diagram, reveals three types of dispersed intermediate particles, which are described in detail in the next section.

2.3.3.1 Constituent intermetallic particles (IMPs)

The IMPs are formed by liquid-solid eutectic reaction during the solidification of the aluminium alloy. These particles are rich in alloying elements and are identified as Al$_2$Cu, Al$_2$CuMg and Al-Cu-(Mn-Fe)Si. Characterized by comparatively large coarser sizes ranging from 1-50 µm, and also by spherical and irregular shapes, particles commonly appear in the microstructure as colonies of different types. Under rolling and extrusion, these particles can be broken up and found as aligned constituents, forming bands [2]. Constituent particles can be found in clusters of different types of intermetallic compound. These particles have no effect on the strength of the alloys because of their coarse size (they cannot stop the movement of dislocations). The high concentration of alloying elements in constituent particles results in the formation micro-galvanic cells with α-Al, resulting in localised corrosion [24]. Hence intermetallic particles are undesirable in the microstructure.

2.3.3.2 Dispersoids

Distinguished by their nano size, ranging from 0.05 to 0.5 µm, dispersoids are created during homogenization (500°C for 12-24 hours) of aluminum alloys, from the additions of Cu, Mn, Cr and Zr. Dispersoids are insoluble particles in the form of Al$_{20}$Cu$_2$Mn$_3$, Al$_3$Zr, Al$_{12}$Mg$_2$Cr Al$_2$Mn$_3$Si, and Al$_2$Fe$_3$Si particles [25]. They are homogenously dispersed, and function as grain refiners affecting re-crystallization behaviour. Grain refinement is very important for mechanical properties, such as fracture toughness [26, 27].
2.3.3.3 Precipitates

As the process of ageing starts, $\alpha_{ss}$ (solid solution) starts to decompose causing nucleation and growth in the microstructure of precipitates with different shapes, such as laths, needles, disks and plates, with small sizes, ranging from a few angstroms to 0.1 µm\(^5\),\(^{25}\). Precipitates such as Guinier-Preston (GP) zones, $\theta''$ and $\theta'$ phases and $\theta$-phase ($\text{Al}_2\text{Cu}$), S' and S- phase ($\text{Al}_2\text{CuMg}$) in 2xxx series alloys are responsible for strengthening the alloys. However, S-phases can significantly reduce the corrosion resistance, as the presence of these precipitates along the grain boundary, leads to intergranular corrosion (IGC). Nevertheless, S-phase particles are known to control the properties of AA2024 alloy during ageing\(^{28}\).

2.3.4 Precipitation hardening

Precipitate hardening can be considered as a kind of deformation, resulting in an increase of strength and hardness in aluminium alloys.

2.3.4.1 Precipitations of $\text{Al}_2\text{Cu}$ phase in Al-Cu alloys

For Al-Cu alloys, precipitates are responsible for their high performance. Figure 2.3 shows the left part of the binary Al-Cu phase diagram. Just after quenching, the formation of metastable phases starts to take place.

![Al-Cu phase diagram](image.jpg)

Figure 2.3: Al-Cu phase diagram showing the metastable GP1 zone, $\theta''$ and $\theta'$ solvuses\(^{29}\).
The first phase to form, which is fully coherent with the aluminum matrix $\alpha$, we the GPB (Guinier Preston Bagaratsky) zones, followed by intermediate $\theta''$ and $\theta'$ phases and finally before the stable $\theta$ phase ($\text{Al}_2\text{Cu}$) \[^{30}\] as follows:

$$\alpha_{SS} \rightarrow \text{GPB zones} \rightarrow \theta'' \text{ phase} \rightarrow \theta' \text{ phase} \rightarrow \theta \text{ phase (Al}_2\text{Cu)}$$

GPB zones are formed homogeneously in the microstructure, as a result of solute atoms accumulation in the lattice forming strengthening phases \[^{9, 23, 31}\]. They form a monolayer of copper atoms on Al matrix plane with a high degree of coherence, \[^{32}\] see Figure 2.4 and a disc like morphology of 0.4-0.6 nm thickness and 8-10 nm diameter \[^{33}\]. As the ageing time elapses and the $\alpha_{SS}$ decomposition, progresses, GPB dissolves or changes to the semi coherent intermediate $\theta''$ phase with sizes ranging from 1 to 4 nm thick and 10-100 nm in diameter but with two layers Cu of atoms separated by a layer of aluminum atoms \[^{33}\], as illustrated in Figure 2.4. The appearance of this $\theta''$ phase in the matrix causes strain in the matrix, as illustrated in Figure 2.4 (b) and results in further increase of hardness and in tensile strength of the alloy. As ageing progresses, the $\theta'$ phase starts to nucleate heterogeneously on dislocations with platelet shapes of thickness 10 to 150 nm and forming a tetragonal structure semi-coherent with the aluminium matrix \[^{34}\]. Further increase of ageing causes the formation of $\theta$ phase with composition $\text{Al}_2\text{Cu}$, accompanied by a reduction of hardness. This phase has a body centered tetragonal structure, and is incoherent with the aluminum matrix.
Figure 2.4: (a) Structure and morphology of $\theta''$, $\theta'$ phases and $\theta$ phase ($\text{Al}_2\text{Cu}$) where, Al atoms are indicated by white dots and Cu atoms by black dots, (b) shape of $\theta''$ phase in the aluminum matrix; the circular dotted line indicates an area strained by $\theta''$ phase and (c) TEM micrograph of a fine and uniform dispersion of $\theta'$ precipitates in Al-1.7Cu-0.01Sn alloy; the needle shaped $\theta'$ phases are nucleated on spherical shaped Sn particles $[^{29}]$. If precipitates grow in size and decrease in number, the strength of the alloy is decreased. This is called over ageing. Hence, there is a direct relationship between hardness and the sequence of, formation of GPB zones, $\theta''$, $\theta'$ and $\theta$ phases with ageing time.

2.3.4.2 Precipitations of $\text{Al}_2\text{Cu}$ Mg phase in Al-Cu-Mg alloys

Precipitation hardening is dependent on the composition ratio in the alloys, $[^2, 5, 35]$. The phase diagram of the ternary Al-Cu-Mg system is well known $[^{36}]$. The rich part corner of Al-Cu-Mg phase diagram at 190ºC is shown in Figure 2.5.
Two sequences of precipitation can occur during the decomposition of a solid solution Al-Cu-Mg alloy\textsuperscript{[14]}:

i) in the (\(\alpha+\theta\)) phase region

\[
\begin{align*}
\alpha_{SS} &\rightarrow \text{GPB zones} \rightarrow \theta'' \text{ phase} \rightarrow \theta' \text{ phase} \rightarrow \theta \text{ phase} \\
(\text{Al}_2\text{Cu})
\end{align*}
\]

ii) in (\(\alpha+S\))

\[
\begin{align*}
\alpha_{SS} &\rightarrow \text{GPB zones} \rightarrow S'' \text{ phase} \rightarrow S' \text{ phase} \rightarrow S \text{ phase} \\
(\text{Al}_2\text{CuMg})
\end{align*}
\]

GPB (Guiner-Preston - Bagaratsky) zones, \(S''\) and \(S'\) are metastable phases which are coherent and semi coherent with the aluminum matrix and \(S\) is the final equilibrium state. It should be noted that, different material characteristics are dependent on the alloy composition (Cu content and Cu/Mg ratio) beside ageing parameters and phase distributions \textsuperscript{[32]}. The mechanism of precipitation and details of the decomposition have been extensively studied \textsuperscript{[29, 30, 37-41]}, but are still controversial. Lack of evidence exists, in particular at the early stage of ageing, whether to consider GPB zones or Cu-Mg co-clusters and \(S''\), as well as counting the distinction between semi coherent \(S'\) and incoherent \(S\) phase. It is generally, accepted that, \(S'\) and \(S\) phases are very similar in chemical composition as well as in crystal structure with slight variation in lattice parameters \textsuperscript{[41-43]}. The authors suggest that the stage between \(S'\) and \(S\) phases is continuous rather than discrete hence, they consider \(S'\) phase as \(S\) phase. S phase morphology viewed in the \(<100>_{\text{Al}}\) direction with elongated direction along \(<100>_{S}\)
with \{210\} \text{Al} habit plains \cite{30} reveals laths and needles shapes, with a heterogeneous distribution on dislocation lines \cite{44}, as shown in Figure 2.6 (a) and (b) respectively.

![Figure 2.6: Al\textsubscript{2}CuMg precipitate particles in an AA2xxx (Al-Cu-Mg) alloy. (a) Dark field scanning transmission electron image showing lath and needle shapes \cite{2}. (b) Bright field TEM micrograph of S-phase with electron diffraction pattern \cite{44}.](image)

There are a number of models that have been proposed for the crystal structure of S'' and S phase (see Figure 2.7(a-e)) \cite{41}, such as Cuisiat's model \cite{45} in Figure 2.6; (a), Wolverton model \cite{46} in (b), Perlitz and Westgren's (PW) model \cite{47} in (c), Mondolofo model \cite{14} in (d) and Jin, Li and Yan model \cite{48} in (e).

![Figure 2.7: (a) and (b) proposed models for S''- phases, (c), (d) and (e) proposed models for S- phase \cite{41}.](image)

The structure of the second stage of S'' phase has not been confirmed, with different proposed structures as orthorhombic \cite{30,49,50}, cubic \cite{37}, tetragonal \cite{46} or monoclinic \cite{39}. Perlitz and Westgren \cite{47} used X-ray diffraction to establish a structure for S-phase where their establishment was supported by later studies \cite{38,44}. It was found that the S-phase composition is Al\textsubscript{2}CuMg, with an orthorhombic structure and with
lattice parameters of \( a_s = 0.400 \) nm, \( b_s = 0.923 \) nm and \( c_s = 0.714 \) nm, as illustrated in Figure 2.7(c).

The strength of Al-Cu-Mg alloys depends highly on the precipitates formed during ageing. The Cu/Mg ratio in precipitate phases, in particular S phase, is crucial in determining the alloy strength. It was found that S phase dominates the precipitation hardening in the peak-aged condition for both stretched and non stretched alloys \(^{41, 51}\). Hardening precipitate formation is related to the alloy composition, where precipitates such as \( \text{Al}_2\text{CuMg} \) \(^{23, 52-54}\) are dominant in AA2024 alloy, while \( \text{Al}_2\text{Cu} \) precipitates are dominant in AA2017 \(^{6, 15, 54, 55}\).

About sixty to seventy percent \(^{44}\) of hardening (total response for ageing at elevated temperature) particularly in Al-Cu-Mg \(^{2, 23, 56-59}\) alloys occurs because of the formation of GPB zones (Cu-Mg co-clusters) as a result of solute atoms such as Cu and Mg accumulated along preferred crystal directions in aluminium lattice. Consequently, strengthening phases are formed where S’-phase is considered the intermediate phase and the maximum of hardness is reached when the S-phase \( \text{Al}_2\text{CuMg} \) is formed after the alloy being left constantly for a period of time \(^{23}\).

### 2.3.5 Mechanical properties enhancement and tempering designation

The mechanical properties, such as strength, in 2xxx alloys series respond significantly to age hardening at room temperature and also to artificial ageing at elevated temperatures. Techniques such as annealing and work hardening or strain hardening \(^{3}\) are also used to enhance their performance.

#### 2.3.5.1 Annealing

Since strength depends on the density of precipitates and not on the particle size, by annealing, the rate of nucleation can be increased without increasing their size. In view of the fact that the growth and shrink age of precipitates can occur, the annealing duration and temperature range play a major role. For example, if the annealing duration is too long or the temperature is too high, this can lower the strength of the alloy. In general, temperatures ranging from 400 to 427°C for a minimum period of 2 hours are applied, followed by subsequent slow cooling in a
furnace to release internal stress, such as stresses caused by cold working. The annealing duration is dependent on the amount of cold work and the thickness of the material plate. Annealing between cold work operations can be done at 250°C for 2 hours, followed by air cooling. Hence, in artificial ageing, time duration and temperature selection, tempering process and alloy composition are important factors for achieving the required properties.

2.3.5.2 Work hardening

Alloys undergo work hardening by hammering causes strain hardening, making them gain strength by plastic deformation. Strengthening of metals occurs because of obstacles to dislocation movements within the crystal structure. When the density of dislocations is increased and grains are deformed, second phases within the matrix prevent dislocation movement and strengthening is obtained.

2.3.5.3 Alloy temper designation

According to the techniques described above, the mechanical properties of aluminium alloys can be modified by different tempers, via selecting the temperature and time of heat treatment duration, to change the size, volume fraction and type of precipitated particles that greatly affect the mechanical properties of the treated alloy. These techniques and others are designated with different tempers as shown in Table 2.2.

Table 2.2: Temper designations for techniques applied for alloy performance enhancement.

<table>
<thead>
<tr>
<th>Temper</th>
<th>Enhancement techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>As-fabricated</td>
</tr>
<tr>
<td>O</td>
<td>Annealed</td>
</tr>
<tr>
<td>H</td>
<td>Strain- or work-hardened</td>
</tr>
<tr>
<td>W</td>
<td>Solution heat Treated</td>
</tr>
<tr>
<td>T</td>
<td>Treated</td>
</tr>
</tbody>
</table>

A second treatment is represented by the first suffix digit, for example, cold worked. A second suffix digit indicates second cold worked and annealed[1] as in Table 2.3.
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Table 2.3: Mechanical properties of AA 2024 at different tempers \(^{[1, 62]}\).

<table>
<thead>
<tr>
<th>Temper</th>
<th>Temper details</th>
<th>Tensile Strength (MPa)</th>
<th>Yield strength (MPa)</th>
<th>Hardness (HB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Annealed</td>
<td>185</td>
<td>75</td>
<td>47</td>
</tr>
<tr>
<td>T3</td>
<td>Solution heat treated, cold worked and natural aged.</td>
<td>485</td>
<td>345</td>
<td>120</td>
</tr>
<tr>
<td>T351</td>
<td>Solution heat treated at 495°C, quenched, stretched 1.5-3% and natural aged for several months</td>
<td>470</td>
<td>325</td>
<td>120</td>
</tr>
<tr>
<td>T4</td>
<td>Solution heat treated and naturally aged.</td>
<td>470</td>
<td>325</td>
<td>120</td>
</tr>
<tr>
<td>T6</td>
<td>Solution heat treated and artificial aged at 190°C for 12 hrs.</td>
<td>475</td>
<td>395</td>
<td>-</td>
</tr>
<tr>
<td>T8</td>
<td>Solution heat treated, cold worked and artificially aged at 190°C for 12 hrs.</td>
<td>480</td>
<td>450</td>
<td>-</td>
</tr>
</tbody>
</table>

More common heat treatment tempers are added as suffix letters and digits to the alloy number. For example, temper T351 means that the alloy is solution heat treated, quenched, stretched 1.5-3% and naturally aged for several months \(^{[1]}\). In general T3 and T4 are used to indicate naturally aged tempers with combination of high strength and good damage tolerance as in AA2024-T3 alloy. AA2024-T351 alloy is one of 2xxx heat treatable aluminium alloys and is the focus of this study.

2.4 Aluminium alloy 2024

AA2024 alloy belongs to the aluminium-copper alloy 2xxx series characterized by high strength, but suffers from low corrosion resistance. In general, this series is used where strength and toughness are required. Therefore, AA2024 alloy is normally used in aircraft structure, rivets, truck wheels, and screw machine products.

2.4.1 Chemical compositions

It is well-known that the desired mechanical properties of aluminium alloys especially high strength are developed, as a result of a heterogeneous microstructure which is produced by careful addition of alloying elements and heat treatment \(^{[20]}\). The additives in AA2024 alloy are within the range limit of their solubility in the
aluminium solid solution. The chemical compositions of AA2024 alloy in weight percentage as a maximum and a minimum are presented in Table 2.4 \[62\].

Table 2.4: Composition limits of AA2024 in wt.\% \[62\].

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Zn</th>
<th>Cr</th>
<th>Ti</th>
<th>Others</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>3.8</td>
<td>1.2</td>
<td>0.0</td>
<td>0.30</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Bal</td>
</tr>
<tr>
<td>Max.</td>
<td>4.9</td>
<td>1.8</td>
<td>0.9</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25</td>
<td>0.10</td>
<td>0.15</td>
<td>0.15</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Copper is the major alloying element and plays a major role in strengthening of aluminium. It is added in a percentage within the solid solubility. The maximum solid solubility of copper in aluminium is 5.67 weight percent at 548°C and decreases to less than 0.25 weight percent at room temperature \[11\]. Magnesium accelerates the hardening process by enhancing the strength through precipitation of particles during aging. The presence of manganese increases the resistance of aluminum against pitting corrosion \[63\].

### 2.4.2 Microstructure development in Al-Cu alloys

Microstructures developed for AA2024 alloy are not well understood in the scientific literature, in particular with respect to the corrosion behaviour \[2\]. This can be related to the existence of combination of equilibrium and non-equilibrium phases resulting in complex microstructures. Chemical composition and presence of Cu, Mg and other elements alongside impurities such as Si and Fe produce insoluble compounds distributed uniformly in the aluminium matrix. These intermetallics are identified as Al\(_2\)Cu, Al\(_2\)CuMg, Al\(_2\)Cu\(_2\)Fe, Al\(_3\)Cu\(_2\)Fe, Al\(_{12}\)Si(FeMn)\(_3\), Al\(_{20}\)Cu\(_2\)(FeMn)\(_3\), Al\(_{20}\)Cu\(_3\)Mn\(_3\) in AA2024-T3 with different electrochemical behaviour of anodic and cathodic cells \[52, 63, 64\]. As explained earlier, intermetallic particles with their comparatively large size, up to 50 \(\mu\)m, are randomly distributed in the AA2024 alloy microstructure with spherical and irregular shapes, and are visible with low magnification optical microscopy. With solubility < 1 wt.\%, Mn, Zr and Cr are the essential alloying elements for forming dispersoids which do not dissolve during homogenisation. The main dispersoids in AA2024 are Al\(_{20}\)Cu\(_2\)Mn\(_3\) (called T-phase) which appears as rod-like shapes with \(<010>\) direction of growth \[41, 65\], with lattice parameters \(a = 2.24\) nm, \(b = 1.25\) nm and \(c = 0.775\) nm \[65, 66\], making them much smaller than the intermetallic particles with sizes range from 0.02 to 0.5 \(\mu\)m \[36\]. In
AA2024 alloy Cu and Mg are the highest wt.% alloying elements compared to other elements where, they provide precipitate enhancement. Precipitates are formed during natural ageing by nucleation and growth from supersaturated solid solution. They can be in different shapes such as laths, needles and plates with small sizes ranging from a few angstroms to 0.1 µm \(^5\). Cu in aluminum does not simply precipitate, but rather it forms metastable precipitates phase, before finally forming the equilibrium phase, such as Al\(_2\)Cu called \(\theta\) phase and Al\(_2\)CuMg S-phase. The S phase (Al\(_2\)CuMg) is one of the key strengthening precipitates in AA2024 alloy. However, this phase can cause a significant reduction in the corrosion resistance \(^{12}\). A preferential growth of precipitates at grain boundaries leads to copper-depleted zones, as a result of Cu consumed by the formation of these precipitates, as suggested by Zhang et al \(^{67}\) in their studies on AA2024 alloy, accumulation of S-phases along the grain boundaries in a chain formation lead to intergranular corrosion.

### 2.5 Fundamentals of corrosion

Corrosion is an electrochemical reaction of a metal with its environment \(^{68}\). For corrosion to occur, four components are necessary:

1. An anode (an active metal), where electrons are produced, or lost.
2. A cathode (a more noble metal (less active), where electrons are consumed, or gained.
3. A conductor for the transport of electrons
4. An ionic conductor which is also called electrolyte for transport of ions in a solution.

If one of the four components is missing, corrosion cannot occur \(^{68}\). There are two types of reaction occurring on the surface of a corroding metal, i.e. oxidation and reduction reactions. Oxidation reactions release electrons at the anode to be consumed by reduction reactions at the cathode. Corrosion occurs at a rate determined by the equilibrium between these opposing electrochemical reactions. A potential difference between the anodic and cathodic reactions on the metal surface represents the driving force for the corrosion reaction.

### 2.5.1 Electrochemical reactions
Electrochemical reactions result in an electrical current which depends on the difference in potential between the metal and the solution. The metal is oxidized forming $M^{n+}$ cations of the metal which are freed into the solution $[^{6}]$:

$$M \rightarrow M^{n+} + n \, e^- \quad (\text{Loss of electrons, resulting in anodic current (-ve current)})$$

A flux of electrons within the metal is called anodic current flow $I_a$, by equal consumption of these electrons from the ions in the solution and transformed to another chemical species. Ions are reduced in the solution resulting in a cathodic current flow $I_c$ flowing from the solution to the metal.

$$M^{n+} + n \, e^- \rightarrow M \quad (\text{Reduction of ions, resulting in cathodic reduction current } I_c \,(+ve \, \text{current})$$

When there is no external source for electric current, the circuit formed by the metal and the solution is an open electric circuit. This means the anodic current and the cathodic current are flowing in opposite directions at equal rates. At this point, the intersection between two polarization curves, defines the corrosion intensity $I_{corr}$ and the corrosion potential $E_{corr}$ which is also called solution potential $[^{69}]$.

The study of corrosion phenomena is done through these polarisation curves which are determined experimentally, either by varying $I$ and measuring $E$, or by varying $E$ and measuring $I$.

![Figure 2.8: Anodic and cathodic polarization curve $[^{6}]$.](image)

Kinetics of anodic and cathodic electrochemical reactions are represented by the relationship between the potential $E$ and the corresponding electrical intensity $I$ $[^{6},^{68}]$. The driving force for a corrosion reaction is the potential difference between anodic
and cathodic reactions on the metal surface. Under this driving force a current flows through the corrosion cell \cite{70, 71}. The standard electrode potential for a reaction is related to the change in free energy by the equation.

\[ \Delta G^\circ = -RT \ln k \quad (2.1) \]

Where \( \Delta G^\circ \) is the standard Gibbs free energy change of the reaction, \( R \) is the universal gas constant, \( T \) the absolute temperature and \( k \) is the equilibrium constant.

\[ \text{Me} \rightarrow \text{Me}^{n^+} + ne^- \text{ equals Me}^{n^+} + ne^- \rightarrow \text{Me} \]

The potential of this electrode is then given by the Nernst equation:

\[ E = E^0 + \frac{RT}{nF} \log [\text{Me}^{n^+}] \quad (2.2) \]

Where \( n \) is the number of electrons involved (valence electrons) and \( F \) is Faraday’s constant, \( E^0 \) is the standard potential for the metal and \([\text{Me}^{n^+}]\) is the concentration of the metal ions in the solution.

Figure 2.9: Pourbaix diagrams for the Al-H$_2$O system at 25\(^\circ\)C \cite{71}.

The Nernst equation is very important in electrochemistry as it relates the cell potential \( E \) to the standard potential \( E^0 \) and concentration of the electro-active ion \cite{68, 72}. It is used for construction of Pourbaix diagrams shown in Figure 2.9, which
shows the thermodynamically most stable species at different combinations of electrode potential, pH and ion activity \cite{68,73}.

The Pourbaix diagram for the Al-H\textsubscript{2}O system, Figure 2.9, shows different regions for the behaviour of aluminium in water. In the corrosive region, corrosion occurs by general dissolution of the metal. In the immune region, the metal is immune because the potential of the metal is so far depressed that the reaction is not thermodynamically possible. In the passive region, the potential of the metal is elevated and the metal becomes covered with a protective oxide film, isolating the metal from its environment. The metal is possibly resistant to corrosion in areas where the film is stable, because this thin layer, usually based on oxide, leads to a decrease in the rate of the anodic reaction.

2.5.2 Electrochemical polarisation (\(\eta\))

The current density due to the anodic or cathodic reaction at \(E_{\text{corr}}\) is called the corrosion current density, \(I_{\text{corr}}\), and is a measure of the corrosion rate. Hence polarization can be defined as potential change from the equilibrium potential to the corrosion potential \cite{85}. When the metal is not in equilibrium with the solution \(|I_a| > |I_c|\) the metal is corroding, where \(|I_a| < |I_c|\) the metal is plated from solution. This means that Nernst equation is not obeyed so the actual potential is different from the equilibrium potential which can be obtained by subtracting \(E - E_0 = \eta\) which is known as the polarization potential or overvoltage.

A polarization curve of metal that shows active-passive behaviour is shown in Figure 2.10, which represents the potential versus current density. The polarization curve shows three specific behaviours: active, passive and transpassive.

To be noted is the fact that the anodic polarization (dissolution) curve in Figure 2.10 is only possible for those metals capable of passivation, i.e able to form an oxide layer which protects the metal from further corrosion. Examples of metals and alloys which passivate include titanium, cobalt - chromium, stainless steels and aluminium.
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From the polarisation curve, curves AO (cathodic) and OD (anodic) represent the net behaviour of the cathodic and anodic reactions respectively. The Tafel lines are extended along the slope of cathodic AO and anodic curves/regions OD with dashed lines AB and CD respectively. These extended dashed lines cross each other at the point O. At this point, the sum of currents (anodic and cathodic) is zero. At point O, the potential is called the corrosion potential \(E_{\text{corr}}\) or open circuit potential and the current density \(I_{\text{corr}}\) can be evaluated. For potentials higher than this point, the corrosion current density increases as potential value increase and reaches a maximum at the passivation potential \(E_{\text{pp}}\). Further increase in potential over \(E_{\text{pp}}\), a passive region from point E to the point F is formed, because of aluminium forming an oxide film \(\text{Al}_2\text{O}_3\) on the surface, reducing the corrosion rate, where the formed oxide film is characterised by poor ionic/electronic conductivity. The stable growth of the passive film accompanied by a sharp drop in current density which is then maintained at a steady low value called the passive current density. A sudden rapid increase in current as indicated at point F is the pitting potential \(E_{\text{p}}\) and defined as breakdown of the passive film where pits grow and propagate with the breakdown of the oxide layer above \(E_{\text{p}}\).
2.5.3 Corrosion behaviour of pure aluminium

The corrosion behaviour of aluminium greatly depends on the properties of its surface and near surface. Pure aluminium has a good corrosion resistance because of a rapid reaction with oxygen in the air to form $\text{Al}_2\text{O}_3$ according to the reaction:

$$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$$

The thickness of such film can grow in the range from 1 to 10 nm $^{[68, 76]}$ and it reforms immediately if scratched or damaged. It consists of two layers, the inner layer is compact while the outer layer is porous $^{[6]}$. However for pure aluminum there still exists a small amount of residual impurities which can act as initiation sites for corrosion attack. The most common residual impurities are iron, silicon and copper. Iron and silicon have low solid solubility in aluminum and form fine segregates at cellular boundaries during solidification. Depending on their size, distribution and reactivity, such segregates affect the local properties of the oxide film $^{[6, 77]}$. The oxide film is stable in neutral solutions, it corrodes rapidly in alkaline media and dissolves in acid media $^{[17]}$. The chemical composition of the passive film at ambient temperature is $\text{Al}_2\text{O}_3.3\text{H}_2\text{O}$ $^{[78]}$, called Gibbsite, which is the stable oxide of aluminum $^{[79]}$. The Pourbaix diagram of aluminum in Figure 2.9 shows the passive region has a pH range from 4 to 8.5. Thermodynamically, it represents the stability region of the oxide film ($\text{Al}_2\text{O}_3$) on the surface of the aluminum. Before or beyond this region, aluminum suffers corrosion. At pH less than 4, $\text{Al}^{3+}$ ions are produced and water is decomposed and hydrogen is produced; at higher pH value than 8.5, aluminum dissolves and $\text{AlO}_2^-$ (aluminates) is formed as corrosion product. Hence, in acid and alkaline environments the oxide film $\text{Al}_2\text{O}_3.3\text{H}_2\text{O}$ is described as unstable thermodynamically.

2.5.4 Corrosion behaviour of aluminium alloys

The corrosion behaviour of aluminium alloys is dependent on the existence of intermetallic particles on the surface of the alloy $^{[80]}$. These intermetallic particles have different electrode potentials from the $\alpha$-Al matrix, creating microgalvanic cells (anodic sites). On the other hand, these intermetallics result in a deformed and thinner oxide film layer, allowing the alloy to be more prone to corrosion $^{[81, 82]}$. 


For aluminium-copper alloys, e.g. AA2024-T351 alloy, due to the large difference of electrode potentials between the copper-containing particles and the aluminium matrix, the resultant galvanic cells initiate corrosion in the presence of aqueous solution \[^{\textsuperscript{83}}\]. In addition, the thinner \(\text{Al}_2\text{O}_3\) film grown on top of those intermetallic particles leads to an increase in the rate of dissolving film thus accelerating corrosion. The dissolution of aluminium in aqueous solution is as follows \[^{84}\].

The dissolution of aluminium in water:

\[
\text{Al} \rightarrow \text{Al}^{\text{+3}} + 3\text{e}^- \\
\]

It undergoes a possible hydrolysis reaction as follows:

\[
\begin{align*}
\text{Al}^{\text{+3}} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}^{\text{+2}} + \text{H}^+ \\
\text{Al} + 2\text{H}_2\text{O} & \rightarrow \text{AlO}_2^- + 4\text{H}^+ + 3\text{e}^- \\
\text{Al} + 2\text{H}_2\text{O} & \rightarrow \text{Al(OH)}^{\text{+2}} + \text{H}^+ + 3\text{e}^- \\
\text{Al} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ + 3\text{e}^- \\
2\text{Al} + 4\text{H}_2\text{O} & \rightarrow \text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} + 6\text{H}^+ + 6\text{e}^- \\
\end{align*}
\]

Dissolution of aluminium in chloride

\[
\text{Al}^{\text{+3}} + \text{Cl}^- \rightarrow \text{AlCl}^{\text{+2}} \\
\]

A faster reaction is:

\[
\text{AlO}_2^{\text{+2}} + \text{Cl}^- \rightarrow \text{Al(0H)} \text{Cl}^+ \\
\]

The dissolution of aluminium in sulphate aqueous solutions is as follows \[^{84}\]:

\[
\begin{align*}
2\text{Al}^{\text{3+}} + 3\text{SO}_4^{2-} & \rightarrow \text{Al}_2(\text{SO}_4)_3 \\
\text{AlO}_2^{\text{+2}} + \text{SO}_4^{2-} & \rightarrow \text{Al(OH)SO}_4 \\
\end{align*}
\]

The above reactions illustrate the reactions leading to the corrosion of aluminium in aqueous electrolytes, and localized corrosion such as pitting corrosion, intergranular corrosion and stress corrosion cracking of aluminium alloys.
2.5.5 Pitting corrosion

Pitting corrosion is generally associated with localised breakdown of the protective film on the surface of a metal when exposed to environment containing aggressive Cl\(^-\) ions \[2\]. For aluminium and aluminium alloys, in particular Al-Cu alloys, the intermetallic particles such as precipitates and constituents are preferred sites for pits formation or initiation because of different electrode potentials between the particles and surrounding matrix \[12, 85, 86\]. Initiation of pitting corrosion is assisted by adsorption of chloride ions on the oxide surface, penetrating through the oxide film via vacancies and interacting with the substrate \[12, 87\]. As a consequence, the corrosion rates can be six order of magnitude \[88\] higher than those observed for passive surface. The corrosion rate which is governed by the dissolution rate of the thin film is \(10^{-13}\) ms\(^{-1}\) (equivalent to a current density of \(I_{\text{pass}}\) of the order \(10^{-2}\) Am\(^{-2}\)) \[88\].

Pits usually grow in uneven shapes, and undercut the surface because of favourable diffusion paths and have a tendency to follow grains that are elongated \[12, 89\]. Pitting corrosion propagates into a metal in a hemispherical hole, or in crystallographic planes with propagation rate in an order of \(10^{-7}\) ms\(^{-1}\) (\(I_{\text{pitting}} = 10^4\) Am\(^{-2}\)) \[88\].

2.5.5.1 Stages of pitting corrosion

Pitting corrosion in aluminium alloys follows three stages:

1) Pits initiation: The presence of intermetallic particles on the surface work as preferential sites for pits to initiate, because of difference in potentials with the substrate.

2) Metastable pits: Pits initiate and then grow up to a point below the critical pitting potential and then re-passivate for a short time (at low current pits repassivate). At the end of this stage the protective thin film breaks down.

3) Pits stabilization: Pits propagate again and reach stability in growth. This occurs when the potential reaches a certain level called critical pitting potential (i.e. \(10^{-2}\) A/cm\(^2\) is required for stable growth of pits to be maintained in the aggressive solution) \[12, 73, 90\]. There are several factors
playing important roles in the process of pitting corrosion in aluminium and aluminium alloys.

2.5.5.2 Influence of surface oxide film

It is well-known that physical, electrical and mechanical properties of a thin passive oxide film significantly affect the resistance of metals to pitting corrosion. The high resistance of pure aluminium to corrosion is accredited to the presence of Al$_2$O$_3$ on the surface $^{[6, 83, 91, 92]}$. The passive film remains stable in environment with a pH range of 4 to 9, and when damaged it can undergo self-repairing in the presence of oxygen to protect the underlying metal from corrosion $^{[12]}$. In an environment containing aggressive Cl$^-$ ions, the chloride anions with high diffusivity can interfere with passivation and dissolve the thin film $^{[88, 93]}$. The processes which can lead to the collapse of the film are dependent on both elemental composition and structure of the thin film.

2.5.5.3 Influence of alloy composition

Alloying composition determines the formation of second-phase particles such as Al$_2$CuMg and Al$_2$Cu that appear on the aluminium alloy surface. As described earlier, the presence of such intermetallics on the surface creates galvanic cells or anodic sites for pitting corrosion and produces defects in passive film. Alloying noble elements like Mo, Cr, W, Nb or Cu increase the pitting potential, where alloying active elements like Ga, Hg, Mg or Zn decrease the pitting potential. Alloys containing high alloying levels of Cu are basically more prone to pitting corrosion than those with lower levels or no Cu $^{[94]}$. However, it was found that the presence of alloying elements such as in solid solution, considerably improve the resistance to pitting corrosion $^{[94-98]}$. Therefore, the solid solution can form the highest corrosion resistance $^{[5]}$.

Beside the presence of Cl$^-$ ions, pitting corrosion mechanism in Al-Cu alloys is primarily based on the presence of Cu-rich intermetallic particles as seen in Table 2.5, which are nobler than the matrix, and working as small local cathodes. But with the increase of copper concentration in $\alpha$-Al solid solution up to the solid limit they can raise the corrosion potential and hence increase the corrosion resistance to galvanic attack $^{[15, 94, 98]}$. Moreover, voltage component calculations done by
Ramgopal et al.\(^{[99]}\) indicate that the main role of the alloying elements is to alter the surface over-potential for metal dissolution and thereby shift the position of the polarization curves on the potential axis.

Table 2.5: Atomic percentage of elements in nominated phases.\(^{[54]}\)

<table>
<thead>
<tr>
<th>Phase assignment(^a)</th>
<th>Colour code</th>
<th>Al</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al matrix</td>
<td></td>
<td>96</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al(_{10})(Cu,Mg)</td>
<td></td>
<td>90</td>
<td>7</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)Cu(_2)Fe(_2)(Si,Fe)(_3) (Si,Mg)(_2)</td>
<td></td>
<td>90</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Al(_2)Cu(_2)Mg (S-phase)</td>
<td></td>
<td>61</td>
<td>20</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)Cu (θ-Phase)</td>
<td></td>
<td>70</td>
<td>27</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)Cu(_2)Fe</td>
<td></td>
<td>70</td>
<td>18</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Al(_3)(Cu,Fe,Mn)</td>
<td></td>
<td>73</td>
<td>11</td>
<td>0</td>
<td>4</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

2.5.5.4 Effect of electrolyte concentration

Pit nucleation rate increases with an increase in Cl\(^-\) ion concentration and applied anodic potential, during polarisation testing.\(^{[100]}\) However, Berzins et al.\(^{[101]}\) suggested that, there is no threshold for the chloride concentration below which pitting will not occur. In fresh water, the chloride ions directly affect the corrosion potential of aluminium. The higher the chloride ion concentration, the more negative the corrosion potential is, resulting in a faster corrosion of a metal.\(^{[102]}\) The outcome is that chloride ions accelerate the corrosion process. Whether due to oxide film breakdown or supporting the anodic reaction an explanation is still unclear.\(^{[102]}\)

2.5.5.5 Pit chemistry

Two electrochemical reactions, i.e. anodic and cathodic reactions, occur in a pit as illustrated in Figure 2.11. Anodic reaction proceeds with dissolution of aluminium at the base of the pit.

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- 
\]

In order to initiate pitting, aggressive anions are necessary. Chloride anions can migrate from the bulk electrolyte to pits in order to satisfy charge neutrality. This leads to the decrease in pH by hydrolysis as follow:

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ 
\]
In neutral/alkaline environment:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \] (Hydrogen evolution)
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] (Oxygen reduction)

2. Literature Review Part I

Al\(^{3+}\) + H\(_2\)O + Cl\(^-\) \rightarrow H\(^+\) + Al(OH)Cl

2H\(^+\) + 2e\(^-\) \rightarrow H\(_2\)

2Al + 6H\(^+\) + 4 Cl\(^-\) \rightarrow 3H\(_2\) + 2AlCl\(_2\)

2.5.5.6 Effect of variation in pH

The effect of pH on pit development was studied by Duan Weng and Shizhong Huo \(^{[104]}\). They found that the pit’s growth in aluminium in seawater (3–4% NaCl) was autocatalytic in the early stage. This can be related to pH decrease and chloride concentration increase within the pit as a result of the formation of hydrogen ions by hydrolysis of aluminium ions. Furthermore, the violent hydrogen release from pit causes the fluctuation of anodic current. McCafferty et al \(^{[105]}\) calculated the pH within the internal pit to be around 2.28. However, over a range of pH values of 4 to approximately 8.5, the pitting potential was found to be independent of pH \(^{[105]}\).
Tabrizi et al. \cite{107} studied the effect of pH values from 8 to 13 for alkaline solutions on corrosion rate of aluminium in long term corrosion, and showed that the corrosion rate increased rather slowly with an increase in pH value from 8 to 10; however, when pH value is above 10, much larger increase in corrosion rates were obvious. Their interpretation was that below pH value of 10, the specimens developed pit-like morphology under the thin film. At pH value of 11, cavities developed in the crystalline film can allow greater solution access result in an increase in corrosion rate. At pH value of 12, cavities developed into pits followed by rapid disintegration and dissolution of the exposed substrate \cite{107}.

2.5.5.7 Effect of temperature

Temperature can greatly affect passive film stability, for instance, the oxide film on aluminum surface can be unstable at temperature above 230°C \cite{6,91,108}. Further, in chloride solutions pitting potential $E_{\text{pit}}$ of aluminum decreases very slowly with an increase in temperature from 1 to 30°C and decreases faster with the increase of temperature up to 70°C. It was found that, at lower temperatures, the film is a single layer of bayerite, while at higher temperatures it consists of an inner layer of pseudo-boehmite and an outer layer of bayerite \cite{109}.

2.5.6 Effects of intermetallic particles in AA2024-T3 alloy on corrosion properties

Localized corrosions in AA2024-T3 alloy often occurs in the vicinity of copper-containing second phase particles \cite{94}. It can strongly depend on anodic/cathodic activities of Cu-rich intermetallic particles such as S-phase (Al$_2$CuMg), θ-phase (Al$_2$Cu), and particles of varying composition containing Al, Cu, Mn, and Fe with copper as the main alloying element. AA2024-T3 alloy is considered as one of the most corrosion-prone aluminium alloys and its performance can be severely impaired when exposed to aggressive environment. Its corrosion is thought to be governed by the galvanic activities between the particles and matrix, i.e. the type of the intermetallic particles. If the particle is nobler with respect to the aluminium matrix, the aluminium will preferentially corrode, while if the matrix is nobler, then the particle will corrode \cite{110}. Table 2.6 shows the data of open circuit potential and corrosion current density of various intermetallics in AA2024 alloy.
Table 2.6: OCP and corrosion currents for various intermetallic particles \[^{[111]}\].

<table>
<thead>
<tr>
<th>Intermetallic particles</th>
<th>OCP (0.1 M NaCl) mV</th>
<th>$I_{corr}$ OCP of 2024 A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{CuMg}$</td>
<td>-830</td>
<td>$9.3 \times 10^{-3}$ (anodic)</td>
</tr>
<tr>
<td>$\text{Al}_2\text{Cu}_x\text{Fe}$</td>
<td>-640</td>
<td>$3.8 \times 10^{-4}$ (anodic)</td>
</tr>
<tr>
<td>$\text{Al}<em>x(\text{Fe}</em>{0.5}\text{Mn}_{0.5})_y$</td>
<td>-609</td>
<td>$4.1 \times 10^{-5}$ (anodic)</td>
</tr>
<tr>
<td>AA2024-T3</td>
<td>-555</td>
<td>$6.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{Al}_2\text{Fe}$</td>
<td>-484</td>
<td>$2.5 \times 10^{-6}$ (cathodic)</td>
</tr>
<tr>
<td>$\text{Al}_2\text{Cu}$</td>
<td>-406</td>
<td>$1.7 \times 10^{-6}$ (cathodic)</td>
</tr>
</tbody>
</table>

2.5.6.1 Al-Cu-Fe-Mn

With composition of 73 Al, 11 Cu, 10 Fe and 4 Mn (at.%) \[^{[54]}\], an AlCu(Fe-Mn) intermetallic particle is nobler than the surrounding aluminium matrix and it works as a cathode in the process of corrosion \[^{[55]}\]. This can increase reactivity of the surface leading to non-uniform dissolution in the presence of aggressive electrolyte \[^{[112]}\].

2.5.6.2 $\theta$-phase ($\text{Al}_2\text{Cu}$)

$\text{Al}_2\text{Cu}$ ($\theta$-phase) contains about 70 Al and 27 Cu (at.%) \[^{[54]}\]. The presence of Cu in the $\theta$-phase supports cathodic transfer reaction \[^{[113]}\]. It has a cathodic behaviour with respect to the Al matrix \[^{[55,114]}\]. The OCP of $\theta$-phase is higher than that of pure Al in solutions with pH values between 2 to 12 \[^{[113]}\]. In aerated/deaerated solutions containing 0.2 to 1.0 M chloride ions, the OCP of $\theta$-phase ranges from -590 to -700 mV \[^{[55]}\]. The higher potential of $\theta$-phase with respect to the aluminium matrix plays an important role in determining the susceptibility of Al-Cu alloys to localized corrosion. Scully et al \[^{[115]}\] suggested that the presence of $\text{Al}_2\text{Cu}$ phase can make the potential of the Al matrix sufficient to promote pit initiation. It was also reported that the precipitation of $\theta$-phase at the grain boundaries make Al-Cu alloys susceptible to intergranular corrosion \[^{[95,114]}\].

2.5.6.3 S-phase ($\text{Al}_2\text{CuMg}$)

Chemical composition of S-phase $\text{Al}_2\text{CuMg}$ is 56.3±3.8Al, 20.4±1.5 Cu and 21.9±2.4 Mg in at.% \[^{[111]}\]. S-phase ($\text{Al}_2\text{CuMg}$) is anodic with respect to the aluminium matrix \[^{[12,116,117]}\], causing severe pitting corrosion of the alloy when exposed to a chloride-containing environment \[^{[52,117,118]}\]. However, Buchheit et al \[^{[52,117,118]}\] found that it supports rapid anodic and cathodic reactions because of its
corrosion potential ranging from -0.88 to -0.93 vs. SCE (in neutral chloride solution), causing subsequent Cu release and dissolve by a dealloying process, as described in Figure 2.12.

![Figure 2.12: Schematic illustration of corrosion mechanism of Al₂CuMg phase in Al alloys](image)

The S-phase dissolution leaves Cu-rich particle remnants or as a residue, which were cathodic to the aluminium matrix and consequently caused the peripheral formation of pits around the particle. As illustrated more in Figure 2.13 for Al₂MgCu phase corrosion mechanism during the immersion of AA2024 in chloride solution S-phase makes approximately 60% of the second phase particles in the alloy \(^{[52]}\) and occupies 2.7% of the total surface area \(^{[12]}\). Nevertheless, the presence of S-phase is a major contributor to the poor corrosion resistance of AA2024 alloy. Moreover, S-phase in Al-Cu alloys is responsible for the initiation of intergranular corrosion which could also lead to stress corrosion cracking (SCC) \(^{[26]}\).
Pits initiated on the surface could transform into intergranular corrosion along the grain boundaries and the intergranular path length become more dependent on grain orientation. Elongated grain orientation such as in AA2xxx and AA7xxx alloys could enhance IGC [93, 120]. IGC is common in age-hardened Al-Cu alloys especially in AA2024 and Al-Zn-Mg-Cu alloys [6, 67, 116, 121, 122]. The pitting potential difference between the precipitated particles and the adjacent matrix was suggested to be the cause for IGC initiation [53, 95, 114, 123]. Besides the aggressive environment, alloying elements greatly affect the susceptibility of the alloy to IGC. It is well-known that IGC occurs in Al-Cu alloys [95, 114, 116, 123]. It develops with a small anodic cell in contact with a large cathode. In aged Al-4%Cu alloy, the Cu-depleted zone and θ-phase with the presence of aggressive species such as chloride ions, accelerates the process of IGC [10]. It was found that the highest susceptibility of intergranular corrosion for aged Al-4Cu occurs at ageing temperature of 170°C for 2.4 hour [124]. For AA2024 alloy, a higher susceptibility was found at 195°C for 8 hours. Hence, it
is strongly suggested that the presence of copper rich-particles at the grain boundaries as a result of precipitation and decomposition from the solid solution and with a formation of anodic Cu-depleted regions adjacent to the boundaries cause the propagation of IGC \cite{95, 123, 125}. The difference in potentials between the grains (with higher potential) and Cu-depleted zone (with lower potential) is the main factor responsible for IGC attack \cite{95, 123}. Intergranular corrosion in AA2024-T3 alloy was reported by Lumsden et al \cite{126} showing that copper-depletion in the zone adjacent to grain boundaries is the cause of IGC, where the copper content at the depleted zone was found to be approximately 0.2 wt\%. However, the measurement of pitting potentials for grain boundary and grain body regions in aged AA2024 aluminium alloy, by Urushino et. al \cite{123}, showed the values of -650 and -610 mV_{SCE} respectively. Another study reported that the intergranular corrosion of Al-Cu alloys is attributed to the difference in corrosion potential between the matrix and the grain boundaries \cite{95, 114, 123}.

\subsection*{2.5.8 Exfoliation corrosion}

Exfoliation corrosion is a form of intergranular corrosion associated with high strength aluminium alloys. Alloys that have been extruded or otherwise worked intensively, with a microstructure of elongated grains, are mostly prone to this damage \cite{127}. In exfoliation corrosion, a separation or detachment of non-corroded layer or layers from the bulk alloy occurs due to the action of the volume of the corrosion products at the interface of the separation \cite{128}. It was suggested that the initiation of exfoliation corrosion is related to the breaking down the passive film \cite{13}. AA2xxx, AA5xxx, and AA7xxx alloys with elongated microstructure have high susceptibility to exfoliation corrosion while aluminium alloy series AA1xxx, AA3xxx and AA6xxx have excellent resistance to exfoliation corrosion \cite{13, 93, 128}.

\subsection*{2.5.9 Stress corrosion cracking (SCC)}

Stress-corrosion cracking is brittle in macroscopic appearance within the material. SCC initiates due to the combination of tensile stress (applied or residual) and specific aggressive environments, such as halides ions even in a small concentration. However, dry air and nitrogen prevent SCC development \cite{10, 13}. The effect of an electrolyte is to cause the metal to fail prematurely at lower stresses due to stress-corrosion cracking,
as indicated in Figure 2.14. Both film rupture and anodic dissolution take place in the process of SCC in AA2xxx aluminium alloys \cite{129}. However, anodic dissolution and hydrogen-induced cracking occur in the mechanism of SCC in AA7xxx aluminium alloy \cite{93}. Compression stress tends to decrease susceptibilities to SCC, because it acts as a crack closer, conversely tensile stress accelerates the crack opening \cite{130, 131}. SCC can be minimised by relieving of residual stress, avoiding applied stress as well as by reducing the precipitation of second phase particles at the grain boundaries \cite{128}.

![Figure 2.14: Schematic diagrams of four stages in the initiation of stress-corrosion cracks which takes place in an intergranular corrosion cracking form. $\sigma$ denotes the direction of applied stress and the fourth stage is the propagation stage.](image)

**2.5.10. Other forms of corrosion**

Pitting corrosion, IGC, SCC and exfoliation corrosion are the areas of concern in this research. Though still other forms of corrosion, such as uniform corrosion, crevice corrosion and de-alloying, can cause damage to the alloys under specific conditions.
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2175.


Chapter 3

Literature Review Part II

Laser Surface Engineering

3.1 Introduction

The first part of this chapter focuses on the fundamentals of lasers and laser beam interactions with materials, and gives a brief introduction to laser surface engineering, with an emphasis on laser surface melting. The second part presents a literature review of laser surface melting of various aluminium alloys for the improvement of corrosion resistance. The factors affecting the corrosion properties of laser-melted surfaces are discussed by considering the types of lasers applied and the category of aluminium alloys treated.

3.2 Lasers

LASER stands for Light Amplification by Stimulated Emission of Radiation \(^1\). A laser is made of three components, i.e. a laser medium, a pumping source and an optical resonator, as shown in Figure 3.1.

![Figure 3.1: Basic components of a laser system.](image)

Laser radiation occurs when a medium undergoes transition from higher to lower energy levels emitting photons that excite other photons. Each photon has an energy \( hv \), where \( h \) is Planck’s constant with value equal to \( 6.626 \times 10^{-34} \) J s and \( v \) is the frequency. Stimulated emission takes place as photon numbers increase with the
same characteristics of the original photons, stimulating other emission of photons with coherency (same frequency and direction) as shown in Figure 3.2.

Figure 3.2: (a) Spontaneous emission, (b) stimulate emission and (c) absorption \(^2\).

Stimulated emission is a release of photons from decaying electrons from a higher to a lower state. In the laser, electrons are reserved in higher state with more numbers called population inversion. Population inversion is essential for the emission process and provided by an external pumping source. The emitted radiation is the amplified by a resonator. A resonator is made of two mirrors; one is a total reflector on one side of the cavity and the other mirror is a partial reflector on the other side (see Figure 3.1). This allows an appropriate fraction of the radiation out as a parallel beam, while the rest is circulating within the cavity to maintain the laser action \(^2, 3\). Characteristics of the laser beam, such as wavelength, pulse width, and energy, depend on the type of laser medium.

3.3 Categories of lasers

Many types of lasers are available, but only a small number of lasers are useful for surface treatments of materials. Lasers can be classified into solid-state lasers, gas lasers, diode lasers and others, as listed in Table 3.1.

3.3.1 Solid-state lasers

Generally, solid-state lasers are characterised by a solid active medium material. There are many types of solid state lasers with wide range of wavelengths. Nd:YAG (Neodymium: Yttrium-Aluminium Garnet) laser of a wavelength in the near infrared at 1064 nm, Ruby laser of a wavelength in the visible light at 694.3 nm.
3.3.2 Gas lasers

A gas laser is a laser in which an electric current is discharged through a gas to produce coherent light. Electrons in a discharge transfer energy to atoms or molecules in a laser gas, typically through at least one intermediate step. Then excited gas emits radiation that resonates within a laser cavity and emerges to form a laser beam (e.g. CO$_2$, Excimer).

3.3.3 Semiconductor lasers

For a semiconductor laser, the active medium is a semiconductor. The most common type of semiconductor laser is the diode laser, which is formed from a p-n junction and powered by injected electric current. The current flows in the radiation direction through a junction between two segments of semiconductor with different doping. Electrons are raised into excited states so that radiation is emitted.

Other types of lasers include X-ray lasers, Fibre lasers, Tunable Dye lasers and Free-electron lasers.

3.3.4 Laser classification

A laser can be classified as operating in either a continuous or a pulsed mode. A laser with CW mode of operation has a stable and continuous pump source to maintain the required population inversion for lasing. In pulsed lasers, output power varies with time. The pulse energy can have a great effect on a surface if kept at a given place for a period of time. On the other hand, if the same energy is spread over longer time, the energy will have less effect. A number of techniques have been used to achieve laser pulses such as mode locking, Q-switches and electric switching.

**Mode locking**: in mode locking, pulses are separated by the time that a pulse takes to complete one round trip in the resonator cavity. Such a pulse of short temporal length has a spectrum, which contains a wide range of wavelengths. As a result of this, the laser medium must have a broad enough gain profile to amplify them all. The emitted short pulses are of duration of the order of tens of picoseconds down to less than 10 femtoseconds.

**Q-switching**: in a Q-switched laser, when the population inversion is produced in the same way as in a CW laser, is left to build up in the cavity and the pumped energy is
stored in the laser medium. The high energy is released in a pulse with short time duration. This pulse is characterized by high power.

3.4 Main types of lasers used in material processing

3.4.1 CO\textsubscript{2} Lasers-the gas laser

CO\textsubscript{2} laser works with a mixture of CO\textsubscript{2}, N\textsubscript{2} and He gases. When electrically discharged, nitrogen molecules vibrate and get excited to a meta-stable state which is close to the energy state of CO\textsubscript{2}, and excitation of molecules occur by collision with the excited nitrogen molecules. The collisions are enhanced by the presence of helium. The decay of molecules produces a laser beam with a wavelength of 10.6 µm. The output power can reach up to 25 kW, which is much needed in the field of material processing. However, the CO\textsubscript{2} laser suffers from high reflectivity by metals which require graphite or sand blasting of the surface of materials for absorption enhancement.

3.4.2 Nd:YAG lasers

The solid state laser works with a lasing medium consisting of a neodymium ions doped in yttrium aluminium garnet, Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} crystal. These lasers are optically pumped either by flash lamp or a diode laser. The Nd:YAG crystal has four energy levels. The molecules in the ground state are excited by absorbing light from the pumping source and excited to the upper state (the fourth energy level), with the decay lead to lasing. The Nd:YAG laser wavelength is in the near infrared region, with a value of 1.06 µm, and it can operate in both pulsed and continuous mode where the former uses Q-switching mode.
### Table 3.1: Typical lasers for industrial applications \[^4\]  

<table>
<thead>
<tr>
<th>Type of lasers</th>
<th>Wavelength</th>
<th>Average power</th>
<th>Operating mode</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid state lasers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd:YAG laser</td>
<td>1.06 µm</td>
<td>1 W - 8 kW</td>
<td>Continuous and pulsed modes</td>
<td>Materials processing (welding, drilling, trimming, marking), medicine, Spot welding, drilling</td>
</tr>
<tr>
<td>Ruby laser</td>
<td>0.6934 µm</td>
<td>Up to 300 W</td>
<td>Pulsed mode</td>
<td></td>
</tr>
<tr>
<td><strong>Gas lasers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ laser</td>
<td>10.6 µm</td>
<td>1 W – 25 kW (100 MW in pulsed mode)</td>
<td>Continuous, pulsed modes and TEA</td>
<td>Materials processing (welding, drilling, heat treating), medicine, isotope separation</td>
</tr>
<tr>
<td>Excimer laser</td>
<td>193 nm, 248 nm, 308 nm (and others)</td>
<td>Up to 1 kW</td>
<td>Pulsed modes</td>
<td>Micro-machining, laser chemistry, medicine</td>
</tr>
<tr>
<td>HeNe laser</td>
<td>632.8 nm (most prominent)</td>
<td>1 mW - 1 W</td>
<td>Continuous</td>
<td>Measurement holography</td>
</tr>
<tr>
<td>Argon ion laser</td>
<td>515, 458 nm (several)</td>
<td>1 mW - 150 W</td>
<td>Continuous and pulsed</td>
<td>Printing technology, pumping laser for dye laser stimulation, medicine, semiconductor processing</td>
</tr>
<tr>
<td>Dye laser</td>
<td>Continuous between infrared and ultraviolet (different dyes)</td>
<td>1 mW - 1 W</td>
<td>Continuous and pulsed modes</td>
<td>Measurement, spectroscopy, medicine</td>
</tr>
<tr>
<td><strong>Semiconductor diode lasers and fiber laser</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diode pumped laser</td>
<td>Infrared</td>
<td>up to 6 kW</td>
<td>Continuous and pulsed modes</td>
<td>3D welding, heavy industry applications (welding and cutting)</td>
</tr>
<tr>
<td>Fibre laser</td>
<td>Infrared</td>
<td>100 kW</td>
<td>Continuous and pulsed modes</td>
<td>“On ship” cutting &amp; welding, “in field” concrete &amp; rock cutting</td>
</tr>
</tbody>
</table>

### 3.4.3 Excimer lasers

Excimer lasers are gas discharged lasers, which emit pulses of 10 ns to 50 ns in the ultraviolet (UV) region. They are considered the most dominant lasers in the UV with their wide applications. Depending on the gas mixture, atomic transitions from
different gases are used to generate light pulses at various wavelengths as shown in Table 3.2.

Table 3.2: Types of excimer lasers [5].

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Active Gas</th>
<th>Relative Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>Argon fluoride</td>
<td>60</td>
</tr>
<tr>
<td>248</td>
<td>Krypton fluoride</td>
<td>100</td>
</tr>
<tr>
<td>308</td>
<td>Xenon chloride</td>
<td>50</td>
</tr>
<tr>
<td>351</td>
<td>Xenon flouride</td>
<td>45</td>
</tr>
</tbody>
</table>

The word excimer stems from two words, excited (molecules in the excited states) and dimer, two atoms form a molecule (diatomic molecule formed from two different gases) [6]. A mixture of a noble gas such as argon, krypton, or xenon and a halogen gas as fluorine or chlorine, is electrically discharged, stimulating molecules to higher levels, as illustrated in Figure 3.3, emitting coherent stimulated laser beam in the ultraviolet region of the spectrum light.

![Excimer (KrF) energy levels](image)

The energy is contained in a single pulse, and measured in millijoules (mJ). Excimer lasers range from a few mJ’s to 1000 mJ. A practical power output of the use of excimer lasers can be obtained by the use of number of pulses per second, which is also called the repetition rate. The average output power is the product of energy per pulse and the repetition rate [5].

**Pulse duration**: Pulse duration is the full width of a temporal pulse at half maximum and usually denoted by FWHM.
Each pulse contains energy $E_{\text{pulse}}$ (Joule) for a train of pulses with repetition rate $f$ (Hz) (frequency).

$$E_{\text{pulse}} = \frac{P}{f} \quad (3.1)$$

Where $P$ (W) is the average power defined as the energy per repetition rate. The peak power is the energy within a single pulse

$$P_{\text{peak}} = \frac{E_{\text{pulse}}}{\Delta t} \quad (3.2)$$

As an example, an energy of 40 mJ for an excimer laser operating at 500 Hz produces 20 W as an average power.

The advantages of excimer lasers such, as short wavelength with high photon energy focused in small spot size with high peak power, is that they can be efficiently used in the material engineering with high reduction of heat affected zone. Their laser radiation can be absorbed by most of industrial materials, even by materials with high reflectivity such as aluminium. Metals have a high reflectivity, because of their radiation of excess energy during interaction with light. Nevertheless, lasers with short wave length generate photons with high energy which can be absorbed by greater number of electrons, lowering reflectivity and enhancing absorptivity of a metal surface.

An excimer laser with high photon energy of 5 eV coupled with 248 nm wavelength, can effectively melt the surface of aluminium alloys up to a depth of 14 µm$^{9,10}$. This is done with smaller heat affected zones and much faster cooling rates without affecting the bulk material. Such an effect is not achieved by thermal interaction of longer wavelength lasers as in Nd:YAG laser, or CO$_2$ lasers as shown in Figure 3.5.
3. Literature Review Part II

3.5 Laser beam interaction with materials

3.5.1 Beam absorption

When a laser light strikes a metal surface, part of the radiation is reflected and the remaining is absorbed into a material surface. The attenuation of light in the material is caused by electron transition excitation. The absorption process is governed by the nature of the interaction between the laser light and the material type. The absorbed light propagating through a medium is given by the Beer-Lambert equation:

\[ I(x) = I_0 \exp(-\alpha x) \]  

(3.3)

Where \( I_0 \) is the intensity at \( x = 0 \) and \( I(x) \) is the intensity after a distance \( x \).

Since the medium is characterised by refractive indices \( n \) and \( k_a \), thus the attenuation coefficient is given by

\[ \alpha = 4\pi k_a / \lambda \]  

(3.4)

At ultra-violet wavelengths, transparent materials have \( \alpha < 1 \) cm\(^{-1}\), while metals have \( \alpha = (2-3) \times 10^6 \) cm\(^{-1} \) \([7]\). The inverse of this value \( \alpha^{-1} \), can give the penetration depth of the laser radiation \([7]\).

Besides wavelength, laser light is also characterised by surface radiation. Roughness, temperature, presence of oxide layers is important in determining the coupling of the laser radiation to solid material \([7]\). For light absorption through a medium, the interaction between the photons and electrons causes vibrations of the lattice to generate heat and temperature rise within a thin layer of the surface.
Generally, materials with low absorption of laser radiation are characterised by high conductivity. Thus, metals such as aluminium, copper and silver with high conductivity have higher reflectivity compared with metals like carbon steels as shown in Figure 3.6 (a) \[^1\]. However, the reflectivity is reduced significantly at short wavelengths (ultraviolet region), such as wavelengths of excimer lasers. A decrease in reflectivity is accompanied with a rise of surface temperature and absorptivity is enhanced, as shown in Figure 3.6 (b). As the surface temperature rises, the phonon population increases, resulting in more phonon–electron energy exchange. This exchange in energy gives electrons a high probability of interacting with the structure rather than oscillating and re-radiating \[^1\].

The relationship between absorptivity and reflectivity in metals can be obtained by using the equation

\[ A = 1 - R \] \hspace{1cm} (3.5)

A is the absorptivity and R is the reflectivity. Since metallic materials are opaque, the complex refractive index, \( m = n - ik_a \) is considered. The reflectivity at normal incidence can be expressed by \[^1\]:

\[ R = \frac{[(n -1)^2 + k_a^2]/(n + 1)^2 + k_a^2} \] \hspace{1cm} (3.6)

since \( A = 1 - R \)

\[ A = \frac{4n}{(n + 1)^2 + k_a^2} \] \hspace{1cm} (3.7)
For metallic materials, $n$ and $k_a$ are functions of wavelengths and temperature. They are relatively slow varying functions of wavelength $\lambda$ over the range $0.4 < \lambda < 1.0 \mu m$. In this range, the absorptivity is higher. For laser beams used for metal processing with longer wavelength, both $n$ and $k_a$ increase rapidly with $\lambda$, which means a decrease in the absorptivity. Hence, as mentioned earlier, lasers with short wavelengths are more absorbent by metallic materials than lasers with longer wavelengths such as CO$_2$ lasers. Commonly used metals in laser materials processing with their absorptivity of different types of lasers are shown in Table 3.3.

Table 3.3: Absorptivity of various metals for various type of lasers

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ar Laser (0.5 µm)</th>
<th>Ruby laser (0.7 µm)</th>
<th>Nd-YAG laser (1.06 µm)</th>
<th>CO$_2$ Laser (10.6 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>0.09</td>
<td>0.11</td>
<td>0.08</td>
<td>0.019</td>
</tr>
<tr>
<td>Copper</td>
<td>0.56</td>
<td>0.17</td>
<td>0.10</td>
<td>0.015</td>
</tr>
<tr>
<td>Gold</td>
<td>0.58</td>
<td>0.07</td>
<td>-</td>
<td>0.017</td>
</tr>
<tr>
<td>Iron</td>
<td>0.68</td>
<td>0.64</td>
<td>-</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Moreover, for wavelengths longer than 5 µm, reflectivity is more dependent on the material electric conductivity. The refractive index for a metal is proportional to

$$(\sigma_e / 2\pi \mu_m \nu)^{1/2}$$

(3.8)

Where $\sigma_e$ is the electric conductivity and $\mu_m$ is the magnetic permeability.

In order to increase laser radiation absorption of some high reflective metals, such as Al or Cu, it is very common to apply a thin coating of highly absorbing material on the surface of the metal, such as graphite.

Effect of surface conditions

The surface roughness has a significant effect on absorption, due to the multiple reflections in the undulations. To stimulated absorption, sandblasted or ground surfaces are used to develop greater energy coupling compared with smoother surfaces. Furthermore, the presence of an oxide layer increases laser beam absorption, particularly for iron and steels that exhibit darkened oxidised surfaces. The effect of temperature on the absorption of beam energy is evident, where the degree of laser beam absorption can varies with temperature of materials. For
example, an increase in temperature of a workpiece results in increased laser beam absorption.

### 3.5.2 Laser-induced heating/melting process

As mentioned above, an absorption can play a dominate role in laser materials processing. When the laser energy is absorbed at the surface through photon interaction with metal, electrons in the conduction band are left with increased kinetic energies, which cause collisions with lattice molecules and excite lattice phonons to higher energies. The electron excess energy gain from both the laser and the number of collisions result in a high temperature \(^{[13, 14]}\). Since the mean free collision time in the process of energy transfer is \(10^{-12} \text{ to } 10^{-14} \text{ s}\) \(^{[15]}\) with laser pulse width is in the range \(10^{-6} \text{ to } 10^{-12} \text{ s}\), then the absorbing electrons can have sufficient time to undergo many collisions, that involve phonons, electrons, ions and defect structure resulting in a complex heating pattern \(^{[12, 16]}\). The laser energy is instantly converted to heat once the absorption took place. Thermal diffusivity \(\alpha\) \([\text{m}^2/\text{s}]\) can be expressed by the following equation:

\[
\alpha = k_\tau / \rho_1 C_p
\]  \hspace{1cm} (3.9)

Where \(k_\tau\) is the thermal conductivity \([\text{J/s m K}]\), \(\rho_1\) is the density of the material \([\text{kg/m}^3]\) and \(C_p\) is the specific heat \([\text{J/kg K}]\).

Materials with higher thermal diffusivity require longer time for surface temperature to rise \(^{[13]}\). However, Yilbas \(^{[17]}\) analytical solutions for the heat conduction mechanism concluded that, time at which the maximum temperature occurs is a function of pulse parameters and not of material properties. The latter become important in the case of a short laser pulse in the range of \(10^{-9} \text{ s}\). Besides, surface maximum temperature is independent on the absorption depth, where its absorption dependency was in the initial stages of the pulse.

### 3.6 Laser surface engineering

The laser surface engineering involves the use of high-power laser beams to heat a material to a required temperature, followed by a rapid cooling as a result of heat conduction to the bulk. By means of laser surface engineering techniques, materials may have their surface microstructure and chemical composition modified, as a
result of properties such as wear, friction, corrosion, hardness, abrasion, oxidation resistance and electrical conductivity are altered. Furthermore, the laser energy can be used to change the surface characteristics of a material, such as laser transformation hardening in laser melting. The thickness of the modified layer can covers a range from nanometres to millimetres.

3.6.1 Laser processing parameters

In laser surface engineering, a laser beam interaction with a material surface can depend on several factors, for example wavelength $\lambda$, power density (for a CW laser), energy density (for a pulsed laser) and interaction time. Both power density and energy density depend on beam dimension of radius $r_b$. When traverse velocity is $v$ and beam spot size of $r_b$, the laser beam interaction time $2r_b/v$ (for CW laser beam) in a combination of power density and beam size determines maximum surface temperature and the melt depth. An increase in velocity decreases interaction time and lead to a lower surface temperature and shallower melt depth under the same power density and beam dimension$^{[18]}$. The variation in the input energy density leads to control the depth of the melt pool and hence, the control the volume of the molten material. Other important factors are the thickness of the work-piece and its surface absorptivity of the laser energy.

In practice, there is often a requirement to produce surface modification over a large area. Partial overlapping of the laser melted tracks can be applied to cover a large area of the surface. The overlapping can be up to 50%. However, overlapping of laser tracks can develop heat build up in the work-piece, resulting in re-heating of part of previous track, leading to different microstructural changes within the re-heated regions and porosity developments.

3.6.2 Various physical processes in laser surface engineering

As discussed earlier, the laser material processing is controlled by two laser operating parameters, i.e. laser power density and interaction time. The combination of these two parameters leads to the characterisation of materials processing as heating, melting and vaporisation as shown in Figure. 3.7.
3. Literature Review Part II

Figure 3.7: Description of laser materials processing map against power density and interaction time [19].

3.6.2.1 Heating

Heat-treatment of materials normally refers to the processes in which the temperature of materials does not exceed their melting temperature. Heating by the laser mainly includes a transformation hardening and an annealing. A laser transformation hardening is a solid state transformation process that occurs on the surface, for instance, if steel is heated above a transformation temperature to form austenite without being melted followed by subsequent rapid cooling, martensite is formed. The advantages of using a laser as a hardening tool lies in the possibility of a local treatment with: (i) a minimum heat input to the substrate, (ii) less thermal distortion and (iii) a relatively shallow depth of hardening, without affecting the desirable properties of the substrate metal, such as toughness. However, for large surface area treatments, the overlapping is used and can result in re-heating part of the previous track. This tempering effect leads to hardness reduction to form hard and soft regions alternatively.

3.6.2.2 Melting

By increasing the power, the material changes phases via changing in atoms mode from vibrating in the solid crystal to a state of free rotation and melting occurs. The laser surface melting (LSM) is characterised by the absence of the incorporation of any additional alloying elements to provide property enhancement of the surface layer. On the other hand, laser surface alloying (LSA) and laser surface cladding
LSC involve melting and mixing of added materials within the molten pool. These processes produce a surface layer having a chemical composition and properties different from those of the substrate material. The major difference between LSA and LSC is the dilution, where dilution in laser cladding is normally controlled within 5%, while the one in laser alloys is much higher.

Since this thesis only involved with surface melting process, LSM is discussed in details in the next section.

3.6.2.3 Vaporisation

When energy is further increased, surface of materials reaches boiling temperature to be vaporised and or even form plasma where plasma temperature can reach $10^8$ K \cite{17,18}, particularly when there is an inert gas around. This vaporisation process can be used for welding, drilling and other processes, which are not the subject of this thesis.

3.7 Laser surface melting

Since laser beam can be focused to a very small spot size generating extremely high power density, the laser beam can provide a rapid heating rate up to $10^{11}$ K s$^{-1}$ on the surface \cite{19-21}. Once absorption takes place, heat conduction is generated and surface temperature rises. The material starts to change phase entering into a liquid phase. As the melting arises, the thermal conduction, convection and transfer of energy within the material take place. The region near surface, rapidly reaches its melting point, a liquid/solid interface starts to move through an alloy and diffusion of elements commences in the liquid phase. A melt goes beneath the surface forming a melt pool and the maximum melt depth has been attained at this stage. As the laser beam moves away an instant cooling process initiate through self-quenching to form non-equilibrium structures where compositions have insufficient time for diffusion or precipitation \cite{4,23}. Solidified metal behind the liquid/solid interface cools so rapidly that solid state diffusion may be negligible and inter-diffusion continues. As the initiation of solidification starts, interface velocity is momentarily zero at region of maximum melt depth and then rapidly increases and moves up towards the surface \cite{24}. Fast cooling rates occur as a result of the substrate acting as heat sink. Therefore, a relatively thin melted layer is formed with thickness from few microns up to
The high cooling rates result in the formation of refined microstructure, reduced microsegregation, extensive solid solubility and formation of metastable phases, hence, laser surface melting is used to alter material surface properties through rapid solidification. Different types of lasers provide varieties of processing capabilities with a wide range of processing parameters available to be selected to suit materials property modification. The inhomogeneous structure of untreated surfaces of aluminium alloys suffers from microsegregation in a relatively thin oxide layer, which plays an important role in initiation of pitting corrosion. It is generally accepted that, the improvement in corrosion performance is attributable to the formation of more refined and homogenous microstructure and dissolution/redistribution of intermetallic particles, which result from rapid solidification \(^4\) that made the formed protective oxide film (\(\alpha\-\text{Al}_2\text{O}_3\)) homogenous and chemically stable, protecting the matrix from corrosion. Furthermore, aluminium alloys characterized with high conductivity and high reflectivity to laser, Therefore, laser process parameters must be carefully selected in order to achieve satisfactory results. An excess of surface heating can result in vaporisation of the material, leading to plasma formation which damage the surface with surface roughness affecting corrosion resistance \(^{26, 27}\).

### 3.8 Morphological formation by rapid solidification theory

#### 3.8.1 Introduction

The rapid solidification of alloys has an immense effect on surface properties of the material and can greatly influence their performance in practical applications \(^{28}\). As consequence of high cooling rate, refined microstructures, extended solid solubility, micro-segregation, free crystals and new metastable phases can take place, leading to an increase in corrosion resistance of the materials \(^{28}\). At extremely high cooling, formation of micro-segregation-free structure is possible. This has drawn specific interest by researchers because dendrites and eutectic microstructure can no longer form in the presence of high growth rates at velocity beyond the absolute velocity, as partition coefficient reach unity. For this reason, understanding of the structured transformation through the effect of rapid solidification is required. A considerable amount of work \(^{28, 29-35}\) was carried out to gain the understanding of the solidification processing variables such as alloy composition (\(C_0\)), temperature
gradient (G) and growth rate (V) in relation to the resulted solidified microstructure of its nucleation, solidification, morphology front, type and amount of phases, micro/macro-segregations and its microstructural geometry [28,36]. This can guide to the prediction of resulting microstructure in terms of grain size, shape, distribution and extent of segregation.

3.8.2 Solidification variables

As result of laser surface melting, liquid is formed and then solidified. It is well known that, a distribution of a solute occurs as the crystal solidifies from a melt of impure metal or alloy [34]. In all solidification processes starting with nucleation and continuing with growth, the main role of nucleation is to permit the development of large volume under cooling of liquid into which growth can occur quite rapidly [37]. Formation of a solid in a liquid begins with an initiation of the nucleation process followed by the growth of atoms from the liquid attached to the solid [38]. These are controlled by:

i) Thermal gradient (G) across solid/liquid interface

ii) Under-cooling is defined as the driving force of solidification resulted from the rapid cooling of the liquid at liquid/solid interface.

iii) Interface growth rate (V).

Before solidification takes place, a liquid undergoes a quick temperature drop below the freezing point. This is called thermal under-cooling. In the case of alloys, a composition change may occur due to such temperature drop. This would be compatible with liquids alloy compositions required temperature, leading to constitutional under cooling. Therefore, constitutional under cooling greatly affect the resulted solidified microstructure. This effect is related to the thermal gradient $G$ of both solid and liquid at the interface, where the thermal gradient control the interface stability and morphology. In addition, a convective flow can disturb a liquid within a melt-pool, in response to thermal gradient which in return affects the solidified structure.
3. Literature Review Part II

3.8.3 Influence of convection on the homogeneity of the LSM melt-pool

A convective flow in the laser melted pool is caused by a large difference between temperature of the surface at the centre and at edges of the melt-pool. The maximum surface temperature is at the centre and the minimum is at the edges \[^{41, 42}\]. Fluid flow during laser melting can influence solute distribution in the liquid and structure of the solidified material \[^{40}\].

The convection in the melt pool plays a major role in the process of solidification where it can influence the geometry of the pool, pool shape, undercut and ripples. It can also result in defects such as porosities and lack of fusion. Convection is also largely responsible for mixing and effecting the composition of the melt pool. Heat transfer and cooling rate are greatly enhanced in the presence of convection \[^{39}\]. The homogeneity of solute redistribution during laser surface melting can only be explained by the presence of convection currents within the pool \[^{40}\].

Srinivasan and Basu \[^{41}\] suggested that Reynolds number and Prandtl number should reveal the nature of the flow during laser melting. When Reynolds number is large or the fluid has high Prandtl number, temperature field is greatly influenced by convection otherwise conduction governs and the convection plays a minor role. In pure liquid metals, surface energy increases with decrease in temperature, this gives an outward directed flow at the surface \[^{73}\]. The flow descends at the edges of the melt pool towards the bottom and it rises again in the middle of the pool as seen in Figure 3.8. At surfaces, temperatures are much higher than in the lower parts of the melt pool \[^{44, 45}\].

![Figure 3.8: Schematic diagram of convective flow working as a mixer in the melt pool \[^{44}\].](image)

Some authors \[^{45, 47}\] suggested that convective flow works as a perfect mixing in the melt pool. Mixing of solutes due to convection will tend to level solute concentration in a liquid \[^{34}\]. In case of alloys where a solute layer starts to accumulate at the
interface, convection must be extremely rapid to remove a high solute concentration formed adjacent to a growing interface before it solidifies \[^{34}\]. Particles in solute travel in a rather long path before they freeze into re-solidifying surface. As result, molten material can be well mixed leading to a uniform distribution of composition within the melt pool \[^{39}\]. This compositional change is accompanied by temperature change resulting in a variation of surface tension across the melted pool \[^{42}\].

The presence of strong convection can help in the process of refinement of re-solidified microstructure through enhancement of mass transfer at solid-liquid interface. This can reduce solute boundary layer thickness, leading to the decrease in the length of the columnar dendrite zone, favouring equiaxed crystals \[^{48}\], as it will be described in more details in the next section. Mehrabian et al \[^{49}\] studied the relationship between microstructure and fluid flow patterns using a CO\(_2\) laser beam with a power density of \(10^6\) W cm\(^{-2}\) on aluminium-copper alloy. The results of the structure analysis showed the existence of strong convection at the middle of the melt pool. However, if there is insufficient time for this to be complete, a layer or layers of frozen solute appear in the solidified structure after re-solidification \[^{44}\].

### 3.8.4 Constitutional Under-cooling theory

Principle of constitutional under-cooling was first presented by Tiller et al \[^{34}\], and conditions of planar growth with equilibrium partitions was predicted. Stability condition for the interface is at equilibrium temperature. Temperature of a liquid in front of the solid/liquid interface must be above the liquidus in order for a stable plane front solidification to preserve. For example, if protrusion occurs on the flat surface as result of the instability of the interface it will be in superheated surrounding and the protrusion melts back to a flat front. This can only occur in pure substance, because of the absence of solute effect. Hence, the thermal gradient controls the stability of the interface \[^{26,50}\]. Conversely, in unstable interface front, temperature of a solute which was rejected from the solid, because of its low solid solubility, piled up in front of the interface with lower temperature (this temperature was gained from the solidified surrounding before rejected to the solid liquid interface) below the equilibrium liquidus temperature. This creates instability in a liquid region near the interface by making the surrounding in a super-cooling condition. Hence, this is called constitutional under cooling and can only occur in a
multi-component system such as alloys. Moreover, in constitutional under cooling crystal growth and morphology are controlled by elemental diffusion where in thermal cooling is controlled by heat flow \(^{[50]}\). Therefore, it is the constitutional under-cooling which influences the solidification microstructure in alloy solidification.

During solidification, solute is rejected in front of the solid/liquid interface due to low solubility of the solute in the solid solution. This leads to piling up of the solute ahead of the solidified front. As composition changes ahead of the solidification interface, temperature must be less than or equal to the solidus temperature \(T_s\) in order for gain growth to occur, creating under-cooling zone. Since the liquid is ahead of the solidification front which exist below its freezing temperature, this zone is the constitutional under-cooling region or zone, as indicated in Figure 3.9 (a-b) \(^{[51]}\) where the ratio \(G/V\) controls planar interface stability.

![Figure 3.9: Constitutional super-cooling, with super cooling arisen from compositional effects. (a) Profile of the composition across the solid/liquid interface. (b) Liquid temperature ahead of solidification front follows line \(T_L\). The constitutional super-cooling arises when \(T_L\) lies under the critical gradient \(^{[51]}\). (c) Constitutional diagram for a solute which lowers the freezing point of the solvent \(^{[34]}\).](image)

\(G/V\) ratio is expressed by the following equation:
3. Literature Review Part II

\[ \frac{G}{V} \left( \frac{m_{L}C_{x}}{D_{L}k_{c}} \right) \left( k_{c} - 1 \right) \]  \hspace{1cm} (3.10)

Where \( G \) is the thermal gradient, \( m_{L} \) is the slope of liquidus vs concentration line, \( C_{x} \) bulk solute concentration, \( D_{L} \) is liquid diffusion constant and \( k_{c} \) is equilibrium distribution coefficient.

Since the rate of solute rejection is proportion to the growth rate, the rejected solute must be carried away by diffusion control represented by the distribution coefficient. While the driving force for the solidification is the heat flux, the temperature gradient increases and the liquid concentration \( (C_{L}) \) decreases with distance from the interface accompanied by an increase of liquid temperature \( (T_{L}) \) as shown in Figure 3.9 (a) and 3.9 (b).

Furthermore, during the formation of a single phase, there is a difference in the equilibrium concentration of the solute between the solid and the liquid at the interface with a ratio of solid to the liquid denoted by \( k \), where \( k = C_{s}/C_{L} \) [34]. This ratio is called equilibrium partitions or more common distribution coefficient as expressed diagrammatically by Figure 3.9 (c).

During the formation of the first protrusion, alloy solute rejection occurs at the interface front. Because of deficiency in redistribution of the rejected solute which causes supper-cooling environment, leads to triggering the formation of other protrusions. For example, if interface instability develops, a first protrusion forms in a super-cooling environment, followed by formation of other protrusions. Protrusions grow faster than the surrounding solid and develop into long arms or cells growing parallel to the direction of heat flow as illustrated in Figure 3.10.
Figure 3.10: A planer front breaks down as protrusions form on it and grow faster as result of constitutional super-cooling forming columnar [51].

They will grow faster than the surrounding solid and develop into long arms or cells uniformly spaced growing parallel to the direction of heat flow as illustrated in Figures 3.11 (a) and 3.12 (b) where the spacing is related to the cooling rate.

Figure 3.11: Illustration of (a) planar growth and (b) cellular growth in a constitutional super-cooling process [51].

With an increase of growth rate, $G/V$ ratio passes through several critical values where the growth undergoes a mode change [52, 53]. Therefore, cellular growth occurs at higher cooling rate than planar growth. Cell spacing of cellular growth is related to the cooling rate. An increase in cooling rate causes a decrease in size cell. Cellular grain growth direction is controlled by heat flow with limited influence of crystallography. As cooling rate gain momentum, the influence of the crystallography is increased with a fast growth of directions, leading to the transition from cellular to dendrites as shown in Figure 3.12.
Further increase in growth rate results in dendritic growth which is influenced by the crystallography, where two forms of dendrite exist in columnar and equiaxed. Growth of columnar dendrites is parallel to each other along crystallographic direction without influence of heat flow. For equiaxed dendrites, the growth grows in separate grain with different orientation from the columnar depending on crystallographic where the effect of cooling rate is inversely proportion to the dendrite arm spacing \([42]\). Since the dendrite arm spacing \(\lambda_a\) depends on the cooling rate \(U\), the relationship is defined by the following equation \([54]\):

\[
\lambda_a = a U^{-n}
\]  

(3.11)

where \(a\) is a positive constant typical of the material and \(n\) varies between one–half and one-third \([54]\). However, refinement of dendritic microstructure with an increase of cooling rate is limited, because of localization of diffusion with respect to both sizes of microstructure and to width of the interface in rapid solidification \([55]\).

### 3.8.5. Rapid solidification of microstructure formation based on constitutional under-cooling

High cooling rate means rapid growth rate, characterising rapid solidification. It increases homogeneity of re-solidified solid solution and extends its solid solubility. This phenomenon of extending solid solubility is termed as solute trapping \([29]\). Moreover rapid interface growth rate controls the formation of re-solidified microstructure and it is considered as the most important parameter in the rapid solidification process along with the cooling rate \(U = GV\).
In general, at low growth rate, evolution of microstructure obeys the well-known relationship \[ d^2V = \text{constant} \] (3.12)

Where \( d \) is either the eutectic spacing \( \lambda \) or dendrite arm spacing and \( V \) is the growth rate of the solid/liquid interface. In addition, the rate of solute rejection is proportion to growth rate, therefore the rejected solute must be carried away by diffusion a distance \( l_d \) [31].

\[ l_d = \frac{2D}{V} \] (3.13)

Where \( l_d \) is the diffusion distance and \( D \) is diffusion coefficient and \( V \) is the growth rate.

As growth rate increases, diffusion distance decreases. At extremely high growth rate (rapid cooling rate), the movement of solid/liquid interface becomes high, and certain new boundaries are reached and modification of microstructure develops [56]. As growth rate reaches critical growth \( V_c \) boundary which is of order of several centimetres per seconds [55], diffusion becomes localized with respect to microstructure, because diffusion distance becomes shorter compared with the extent of the microstructure scale. This occurs when Peclet number (\( P = Vd/2D \)) is larger than unity and equation (3.12) is no longer valid with typical growth rate. Further increase in the growth rate, the interface movements becomes higher and greatly reducing diffusion distance to a range comparable to its width which is in order of several atomic distances [29, 55]. As a result, solute atoms are frozen into solid at the same composition as it reaches to the interface. In this situation, local equilibrium is lost at solid/liquid interface and the solute is trapped. When growth rate of interface reaches velocity of sound, upper limit is reached and growth at velocity of order of \( 10^3 \) m/s [55, 57], as illustrated in Figure 3.1.
Figure 3.13: Range of growth rates in normal and in rapid solidification processing $^{[55]}$.

An example for a solute trapping is what occurs in rapid solidification induced by laser surface melting that is characterized by high cooling rates and large undercooling.

In laser surface melting, the interface $V$ increases rapidly from zero at the bottom of the pool to the maximum at the surface. Since $V$ is zero at the bottom of the melt pool (as solidification is initiated), the thermal gradient $G$ has the highest value and is strongly dependent on the absorbed power $^{[53]}$. As the growth velocity $V$ of an interface increases from near zero to large values under the condition of positive temperature gradient, where heat flows from the melt into the solid, a great variety of solidification front morphologies develop in an alloy. Plane front, cells, dendrites, cells, bands and plane are produced in sequence $^{[30, 31, 50, 55-58, 59]}$, as shown in Figure 3.14 and Figure 3.15 with respect to the growth velocity of the interface where the rapid solidification covers the range from $10^{-2}$ to $10^{3}$ m/s of growth rates.
Figure 3.14: A schematic illustration of the sequence of morphologies resulting for solidification process, where transformation of microstructure is a function of solidification rates [60].

Figure 3.15: Schematic interface response function diagram for plane front growth $T_p$ and dendritic growth $T_D$. Various microstructures growth with respect to an increase of growth velocity, between $V_c$ and $V_a$, cells/dendrites grow at higher temperature with stable growth. Between $V_a$ and $V_{T_{\text{max}}}$, a banded structure grow because of oscillatory instability. These microstructures can be determined by the maximum growth temperature criterion [55, 61]. Letters P, C, D and B indicate the morphologies: planar, cellular, dendrite and banded, respectively.

Once driving force of solidification is established, thermal gradient $G$ influences solidification structure and growth rate $V$ influences scale of solidification, solute distribution and under cooling. Therefore product of thermal gradient $G$ multiplied by growth rate $V$ is the cooling rate $U$ [55, 62].

$$U = GV$$

The cooling rate is an important parameter in solidification process. As a cooling rate of a melted pool increases, microstructure becomes finer. In continues lasers, cooling rate is dependent on parameters of laser beam such as energy flux, beam diameter and scanning velocity, where in pulsed lasers, it is dependent number of pulses and pulse duration [53].
For simplicity, transformation of interface morphology can be explained by considering a single-phase solidification and precipitation of additional phases is avoided. From Figure 3.15, when $V$ is small, the smooth interface growth remain planar (steady state) up to a critical growth rate $V_c$ which is defined by the constitutional under-cooling \(^{[34, 35]}\) by the equation \(^{[31]}\).

$$V_c = GD/\Delta T_0$$  \hspace{2cm} (3.15)

Where $G$ is the temperature gradient at the interface and equal to $(G_s+K_LG_L)/(K_s+K_L)$; $K_s$ and $K_L$ are thermal conductivity for the solid and the liquid respectively. $U_0$ equilibrium freezing range [K] and equal to $C_0m_{v}(k_{v}-1)/k_v$ and it represents the equilibrium liquid/solid difference at low velocities while at extremely high velocities $U_0$ approaches zero \(^{[31]}\).

Beyond the critical velocity $V_c$, the interface exhibits different morphologies, steady cellular morphology becomes unstable as the growth rate increases and dendritic patterns are developed \(^{[35]}\). For higher growth rate dendritic patterns disintegrate into rapidly moving cells. When growth rate reaches absolute value $V_a$, banded structure start to develop. According to Gill et al \(^{[63]}\) banding is caused by repeated cycling between dendritic or eutectic and plane front growth. This transition occurs very abruptly and the resulted bands are of successive light and dark in parallel to the solid liquid interface. The light bands were segregation free zones and the dark bands have cellular structure as illustrated in Figure 3.13 \(^{[63, 64]}\).
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At the growth rate of $V_{T_{\text{max}}}$, absolute stability is reached and region micro-segregation- free of plane front growth is formed. This criterion of absolute stability is independent of temperature gradient felt by the interface \[^{65}\]. The velocity of absolute stability can be simply calculated by using:

$$V_a = \frac{D U}{\Gamma k}$$ \hspace{1cm} (3.16)

Where $U$ is cooling rate, $\Gamma$ Gibbs-Thomson parameter measured in K/m, $D$ diffusion coefficient and $k$ partition coefficient.

In the region of instability, the growth rate is inversely proportional to the composition, but the absolute stability boundaries occur at growth rate that increase with an increase of composition \[^{66}\].

Figure 3.16: The banded microstructure in Al-Cu alloy system \[^{63, 64}\].

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3.9 Solidification microstructure of aluminium alloys after LSM

Laser surface melting has been applied for surface treatment of different materials for over three decades. Microstructure changes and properties produced by LSM are different from those produced by solidification by casting. In LSM process, the melt can be resolidifies with an enormous cooling rates in a range of $10^4$-$10^8$ K/s \(^{67}\) for a CW laser and it can reach up to $10^{11}$ K/s \(^{46}\) for short pulsed excimer lasers, compared with less than $10^2$ K/s in conventional solidification by casting \(^{53}\).

Aluminium alloys are regarded commercially important in many sectors of industry. In particular, Al-Cu (AA2xxx) alloys are widely used in aerospace industry because of their high strength to weight ratio and good damage tolerance. However, this series of alloys suffer from low localised corrosion resistance, particularly in an environment containing chloride ions, due to the presence of second-phase intermetallics. This makes LSM technique a potential method to be applied to generate refined solidification microstructure with dissolution of second-phase intermetallics through both extremely rapid melting and rapid solidification, to achieve improvement in their corrosion resistance. There have been some publications \(^{53, 68-79}\), applying LSM by using different types of lasers such as CW-CO\(_2\), CW-Nd:YAG and CW high power diode lasers, as well as short pulsed laser such as excimer laser, which revealed rapid solidified microstructures with extended solid solution solubility, refined microstructure and non-equilibrium phases.

Noordhuis and Hosson \(^{71}\) reported the use of 1.3 kW CW CO\(_2\) laser beam to melt the surface of 2024-T3 alloy with variation in laser scanning velocity at a fixed power density, to study the nucleation of precipitates. Finer microstructure features of cellular structure were developed during solidification. Different stages of the precipitation sequence affecting hardening behaviour after laser melting were reported.

Another important study was conducted by Munitz et al \(^{53}\) on Al-4.5% Cu-alloy using $1.5 \times 10^{10}$ W/m\(^2\) of a CW CO\(_2\) laser beam with spot size of 380 µm in diameter. The major impact of rapid solidification was the refinement of microstructure. Their results showed that interdendritic arm spacing changed from about 100 µm in the cast substrate to less than 1 µm in the re-solidified alloy with
the verification of cooling rate of $10^6 \, ^\circ C/s$. However, the convection was found not sufficiently vigorous enough to produce a homogenous melt.

Gill et al $^{[80]}$ used 1.7 kW CW CO$_2$ laser on aluminum-copper alloy with higher concentration of copper up to 28 wt.%. The microstructural analysis showed several growth morphologies under local growth velocities in which regular eutectics was at up to $\sim 0.2 \, m/s$, dendritic/cellular structures were from $\sim 0.05-0.6 \, m/s$, and band structures were from $\sim 0.6 \, m/s$. However, there were differences with respect to the microstructures previously reported by Zimmermann et al $^{[81]}$ in which at eutectic composition where the appearance of a small initial region with a cellular-like morphology at the edge of laser tracks, and the eutectic-dendritic transition at velocities in the range of 0.05-0.15 m/s.

Watkins et al $^{[82]}$ reviewed studies on the CW CO$_2$ laser surface melting of AA2014-T6 alloys containing 4 wt.% Cu. The microstructure consisted of a planar front zone and dendritic structure. These dendrites contained $\alpha$-Al matrix with either Al$_2$Cu precipitates or Al$_2$Cu-Al eutectic as interdendritic phase.

Li et al $^{[84]}$ reported that CuAl$_2$ precipitates were present but with no evidence of S-phase (Al$_2$CuMg) formation after a CW CO$_2$ laser melting of 2024-T351. This was believed to be related to vaporization of Mg during laser surface melting process.

The interpretation of micro-segregation of copper under rapid solidification observed in other studies $^{[85]}$ on AA2014-T6 alloy was linked to lower Cu concentration at the planar front zone compared to the equilibrium value. In addition, it was shown by the same authors in another study $^{[85]}$ that, micro-segregation occurred within the planar front zone of the laser melted layer and microstructural coarsening occurred in the heat affected zones caused by overlap-reheating.

Earlier study on formation of porosity in the melted layer of AA2024-T6 by using pulsed Nd:YAG laser was conducted by Kim and Weiman $^{[67]}$, at an incident energy density 440 J/cm$^2$. They suggested that the cause of porosities was as a result of the trapped internal hydrogen during LSM process of the material. The hydrogen was believed to be presented in the substrate due to manufacturing process. The hydrogen were accumulated and expanded by melting which were trapped and form porosity.
Microstructure resulted from a 3 kW CW Nd:YAG laser reported by Chong et al. [4] on AA2014-T351 alloy was described as columnar cells that had grown epitaxially from the matrix, followed by planar-front zone. It was evident that the variation in the cooling rates affected the solidification structure scale. Dendrite spacing was reduced from 5 µm at the matrix/melted layer interface (fusion boundary) to 2 µm at the surface as shown in Figure 3.17 [4].

In order to cover a large area, overlapping of individual tracks is required. This can be done at different overlapping ratio ranging from 30% to 50% in most cases. Overlapping leads to re-melting and re-heating of previous track, consequently changes in microstructures do occur. The change in microstructure for carbon steel could affect microhardness within re-heated regions due to back-tempering effect. This may influence the surface behaviour in various ways. Some manufacturers that use the laser hardening technique always specify an overlap ratio between 10 and 20% so that the soft area with minimum hardness in the overlap region between passes is around 10-20% [48]. A 30% overlap ratio by a CW CO₂ LSM of AA2024 alloy conducted by Hanna et al. [87], displayed formation of a non-uniform cellular structure on the surface. Chong et al [4, 48] reported that, microstructure with the re-melted region began with expitaxial growth from previous melted substrate and a layer of cellular structure was clearly presented between laser tracks as shown in Figure 3.17 and Figure 3.18. The layer became coarser with increase in the overlapping ratios. It was also suggested that, this coarsening may promote copper segregation. In addition the content of copper in the cellular layer was lower than in dendritic cores as more copper went into the solid solution [4].

Figure 3.17: SEM images showing the effect of variation of growth rate on the resulting microstructure from the rapid solidification process caused by 3 kW CW Nd:YAG LSM of AA2014-T351alloy [4, 48].
Yue et al. [87] used a 500 W CW CO$_2$ laser with 30 mm/s scanning speed velocity to produce a melted layer with a thickness around 300 µm. Within the laser-melted layer, coarse second-phase particles that were present in the substrate were removed and fine cellular/dendritic structures were formed within the melted layer, as shown in Figure 3.19. Micro-segregation of copper was detected at interdendritic regions as well as at the boundary between the fusion zone and the substrate.
Figure 3.20: Typical microstructure images of cell spacing variation with melted layer thickness caused by different types of pulsed lasers in LSM on 2024-T3 alloy \(^{[77]}\).

Since the solidification front accelerates from the fusion boundary towards the surface of the melt pool, the depth of the melted layer affects the growth behaviour. A study done by Ryan \(^{[77]}\) illustrated the variation of microstructure refinement that resulted from different types of lasers used in LSM processes with respect to the depth of the melted layer of AA2024-T3 alloy. The high cooling rate, such that produced by using of excimer laser, creates a thin melted layer in comparison with that created by Q-Switched CO\(_2\) laser, as shown in Figure 3.20.

This study also included a modelling for the variation of growth velocity with the melted layer depth that resulted from use of a short pulsed 308 nm XeCl excimer laser, with pulse length of 25 ns and fluence of 10 J/cm\(^2\). The results are illustrated in Figure 3.21 \(^{[77]}\) which it indicates the existence of a growth velocity value below the velocity required for planar solidification when the solidification front velocity accelerates from zero at the bottom of the melted layer. This region is regarded as a transient region, which initiated independently of the depth, but as the depth increases the thickness of the region increases. Typically, for short pulse excimer laser LSM the solidification interface returns to the surface at growth velocities of 1-10 m/s under a cooling rate up to \(10^{11}\) K/s \(^{[46, 88, 89]}\). The absolute velocity for solidification at stability planar growth was estimated at 5 m/s \(^{[77]}\).
Solidification by excimer LSM of AA2024 aluminium alloy was greatly influenced by the matrix due to the conduction effect. Results reported by Ryan et al [77] showed solidification structures of AA2024-T3 under an excimer laser had a melted layer with planar growth as shown in Figure 3.22.

The AA2024-T3 melted layer has a grain structure that grows epitaxially upwards, which is a well recognized phenomena that occurs in a partially melted layer with positive thermal gradient during re-solidification, where these is no energy barrier for heterogeneous nucleation when the liquid and substrate are the same material [42, 77].
Arias et al. [74] used a 3.3 kW CW diode laser for LSM on AA2017-T4 alloy with variation of processing conditions to investigate the effect of the laser process parameters on the surface of the alloy. Similar microstructures of fine dendrites equiaxed cell structure for all the conditions at the interface and the melted layer were formed, as shown in Figure 3.23. The second phase particles are melted and solidified in fine dendritic patterns as in Figure 3.23 (a) and in Figure 3.23 (b) where large particles can be observed before and after LSM but with different distribution in the matrix, as shown in Figure 3.23 (c).

![Figure 3.23](image)

Figure 3.23: (a) Optical image of the dendritic microstructure of the melted layer produced by LSM on AA2017 alloy using a 3.3 kW CW diode laser. (b) SEM image of the fine dendritic structure produced by the rapid solidification of laser-melted second phase particles shown in (c) [74].

Similar results of microstructures were obtained by Xu et al. [90] using a Nd:YAG laser that produced a fine dendritic microstructure of several hundred microns in depth. The coarse second-phase particles that were present in the as-received material were eliminated and fine interdendrites were formed instead, as shown in Figure 3.24. The refinement of microstructure and elimination of coarse second-phase particles, as a result of LSM in the laser-melted layer was believed to be able to improve the corrosion resistance.
3.10 Previous work on corrosion behaviour of LSM in aluminium alloys

It is well known that grain boundary precipitates, second phases, inclusions and segregated interface, as discussed in the previous Chapter 2, are common sites for corrosion initiation, leading to degradation of alloys such as aluminium alloys, by corrosion attack. As described above, it is possible to melt these second phase particles to produce refined microstructures on the surface of the bulk material with elimination or minimizing second-phase particles due to rapid quenching within the melted layer. The dissolution of second-phase particles may create a supersaturated solid solution. As a result, it might be possible to enhance the corrosion resistance of laser-melted alloys.

As discussed earlier, the typical thicknesses of laser-melted layers range from a few micrometres to a few hundred micrometres, controlled by the laser power density and interaction time. As a result, LSM processes may be divided into two classes: namely, thick-layer melting and thin-film melting, depending on melt depths. The thick-layer melting process, typically with melted thickness in the range of 50 μm to a few hundred micrometres, involves the use of either energy pulses of duration from
1 to 20 ms or continuous-wave (CW) radiation, resulting in cooling rates of $10^4$–$10^8$ K/s \[^{[67]}\]. Under these conditions, cellular/dendritic microstructures are formed with elemental segregation along cellular/dendritic boundaries. In contrast, the thin-film melting process involves the use of short energy pulses (width range from some nanoseconds up to a few milliseconds), such as an excimer laser. A typical melted thickness is a few micrometres, with cooling rates up to $10^9$–$10^{11}$ K/s \[^{[46]}\]. In this regime, significantly reduced solute re-distribution could occur, to achieve no chemical segregation with the same composition as the liquid. Therefore, both types of LSM may generate completely different microstructures and hence corrosion properties.

LSM has been recognized as a useful method for protection of surfaces against corrosion. Aluminium alloys are subject to laser surface treatments to improve their corrosion resistance by modifying the surface characteristics and microstructure through rapid melting and rapid solidification. Creation of these types of surface microstructures are primarily dependent upon laser parameters such as wavelength, scan speed for continuous and pulse duration of lasers, besides other material properties such as composition and structures. This section reviews the previous studies on laser surface melting of various aluminium alloys, in particular Al-Cu alloys.

### 3.10.1 LSM thick-layer melting of aluminium alloys using a long-pulse or CW lasers

Historically, CW lasers have been used for laser surface melting of steel and aluminium alloys to improve corrosion resistance \[^{[91-93]}\]. Early efforts by Moore et al \[^{[94]}\] to study the influence of CW CO$_2$ laser for LSM of AA2024-T3 alloy, showed no improvement of pitting corrosion resistance because of the presence of cracks and pores in the surface. Li et al \[^{[83]}\] used a 2 kW CO$_2$ laser to melt the surface of AA2024-T3 alloy. The results showed no significant improvement in the pitting potential of laser-melted AA2024–T3 alloy. However, the shift in corrosion active sites from second phase precipitates to $\alpha$-Al dendrites resulted in elimination of intergranular corrosion at the penalty of a smaller number of large pits. This change of corrosion behaviour was believed to be attributed to the changes in the distribution and composition of the second phase particles on the surface of the alloy.
Liu et al [84] achieved a positive shift of 165 mV in the pitting potential in laser-melted AA2014-T6 alloy using a 3 kW CW Nd:YAG laser, tested in deaerated 1 M NaCl solution. Pitting corrosion was observed along the planar front zone where Cu depletion was found. Pits initiated in this zone were related to the coarsened second phase particles of the re-heated region by the overlapping effect. In addition, overlapping of the beam tracks to cover large areas produced cellular layers of the laser treatment that were prone to pitting. The refinement of the second phase particles acted as a corrosion barrier limiting the number and depress of pits formed (much lower density pits number) although pits were of larger size than those of the as-received alloy. Another work from the same authors [95], reported a comparative study of corrosion performance of AA2024-T351 alloy and AA2014 alloy after LSM using a 2 kW CW CO2 laser. Results showed an improvement of pitting corrosion resistance for the laser-melted of AA 2014-T6 alloy, but no improvement for AA 2024-T351 alloy. It indicated that the refinement of microstructure with finer intermetallic particles did not play an important role in corrosion performance. This was explained by the extension of copper solubility in the α-Al matrix caused by LSM. For AA 2014-T6 alloy, due to the cathodic nature of dominant phase in the substrate of Al2Cu relative to the α-Al solution, the rise of corrosion potential of α-Al solution reduced galvanic coupling between Al2Cu and α-Al matrix thus improving pitting corrosion resistance. Hence, the driving force for pitting corrosion in the α-Al solution was reduced. However, for AA 2024-T351 alloy, due to anodic nature of the dominant phase Al2CuMg in the matrix relative to the α-Al solution, the extension of copper solubility in the α-Al matrix increased the driving force for pit initiation due to the increased potential difference between the two phases. Therefore the laser melting promoted the pitting corrosion of the AA 2024-T351 alloy.

Hanna et al [86] used a 1 kW CW CO2 to melt the surface of AA2024-T3 alloy, resulting in a very fine cellular/dendrites microstructure which was tested for pitting corrosion in 0.5 M NaCl solution. The pitting potential was not improved in comparison to the as-received alloy because of non-uniform structure at subsequent laser tracks.

A 2 kW CW Nd:YAG laser surface melting of AA7075 alloy was conducted by Yue et al [87] for improvement of stress corrosion cracking (SCC) behaviour. In general, SCC resistance of the alloy was significantly improved by LSM. The improvement
was attributed to the removal of the coarse constituent particles and planar grain boundaries [87].

A recent study by Xu et al [90] employing a CW Nd:YAG laser for surface melting of AA6013 alloy was aimed at improving the pitting corrosion and pitting corrosion fatigue resistance. Electrochemical measurements recorded an increase in corrosion potential and reduction in corrosion current density. Hence, the pitting corrosion resistance of laser-treated AA6013 alloy was increased after laser melting. The improvement was accredited to the refinement of microstructure and the presence of AlN phase at the surface [90]. The formation of the AlN phase resulted from the chemical reaction of molten aluminium with N2 [87] during laser melting process. With regard to fatigue crack propagation, the interdendritic boundaries are vulnerable to corrosion cracks due to the presence of refined second-phase particles [91].

LSM studies [72, 93, 96] carried out on Al-Si alloys with different percentage of silicon contents, showed significant improvement in pitting corrosion in 3.5 wt % NaCl solution. However, the effect of LSM became less significant in high Si content alloy [93]. For a higher Si content-containing Al-Si alloys, after laser melting the hardness was found increase due to the supersaturated silicon content. In addition, Al-Si alloys with higher silicon content provided better corrosion resistance in H2SO4 and HNO3 solutions. However, in 10% HCl and 5% NaCl solutions, laser-melted Al-Si alloys suffered from more severe corrosion attacks [72, 96].

From the previous work described above, it could be concluded that improvement of corrosion resistance using LSM with CW high power lasers is related to refinement of the microstructure and extending solid solubility of copper in α-Al. However some alloys with anodic second-phases such as Al2CuMg (S-phase) in 2024-T351, did not show any improvement. On the contrary, it showed even worse corrosion resistance compared to the performance of as-received alloy without LSM.

3.10.2 LSM thin-film melting of aluminium alloys using short-pulsed lasers

Pulsed lasers deliver high energy density on the material surface in a short time, resulting in melting and solidification taking place within ns - μs time scales depending on the pulse width, while absorption of photons and their conversion to
heat occurs on faster time scales \cite{88}. Such irradiation induces rapid heating and cooling with a typical cooling up to $10^{11}$ K/s \cite{46,88,89} that promotes development of a solidification front which can progress at a rate of several meters per second. This progress of growth rate can surpass the critical velocity where transition from cellular to planar front takes place leading to the formation of micro-segregation-free material within the solidified layers. The resultant microstructures are expected to consist of a highly supersaturated solid solution \cite{97}, with dissolution of second-phase particles that would benefit the improvement of corrosion resistance \cite{98}.

Bonora and co-workers \cite{99} were the first to study corrosion behaviour caused by LSM of pure aluminium using a Q-switched ruby laser with 15 ns pulse duration and energy density ranging from 1-5 J/cm\(^2\). Under such conditions, a cooling rate near $10^{11}$ K/s was achieved. The results showed that the pitting potential after LSM remained unchanged, but the passive current density was lower than that of the as-received under both potentiostatic and potentiodynamic conditions. It was concluded that the cause of lower passive current density was related to the formation of inert amorphous aluminium in the microstructure after LSM. A similar study was performed by Hagans and Yates \cite{100}, using a Q-switched Nd:YAG laser with 5 ns pulse duration and 4 mJ per pulse.

McCafferty et al \cite{101} used a single pulsed CO\(_2\) laser with pulse duration of 1 µs and 5x $10^8$ W peak power density on AA3003 alloy and produced a melted layer with depth of 10 µm. The modified microstructure displayed an improvement in uniform corrosion resistance in hydrochloric acid and in sodium citrate, but no improvement in pitting resistance in 0.1 M NaCl solution and also there was an increase in the free corrosion potential by 300 mV.

Padovani et al \cite{102} applied excimer laser surface melting technique on friction stir welds in AA2024-T351 for improvement of corrosion resistance within the weldments. A melted layer around 5 µm of thickness was formed with a refined microstructure, where constituent particles were dissolved and the alloying elements retained in aluminium solid solution. After immersion test in 0.1 M NaCl solution, the AA2024-T351 friction stir welds with laser treatment showed improved corrosion resistance, with more uniform and less intense corrosion attack compared to the weldment without laser treatment. The improved corrosion resistance was
related to the decrease in the anodic and cathodic activities in the weld region compared with the matrix. A scratch test was also conducted by intentionally made scratches on the surface of laser-treated and untreated alloy. The laser-treated surface showed better corrosion resistance. This was believed to be due to the higher corrosion potential of the melted layer with respect to the as-received but with low cathodic reactivity, which is responsible for the driving force of galvanic coupling between melted layer and the matrix. However, corrosion propagation at the melted layer/matrix interface produced partial delamination (exfoliation), which causes partial removal of the melted layer thus lowering the protection capability of laser surface treatment.
3.11 References


3. Literature Review Part II


3. Literature Review Part II


3. Literature Review Part II

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3. Literature Review Part II


Chapter 4

Experimental Procedure and Characterization Techniques

4.1 Introduction

This chapter describes the materials and the accomplished experimental work and various characterization and testing techniques. It covers the laser surface melting and anodising procedures. The techniques involved in microstructural characterisation include scanning electron microscopy (SEM), equipped with energy dispersive X-ray spectroscopy (SEM/EDX), transmission electron microscopy (TEM), scanning Kelvin probe force microscopy (SKPFM), X-ray diffraction (XRD). Corrosion tests include potentiodynamic polarization and immersion in sodium chloride solution and exfoliation corrosion (EXCO) tests.

4.2 Materials

This research was conducted on aerospace aluminium alloy AA 2024-T351, supplied commercially in the form of 10 mm thick plate. A sample was sent to Inco-Test laboratory for chemical analysis. Table 4.1 shows the chemical composition of the alloy provided in a certified report by Inco-Test.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>4.30</td>
<td>1.41</td>
<td>0.61</td>
<td>0.17</td>
<td>0.04</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Only the main elements of the alloy are presented; however, the other minor elements, such as zirconium, chromium, titanium and others were not measured in Inco-test.

4.3 Sample preparation for LSM

The supplied plates of AA2024-T351 alloy were cut into small pieces in dimensions of 20 mm x 15 mm for the following laser process. The sample surfaces were then mechanically ground to remove the surface oxide produced during manufacturing and any other surface defects and contaminants, such as oil grease. Mechanical grinding was achieved using 600, 800, 1200 grit SiC sandpaper successively. During grinding, running water was applied
continuously to avoid any thermal effects induced by grinding. The ground samples were rinsed by deionised water, ultrasonically cleaned in ethanol and then dried in cool air for the following laser process. The grinding also served the purpose of producing sample surfaces with a certain degree of roughness, to enhance the absorption of the laser beam. In addition, the ground surfaces, up to 1200 grit, were used for corrosion tests in comparison to the surface after laser treatment.

4.4 Laser Surface Melting (LSM)

4.4.1 The Laser

A KrF excimer laser (GSI Lumonics Pulse Master, PM-840) with an output ultraviolet wavelength of 248 nm was used in this project, as shown in Figure 4.1. The laser beam has a full width at half maximum (FWHM) pulse duration of 13–20 ns, a maximum repetition rate of 200 Hz and maximum pulse energy of 450 mJ. The output laser beam was non-polarized and had a rectangular intensity profile, as shown in Figure 4.2. The beam intensity distribution was not entirely uniform; one side the left was slightly higher than the other side the right.

Figure 4.1: The KrF Excimer laser used in the project.
4. Experimental Procedure and Characterization Techniques

Figure 4.2: The excimer laser beam intensity distribution, (a) in two-dimensions and (b) three-dimensions.

Figure 4.3: Excimer laser surface melting process setup.

The setup for the laser surface melting process is shown in Figure 4.3. The beam was focussed by a fused silica plano-convex lens with a diameter of 50 mm and focal length of 200 mm. The samples to be treated were placed on the focal plane, i.e. at a distance of 200 mm from the lens. The beam size on the sample surface was approximately 3.5 mm x 1.75 mm. The samples were mounted on an X-Y moving stage which was controlled by an ESP.
motion controller for scanning speed and travel distance. The X-Y moving stage was moved along the length of the laser beam, i.e. 1.75 mm. In order to cover a large area, a 20% overlap ratio was used \[1, 2\].

4.4.2 Surface conditions prior to LSM

Since surface absorption of a laser beam is highly dependent on surface conditions, three surface conditions of AA2024-T351 were applied to investigate the effect of surface conditions on the laser surface melting behaviour.

1) As-received: the as-received alloy surface contained heavy oxide films produced during material production and heat treatment.

2) Ground surface: surface deformation and oxidation during manufacturing processes have been removed by grinding; the ground surface (up to 1200 SiC grit) exhibited a certain degree of roughness for enhancing laser beam absorption.

3) Carbon-coated: For a high reflective material such as aluminium, graphite is commonly applied as a thin coating layer on the surface of the material. Hence, a thin graphite layer was applied after the sample surface was ground using 1200 grit to remove any deformation and create a uniform surface.

![Image](image.png)

Figure 4.4: Three surface conditions prepared for laser irradiation. a) as-received, b) ground to 1200 grit and c) ground to 1200 grit and then graphite-coated. Note the marks are laser-treated regions.

4.4.3 Laser processing parameters

In order to investigate the influence of the laser operating parameters on melting behaviour of AA2024-T351 alloy, two main laser operating parameters, i.e. laser fluence and number of laser pulses, were varied.
4. Experimental Procedure and Characterization Techniques

**Laser fluence**: fluence indicates the energy density per laser pulse. The laser fluence, is controlled by either adjusting the laser beam energy or the irradiation area on the sample surface, or both. The laser beam energy is controlled by changing the input voltage.

**Number of laser pulses**: the required number of laser pulses is determined by a number of processing parameters, including the size of the laser beam, scanning velocity and laser frequency.

![Figure 4.5: Illustration of laser beam scanning.](image)

When a laser beam, in dimension of X-Y and frequency, f, scans along the X-axis as shown in Figure 4.5, at scanning speed of v, the interaction time between the laser beam and work piece, t, can be calculated as:

\[ t = \frac{X}{v} \quad (4.1) \]

The number of laser pulses per unit area, N, will be:

\[ N = t \times f \quad (4.2) \]

Where f is the laser beam frequency.

For example, when a laser beam of dimensions is 3.5 mm x 1.75 mm is scanned at a scanning velocity of 1.75 mm/s with a pulse frequency of 10 Hz, the number of laser pulses per unit area will be:

\[ N = \frac{1.75}{1.75} \times 10 = 10 \]

In this project, the laser processing parameters used for laser surface melting of AA2024-T351 alloy are shown in Table 4.2. The laser fluence was fixed as 7.0 mJ/cm², and the number of laser beam pulses was 10, 25 and 50.
Table 4.2: Optimum laser conditions for LSM treatment applied to AA2024-T351 used in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser pulse energy, mJ</th>
<th>Beam size, mm²</th>
<th>Laser fluence, mJ/cm²</th>
<th>Frequency, Hz</th>
<th>Scanning velocity, mm/s</th>
<th>Number of pulses per unit area</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3</td>
<td>420</td>
<td>3.5 x 1.75</td>
<td>7</td>
<td>20</td>
<td>0.7</td>
<td>50</td>
</tr>
<tr>
<td>M4</td>
<td>420</td>
<td>3.5 x 1.75</td>
<td>7</td>
<td>10</td>
<td>0.7</td>
<td>25</td>
</tr>
<tr>
<td>M5</td>
<td>420</td>
<td>3.5 x 1.75</td>
<td>7</td>
<td>10</td>
<td>1.75</td>
<td>10</td>
</tr>
</tbody>
</table>

4.5 Anodising

Anodising generates a metallurgically bonded finish that is resistant to corrosion. Samples to be anodised of as-received AA2024-T351 alloy and laser-treated were immersed in 0.46 M sulphuric acid electrolyte at room temperature. A two-electrode cell was used, in which the sample to be anodised was the working electrode and a pure aluminium plate was the counter electrode. A DC (direct current) electric current was passed between the aluminium alloys, i.e. the anode (positive terminal), the electrolyte and the cathode. As a result, the water in the electrolyte breaks down and oxygen is deposited at the anode and combines with the aluminium to form an oxide film. The sulphuric acid tries to break up or dissolve the oxide film and produces a porous oxide film with hexagonal cells, each containing a pore. Once the required treatment time is reached the sample is removed from the electrolyte and rinsed in deionised water to remove the acid from the pores. Since the anodic film is relatively porous, the pores were sealed. The sealing process was carried out in boiling water for 30 minutes and then the as-received alloy and laser-treated alloy samples were ready to undergo corrosion testing. Figure 4.6 shows the schematic illustration of the anodising process.
4. Experimental Procedure and Characterization Techniques

4.6. Microstructural Characterisations

4.6.1 Sample preparation for metallographic examination

AA2024-T351 alloy samples after various treatments were sectioned, mounted in Araldite resin mixed with hardener in a ratio of 10:1 and left in air to dry. The mounted samples were ground using 600, 800, 1200 and 4000 grit SiC sandpapers in ascending order. The samples were then polished using diamond suspension and lubricant on nylon cloth. The final polishing step was conducted using a colloidal suspension of 0.3 μm silica. Ultrasonic cleaning was then carried out in alcohol for degreasing. Some of the samples after polishing were chemically etched to reveal the microstructure. Keller’s solution, containing 2.5 ml HNO₃, 1.0 ml HCl, 1.5 HF, 95 ml H₂O, was used as etchant. The samples were exposed to the Keller solution for 15 s, and then rinsed using deionised water and dried in air.

4.6.2 Optical microscopy (OM)

An optical microscope was used for observation of any variation in morphology or microstructure of both the surface and cross sections of the melted layer of the laser treated samples. It was also conducted for preliminary observation of the effect of corrosion on the morphology and microstructure, before use of SEM. Polished sample surfaces were also inspected by optical microscope for particle-matrix cavitation or local corrosion. The optical microscope employed in this project was a Reichert-Jung-MeF3 microscope, with a Kyocera-
Yashica 108 Multi-program digital video camera. The microscope was connected to a personal computer (DELL, Dimension L933R). The Olympus BHM microscope was fitted with a number of fixed magnification lenses from 5X magnification to 80X magnification.

4.6.3 Scanning electron microscopy (SEM)

Microstructural characterisation of the AA2024-T351 alloy before and after various treatments was accomplished via the use of three types of scanning electron microscope equipped with EDX microanalysis facilities, including a Philips XL-30 Field Emission Gun-Scanning Electron Microscope (FEG-SEM), EVO50 and a Carl Zeiss ULTRA 55.

4.6.3.1 Samples prepared for SEM

Specimens prepared for FEG-SEM were carbon coated with 100 nm of carbon and mounted on standard 25 mm SEM stubs using electrically-conducting, double-sided adhesive carbon tape. For samples in a non conductive resin, a line trace of silver liquid was used to connect the stub to the sample to avoid charging of the sample. Secondary electron and backscattered electron imaging was carried out using a beam energy of 20 kV and a probe current of approximately 140–145 pA.

4.6.3.2 Background and details on the types of used SEM

Scanning electron microscopy (SEM) is an efficient tool for topographical and microstructural investigation of various types of materials at greater depth of focus. Generally, SEM consists of the high tension system for generating an electron beam. At the top of the column in Figure 4.7, the electron gun generates an electron beam and the vacuum system inside the chamber allows electrons arrive at the specimen without losing energy. As the beam arrives at the specimen, various kinds of electrons are emitted and then detected, and converted to signals.

Electrons that are reflected from the sample by elastic scattering are the Back-scattered electrons (BSE). BSE are employed for analytical SEM, together with the spectra obtained from the characteristic X-rays. Since the BSE signal intensity is strongly related to the atomic number (Z) of the sample, BSE images can give information about the distribution of different elements in the specimen. X-rays are emitted when the electron beam excites an inner shell electron from the sample, causing a high energy electron to fill the shell and...
release energy. These X-rays are used to identify the composition and measure the abundance of elements in the samples.

Field emission gun scanning electron microscopy (FEG-SEM) is a powerful technique that can deliver an image with resolution at the nanometre scales. This instrument is mostly used to capture a good contrast images at higher magnification from the surface, interface or cross section of films and bulk materials. In addition, FEG-SEM is also equipped with an EDX spectrometer, which is used to analyze chemical compositions at small localized areas of the sample such as grain boundaries, precipitates and second phase particles etc. Other features, including line scan imaging and chemical analysis, are used to identify and verify the chemical nature of nano-particles. In this project, a Philips XL-30, FEG-SEM was used and operated at 15-20 kV, the instrument could resolve features as small as 3.5 nm.

The Zeiss Ultra-55 SEM has a unique design to the final lens; it is electrostatic instead of electromagnetic. This feature allows the microscope to image magnetic materials without distortion created by a magnetic field. This microscope is capable of delivering very high lateral resolution at low voltages. Its resolution can be 1 nm at 15 kV and 1.7 nm at 1 kV. In this project, the sample preparation was the same as described in the latter section on ultramicrotomy, except that the purpose was to produce a freshly polished surface using a dry diamond knife. This means that the diamond-cut had to be made just before placing the sample inside the specimen chamber. This was to ensure there is no time for AA2024-T351
aluminium alloy to form a relatively thick oxide layer, which may result in distortion of the images.

4.6.4 Transmission electron microscopy (TEM)

4.6.4.1 Sample preparation for TEM

TEM requires thin samples for successful transmission of the electron beam. For aluminium and its alloys, sample thicknesses used for TEM are typically less than 150 nm. Two techniques were used for sample preparation including ultramicrotomy and twin-jet electropolishing.

*Ultramicrotomy:*

The purpose of this technique was to produce electron transparent foil or ultra slices of nano-scale thickness suitable for characterisation under TEM. Firstly, samples of dimensions 5 x 8 x 2 mm³ were cut from required regions of the samples to suit the size of the TEM holder. Secondly, the samples were mounted in resin in a TEM sample holder. The surface to be examined was positioned at the bottom of the holder. Epoxy resin was prepared using Agar 100 resin, DDSA, MNA and BDMA in the weight ratio of 24:13:13:1 respectively and kept in an electrical oven at 60°C for 24 hours to cure the resin.

A Reicheit Jung ultramicrotomy was employed for trimming. A fixed sharp glass knife was placed on a moving rotating stage. Sample edges were trimmed to an angle of 35°. The glass knife was replaced by a diamond knife of clearance angle 6° and electron transparent slices were cut. The use of the diamond knife allowed cutting a foil of thickness of 15 nm. The foils were collected onto nickel grid meshes. The meshes were fully dried with filter paper and stored in a dry TEM sample holder box for later examination by TEM.

*Twin-jet electropolishing:*

A Struers Tenupol twin-jet electropolishing machine was used to prepare AA2024-T351 aluminium alloy samples for TEM analysis. 3 mm diameter circles were punched on the surface of as-received samples to a certain depth without penetrating to the other side of the specimen. The punching was done by a sparking technique with 3 mm discs. The depicted discs on the surface were then mechanically ground from both surfaces using 1200 grid SiC sandpaper and water was introduced for cooling during the grinding process. When a
thickness of approximately 100 µm was obtained, the discs were then cleaned in ethanol and dried in cool air. Finally, twin-jet electropolishing was carried out using a mixture of 70/30 ml methanol/HNO₃. Liquid nitrogen was added gradually to the mixture till the temperature decreased to about 30°C below zero.

### 4.6.4.2 Transmission electron microscopy (TEM)

The fundamentals of TEM are based on a beam of electrons transmitted through a transparent thin sample, prepared by ultramicrotomy or twin jet electropolishing. Transmitted electrons are focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or detected by a sensor such as a CCD camera. Owing to the small de Broglie wavelength of electrons, TEM is capable of imaging at a much higher resolution than SEM [4].

TEM can be described briefly as a system of three components. The first component is the illumination system, comprising the electron gun and condenser lenses, which produce a fine electron beam. The beam interacts with the solid matter of the sample, producing different signals. The constituents of the direct electron beam that is transmitted through the sample, or some of the diffracted beams, are used to produce bright field and dark field images, respectively, as shown in Figure 4.8. The second component is the objective lens, located immediately after the sample. Its function is to produce the diffraction pattern and a first magnified image of the specimen. The third component, the magnification system, produces the final image. These optical components of the microscope are arranged in a columnar geometry and rest on a control console, which permits establishment of the operating conditions and handling of the sample. The filament used as the electron beam source is frequently made of W or LaB₆; the latter is brighter, and the quality of the electron beam provides higher resolution. A small electrical current is passed through the filament, heating it to temperatures as high as 2500°C, producing a beam of adjustable size, intensity and convergence. This system works under relatively high vacuum conditions (about 10⁻⁷ Torr) to avoid electrons colliding with the residual gas atoms.

Two types of TEM were employed for the investigation of the nano-scale structure of AA2024-T351 alloy before and after various treatments, including Joel 200 FX (operated at 120 kV) and Tecnai F30 (operated at 300 kV) instruments, both equipped with high angle annular dark field (HAADF) and EDX facilities.
4. Experimental Procedure and Characterization Techniques

The FEI Tecnai F30 is an analytical electron microscope (AEM), which can function as a conventional TEM or a scanning transmission electron microscope (STEM). It has a field emission gun and it can operate up to an accelerating voltage of 300 kV. It includes both an energy dispersive X-rays detector and an electron energy loss spectrometer (EELS) for elemental analysis. The spot size can be reduced to < 0.3 nm for the chemical analysis and micro diffraction studies. The resolution can be 0.2 nm for point to point analysis and 0.102 nm for line analysis.

4.6.5 Electron Backscattered Diffraction (EBSD)

Electron backscattered diffraction (EBSD) is a SEM technique applicable to crystalline materials. EBSD allows identification of phases and discrimination between phases within materials. EBSD is conducted using a SEM equipped with an EBSD detector. A typical experimental set up is shown in Figure 4.9. For an EBSD measurement, a flat/polished crystalline sample is placed into the normal position in the SEM chamber, but is highly tilted (~70° from horizontal) towards the diffraction camera to increase the contrast in the resultant
electron backscatter diffraction pattern. These patterns are effectively projections of the geometry of the lattice planes in the crystal, giving direct information about the crystalline structure and crystallographic orientation of the grain from which they originate. The diffraction signals come from the top few nanometers of the crystal lattice as EBSD is a surface-sensitive technique.

![Figure 4.9: Typical setup in EBSD.](image)

In order to carry out EBSD characterization, after grinding and polishing, AA2024-T351 alloy samples were electro-polished in a stirred solution containing a mixture of 70% ethanol and 30% perchorlic acid, under a temperature below 10°C, which was maintained using ice surrounding the exterior circumference of the container. An aluminium sheet was inserted in the container and connected to the negative terminal of a DC power supply and the sample was connected to the positive terminal. The applied potential was 20 V set for 60 s at a temperature near zero. Then samples were rinsed using ethanol and dried in cool air.

### 4.6.6 X-ray diffraction (XRD)

X-ray diffraction (XRD) is commonly used to identify the crystallographic structure of materials, along with other information on the physical state of the samples, such as grain size, surface texture and crystal perfection. X-rays phase analysis is based on the fact that when monochromatic x-rays with wavelength $\lambda$ strike a polycrystalline sample at an angle $\theta$, grains with interplanar spacing $d$ diffract the radiation at the same angle, according to Bragg’s law. When x-rays fall on atoms of all the planes in a crystal, each atom scatters a small fraction of the incident beam (see Figure 4.10). A strong reflection occurs when the
angle of reflection equals the angle of incidence. The maximum signal intensity of XRD occurs when x-rays interfere constructively and this takes place when Bragg’s law is satisfied:

\[
n\lambda = 2 d_A \sin \theta \quad (4.3)
\]

where \( n \) is an integer and \( \lambda \) is the wavelength of the x-rays, and \( d_A \) is the distance between planes of atoms.

In this project, AA2024-T351 alloy before and after laser melting was investigated using low-angle XRD. Low angle XRD, also known as grazing incidence x-ray diffraction, uses small incident angles from 0.1 to 10° for the incoming x-rays, so that diffraction can be made surface sensitive. It is used to study surfaces and layers because wave penetration is limited. The incident angle used was on the laser treated samples to avoid x-rays reaching the bulk material because the melted layer of the samples is < 10 μm thick.

**4.6.7 ADE Phase shift microXam white light interferometer**

The surface topography was assessed using ADE phase shift MicroXam white light interferometer equipped with the TalyMap platinum software. The interferometer can perform topography surface measurements using coherence peak scanning which uses a filtered white light from a halogen lamp and phase measurements using a band width green light for phase shift. By acquiring a sequence of images of the deformed fringe pattern, the surface topography can be detected.
4.6.8 Scanning Kevin Probe Force Microscopy (SKPFM)

In principle, SKPFM (see Figure 4.1) is a scanning probe instrument for measuring a potential offset between a probe tip and a surface of a metal. SKPFM produces a map on the submicrometer scale of the potential distribution across a sample. The surface topography and potential distribution can be measured simultaneously using electrically conducting probe tips. The AFM cantilever works as a reference electrode, forming a capacitor with the metal surface. Using tapping mode, a profile of sample topography can be determined along a line of a scan. To determine the potential during the second scan, an AC voltage of ±1 V is applied to the tip, so as to create fluctuating dipole at the tip. This dipole will make the cantilever fluctuate, which can be detected by AFM. Along the rescanned line, a ramp of DC voltage is added at each point to the AC signal; the DC is determined by nulling out the cantilever fluctuation. At this point, the same value of potentials occurs at the tip and at the sample and a map of a relative potential of the surface with respect to tip is established. Because of the nulling method and the applying of voltage to the tip, the output signal is inverted. The inversion of the signal is necessary to obtain the expected potential polarity measurements which are relative to the potential of the tip \[^5\].

![Figure 4.11: Kelvin probe force microscopy, a conducting cantilever is scanned over a surface at constant height in order to map the work function of the surface \[^6\].](image)

SKPFM is particularly useful for studying corrosion phenomena. SKPFM generates a map of the potential distribution across a sample with a resolution of at least 100 nm. SKPFM is a useful tool to assess the practical nobility of a surface. In this project, this technique was applied to the heterogeneous microstructure of AA2024-T351 alloy before and after laser melting to provide evidence regarding the shape, position, compositional inhomogeneities and local practical nobility of copper-rich intermetallic particles, as well as the change in
various intermetallics and aluminium matrix after laser melting. The AA2024-T351 alloy samples were polished up to 1 µm. For the laser-melted AA2024-T351 alloy, the scanning was done over an area of cross section covering the melted layer, the interface and part of the matrix.

### 4.6.9 Residual stress analysis

In general, stress, \( \sigma \), is defined as force per unit area within a material that arises from externally applied forces. Strain, \( \varepsilon \), is defined as relative deformation or change in shape and size of elastic, plastic and fluid materials under applied forces. Hence,

\[
\sigma = \frac{F_n}{A} \quad (4.4)
\]

where \( F_n \) is the force exerted on the surface and \( A \) is the area and

\[
\varepsilon = \frac{\Delta d}{d_o} \quad (4.5)
\]

where, \( \Delta d \) change of length and \( d_o \) is the initial length

stress/strain = Young’s modulus, \( \xi \)

\[
\sigma /\varepsilon = \xi \quad (4.6)
\]

Since tensile stress is the stress that is applied to an object by pulling on it, or attempting to stretch it, positive values of stress indicate tensile stress. Conversely, given that compressive stress is the stress applied to materials resulting in their compaction (decrease of volume), so negative values of stress indicate compressive stress.

Residual stresses remain in a material or body without application of an external load. A residual stress usually originates during manufacturing and processing of materials due to heterogeneous plastic deformations which occur during bending, rolling or forging. In addition, thermal gradients introduce residual stresses into a material due to differential expansion after a metal is heated or cooled. Both thermal treatment and restraint of the component must be present in order for residual stresses to be generated. In general, tensile residual stress in the surface of material is undesirable because it can contribute to stress-corrosion cracking, fatigue failure and quench cracking.

The effect of residual stress is the same as common mechanical stresses however, the latter can be accurately calculated with a degree of accuracy while the residual stresses are hard to
predict. Subsequently, a reliable method to measure residual stresses directly with minimum damage to the surface is essential. There are several residual stress measuring methods such as x-ray diffraction, ultrasonic methods, magnetic methods and hole drilling and strain gauge techniques. The X-ray diffraction method has been used in this project to calculate the residual stresses in AA2024-T351 alloy caused by LSM.

X-ray diffraction method is widely used as a non-destructive technique for residual stress measurement. Since residual stress in the material forces the inter-planar spacing of the material to change, these changes in the inter-planar spacing “d” can be used with the Bragg’s equation to detect elastic strain “ε” through a change in the Bragg scattering angle, as shown in equation 4.7:

\[ \varepsilon = \frac{\Delta d}{d_0} = -\cot \Theta \Delta \Theta \]  

(4.7)

Therefore, stress can be evaluated from strain values using Young’s modulus and Poisson ratio which is the ratio of the decrease in thickness to the increase in length.

4.7 Corrosion tests

4.7.1 Electrochemical measurement

4.7.1.1 Sample preparation:

Samples to be tested were firstly ground by different SiC sandpapers and then polished to a mirror finish. To ensure a good electric connection during electrochemical measurement, a small hole was drilled using an electric drill on one of the short sides at the cross section of each laser treated sample as well as as-received one. Using a drill bit of diameter just little smaller than the diameter of the aluminium rod, the aluminium rod was cut into a suitable length and fixed to the sample by inserting it into the hole with enough pressure using small hammer. Samples were coated all around using 45-stopping of lacquer, excluding this irradiated area of 1 cm² of the surface to be exposed to the testing solution. The insulating liquid was spread on the surface via a small brush. Samples were ready for investigation after being left for 24 hours to dry. At the end of the corrosion experiment, the samples were dipped rapidly into de-ionized water and then rinsed thoroughly in double-distilled water and dried in a cool air stream.
4. Experimental Procedure and Characterization Techniques

### 4.7.1.2 Anodic polarization test

Anodic potentiodynamic polarization experiments were performed using a solartron 1286 potentiostat and a conventional three electrode cell employing a platinised titanium counter electrode and saturated calomel as the reference electrode (SCE).

Polarisation studies were carried out on as-received and the laser-treated Al 2024-T351 alloy in 1 M reagent grade NaCl solution at 25 ± 2 ºC. The solutions were deaerated by purging with nitrogen for at least 75 minutes. Samples were then immersed in the solution for 60 minutes to stabilize the open circuit potential. Potentiodynamic polarization curves were then determined at a potential scan rate of 0.167 mV/s for Al 2024-T351 alloy; purging nitrogen was continued throughout the test. After the tests, samples were subsequently cleaned for 5 minutes in ethanol using an ultrasonic bath, followed by observations using optical microscopy (OM) and SEM for the corrosion morphologies.

### 4.7.2 Immersion tests

Samples of laser treated and as-received alloys were exposed to 1 M NaCl solution for 24 hours and left open to air at room temperature.

### 4.7.3 EXCO tests

#### 4.7.3.1 Solution preparation

The exfoliation and intergranular corrosion behaviour were investigated in a comparatively severe EXCO immersion test, rather than the MASTMAASIS which is widely used for evaluating sensitivity of aluminium alloys to exfoliation corrosion [7]. The used EXCO test was based on the ASTM G34-01 standard [8]. It contains 4 M (234g) NaCl, 0.5 M (50g) KNO₃ and 0.1 M (6.3 ml) HNO₃ diluted to one litre of deionised water in a flask with stirring magnet rod. The flask was put on the stirring machine for at least one hour to make sure all the components were dissolved at room temperature.

#### 4.7.3.2 Sample preparation

After coating the samples using 45-stopping of lacquer and let to dry for one day, lacquer bee wax was applied to the samples for extra sealing.
4. Experimental Procedure and Characterization Techniques

4.7.3.3 Corrosion exposure

Samples were laid horizontally with the investigated surface facing up in 1000 ml beaker with plastic rods fixed at the bottom to ensure samples were not touching the bottom of the beaker. Around 500 ml of the EXCO solution poured from the flask slowly into the beaker covering all samples. The environment surrounding the samples had a pH around 0.4 and a temperature of 25 ± 3°C. The test was conducted for 6 hours and repeated several times for reproducibility.

4.8 Nano-indentation measurements

Hardness measures the capability of a material to withstand external force while maintaining its structure and form. Nano-indentation measures the hardness of small volumes of surface materials. The technique uses small loads and tip sizes. The indentation area can be in the range from nano to micro metres. The technique employs a Berkovic tip, which has a geometry of three sided pyramid, in the indentation process. The penetration depth is recorded leading to determining the area of indent geometry of the tip. Hence load and depth of penetration is measured and values are recorded and plotted on a graph to create a load-displacement curve as shown in Figure 4.12 \[9\]. The depth and area of the indent are correlated with the hardness. Other properties such as elasticity, adhesion, creep, and tribological features can also be calculated from the indentation data. However, in this project, only hardness was considered.

Figure 4.12: Typical Loading and Unloading Curves for Nanoindentation Tests. \[9\].
4.9 References


8. Standred Testing Metod for Exfoliation Corrosion susceptibility in 2XXX and 7XXX series aluminium alloys (EXCO test), AMST Standard G34-01, A. Internatinal, Editor. 2007: West Conshohocken, PA USA.

Chapter 5

Microstructural Characterization of As-received AA2024-T351 Alloy

5.1 Introduction

As discussed in Chapter 2, the microstructure of Al-Cu alloys, in particular AA2024-T351 alloy contains various phases that form during fabrication and heat-treatment processes, including precipitates, dispersoids and constituent particles. The microstructure affects the mechanical properties, as well as corrosion resistance. Although AA2024-T351 alloy has been chosen extensively to be used in aerospace industry, the corrosion resistance of this alloy, particularly localized corrosion, is a major drawback during its service in environments containing chloride ions.

This chapter presents the microstructural characteristics of as-received AA2024-T351 alloy that have been investigated in the project. The microstructural characterization was carried out using SEM/EDX, TEM/EDX and XRD, in terms of phases, distributions and morphologies of second-phase particles and grains. In addition, surface potential measurements were conducted using scanning Kelvin probe force microscopy (SKPFM).

5.2 Microstructure of as-received AA2024-T351 alloy

5.2.1 Constituent intermetallic particles

5.2.1.1 Distribution

Figure 5.1 is a general view of the as-received AA2024-T351 alloy showing a relatively uniform distribution of various intermetallic particles in the aluminium matrix. The intermetallic particles (IMPs) are variable in size and shape.
Figure 5.1: Backscattered SEM image showing a typical microstructure of the as-received AA2024-T351 alloy.

5.2.1.2 EDX analysis of IMPs

A general view of the elemental distribution of Cu, Mg, Mn, Fe, and Si within the aluminium matrix is shown in Figure 5.2. The bright areas in each mapping image represent the presence of the indicated elements. In order to identify each individual particle, a combination of SEM/EDX analysis was carried out, involving analyzing nine spectra locations of different particles based on their shapes and sizes, as shown in Figure 5.3.

EDX analysis for each individual particle, as marked in Figure 5.3, reveals the presence of various phases of the as-received AA2024-T351 alloy. These particles can be distinguished to some extent by their sizes and shapes. A spherical shape, later given as 1-3 µm in size containing Al-Cu, was presumably the 0-phase. Al-Cu-Mg particles with nearly spherical shape, of size later given as 5-10 µm, was most likely to be S-phase. Al-Cu-Mn-Fe and Al-Cu-Mn-Fe-Si are comparatively large in size, up to 50 µm, with irregular shapes. These results are in agreement with the AA2024-T351 alloy microstructure reported in the literature review presented in Chapter Two. Further XRD analysis was required to confirm the composition of the phases.
Figure 5.2: EDX mapping of the as-received AA2024-T351 alloy showing alloying element distributions in the aluminium matrix.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

Figure 5.3: (a) SEM micrograph of a cross sectional view of a random distribution of intermetallic particles in the AA2024-T351 alloy microstructure, where nine particles were selected for EDX analysis and (b) at higher magnification. The SEM micrograph of (b) displays a round shape, micron-size particle.

Figure 5.4: EDX spectra for analysis of particles marked 1, 2, 5 and 6 in Figure 5.3, showing different types of particles.
5.2.1.3 XRD Analysis

Further analysis of various phases of the as-received AA2024-T351 alloy was made by XRD, from which phases were identified as shown in Figure 5.5. It can be seen that the as-received AA2024-T351 alloy consists of $\text{Al}_2\text{CuMg}$ (S-phase), $\text{Al}_2\text{Cu}$ ($\theta$-phase) and $\text{Al}$ (Cu-Fe-Mn) as well as the $\alpha$-$\text{Al}$ matrix.

Figure 5.5: XRD patterns of the as-received AA2024-T351 alloy.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

5.2.2 θ-phase investigation

Figure 5.6 (a) shows the SEM image of a typical phase, which is rich in aluminium and copper, as indicated by EDX spectra in Figure 5.5 (b). A rough percentThe phase consists of around 67 at% of aluminium and 33 at% of copper, and is believed to be Al$_2$Cu, i.e. θ-phase. Such phase can be spherical or another symmetrical shape and the sizes are in a range from 1-3 µm for single particles. This phase can also be found in clusters together with S-phase, as described later.

Figure 5.6: (a) SEM micrograph displays the shape and size of θ-phase particle and (b) EDX spectra of θ-phase.
5.2.3 S-phase investigation

Figure 5.7 (a) shows a typical phase which is roughly spherical in shape and 5 -10 µm in size and which appears white colour and light gray in the scanning electron micrographs. The line scan of the magnified particle confirms the presence of Al, Cu and Mg, indicating the S-phase. In general, these particles are free from Mn and Fe, making them to be distinguished easily from Al-Cu-Mn-Fe (Si) with their shape irregularity. XRD results confirms the presence of S-phase, with relatively strong peaks evident (Figure 5.5).

The SEM micrograph of Figure 5.8 (a) shows a group of mostly round shaped intermetallic particles distributed randomly in the alloy microstructure. Apart from the group, there is an irregular shaped particle marked by the yellow dashed circle. Results of EDX elemental mapping of these particles are displayed in Figure 5.8 (b)-(f) where the roughly spherical particles were mostly found to contain Al, Cu and Mg, suggesting such phase to be S-phase compared to the irregular shaped particle that consisted of Al-Cu-Mn-Fe.

![S-Phase](image)

Figure 5.7: (a) SEM micrograph revealing S-phases with varied sizes and roughly spherical shapes with contrasted colours. (b) EDX line scan of two different size S-phase particles revealing the elements in the S-phase.
Figure 5.8: (a) SEM micrograph of intermetallic particles and (b)-(f) EDX elemental mapping for the as-received AA2024-T351 alloy. The irregular shaped particle verged with yellow, contains Al-Cu-Mn-Fe compared to the roughly spherical S-phase particles containing Al-Cu-Mg.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

5.2.4 Al-Cu-Mn-Fe-(Si) particles analysis

Al-Cu-Mn-Fe-(Si) particles are distinguished by comparatively large size, around 8 µm, with irregular shapes. Figure 5.9 (a) is a BSE micrograph of a typical Al-Cu-Mn-Fe-Si particle. The particle displayed variation in brightness. This means the distribution of elements is not uniform within the particle. EDX line scan was performed on the particle; results are shown in Figure 5.9 (b). It is evident that the darker area contains more Fe and Mn with a very low presence of Cu; in the bright area, the presence of Cu is evident.

Figure 5.9: (a) Backscattered SEM image of Al-Cu-Mn-Fe-Si showing bright and relatively dark areas and (b) EDX line scan across the particle.

Figure 5.10 shows EDX mapping which illustrates elemental distributions within the irregular shape particles. Each element was assigned a different colour. The black colour means no presence of the assigned element. A reduced amount of aluminium in the particle is displayed in image (iii). Image (iv) shows the distribution of copper with bright colour intensity particularly on the bottom right of the particle with light blue marked colour. This type of particle is distinguished by the absence of Mg as indicated by mapping image (v), and by the presence of both Fe and Mn. The mapping images of Fe and Mn (vi) and (vii), respectively, show uniform distributions of these elements within the particle. Image (viii) shows the distribution of silicon in the particle mostly concentrated in the upper left part.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

Figure 5.10: EDX mapping showing the presence and distribution of various alloying elements within the irregular shaped particles. (i) SEM micrograph of the irregular-shaped particle. (ii) Element distribution. (iii) Aluminium, (iv) Copper, (v) Magnesium, (vi) Iron, (vii) Manganese and (viii) Silicon.
Further EDX mapping analysis of different, irregular-shaped constituent particles has been conducted. Results are displayed in Figure 5.11. Figure 5.11 (a) is a SEM micrograph of two irregular shape intermetallic particles. EDX elemental mapping of the two particles are shown in Figures 5.11 (b)–(h). The particle at the top was found to consist of an Al-Cu-Mg, indicating S-phase (Al$_2$CuMg). However, at an area at the far right of the same particle, there is no Mg, only Al and Cu. This is evidence of the presence of Al$_2$Cu particles forming a cluster with S-phase, as illustrated in Figure 5.11 (b). At the bottom, mapping of a larger irregular-shaped particle revealed the presence of Al, Cu, Fe, Mn and Si. Copper is found on periphery of the particle. Mn and Fe are uniformly distributed within the particle. Silicon is also present with a lower concentration. Further analysis by EDX has indicated the presence of an Al-Cu-Mn-Fe-Si intermetallic particle. At higher magnification of EDX mapping, Figure 5.11 (g, h) show the copper distribution at the top particle of Figure 5.11(a), indicating Al$_2$Cu next to the S-phase, is evident.
Figure 5.11: (a) SEM micrograph of two different IMPs. (b)-(f) EDX elemental mapping of the two IMPs, (g) Al$_2$CuMg cluster at higher magnification and (h) increased magnification of the marked region with the red circle, illustrating an Al$_2$Cu phase.
5.2.5 Dispersoids and grain boundary precipitates

Due to the small sizes of the dispersoids, high resolution FEG-SEM and TEM were employed to examine such fine particles in the grains and at the grain boundaries. Figure 5.12 shows the FEG-SEM micrograph of a sample surface with diamond knife finish, illustrating the presence of the particles in the aluminium matrix. The particles are elongated in one direction. The long axis of the dispersoids is usually parallel to the rolling direction of the alloy sheet. There is a variation in sizes among those particles and the lath shape is the most common type with average size of 200-400 nm.

![Figure 5.12: FEG-SEM micrograph of the dispersoids.](image)

A combination of FEG-SEM equipped with EBSD and TEM equipped with high angular annular dark field (HAADF) imaging in addition to EDX analysis facilities was employed to gain further evidence by analysis of twin-jet electro-polished thin film foil and ultramicrotomed specimens.

Figure 5.13 shows a dark-field TEM image of the dispersoids in the aluminium matrix. Three dispersoids were selected, marked with 1, 2 and 3, for chemical compositional analysis. The EDX analysis results showed particles 1 and 2 have the similar contents of Al, Cu and Mn, whereas particle 3 showed less Mn. A minor addition of Mn to Al-Cu series alloys can modify the precipitation process, forming
fine precipitates that restrict grain boundary movements resulting in a greater age hardening \cite{1} and enhancing toughness \cite{2, 3}. From the particle shape and elemental contents could be consistent with $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ phase.

Figure 5.13: TEM micrograph of the laths with EDX analysis of the three selected particles numbered 1, 2 and 3.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

5.3. Grain boundary precipitations

EBSD and FEG-SEM were employed to reveal grain boundary structure of AA2024-T351 alloy. The effect of the grain orientation on the development or enhancement of corrosion, such as intergranular corrosion, can be discussed in terms of grain boundary precipitates and grain stored energy. Figure 5.14 is a SEM image of the electro-polished specimen reveals grains and grain boundaries of the alloy with two different colour contrasts, i.e. bright and dark. The SEM images display grain shape, boundary as well as grain orientation. Figure 5.14 displays bright and dark grains. It has been reported that brighter grains have higher stored energy than the darker ones [4].

Grain boundaries with high stored energies have high susceptibility to corrosion, such that pits initiated on the surface may be transformed into intergranular corrosion along the grain boundaries. Consequently, intergranular path length becomes more dependent on grain orientation. Elongated grain orientation such as in AA2xxx and AA7xxx alloys could enhance IGC [5, 6].

Figure 5.15 shows EBSD grain mapping and distribution of misorientations of grain boundaries. The EBSD map reveals different grain sizes, grain boundaries and sub-grains. Figure 5.16 (a) shows the width of grain. The shortest grain width is around 20 µm while the widest is 200 µm. The grains appear in varied degree of brightness which is related to the grain energy stored. Grain stored energy is determined by the average dislocation density developed during quenching and cold work. The more dislocations generated in grains, the higher stored energy these grains will have [4]. The calculation of the grain boundary misorientation and grain energies is beyond the scope of this study. Figure 5.16 displayed large intermetallic particles in the grains and intersecting the grain boundary. Figure 5.16 (c) is an increased magnification of BSE image of the grain boundary as indicated by the square in (b). Three particles of disk shapes of sizes 72 nm, 130 nm and 172 nm are located at a grain boundary, separated by a distance of around 1000 nm and 500 nm, respectively. These resulted from the decomposition of the solid solution αss, generating precipitates with different shapes, such as laths, needles, disks and plates, with sizes ranging from a few angstroms to 0.1 µm [7, 8]. S-phases particles are
known to control the properties of AA2024 alloy where it evolved during aging \[^9\]. If these particles were S-phases, a significant reduction of corrosion resistance can occur to alloy due to the gathering of these precipitates along the grain boundary forming a chain, leading to intergranular corrosion (IGC).

![SEM micrograph showing a general view of the as-received AA2024-T351 alloy, with surface grains elongated along the rolling direction with dark and bright colour contrast.](image1)

![EBSD grain orientation map in Euler’s colour. The grain colour variation is related to their crystal lattice orientation where similar colours indicate similar orientation.](image2)
5. Microstructural Characterization of As-received AA2024-T351 Alloy

Figure 5.16: BSE micrographs of grains showing (a) grain orientation and sizes, (b) increased magnification of the bright grain with 44 µm length in (a), and (c) the high magnification of the selected region marked in (b), showing precipitation at grain boundary.

As different grain boundaries with relative grain energies can influence intergranular corrosion, precipitation and solute depletion\textsuperscript{10}, an investigation of grain boundary precipitates was conducted by conventional and high resolution transmission electron microscopy on twin-jet electro-polished thin film foils of AA2024-T351 alloy. The results are displayed in Figure 5.17 which illustrates two grain. By contrasting, the dark presents grain 1 and the bright region grain 2. The line between the two grains is the grain boundary. There is a relatively dense population of nano-sized particles, with the same orientation. Different shapes of particles are revealed both at the grain boundary and within the grains.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

Figure 5.17: TEM micrograph of a grain boundary between grain 1 and grain 2 with the presence of precipitates at the grain boundary and within the grains.

Figure 5.18 (a) is a TEM image of grain and grain boundary precipitation. A square shape precipitate particle was selected, marked with number 1, for elemental and composition analysis. Figure 5.18 (b) displays line scan results for the selected particle. Al, Cu, Fe and Mn are present where EDX analysis is shown in Figure 5.18 (c). The composition of the particle is consistent with Al (Cu-Fe-Mn).
Figure 5.18 (a) TEM micrograph of grain boundary precipitates and dispersoids. (b) Line scan showing elemental distribution in the precipitate particle at grain boundary position 1 and (c) EDX analysis of precipitate particle at position 1 of the grain boundary.

The circled region in Figure 5.18 was magnified and a number of precipitate particles were selected based on their different shapes and positions at the grain boundary as well as within the grain. Selected particles were numbered from 1 to 4 and results are presented in Figure 5.19 (a-e). Figure 5.19 (a) is a TEM micrograph showing three precipitate particles of size from 200 to 300 nm, two with a needle shape and the middle has a lath shape right at the grain boundary. Two of them were selected and examined. Another two in the grain with square and roughly round shapes, with sizes range from 50 to 200 nm, were selected for EDX examination. Figure 5.19(b) shows EDX analysis results of particle 1 at the grain boundary where aluminium, copper and manganese and a very small peak of iron are detected, respectively. Particle 2 and particle 3 are of square and roughly round shapes, respectively with dimensions around 200 nm. Results of EDX analysis are revealed in Figures 5.19 (b) and (c). Both EDX results show peaks of an aluminium, copper and manganese. The fourth particle with a needle shape located at the grain boundary, exhibits peaks of an aluminium and copper suggesting the presence of second phase particles of Al\textsubscript{2}Cu particles.
Figure 5.19: (a) TEM micrograph of four precipitates at and near the grain boundary. (b-e) EDX spectra showing the elemental composition of the selected precipitates (1-4), respectively.
Further investigation of the content of particle 4 was conducted using a line scan profile and EDX. Results are shown in Figure 5.20. The line scan profile shows a high peak of Cu, indicating the presence of Al₂Cu particle at the grain boundary.

Figure 5.20: TEM micrograph with line scan and EDX analysis of precipitates.

The microstructure analysis results show a good agreement with the finding of the literature for AA2024-T351 alloy, which has been extensively studied. Since the strength of Al-Cu-Mg alloys depends highly on precipitates formed during ageing, with phase morphology consisting of laths and needles shapes \[^{11}\], the Cu and Mg ratio in precipitates phases in particular S-phase is crucial in determining the alloy strength. It was found that S-phase dominates the precipitation hardening in the peak aged condition for both stretched and non-stretched alloys \[^{12, 13}\]. Hardening precipitate formation is related to the alloy composition where precipitates such as Al₂CuMg \[^{14-17}\] are dominant in AA2024 while Al₂Cu is dominant in AA2017 \[^{16, 18-20}\]. However, S-phases can significantly reduce the corrosion resistance, as accumulation of these precipitates along the grain boundary forming a chain that can lead to intergranular corrosion (IGC).
5.4 **Surface Potential of the as-received AA2024-T351 alloy**

Surface potential measurements were conducted on AA2024-T351 alloy using scanning Kelvin probe force microscopy (SKPFM). Surface potential measurements of various intermetallics with respect to the matrix are presented in Figures 5.21-5.24. Figure 5.21 (a) shows the topography map of the as-received AA2024-T351 alloy with second phase particles appearing on the surface. The second-phases can be distinguished by their shapes with different colour contrast. The topographic map displays locations of the second phase particles on the surface; in contrast the colour indicates the height of the patterns. Four particles with different shapes are marked (numbered 1 to 4). For potential measurements in particular particle number 2, that is believed to be S-phase ($\text{Al}_2\text{CuMg}$), can be distinguished by its round shape compared to the irregular shape of the $\text{Al–Cu–Mn–Fe-(Si)}$ particles. The corresponding SKPFM potential map in Figure 5.21 (b) of the as-polished AA2024-T351 alloy provides a much clearer indication of the location of the intermetallic particles on the surface. The particles in white colour show positive potential values as shown in Figure 5.22 (b), which indicates a cathodic behaviour. There are many small particles, which appear as brown dots on the potential map of Figure 5.21 (b). These dots showed negative potential and represent as holes in the surface as illustrated in Figure 5.22 (a). Out of these particles, four intermetallic particles were marked with relation to the shape difference. The scanned particles showed negative potential, as indicated in Figure 5.22 (b), and are anodic second phases.
Figure 5.21: 2-D SKPFM micrographs with scale bar of (a) surface topography and (b) surface potential. Numbers 1-4 are elected particles to be measured for surface potential.

Figure 5.22, shows the line scan results of the selected particles numbered 1 and 2. The line is nearly flat on the main surface and ascends when particle 1 is reached, indicating a positive potential (cathodic) as indicated by the blue arrow. The potential decreased at particle marked with number two, the negative potential value indicating an anodic second phase, as illustrated in the magnified part of the dashed circle.

Figure 5.22 (b) displays the surface potential profile of the line scan. The profile shows three potentials values, the surface potential of the matrix, with a value around 25 to 50 mV, a negative potential of value of -125 to -150 mV at the dip assigned to the anodic second-phase particle and a positive potential value of 300 mV at the peak assigned to a cathodic second phase. Figure 5.22 (c) displays the line scan profile and superimposed on the SKPFM image.
5. Microstructural Characterization of As-received AA2024-T351 Alloy

Figure 5.22: SKPFM micrographs of particles. (a) 3-D surface potential shows anodic and cathodic second-phases, (b) Surface potential profile of the line scan and (c) potential profile superimposed on SKPFM image.
Figure 5.23, illustrates another line scan at a different location on the surface. The potential scan crosses the particles numbered 3 and 4. The potential line profile measurement is depicted in Figure 5.23 (b). The profile behaviour shows two peaks at locations numbered 3 and 4 with positive potential values of 350 and 250 mV respectively. The particles with positive potentials are cathodic. There are two narrow sharp dips and one wider dip between the two peaks with potential values over -70 mV which due to the presence of small anodic particles.

Figure 5.23: SKPFM images. (a) 3-D surface potential illustrates anodic and cathodic second phase particles and (b) surface potential profile of the line scan of particle 3 and particle 4 in Figure (a).

More surface potential measurements were taken on different intermetallic particles on the surface. Figure 5.24 (a), shows a mapping of the surface potential at a selected rectangular area of 60 µm x 60 µm. A large particle of white colour, with irregular shape, appears on the surface and the matrix (α-phase) surface appears in brown colour. The particle could be Al-Cu-Mn-Fe or Al-Cu-Mn-Fe-Si, which is characterized by a cathodic potential. Figure 5.24 (b) demonstrates the surface potential profile of the particle in Figure 5.24 (a). It has a positive potential value of 250 mV with respect to the matrix. The potential difference $\Delta E = \Delta E_{\text{particle}} - \Delta E_{\text{surface}}$ between the highest potential peak value and dip value relative to the surface is 200 mV. Figure 5.24 (c) is a 3-D surface potential mapping of a selected area of the
specimen surface. Table 5.1 summarizes the potential values of the various particles measured.

Figure 5.24: Scanning Kelvin Probe Force micrographs of surface potential measurements of irregular shaped particle. (a) 2D topography, (b) measured surface potential with respect to distance and (c) 3D topography with surface potential measured path.
Table 5.1: Intermetallic particles surface measurements.

<table>
<thead>
<tr>
<th>Particle no.</th>
<th>Particle type</th>
<th>Potential type</th>
<th>Potential (mV)</th>
<th>Potential difference ΔE (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-phase</td>
<td>-</td>
<td>Matrix</td>
<td>Surface potential</td>
<td>25</td>
</tr>
<tr>
<td>A</td>
<td>Al-(Cu-Mn-Fe)-Si</td>
<td>Cathodic</td>
<td>250</td>
<td>225</td>
</tr>
<tr>
<td>1</td>
<td>Al-(Cu-Mn-Fe)-Si</td>
<td>Cathodic</td>
<td>300</td>
<td>275</td>
</tr>
<tr>
<td>2</td>
<td>Al₂CuMg</td>
<td>Anodic</td>
<td>-125</td>
<td>135</td>
</tr>
<tr>
<td>3</td>
<td>Al-(Cu-Mn-Fe)-Si</td>
<td>Cathodic</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>4</td>
<td>Al₂Cu</td>
<td>Cathodic</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The hard intermetallic particles protrude from the surface of a freshly polished sample because of i) the greater hardness compared to the matrix; ii) differential polishing rates and dissolution reactions during polishing, with a lower rate of polishing of the particles compared to the matrix [15, 21, 22]. The SKPFM potential value for S-phase (Al_2CuMg) particles shows a negative potential of around -150 mV with a standard deviation of 25 mV. Taking account that measured potential values of the particles are not inverted, this value is very good in agreement with the value observed by other researchers of +150 mV [22, 23]. Similar observations for the cathodic particles, with values up to 250 mV, showed agreement with the values in literature. Hence the surface potential map revealed a surface potential of around 150 mV of the S-phase where S-phase form 60% of the population of the surface as reported by Buchheit [14]. In addition, the open circuit potential (OCP) and corrosion current density of S-phase in 0.1 M NaCl solution was reported to have value -830 mV and 9.3 x 10^{-3} A/cm^2 respectively [24]. This suggests a galvanic coupling can occur between the S-phase and the respective aluminium matrix. Where the aluminium will preferentially corrode, if the particle is nobler otherwise the particle will corrode if the matrix is nobler [25].

5.5 Conclusions

- The main intermetallic particles of AA2024-T351 alloy such as spherical shaped S-phase particles, round shaped Ө-phase particles and irregular shaped Al-Cu-Mn-Fe-(Si) particles have been identified by their shapes, sizes and chemical compositions. Each particle was studied and analysed in details using SEM/FEG SEM, EDX line scan and EDX element mapping.

- Ө-phase particles (Al_2Cu) were found with dimensions from 955 nm to 1.21µm wide and 1.33 µm to 1.51µm long, containing copper content of 33 at% of copper. S-phase with typical size has copper content in the range of 32 - 40 at%. The S-phases were observed to have a higher population density compared to the other particles. Irregular shape particles of Al-Cu-Mn-Fe-(Si) are distinguished by comparatively large size around 8 µm. The distribution of elements is not uniform as indicated by the variation in the
brightness. Copper is evident in the bright area, while more presence of Fe and Mn in the darker area. At higher magnification EDX mapping, it is evident that part of irregular shape particle could contain Al$_2$Cu particles.

- Small sized particles in the range of nanometres were observed by TEM on samples thin film foil prepared by twin-jet electropolished. Dispersoids were identified that contain Al, Cu and Mn. EBED mapping showing the grain orientations in the AA2024-T351 alloy microstructure. Precipitates of different shapes and brightness at the grain boundary were examined. EDX and line scan results indicated the presence of Al$_2$CuMg, Al$_2$Cu and Al$_{20}$Cu$_3$Mn$_3$ in laths and rod like shapes lined at the grain boundaries.

- SKPFM study of potential surface measurements of Al$_2$CuMg was define and found to have anodic potential different from the matrix in a range of -125 to -150 mV. Cathodic particles displayed potential up to 300 mV higher than the matrix, where the matrix was taken as reference with value around zero.
5.6 References

Chapter 6

Microstructural Characterization of Excimer Laser-melted AA2024-T351 Alloy

6.1 Introduction

This chapter presents an investigation of microstructures of AA2024-T351 alloy after excimer laser surface melting. It includes the effects of alloy surface conditions and laser operating parameters on surface melting, in terms of surface morphology, melt depth, defect formation, microstructural changes and solute bands formation. The variation of laser operating parameters was based on fixing the laser fluence with variable number of laser pulses. The microstructural characterisation was carried out using SEM/EDX, TEM/EDX and XRD. The surface potential measurements were conducted using Scanning Kelvin Probe Force Microscopy (SKPFM). The surface topography was assessed using ADE phase shift MicroXam white light interferometer equipped with the TalyMap Platinum software. In addition, nano-indentation was used to evaluate the hardness changes of the surface after LSM.

6.2 Influence of surface conditions and laser operating parameters on surface melting

Surface melting by an excimer laser is controlled by the combination of laser fluence and number of pulses, as these parameters affect the surface temperature and melt depth, consequently affecting the melting of second phase particles within the aluminium matrix. In addition, surface conditions of the substrate prior to laser treatment also affect the absorption of the laser beam energy.
6.2.1 Effect of surface conditions

Three different surface conditions were prepared: 1) As-received alloy from the manufacturer, where heavy oxide film, surface deformation and greasy contaminants are present on the surface; 2) Ground surface with final finishing using 1200 grit SiC sandpaper, to ensure removal of the heavy oxide film, surface deformation and contaminants and 3) Ground surface with final finishing using 1200 grit and then coated with a thin layer of graphite using a graphite spray. The purpose of applying the graphite coating was to enhance absorption of the laser beam energy by the substrate. The specimens with these three surface conditions were exposed to a laser beam with variable spot sizes and power outputs to produce different laser fluences.

Figure 6.1 illustrates three laser surface conditions: as-received, 1200 grit ground and graphite coating. These were irradiated at variable laser fluences with a fixed number of pulses of 10 at repetition rate of 10 Hz. Variable laser fluences were achieved by varying laser beam sizes or pulse energies. As shown in Figure 6.1, the marks on the surface after laser irradiation become bigger with increasing pulse energy and laser fluence on each surface condition. In comparison between three surface conditions, from the surface appearance, biggest marks are observed on the surface with graphite coating, representing the highest laser beam absorption.

Figure 6.1: Three surface conditions. (i) as-received, (ii) 1200 grit ground surface and (iii) 1200 grit ground surface with graphite coating. The surfaces were exposed to excimer lasers with two different beam sizes and varied pulse energy.

SEM micrographs of the cross-sections of the three surface conditions are displayed in Figure 6.2. Figure 6.2 (a) and (b) show results of excimer laser radiation on the graphite coating surface condition, revealing a rather rough surface and non-uniform

melted layer. It could be the result of the formation of plumes due to extremely high temperature of the melt where explosive phase change could occur forming mixture of liquid and vapour leaving the surface like an explosion and freezes as depicted in Figures 6.2 (a)-(b). Figure 6.2 (c) is the cross section of the laser melted layer on the as-received surface condition, showing a very thin melted layer with depth of around 2 µm. The large intermetallic particle at the interface is partially melted, leaving short trails of fogy white solutes. However, since the as-received surface presents a certain degree of non-uniformity like non-uniform distribution of heavy oxide, by manufacturing, the laser beam absorption might become non-uniform leading to non-uniform melt layers. Figure 6.2 (d) shows the result of the ground surface, presenting a relatively uniform melted layer with melt depth of 5 µm and more refined microstructure than the matrix.

![Figure 6.2: SEM micrographs of cross sections of excimer laser-treated layers with different surface conditions.](image)

In comparison among the three surface conditions results, it is believed that the ground surface with 1200 grit SiC sandpaper is capable of generating a relatively uniform LSM melted layers with smooth surface, due to the removal of all surface
contaminants. Therefore, only 1200 grit grinding was applied to the AA2024-T351 alloy surface prior to laser surface melting process throughout the project.

6.2.2 Effect of laser operating parameters

In this experiment, the number of laser pulses was fixed at 10, repetition rate was set at 10 Hz and the laser fluence was varied from 1.9 to 7 J cm\(^2\). Figures 6.3 (a-d) present SEM micrographs of cross sections of the melted layers, showing the effects of laser fluence on the melted layers. In general, the melt depth is increased by increasing the laser fluence. When a low laser fluence of 3.5 J cm\(^2\) was applied, only partially melting of the intermetallic particles is observed. The melt depth is less than 2 µm. Under this condition, it is believed that the temperature of the melt pool is not sufficient to completely dissolve the intermetallic particles. When increasing laser fluence to 4.9 J cm\(^2\), the temperature of the melt pool is increased, therefore enhancing the melting of the intermetallic particles, however still not sufficient to achieve fully melting. The distribution of the solutes due to the laser melting results in less homogenization of the melted layer. Further increasing in the laser fluence to 5.4 J cm\(^2\), the melt depth of 5 µm was achieved with improvement of homogenization and refinement of the microstructure as shown in Figure 6.3 (c).

Figure 6.3 (d) displays melted layer in thickness of 5 µm resulted from LSM treatment with a laser fluence of 7.0 J cm\(^2\). The melted layer is relatively uniform with homogenous microstructure. Two large intermetallic particles at the interface between the matrix and laser-treated layer have been partially melted. As a result of a dissolving intermetallic particle, coarse intermetallics and fine dispersoids within the melted layer, the solute enriched bands are evident at the bottom of the melted layer. In general, it can be seen that the increase of laser fluence results in an increase in the melt depth with more complete melting/dissolving of various intermetallics to form refined microstructure.

Figure 6.3: SEM micrographs of cross sections of melted layers produced by varied laser fluence used in the LSM treatment of AA2024-T351 alloy. (a) laser fluence of 3.5 J/cm², (b) laser fluence of 4.9 J/cm², (c) laser fluence of 5.4 J/cm² and (d) 7.0 J/cm². The number of laser pulses is 10.

Therefore, in order to achieve reasonable melt depth, fully dissolution of second phase particles, and uniform microstructure of the melted layer, the optimized laser fluence is 7.0 J cm⁻² (i.e. laser beam size is 1.75 µm × 3.5 µm) for the ground surface condition at the fixed number of laser pulses of 10. Under these conditions, the melt pool temperature is sufficient to fully dissolve the second phase particles without formation of plasma, and also the increase of the temperature results in an increased atomic mobility and solubility than the temperature of the molten material produced by lower fluence, consequently, leading to rapid material homogenization and refinement of microstructure. Since the substrate of the specimen works as a heat sink (high self-quenching rates), excimer LSM can produce solidification front velocities up to several m s⁻¹ with cooling rate up to 10¹¹ K/s [¹]. Such rapid quenching can extend the solid solubility of the elements like copper and silicon in the α-aluminium solid solution.

Based on the results described above, the laser fluence is chosen as 7 J cm⁻², and the specimens are ground by 1200 grit sandpaper without graphite coating. The number of laser pulses is variable throughout the study.

6.3 Surface morphology of excimer LSM-treated AA2024-T351 alloy

Once the surface of AA2024-T351 alloy is melted and re-solidified, morphological changes of surface take place, resulting in certain degree of surface roughness, in addition to the microstructural changes.

6.3.1 Single laser shot

Surface morphologies of the alloy after a single laser shot at the laser fluence of 7 J cm\(^{-2}\) are investigated, using SEM and the white light interferometer and presented in Figure 6.4. There are two distinguished regions, region 1 and region 2, as shown in Figure 6.4 (a). With higher magnification, Figure 6.4 (b) presents a relatively smooth surface for region 1, where Figure 6.4 (c) shows wavy features for region 2.

![Figure 6.4: (a) SEM micrographs showing the morphology of laser-treated surface of AA2024-T351 alloy with two distinct regions, (b) high magnification of region 1 and (c) region 2.](image)

Due to the feature of non-uniform energy distribution of the laser beam, within the laser spot, different temperature distribution is also resulted in. In region 1, the laser energy should be highest, and thereby the temperature within region 1 is also the highest which leads to the liquid to pull away from the hotter to the cooler region forming a smooth surface. For region 2, the wavy or rippled morphology is as result
of a fluid flow away from the point of laser spot impact, enhancing deformation of the melted layers. As a consequence of fast cooling rate where high heating energy was absorbed by the massive substrate (heat sink) \(^{2, 3}\), this deformation in the form of waves or ripples is frozen as they flow.

### 6.3.2 Overlapping effect

In order to cover large areas, overlapping laser melted tracks is often required. This involves re-melting of portion of previously melted track and re-heating portion of previously melted track, as illustrated in Figure 6.5 (a).

In this experiment, an overlap ratio of 20\% was applied. Plan views of the surface morphologies after LSM of AA2024-T351 alloy are presented in Figures 6.5 (b-d). The number of laser pulses was varied from 10, 25 with frequency of 10 Hz and 50 with frequency of 20 Hz, covering an area of 14 mm \(\times\) 6 mm = 84 mm\(^2\). The melted surfaces present wave-like or rippled morphology as previously reported typical for pulsed laser radiation \(^{4}\). The distance between the ripples is varied with the number of pulses. Increasing the number of pulses decreases in the distance, as seen in Figure 6.5. Surface morphology (as shown in Figure 6.5) was also reported by Koutsomichalis et al \(^{5}\), as a distinctive morphology produced by an excimer laser radiation. In addition, the width of melted track is slightly varied with the number of pulses. As the number of pulses increases from 10 to 50 pulses, the width of melted track is increased. As a result, increasing the number of pulses widens the overlap area, particularly the re-heated region. This can be evident from Figure 6.5. In the magnified part for each designated number of pulses, it can be seen that wave tips pointing differently which could be related to the increased number of pulses.

![Diagram of overlap region and (b) SEM surface view of LSM overlap regions](image)

Figure 6.5: (a) Schematic diagram of overlap region and (b) SEM surface view of LSM overlap regions of AA2024-T351 alloy treated with a fixed laser fluence of 7 J cm\(^{-2}\) at different numbers of pulses.

### 6.3.3 Surfaces roughness measurement

The interferometry was utilized for generating 3-D topographical maps of the LSM treated surface by different number of pulses. The surface profiles of the specimens LSM treated at 10, 25 and 50 pulses are shown in Figures 6.6 - 6.8, respectively.

Figures 6.6 (a), 6.7(a) and 6.8 (a) show the SEM images presenting three distinct areas within melted tracks and overlapping regions. In all the SEM images, wavy morphology is evident. As marked on the micrographs, the laser beam scanning direction was to the right for track 1 while that was to the left for track 2. The different scanning directions produce different directions of ripples as indicated. At the edge of the track 2, there is always a distinct area slightly above the surface that is a typical feature, due to solidification of the melt pool generated by laser. Figures 6.6, 6.7 and 6.8 (c-e) show detailed results of the three areas through 3-D mapping. From the 3D mapping examination for all the surfaces produced with different number of pulses, the height and valleys distribution is apparent. The topographical
characteristics of the surface roughness can be measured by S field parameter set, which depends on the height amplitude and the spacing frequency for describing amplitude and spatial information. For topography characteristics, $S_a$ represents mean height; $S_q$ is root mean square length surface, $S_z$ is maximum height of the scale surface and $S_{dr}$ is area increased percentage compared with a flat surface. The measured values of S field parameter set are presented in Tables 6.1 - 6.3 for the number of laser pulses of 10, 25 and 50 pulses, respectively.

Figure 6.6: (a) SEM image of LSM AA2024-T351 alloy treated by 10 pulses with 20\% overlap, (b) 3-D track 1 surface profile. (c) 3-D track 2 surface profile. (d) 3-D overlap region surface profile.

Figure 6.7: (a) SEM image of LSM AA2024-T351 alloy treated by 25 pulses with 20% overlap, (b) 3-D track 1 surface profile, (c) 3-D track 2 surface profiles and (d) 3-D overlap region surface profile.
Figure 6.8: (a) SEM image of LSM AA2024-T351 alloy treated by 50 pulses with 20% overlap, (b) 3-D track 1 surface profile, (c) 3-D track 2 surface profiles and (d) 3-D overlap region surface profile.

Table 6.1: Interferometer measurements for AA2024-T351 treated with 10 laser pulses at laser fluence of 7 J cm$^{-2}$.

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<tr>
<th>Height parameters ($\mu$m)</th>
<th>LSM Areas</th>
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<tr>
<td></td>
<td>Track 1</td>
</tr>
<tr>
<td>$S_a$</td>
<td>2.11</td>
</tr>
<tr>
<td>$S_q$</td>
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<tr>
<td>$S_{dr}$</td>
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Table 6.2: Interferometer measurements for AA2024-T351 treated with 25 laser pulses at laser fluence of 7 J cm$^{-2}$.

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<tr>
<td>$S_q$</td>
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</tr>
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<td>$S_z$</td>
<td>18.8</td>
</tr>
<tr>
<td>$S_{dr}$</td>
<td>33.3 %</td>
</tr>
</tbody>
</table>

Table 6.3: Interferometer measurements for AA2024-T351 treated with 50 laser pulses at laser fluence of 7 J cm$^{-2}$.

<table>
<thead>
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<th>Height parameters ($\mu$m)</th>
<th>LSM Areas</th>
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<td>Track 1</td>
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<tr>
<td>$S_q$</td>
<td>3.9</td>
</tr>
<tr>
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<td>26.2</td>
</tr>
<tr>
<td>$S_{dr}$</td>
<td>24.7 %</td>
</tr>
</tbody>
</table>

As shown in the 3D topography, the LSM results in the formation of ripples and the re-heated area becomes smooth and increasing the number of pulses the distance between ripples decreases. In comparison of the surface parameters, it reveals that increasing in number of pulses, the average value of $S_a$ increases from 2.06 at the 10 pulses, to 3.17 at the 50 pulses. Due to the increases in surface roughness, increasing in the number of pulses also increases in the surface areas from 12.27% at the 10
pulses, 34.7% at the 25 pulses, to 32.3% at the 50 pulses in the reference of a flat surface.

### 6.4 SEM/EDX analysis

A large cross-section of an ultramicrotomed laser-treated specimen with top view is shown in Figure 6.9 (a). The SEM micrograph clearly illustrates the formation of ripples on the surface. The cross-sectional view in Figure 6.9 (b) shows the melted layer. It is evident that the melt depth of the melted layer is not even, reflecting the wavy topography. The succession of valleys and hills results in the difference in thickness of the melted layer. In addition, some pores are evident in the overlap regions.

![Figure 6.9: SEM micrographs of laser-melted layer at 10 pulses at laser fluence of 7 J cm\(^{-2}\), showing (a) angled-view and (b) cross-sectional view.](image)

Under higher magnifications, Figure 6.10 (a) displays a fairly uniform thin melted layer without any coarse intermetallic particles within the melted layer. The dispersoids present in the matrix are not evident, suggesting that all the particles are dissolved and are not precipitated out of the solution after rapid cooling. At the interface, a partially melted intermetallic particle is apparent. The melt depth is around 5 µm with homogenous refined microstructure. Figure 6.10 (b) shows the selected area of the melted layer with the partially melted particles located at the melted layer/matrix interfac. Figure 6.10 (c) is the magnified view of selected area in Figure 6.10 (b), illustrating an EDX line scanning path across the melted layer from the top to the partially melted particle at the interface and then down to the matrix. Figure 6.10 (d) shows the results of line scan profiles. It indicates a uniform elemental distribution within the melted layer, but the peaks of copper and
magnesium are evident on the partially melted particle, and the particle appeared in the matrix. Therefore, it is believed that the laser melting results in uniform distribution of various elements within the laser melted layer.

Figure 6.10: (a) SEM micrograph of cross sectional view of the melted layer and part of the matrix with partially melted IMP at the interface, (b) SEM micrograph of cross sectional view of selected area of the melted layer and part of the matrix for line scan analysis (c) magnified view with EDX line scan trail marked in red line and (d) line scan profile. The alloy was treated by laser fluence of 7 J cm\(^{-2}\) and 50 number of pulses.

Figure 6.11 shows element distribution mapping of the laser-melted layer in comparison with the matrix. It can be seen that, under this magnification, no particular element is found to be enriched or depleted within the melted layer and a generally uniform elemental distribution of all elements are achieved.
Figure 6.11: FEG-SEM/EDS elemental mapping showing laser-melted layer treated by 10 pulses and at laser fluence of 7 J cm\(^{-2}\) at the top. The rest is matrix of 2024-T351 alloy.

Figure 6.12 (a) shows the cross-section of the melted layer treated by 25 pulses. It can be seen that, at the interface between the melted layer and the matrix, two partially melted intermetallic particles are evident. Figure 6.12 (b) shows a SEM micrograph of the part of the molten area with higher magnification, revealing the formation of solute bands resulted from the melting of the top part of the intermetallic particle. The solute-enriched phases which are formed just above the partially melted particles, might be due to the limited diffusion of the solute during laser surface melting. Increasing magnification of the selected area in Figure 6.12 (b), Figure 6.12 (c) reveals the details of the elemental segregation. This segregation reflects its dendritic/cellular feature which is a typical characteristic of rapid solidification of laser melted alloys.
6.5 XRD phase analysis

Figure 6.13 shows the XRD patterns of the laser-melted surfaces treated with varied number of pulses from 10, 25 to 50 pulses at laser fluence of 7 J cm\(^{-2}\), in comparison with the as-received AA2024-T351 alloy. As described in Chapter 5, the as-received alloy shows the presence of a number of intermetallics, including S-phase (Al\(_2\)CuMg), Al\(_7\)Cu\(_2\)Fe(Mn), and Al\(_2\)Cu. After laser treatment, the second phases greatly reduced with the increased number of laser pulses and dissolved within the \(\alpha\)-Al solid solution. It can be seen from the XRD patterns in Figure 6.13 for LSM with 10 laser pulses, that the S-phase (Al\(_2\)CuMg), which is well identified in as-
received alloy, was eliminated in the laser processing, while a small amount of \( \text{Al}_2\text{Cu} \) has been formed. This change of phases from S-phase to \( \theta\)-\( \text{Al}_2\text{Cu} \) might be the evaporation of magnesium during LSM treatment, where the S-phase formation was reported only at critical Cu-Mg and Mg-Si ratios \([6]\). Furthermore, other large intermetallic particles like \( \text{Al} (\text{Cu,Fe,Mn}) \) were still present on the melted surface but with low intensity. The presence of such phases might be due to the relatively shallow melt depth, allowing the intermetallic phases in the matrix beneath the melted layer to be detected by the XRD. Furthermore, it could also suggest an incomplete dissolution of the phases under this condition. When the number of laser pulses is increased to 25 pulses, only tiny peaks representing the intermetallics can be seen suggesting better dissolution of the phases and a deeper melt depth. As the number of laser pulses is increased to 50, no intermetallic particles are evident, indicating a complete dissolution/removal of various intermetallic particles within the melted layer.

![Comparison of XRD patterns of the as-received alloy and laser treated alloy at 10, 25 and 50 pulses and at laser fluence of 7 J cm\(^{-2}\).]

6.6 Solute band formation

Figure 6.14 (a) shows the upper part of the melted layer free from visible particles. However, at the interfacial region between the melted layer and the matrix, a number of solute bands are observed, which are in their form of thin lines aligned parallel to the interface, as marked by the arrows. The distance between the parallel solute bands is around 1 µm as shown in Figure 6.14 (b). The dispersoid precipitates, that are apparent in the matrix and distinguished by lath shapes, are no longer exist within the melted layer. However, a further increased magnification at the melted layer/matrix interface area reveals a number of dispersoids still presented around the bands as illustrated in Figure 6.14 (c).

Figure 6.14: SEM micrographs cross sectional view of solute bands in melted layer treated with laser 25 pulses and at laser fluence of 7 J cm\(^{-2}\). (a) solute bands at the bottom of the melted layer, (b) parallel solute bands separated by 1 µm and (c) increased magnification of solute bands.

Therefore, it is evident that the excimer laser surface melting results in dissolution and removal of second phase particles due to the rapid cooling process. However, the rapid solidification process also results in the formation of solute bands, that will be confirmed later by elemental analysis. It is worth noting that, the formation of such bands is different from the bands formed by the partially melted intermetallics given
in Figure 6.12. The SEM micrographs suggest that this type of the bands has the band thickness less than 10 nm in size as displayed in Figure 6.14 (c).

The TEM was used for further investigating the microstructural characteristics of the melted layers and solute bands. Figure 6.15 (a) shows that the upper region of the melted layer is free from intermetallic particles. The melted layer produced by 10 laser pulses is roughly 5 µm in thickness. It is evident that the homogenous microstructure is achieved after excimer LSM. Furthermore, features of nanocrystalline formed in rapid solidification are also present in some regions of the melted layer. This nanocrystalline re-solidification phenomenon was also reported previously, which occurs when the interface growth front moves at velocities below the interface stability threshold \[7\].

In addition, two solute bands forming two parallel lines along the melted layer/matrix interface are evident. There are a number of scattered dispersoids at the interfacial region. Figure 6.15 (b) reveals a feature of convection flow pattern, suggesting a number of convections within the melt pool take place during laser melting process. The convection might be caused by radial temperature gradient that could be in the order of \(10^2\) to \(10^4\) K mm\(^{-1}\) in the melt pool as reported \[8\], that works as a driving force for mixing, leading to redistribution of the solutes from the dissolved intermetallic particles within the melted layer. With increased magnification of solute bands, Figure 6.15 (c) shows stream-like solutes of dissolved element or elements of thickness around 20 nm and several dispersoid particles with a lath and round shapes, scattered around these streams. Figure 6.15 (d) demonstrates the size of the refined particles compared with a dispersoid particle of size around 80 nm at the top of the micrograph. It can be seen that the refined scattered particles are in a size range of around 5 nm, as shown in Figure 6.15 (e).
Figure 6.15: TEM micrographs of melted layer treated by 10 pulses and at laser fluence of 7 J cm$^{-2}$. (a) The melted layer, (b) Magnified part of the melted layer in (a), (c) Two parallel solute lines at interface with precipitates, (d) and (e) Magnified part of the melted layer showing a featureless structure.
Figure 6.16 (a) shows TEM micrographs of the interface between the laser melted layer and the matrix. The line marked with number 1 is set to cross one of the solute bands. EDX analysis for elemental composition analysis was carried out and results are displayed in Figure 6.16 (b). The elemental profiles cross the solute band show enrichment in copper. Therefore, these solute bands are called copper-rich solute bands.

Figure 6.16: (a) TEM high-angle annular dark-field (HAADF) image of a band shown in Figure 6.15 and (b) EDX elemental profiles shows slight copper enrichment.

Figures 6.17 (a) and (b) show a single and continuous solute band in the white and dark fields, respectively. The latter also shows the selected area for EDX line scan analysis. The result of EDX line scan is shown in Figure 6.17 (c). The solute band is found to be copper-rich and accompanied by iron enrichment. Further investigation of the second solute band and compared with the upper band in the image are shown in Figure 6.17 (d). Figure 6.17 (e) illustrates two solute bands where the one on the top was analysed in comparison with the bottom one in the white and dark field. Figure 6.17 (f) shows the EDX results of the two solute bands in comparison. The bottom solute band is only rich in copper.
Figure 6.17: TEM high-angle annular dark-fields (HAADF) images of solute bands. (a) and (b) show a single and continuous solute band in white and dark fields, (c) EDX elemental analysis of the line scan indicated by 2 in (b), (d) and (e) two parallel solute bands in white and dark field as indicated by the red arrows in (d). (f) EDX elemental analysis of the line scan indicated by 3 in (e).

Figure 6.18 illustrates a few examples representing a complete melting, partial melting of intermetallic particles, solutes and solute rich bands with different intensities. Figure 6.18 (a) shows solute bands in different forms. On the left, indicated by vertical blue arrow pointing upward, the solutes are in circular motion (i.e., convection). A high concentration can be produced by a large irregular intermetallic particle which were not dissolved during laser process. In the middle of Figure 6.18 (a), the red and blue arrow indicates a solute band formed a tail out of the partially melted intermetallic particle. On the right side, a large intermetallic particle of around 5 µm, was partially melted from the top. Figure 6.18 (b) displays the solutes frozen with the wave motion at the edge of the melt pool. Figure 6.18 (c) shows the fine solute bands in straight lines, in the melted layer near the interface. Figure 6.18 (d) reveals the presence of a very fine solute bands around 10 nm near the top of the melted layer.
Figure 6.18: SEM micrographs of various solute bands formed as a result of melting of IMPs and precipitates.

Figure 6.19 (a) shows solute bands segregation located at the interface and other fine solute bands are evident within the laser melted layer. Figure 6.19 (b) illustrates the appearance of dense solutes at the melted layer/matrix interface. In summary, solute bands appear in most parts of the melted layer as fine line with different degree of density. The degree of solute bands density significantly decreases at the upper part of the melted layer. Further, heavy presence of solute bands are found at interface between the melted layer and the matrix with relatively dense in some cases accompanied with segregation. They can be formed by partially melted intermetallic particles and undissolved second phases.

Figure 6.19: SEM micrographs showing thick solute bands at the interface between the melted layer and matrix, and (b) discontinuous solute band in the middle of the melt pool.

6.7 Defects in the melted layer

Defects, such as porosity in melted layers and in overlapped regions have been observed. However, no cracks are found. An investigation was conducted on both the melted layer and the overlap region for 10, 25 and 50 laser pulses at laser fluence of 7 J cm\(^{-2}\).

6.7.1 Melted layers

Figure 6.20 (a) shows part of the melted layer in which a large intermetallic particle in the size of more than 5 µm is found at the interface, and the upper part of the particle is dissolved. Figure 6.21 (b) reveals that a pore in size of 1 µm is present within the melt layer; and also another pore formed next to the unmelted intermetallic particle. Figure 6.20 (c) shows the presence of pores in which one is in diameter of 3 µm. The formation of porosity is usually believed to be from hydrogen presented in aluminium alloys after manufacturing. Such hydrogen attempts to increase its volume within the aluminium in the form of liquid. Due to the extremely short period of time for the hydrogen gas to escape from the melt pool, it is easily trapped in the melt pool to form porosity. Further more, during LSM treatment, the temperature of the melt pool exceeds vaporisation temperature of the magnesium. As a result, when the hydrogen has insufficient time to escape from the melt pool; on the other hand, vaporised magnesium from dissolving various intermetallics as left the melt pool, leaving porosity behind. In general, these types of defects can have a significant effect on the corrosion resistance of the melted layer.

Figure 6.20: SEM micrographs (a-c) showing formation of porosity within the melted layer treated at 10 pulses and at laser fluence of 7 J cm$^{-2}$.

6.7.2 Overlapped regions

Figure 6.21 shows the cross-sections of the overlapped regions treated by 10, 25 and 50 laser pulses, respectively. Figure 6.21 (a) illustrates the overlap of track 1 and track 2 treated by 10 pulses, where a wavy shape is evident within the overlap region. Figure 6.21 (b) displays the presence of small pores in the sizes of around 500 nm within the overlap region. However it is worth noting that the track 1 in thickness 2 µm is almost free from porosity, while the porosity seems only present in the track 2, which is melted twice. Figure 6.21 (c) displays a relatively large number of pores with different sizes within the overlapped tracks. The difference in the overlap regions for the three different laser operating conditions could be possibly related to the temperature of the melt pool, where an increased number of pulses results in higher temperature. When the temperature of the melt pool reaches the vaporisation temperature of magnesium, vaporisation of magnesium certainly contributes to the formation of porosity. In addition, the presence of hydrogen in the aluminium matrix due to manufacturing processes might be another reason. When the surface layer is melted during laser melting process, the hydrogen atoms form
hydrogen gas that tends to escape from the melt pool. However due to the extremely short pulses of 20 nm pulse width, there would be insufficient time for hydrogen gas to escape. Therefore some trapped hydrogen gas forms porosity in the melted layer. It is worth mentioning that within the overlap regions, the formation of porosity becomes more pronounced, due to the re-melting of the solidified alloy.

Figure 6.21: SEM micrographs of overlapped area of 10 (a), 25 (b) and 50 laser pulses (c) at laser fluence of 7 J cm$^{-2}$.

6.8 Surface potential measurement by SKPFM

SKPFM potential measurement of the melted layer was conducted to detect potential difference of various phases in comparison with the matrix. The far left part of Figures 6.22 (a) and (b) show the topography and surface potential maps of the cross-section of the melted layer produced by 10 laser pulses. The results regarding the matrix and intermetallic particles were presented and discussed in details in Section 5.3 of Chapter 5. Therefore, the results of SKPFM presented in this section are limited to the melted layer in this section. The melted layer with refined microstructure is less than 7 $\mu$m in thickness. The surface potential mapping of the melted layer shows clearly that the microstructure within the melted layer is free
from coarse intermetallic particles in comparison with the matrix. For more illustration, the topography and surface potential are mapped and displayed in Figure 6.22 (c). Detailed information of the surface potentials of the selected potential scan along the line A-B is illustrated by the potential profile in Figure 6.22 (d). The point A within the melted layer demonstrates a surface potential of 75 mV with respect to the matrix. The high peak on an intermetallic particle shows the surface potential of 300 mV with respect to the matrix.

Figure 6.22: 2-D SKPFM micrographs with scale bar for sample treated with LSM 10 pulses and laser fluence of 7 J cm\(^{-2}\). (a) surface topography, (b) surface potential of the melted layer, (c) 3-D mapping of the melted layer produced by 10 pulses LSM and (d) the corresponding line profile of the selected location.

Figure 6.23 (a) shows 2-D potential surface mapping of the melted layer of specimen treated with 50 laser pulses. The thickness of melted layer is around 12 µm free from
coarse intermetallic particles or precipitates. The surface potential line scan is taken by two-steps. First part of the line crosses the melted layer and the second part crosses the matrix, passing through the solute band at the interface and over other two separated second phase particles. The profile of surface potential along the line is displayed in Figure 6.23 (b). The surface potential of the melted layer has a relative uniform distribution of potential. There is a peak on the location of the solute band just above the interface between the melted layer and the matrix, with a value of ~100 mV with respect to the matrix. The line profile also show two high peaks, representing the surface potential of the two intermetallic particles in the matrix, with the values of +300 mV and +400 mV with respect to the matrix.

Figure 6.23: (a) 2-D SKPEM topography of the melted layer, solute bands and IMPs, after LSM at 50 laser pulses at laser fluence of 7 J cm$^{-2}$ and (b) the line profile of surface potential.

Therefore, the coarse intermetallic particles in the matrix are completely melted and the elements like copper, silicon, manganese and iron are dissolved into the solid solution of the $\alpha$-phase, resulting in an increase of surface potential within the melted layer with respect to the aluminium matrix. The surface potential of the solute band at the interface shows a higher surface potential around 100 mV, suggesting the possibility of initiating galvanic corrosion that is discussed in Chapter 6.

6.9 Residual stress measurement

It is worth mentioning, that the XRD for the measurement of residual stress is only available for the X-ray penetration depth larger than the melt depth of 5 – 7 µm.
When it is used for thin-film analysis, for example, in our case, the measurement may show a significant error. Nevertheless, the XRD has been applied in our case for LSM of AA2024-T351 alloy to compare the change of residual stresses before and after laser treatment. Generally, laser surface melting results in thermal gradient, leading to formation of thermal stress commonly tensile stress \[12\]. For the laser tracks produced by excimer laser surface melting using 10, 25 and 50 pulses, the residual stress measurement was carried out on the melted surface and also on the ground surface of by 1200 grit SiC sandpaper. A residual stress in the surface layers of thickness 10 to 15 µm of metallic materials can be verified by the measurements of the changes in the lattice parameters of the alloy matrix \[10\]. All the results measured on the surface treated by different number of laser pulses are tabulated and displayed in Table 6.4.

Table 6.4: Residual stress measured values for as received and laser surface treated at laser fluence of 7 J cm\(^{-2}\).

<table>
<thead>
<tr>
<th>Material</th>
<th>Residual stress (MPa)</th>
<th>0° (X-direction)</th>
<th>90° (Y-direction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received alloy ground with 1200 grit</td>
<td>-20.5±15.7</td>
<td>-27.7±16.3</td>
<td></td>
</tr>
<tr>
<td>LSM-10 pulses</td>
<td>50.2±84.3</td>
<td>74.7±99.1</td>
<td></td>
</tr>
<tr>
<td>LSM-25 pulses</td>
<td>98.6±22.5</td>
<td>115.9±25.3</td>
<td></td>
</tr>
<tr>
<td>LSM-50 pulses</td>
<td>73.0±19.8</td>
<td>97.8±19.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4 shows the presence of negative values of the ground surface before laser treatment, while the laser treated specimens reveal positive values in both directions. The negative stress indicates the presence of a compressive stress and the positive value indicates a tensile stress. From Table 6.4, it is evident that the excimer laser surface melting of AA2024-T351 alloy changes the sign of the residual stress on the melted surface from compressive to tensile stress. This is inconsistent with the data obtained by Panagopoulous and Badekas \[4, 10\], who observed a change of residual stress on the surface of an Al-4 wt % Cu alloy from tensile to compressive as a result of excimer LSM.

6.10 Hardness measurement by Nano-indentation

The hardness of the melted layer was measured by nano-indentation in comparison with the hardness of the un-treated alloy. The specimen was subjected to 20 indentations points forming a line of sequences of points, between each pair of points is a distance of 5 µm. The hardness line profile versus indenter numbers of 5 µm crossed distance is plotted and depicted in Figure 6.24.

The hardness value of 0.728 GPa in the melted layer shows an increase with respect to the hardness values of the matrix (0.258 GPa). Such increase in hardness might be attributed to the fact of that various elements like copper, silicon and etc. have been dissolved in α-aluminium matrix leading to solution hardening.

![Hardness Profile](image)

Figure 6.24: Hardness verses distance (calculated based on the number of indents and distance between two indents of 5 µm) measured by nano-indentation.

6.11 Conclusions

Microstructural characterisation of the Excimer LSM of AA2024-T351 alloy has revealed that:

- Surface conditions prior to LSM affects laser surface melting by affecting laser beam absorption. Among the as-received, graphite coated and ground surface with 1200 grit alloy surface conditions, the ground surface is selected...
and used throughout the work based on the uniformity of the melted layers and surface morphology.

- Excimer LSM results in the formation of ripples on the surface. The distance between the ripples decreases with increasing number of pulses.
- Overlapping to cover large area leads to re-melting and re-heating of previously melted track. Increasing the number of laser pulses increases the areas of re-melted zones at the fixed laser fluence.
- At the fixed laser fluence, increasing the number of pulses results in an increase in surface roughness, leading to increase in surface area.
- Under the laser operating conditions in this work, LSM results in thin-layer melting with the thickness in a range of a few microns up to 7 microns. Increasing the number of pulses increases the depth of melted layers.
- LSM results in dissolution of the intermetallics and dispersoids, existed in the as-received condition, within the melted layers.
- LSM results in the formation of solute bands. There are two typical types of bands. One is the formation of discontinuous, thin bands within the melted layers; the other one is the relatively thick bands at the interface between the melted layer and the substrate. The second one is typically enriched copper.
- The LSM layers exhibit uniform surface potential distribution with potential with respect to the matrix, also suggesting that the intermetallic particles are completed dissolved in the \( \alpha \)-aluminium solution.
- The melted layer presents tensile residual stress compared with the compressive stress on the ground surface.
- The nano-indentation measurement shows a slight increase in the hardness of the melted layer with respect to the matrix due to the dissolution of various elements in the \( \alpha \)-aluminium solution leading to solution hardening.
6.12 Reference


Chapter 7

Corrosion behaviour of AA2024-T351 alloy before and after laser treatment

7.1 Introduction

This chapter presents the corrosion behaviour of the AA2024-T351 alloy before and after laser treatment. A series of corrosion tests were carried out, including electrochemical potentiodynamic measurements in aerated and deaerated 0.1 M NaCl solutions, immersion tests in 0.1 M NaCl solutions for 24 hours and exfoliation test in EXCO solution for 6 hours based on ASTM G34-01 standard. Improvement in the corrosion performance after LSM is observed. The corrosion mechanisms of the AA2024-T351 alloy before and after laser treatment in various corrosion environments are discussed.

7.2 Electrochemical behaviour

7.2.1 As-received alloy

The anodic polarization behaviour for the as-received AA2024-T351 alloy in deaerated 0.1 M NaCl solution is shown in Figure 7.1. The polarization curve exhibits semi-passive region from -0.9 V to -0.5 V\textsubscript{SCE}, which is marked by an increase of potential with relatively constant current density value of $2.0 \times 10^{-5}$ A/cm$^2$ at breakdown point of the passive region. This passive region started from just above $E_{corr}$ and over a range of 0.4 V\textsubscript{SCE}. Pitting corrosion commenced for example, pitting potential ($E_{pit}$) occurs at the point -0.51 V\textsubscript{SCE}. In general, the pitting potential is defined by a sudden increase in the current density and can be attributed to the breakdown of the passive film and the start of generation of pits at sites of constituent particles.
7. Corrosion behaviour of AA2024-T351 alloy before and after laser treatment

7.2.2 Laser-melted alloy

7.2.2.1 In Deaerated 0.1 M NaCl solution

The anodic polarization curves in deaerated 0.1 M NaCl solution for AA2024-T351 alloy with and without laser surface melting are shown in Figure 7.2. It can be seen that all the samples exhibit relatively similar pitting potentials. The laser-melted alloys present a decreased current density compared with the as-received alloy. The polarization curves for the laser-treated AA2024 alloy with different number of pulses demonstrate more pronounced passive regions and slightly more positive values of the pitting potential than that of the as-received alloy. It is evident that the excimer laser surface melting considerably reduces the passive current density. The current densities are measured at the break down of the passive region point and show values of 2.0×10^{-5} \text{A/cm}^2, 4.0×10^{-8}\text{A/cm}^2, 3.0×10^{-8}\text{A/cm}^2 and 2.0×10^{-8}\text{A/cm}^2 for the as-received alloy and laser-treated alloy with 10, 25 and 50 laser pulses, respectively, as shown in Table 7.1. The laser-treated alloy shows a lower current density slightly more than two orders of magnitude for the laser treated with 10 and 25 pulses and three orders of magnitude for the laser treated alloy with 50 pulses compared to the as-received alloy measured at the point of breaking potential. Furthermore, the current density for the laser treated alloy with 50 pulses is decreased further compared with the laser treated alloy with 10 and 25 pulses. The corrosion potential, \(E_{\text{corr}}\), values of \(-1.09\ \text{V}_{\text{SCE}}\), \(-1.05\ \text{V}_{\text{SCE}}\) and \(-0.99\ \text{V}_{\text{SCE}}\)

Figure 7.1: Anodic polarization behaviour of the as-received AA2024-T351 alloy in deaerated 0.1 M NaCl solution.
7. Corrosion behaviour of AA2024-T351 alloy before and after laser treatment

for the laser treated alloy with 10, 25 and 50 pulses, respectively compared with a corrosion potential of -0.92 V_{SCE} for the as-received alloy. Both the shift of E_{corr} toward the more negative potential and the decrease in current densities on the laser-treated alloy surface might be associated with the decrease of cathodic activity of the laser-treated alloy.

![Anodic polarization curves](image)

**Figure 7.2:** Anodic polarization curves in deaerated 0.1 M NaCl solution for AA2024-T351 alloy laser treated with 10, 25 and 50 laser pulses and laser fluence of 7 J cm\(^{-2}\) in comparison with the as-received alloy.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>E_{corr} (V_{SCE})</th>
<th>E_{pit}(V_{SCE})</th>
<th>ΔE(V_{SCE})</th>
<th>Current density (A/cm(^2)) at E_{pit} point</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>-0.92</td>
<td>-0.52</td>
<td>0.40</td>
<td>2.0 \times 10^{-5}</td>
</tr>
<tr>
<td>10-pulses</td>
<td>-1.09</td>
<td>-0.50</td>
<td>0.59</td>
<td>4.0 \times 10^{-8}</td>
</tr>
<tr>
<td>25-pulses</td>
<td>-1.05</td>
<td>-0.51</td>
<td>0.54</td>
<td>3.0 \times 10^{-8}</td>
</tr>
<tr>
<td>50-pulses</td>
<td>-0.99</td>
<td>-0.53</td>
<td>0.46</td>
<td>2.0 \times 10^{-8}</td>
</tr>
</tbody>
</table>

**Table 7.1:** Anodic polarization parameters from the polarization curves shown in Figure 7.2.

**7.2.2.2 In aerated 0.1 M NaCl solution**

Figure 7.3 (a) presents the anodic polarization behaviour of the laser-melted AA2024-T351 alloy in naturally aerated 0.1 M NaCl solution in comparison with the as-received. The laser melting has changed the anodic polarization behaviour. It can be seen that the laser-melted alloy demonstrates the passivation behaviour with an increase of pitting potential to the value of -0.48 V_{SCE} compared with the as-received alloy which suffers from pitting corrosion just very slightly above corrosion potential at -0.62 V_{SCE} and a
passivation region of 0.14 V$_{SCE}$ was obtained for the LSM alloy. The current density for the LSM alloy is almost two orders of magnitude lower, reaching a value of $1.0 \times 10^{-8}$ A/cm$^2$, compared with $2.0 \times 10^{-6}$ A/cm$^2$. It is worth noting that both as-received and laser-melted alloys show similar values of $E_{corr}$. Figure 7.3 (b) shows the cathodic polarization behaviour for the laser-treated and as-received alloys in naturally aerated 0.1 M NaCl solution. The cathodic current density for the LSM alloy is typically two orders of magnitude lower compared with the as-received alloy. This decrease in the cathodic response can be possibly related to the removal of intermetallic particles.

Typical surface morphologies after the anodic polarization measurements are shown in Figure 7.4 (a). The as-received alloy suffers from a widespread pitting corrosion and intergranular corrosion. Such corrosion behaviour is significantly modified after laser treatment. The attack in the laser-treated alloys is only evident by closely inspection of the exposed area that revealed pits mainly located in the overlapped regions. This modified corrosion attack as a result of LSM is further confirmed by observations of cross-sections of the laser-treated and as-received alloy.
7. Corrosion behaviour of AA2024-T351 alloy before and after laser treatment

Figure 7.3: (a) Anodic polarization curves and (b) cathodic polarization curves for laser-melted (7 J cm\(^{-2}\) and 10 number of pulses) and as-received AA2024-T351 alloy in aerated 0.1 M NaCl solution.

Figure 7.4: Optical micrographs of the surface morphology after anodic polarization in naturally aerated in 0.1 M NaCl solution. (a) as-received AA2024-T351 alloy and (b) laser-treated (7 J cm\(^{-2}\) and 10 number of pulses) showing few scattered large pits as indicated by the arrows.
The anodic polarization behaviour for the laser-melted alloy indicates the decrease in passive current density up to two orders of magnitude and almost three orders of magnitude for deaerated and aerated 0.1 M NaCl solution, respectively, in comparison with that of the as-received alloy. The high current density for the as-received alloy is attributed to the presence of various intermetallics, for example, the Al$_2$CuMg phases that are distributed in a form of coarse and/or clusters precipitates, in the rolling direction as well as in the form of grain boundary precipitates as discussed in Chapter 5. Both polarization evaluations for the laser-melted surface show improvement in corrosion resistance, suggesting that the excimer laser melting could significantly reduce the magnesium content of intermetallics containing magnesium. As discussed earlier in Chapter 5, vaporisation of magnesium from the anodic S-phase Al$_2$CuMg particles to achieve the phase transformation from S-phase to Al$_2$Cu, and the solute bands in the melted layer. Liu et al.\cite{1} reported that AA2024-T351 alloy treated with a CO$_2$ laser showed no improvement of pitting corrosion resistance and related this to the existence of S-phase of much refined size distributed along the grain boundaries after the LSM. Therefore, such corrosion resistance improvement for AA2024-T351 after excimer laser treatment is considered to be related to the ability of generating an extremely fast cooling by excimer laser radiation which results in dissolution/removal of the large intermetallic particles such as Al$_2$CuMg (S-phase), Al (Cu, Fe, Mn) and a smaller sized particles like Al$_2$Cu phases from the surface layer of the alloy. Due to the dissolution of those intermetallic particles in the $\alpha$-Al matrix by fast cooling, it would be reasonable to expect an extended solid solubility of copper in the solid solution as well as other elements. Furthermore, the higher the number of laser pulses, the better improvement in corrosion resistance achieves, as indicated by Figure 7.2 where the current density was the lowest at 50 pulses. This might be due to the complete removal of those phases, as supported by XRD results in Figure 6.12 in Chapter 6 specifically for the 50 pulse laser-treated.

Looking into electrochemical polarization of the as-received alloy in deaerated condition, the shorter passivation region of 0.37 V$_{SCE}$ in Figure 7.1 is related to the presence of a protective oxide film in an environment containing aggressive Cl$^-$ ions which can interfere with passivation\cite{2,3}. The chloride ions accelerate the corrosion process due to the dissolution of the thin film and pitting is initiated\cite{4}. Extensive pitting appears in Figure 7.4 (a) on the surface of the untreated alloy after anodic
polarization in aerated condition, which can be related to the presence of S-phase which covers 60% of the second phase particles in the alloy \(^5\) that have anodic potential with respect to the aluminium matrix \(^6-8\). This can cause severe pitting corrosion of the alloy when exposed to a chloride-containing solution \(^5, 8, 9\) as shown in Figure 7.4 (a). In contrast, the laser surface treated shows a small number of large pits that were initiated randomly over the melted surface. It is known that high resistance of pure aluminium to corrosion is attributed to a thin film formed on the surface free of intermetallic particles. This suggests that the extended passive regions for the laser-melted alloy and decreased values of passive current density can also be related to enrichment of copper in the alumina passive film, which was reported to improve the pitting corrosion resistance \(^10, 11\). The presence of the film on the refined microstructure melted layer can result in enhancements of the film resistance against the aggressive chloride molecules, leading to larger passive region accompanied by decrease in current density.

7.3 Immersion test in 0.1 M NaCl solution for 24 hours

Figure 7.5 shows the corrosion morphology on the as-received alloy after exposed to 0.1 M NaCl solution for 24 hours. It is evident that the pits are distributed in association with the presence of the intermetallic particles that are believed to be the preferential sites for pits formation. It can be seen from the backscattered SEM images that there are two types of corrosion involved, i.e. 1) dissolution of the particles that are anodic with respect to the aluminium matrix, and 2) dissolution of the Al-matrix around the intermetallic particles that are cathodic to the aluminium matrix, resulting in trenching around the circumference of the particle, as shown in Figure 7.5 (b) and (c).

Figure 7.5(c) illustrates a pit in the middle part; with almost complete dissolution of the particle leaving corrosion products surrounding the pit. Also there are cracks within the corrosion products.
Figure 7.5: Backscattered SEM micrographs showing (a) an overview of pitting corrosion on the surface of as-received AA2024-T351 alloy after immersion in 0.1 M NaCl solution for 24 hours, (b) higher magnification of the pits, some with corrosion products, (c) increased magnification of the particle dissolution and trenching.

Figure 7.6 shows SEM micrographs of the surface view of the corrosion morphology of laser-melted alloy after exposed in 0.1 M NaCl solution for 24 hours. It is clearly revealed in Figure 7.6 (b) that most of the corrosion attacks occurred within the re-heated zone with some corrosion products and a few black pits scattered on both re-heated and overlapped regions. Away from the overlapped region, Figure 7.6 (d) displays the magnified region in the circled area in Figure 7.6 (b), indicating the re-heated region. It reveals a pit with a flower-like corrosion product.
Figure 7.6: (a) SEM micrograph of the corrosion morphology of the laser-melted AA2024-T351 alloy with 10 pulses and laser fluence of 7 J cm$^{-2}$ after immersion in 0.1 M NaCl solution for 24 hours, (b) backscattered SEM image, (c) high magnification of backscattered SEM of the reheated region and (d) backscattered SEM revealing flower-like corrosion product within the track.

Elemental mapping of the areas containing cracked corrosion products on the laser-melted surface with 10 pulses and laser fluence of 7 J cm$^{-2}$ is shown in Figure 7.7. Their corresponding EDX spectra are given in Figure 7.8. Four different areas indicated by the yellow arrows were selected for analysis and the results of analysis are tabulated in Table 7.2.

Figure 7.7: (a) Backscattered SEM micrograph and (b) elemental mapping of the corroded areas on the laser-melted surface with 10 pulses and laser fluence of 7 J cm$^{-2}$ after immersion in 0.1 M NaCl solution for 24 hours illustrating the distribution of O, Mg, Al and Cu.
Figure 7.8: EDX spectra of the four corroded areas indicated in Figure 7.7. (a) Spectrum 1 showing the presence of C, O, Cu, and Al, (b) spectrum 2 showing the presence of O, Cu and Al, (c) spectrum 3 showing the presence of Cl, O and Al and (d) spectrum 4 illustrating the existence of C, O, Fe, Cu and Al.

Table 7.2: Elemental contents in wt. % for the four selected corroded areas in Figure 7.7.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Fe</th>
<th>Cl</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.22</td>
<td>47.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.49</td>
<td>6.96</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>16.20</td>
<td>80.06</td>
<td></td>
<td></td>
<td></td>
<td>3.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>38.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.65</td>
<td>55.75</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>24</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
<td>35</td>
<td>7.85</td>
<td></td>
</tr>
</tbody>
</table>

The immersion test was also carried out for the laser-melted alloys with 25 and 50 laser pulses at laser fluence of 7 J cm\(^{-2}\) in 0.1 NaCl solutions for 24 hours and the corrosion morphologies of both specimens are presented in Figure 7.9 and Figure 7.10, respectively. Figure 7.9 (a) shows a few scattered pits on a rippled surface within the overlapped region and re-heated region. Figure 7.9 (b) is a backscattered SEM image.
illustrating more clearly the shape of the formed pits. There are three pits similar in appearance with different sizes that grew along the line of the overlapped region, as indicated by the yellow arrows. Figures 7.9 (c) and (d) are backscattered SEM images at a higher magnification showing the pit shape. The pit appears as a large ball-shape with a smooth surface cracked in the middle, with corrosion products in a form of tiny ball-shape formation on its surface.

Figure 7.10 displays pitting corrosion on the surface of AA2024-T351 alloy for the 50 pulses laser-treated condition after the immersed test. Figure 7.10 (a) illustrates a few scattered pits within the ripples, with more pits in the overlapped region than that in the tracks. The backscattered SEM image reveals one large pit with corrosion product just on the line of the overlapping where other pits appear as small black dots. The backscattered SEM micrographs in Figure 7.10 (c) show corrosion products, as indicated by the blue arrows. The circled area was magnified and presented in Figure 7.10 (d) and (e). These images show white coloured corrosion products with near squared shape spots accompanied by micro-cracks.

From the above experimental results, it is believed that for AA2024-T351 alloy with and without laser treatment, the chloride ions caused pitting corrosion due to breakdown of the oxide film and the subsequent formation of micro-anodic/cathodic cells, as reported by others \[4\]. It is obvious that all the surfaces show pitting corrosion. However, the numbers of pits as well as corrosion products are reduced significantly for the laser-treated surface. Furthermore, the overlapped region suffers more from pitting than the tracks, with fewer of the fully grown pits.

Generally, the pits are the results of localized corrosion in AA2024-T351 alloy and usually occur in the surrounding area of copper containing intermetallic particles due to the formation of anodic/cathodic cells created by the presence of various intermetallic particles such as S-phase, 0-phase and Al-Cu-Mn-Fe-(Si) \[12\]. Hence the relatively numerous pits on the surface of the as-received alloy are a result of the high density of these particles. Anodic activity causes dissolution of the particles such as S-phase. Cathodic activity causes the corrosion of the matrix forming trench around the cathodic particles, as in the case of Al-Cu-Mn-Fe particles. These two activities are revealed in the SEM micrographs for the as-received alloy in Figure 7.5. The significant reduction of the number of pits is expected in the laser-treated surfaces because the presence of
such particles is greatly diminished, leading to highly reduced anodic and cathodic activities. Such improvement of corrosion resistance can also be related to the refinement of microstructure and the extension of solid solubility \(12-14\) where the presence of alloying elements in particular copper in solid solution can cause significant development in the resistance of pitting corrosion. This was found in the case of laser-treated surface with different number of laser pulses compared with the as-received alloy. However, a few scattered pits still appear on the laser-treated surfaces in particular in the overlapped region and fully grown with dome shape formed pits as shown in Figure 7.9 (b)–(d) for the 25 pulses LSM condition. The overlap region of 25 pulse laser treated alloy, as illustrated in Figure 6.21 (b) reveals significant porosity, which possibly provides paths for the NaCl solution to reach to the copper rich solute bands. There is similarity between the pits formed on a surface treated by 10 pulses LSM condition and 50 pulses LSM condition. However, the pits formed on the surface treated by 25 LSM condition are different in shape, in particular pits that are formed in the overlapped region.

Figure 7.9: (a) SEM micrograph showing the corrosion morphology in the laser-melted AA2024-T351 alloy treated with 25 pulses and laser fluence of 7 J cm\(^{-2}\) after immersion in 0.1 M NaCl solution for 24 hours, (b) backscattered image displaying pits with corrosion products along the overlap region, (c) and (d) higher magnification of the pits.
7. Corrosion behaviour of AA2024-T351 alloy before and after laser treatment

Figure 7.10: (a) SEM micrograph of the corrosion morphology in the laser-melted AA2024-T351 alloy treated with 50 pulses and laser fluence of 7 J cm\(^{-2}\) after immersion in 0.1 M NaCl solution for 24 hours, (b) backscattered image of (a) illustrating pits, indicated by green arrows, in the overlap and reheated regions, (c) backscattered image showing corrosion products, indicated by blue arrows, (d) higher magnification of corrosion products, in the wavy morphology and (e) increased magnification of (d).

7.4 EXCO Immersion test

7.4.1 As-received alloy

Figure 7.11 presents the surface view of the corrosion morphology of the as-received AA2024-T351 alloy after an immersion in the EXCO solution for 6 hours. It is evident that severe pitting corrosion and intergranular corrosion take place during the test. The
network of the micro-cracks on the surface represents the intergranular corrosion attack on the grain boundary.

![Image](image_url)

Figure 7.11: (a) SEM micrographs of the surface of the as-received alloy AA2024-T351 alloy after an EXCO test for 6 hours and (b) increased magnification revealing pitting and intergranular corrosion.

A cross-section of the as-received alloy that was prepared by ultramicrotomy, after the EXCO test for 6 hours is presented in Figure 7.12. The top part of Figure 7.12 (a) is a sketch of the specimen prepared by ultramicrotomy using glass and diamond knives; part (ii) is a backscattered image where the specimen is shown in three dimensions as sketched on the top of the SEM micrograph. It can be seen that a large portion of the area was attacked by intergranular corrosion. The appearance of the cracks at the back of the sample reveals the ability of intergranular corrosion to propagate deeply into the bulk material. The upper part of the specimen on the right side was removed as a result
of the attack. The intergranular corrosion is evident at the back of the sample and penetrated deep into the bulk material. There is an evidence of intergranular corrosion at the back of the specimen. This is an indication of a severe intergranular corrosion occurred to the matrix. Figure 7.12 (a)-(d) show a series of backscattered micrographs at different magnifications for the same area. These backscattered images show that the intergranular corrosion propagated along both longitudinal and long-transverse directions resulting in an extensive corrosion attack along the grain boundaries. In addition, it can also be seen that the intergranular corrosion was accompanied by pitting corrosion leaving a hole-like morphology in the matrix. In addition, trenching phenomena are observed in which the corrosion occurs in the matrix around the periphery of the particles.

Figure 7.12: SEM micrographs of cross-sections of ultramicrotomed as-received AA2024-T351 alloy after an EXCO test for 6 hours. (a) SEM micrograph with severe IGC and a sketch of the specimen illustrating specimen parts, (b) SEM image of corrosion products at the back of the sample, (c) higher magnification of corrosion product at the back of the specimen and (d) increased magnification shows complete detachment of grains.
Figure 7.13 is a backscattered micrograph of the cross-section at higher magnification, illustrating the intergranular corrosion and pitting of the as-received alloy after the EXCO test. Extensive damage to the matrix can be observed. Most of the particles inside the grains were not attacked while the particles along the grain boundaries were corroded. Two selected areas were marked by a red square and a black circle for EDX line scan analysis. Figure 7.13 (b) shows the results of the line scan for the region marked by the red square in Figure 7.13 (a), revealing that the two particles contain copper and magnesium beside aluminium. The phases are likely to be S-phase (Al-Cu-Mg). Figure 7.13 (c) shows the results of the line scan of the corroded region circled in Figure 7.12 (a). Since the particles remained contain aluminium and oxygen, without other elements like copper, magnesium, manganese and iron, it is more likely that the particles were dissolved during the test and changed to aluminium oxide after the test.
7.4.2 Laser-melted alloy

The laser-melted alloys were exposed to the EXCO solution for different periods of time in order to investigate the propagation of the delamination at the melted layer/matrix interface.

Figures 7.14 (a) and (b) are scanning electron micrographs of the surface of AA2024-T351 alloy treated by LSM with 10 pulses and exposed in EXCO solution for 6 hours. Pitting corrosion is evident on the laser-melted surface. The pits appear as black dots non-uniformly distributed on the surface. The pits appear to be more numerous in the re-heated region and in the overlapped, compared with laser tracks. There is also some corrosion products scattered randomly on the surface, similar to that obtained earlier for the immersion in 0.1 M NaCl solution for 24 hours and scattered randomly on the surface.

![Figure 7.14](image)

Figure 7.14: (a) SEM micrograph displays pitting corrosion on the surface of laser-melted alloy treated with 10 pulses and (b) increased magnification reveals dense pitting at the overlap region.

It has been observed that after three hours immersion in the EXCO solution of the laser treated alloy with 10 laser pulses, the delamination of the melted layer occurred, as shown in Figure 7.15 (a). However, there is no evidence of intergranular attack in the matrix. Figure 7.15 (b) at higher magnification shows that the delamination is apparent along the interface between the matrix and the melted layer. After four hours immersion, Figure 7.15 (c) and (d) show the full exfoliation of the melted layer, with corrosion products within the delamination region. An extensive intergranular corrosion attack occurred in the matrix. Figure 7.15 (e) and (f) show the results after six hours exposure to the EXCO test. It is evident that the gap between the delaminated layer and the matrix is wide and intergranular attack of at the matrix increases.
Figure 7.15: SEM micrographs of cross-sections of the laser-melted alloy treated with 10 pulses after EXCO tests for increased immersion time. (a) and (b) EXCO immersion test for 3 hours, (c) and (d) for 4 hours; (e) and (f) for 6 hours.

Figure 7.16 (a-b) reveals the laser-melted layer produced by 25 laser pulses after 6 hours of immersion in the EXCO solution. Intergranular corrosion attack is apparent, both at melted layer/matrix interface and in the matrix. The attack is severe but with less than previously displayed by sample treated with 10 laser pulses condition. The exfoliation at the interface is evident. The presence of intermetallic particle at the layer/matrix interface which was partially melted is conspicuous. Besides the intergranular corrosion attack, Figure 7.16 (b) shows an intermetallic particle at the layer/matrix interface which experienced trenching probably related to the cathodic
nature of particle. Intermetallic particles with such reactivity at such locations possibly promote delamination of the melted layer for the 50 pulses laser treated condition in the EXCO immersion test. Figure 7.16 (c) and (d). Similar intergranular corrosion occurred for the 25 laser pulses condition at both melted layer/matrix interface.

Figure 7.16: (a) SEM micrograph illustrating delamination of the 25 pulses laser-melted layer and intergranular corrosion of the matrix after 6 hours immersion in the EXCO solution, (b) Trenching around an intermetallic particle at melted layer/matrix interface. (c) and (d) Details of LSM 50 laser pulse condition, with delamination of the melted layer and intergranular corrosion attack to the matrix.

In addition to the results presented above from the immersion tests in 0.1 M NaCl solution and EXCO solution, Figure 7.17 displays the results for the 10 pulses laser-treated condition after electro-polishing of the specimen for 60 seconds in order to investigate the possible corrosion attack occurring during the electro-polishing process, particularly at the interface between the melted layer and the matrix. It can be seen that pitting corrosion is evident in the matrix and corrosion at the interface between the melted layer and the matrix, Figure 7.17 (a) and (b). In addition, it is also observed that the region below the melted layer seems to behave differently from the matrix. This is possibly due to the laser irradiation induced heat-affected zones.
7. Corrosion behaviour of AA2024-T351 alloy before and after laser treatment

![Figure 7.17](image)

Figure 7.17: (a) and (b) SEM micrographs of AA2024-T351 alloy laser-treated with 10 pulses and then electro-polished for 60 seconds (c) and (d) back scattered micrographs at higher magnification.

From the above results it is evident that the AA2024-T351 alloy with or without laser treatment all suffer from localised corrosion, including pitting and intergranular corrosion, under all the conducted tests.

It is known that IGC occurs in AA2xxx alloys, in the presence of Cl⁻ ions due to Cu-depleted zones caused by presence of the Al₂Cu and/or Al₂CuMg phases along the grain boundaries [13, 15]. In the present study, the TEM results show that both of these phases exist at the grain boundaries, as rod like shapes, as well as dispersoids Al₂₀Mn₃Cu₂ described in Chapter 5. For the laser-melted alloy, the copper-rich solutes at the interface between the melted layer and matrix described in Chapter 6 are also believed to contribute to the intergranular corrosion initiation when exposed to the EXCO solution. Generally speaking, S-phase (Al₂CuMg) acts as an anode with respect to the adjacent Al-grains and the depleted zone at the grain boundary [8, 9, 15]. This can cause preferential dissolution and the initiation of intergranular attack, as shown in Figure 7.15. On the other hand, θ-phase, acts as a cathode with respect to the matrix [9, 16] promoting dissolution of the adjacent depleted zone of the Al-matrix. However, Boag et'al reported that the presence of θ-phase at the grain boundaries is around 15% [17].

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This suggests that there are other factors that contribute to the intergranular attack. The existence of copper rich solutes might also be associated to the intergranular corrosion. It is known that AA2024-T351 alloy has various intermetallic particles in different forms such as in clusters, colonies, lined and single, etc. as displayed in secondary and backscattered micrographs of Chapter 5 and Chapter 6. These particles have a high probability to be found at the melted layer/matrix interface as lined particles and in colonies, as indicated by the results in Section 6.2. The partially melting of these particles at the melted layer/matrix interface, probably forming copper solute-rich along the plain of the melted layer/matrix interface creating a net work of solutes possibly be responsible for the delamination of the melted layer. Another factor that might contribute to the delamination of the melted layer is the high stored energy of grains located at the laser melted/matrix interface, as suggested by Luo et al. It was reported that IGC is preceded by pitting corrosion based on the fact that the first breakdown of the polarization curve is for the pitting potential and the second breakdown potential is for the IGC. On the other hand, the results obtained by the previously mentioned authors indicated that extensive intergranular corrosion was observed to propagate well into AA2024-T351 alloy matrix before the development of any substantial pits. The results obtained in this study by exposing the samples to the EXCO solution for three hours support their observations.

In general, the severity of IGC is agreed to be related to the maximum depth of the attack. It can also be related to the isolation of the grain from the surrounding matrix (detachment of the grain). A severe intrgranular corrosion and grain detachment have been observed for the as-received AA2024-T351 alloy in this study. Less severity IGC was observed following LSM, decreasing with increase in the number of pulses after laser treatment, suggesting an enhancement of the corrosion resistance of AA2024-T351 has been achieved.

7.5 Conclusions

- Polarization studies of the AA2024-T351 alloy in deaerated and aerated 0.1 M NaCl solution show high current density, due to the presence of various intermetallics.
- Excimer LSM of AA2024-T351 alloy has improved the localised corrosion resistance by reducing the passive current density up to two orders of magnitude and almost three orders of magnitude for deaerated and aerated 0.1 M NaCl solution.
respectively. The higher the number of laser pulses, the better the corrosion performance.

- In contrast to the as-received, the pits as well as the corrosion products were reduced significantly for the laser-treated alloy. This suggests that the extended solid solubility of the solid solution which contained more copper could reduce the number of pits on the surface, where copper in the solid solution increases corrosion resistance.

- The AA2024-T351 alloy displayed severe intergranular corrosion during six hours of EXCO test, causing detachment of grains and exfoliation.

- The laser-melted alloy with a variation of laser pulses reveals significantly decreased degree of intergranular corrosion attack with respect to the increased number of laser pulses. Different degrees of delamination of the laser-melted layer were observed, suggesting that the effect of the presence of the copper-rich bands particularly at the melted layer/matrix alloy interface favours the formation of micro-galvanic activities.
7.6 References

Corrosion Science, 2012. 61(0): pp. 35-44.

Chapter 8

Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

8.1 Introduction

This chapter evaluates the laser surface melting as a pre-treatment method prior to anodizing of AA2024-T351 alloy. AA 2024-T351 alloy treated with the excimer laser under the conditions of 10, 25 and 50 number of pulses at a fixed laser fluence of 7 J cm\(^{-2}\) as anodized at an applied voltage of 12V in sulphuric acid for 4, 12 and 20 minutes, respectively, and then sealed in boiling water for 30 minutes. The Microstructure of the anodic oxide film formed on the alloy was examined using FEG-SEM/EDX and FEG-TEM/EDX, and then compared with the one obtained without laser treatment. Comparative study of the corrosion behaviour of the alloy surfaces with different treatments, as described in Chapter 7, was carried out using immersion test in 0.1 M NaCl solution for 24 hours and also the EXCO test, as well as anodic polarisation test in 0.1 M NaCl solution.

8.2 Anodizing of AA2024-T351 alloy

Figure 8.1 shows the variation of current density with time which was recorded during anodizing at 12 V for the LSM samples as well as the as-received alloy. The curves show an initial surge in current density in the first few seconds followed by a decrease to a minimum value in the next 10 seconds and then an increase to a steady current density after 30 seconds. This is a distinctive response for anodizing aluminium alloys in acid solutions, where the initial stage can be related to barrier film growth followed by a relatively uniform thickening of a porous anodic film in the steady current density region\(^{[1]}\). From Figure 8.1, it can also be seen that the as-received alloy current density of 2.5 mA cm\(^{-2}\) was decreased significantly to a current density value of 0.9 mA cm\(^{-2}\) for the alloy laser-treated with 50 pulses. Moreover, in the steady regions, the current density decreased with an increase in the
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

number of laser pulses. These responses suggest that laser surface melting increased the efficiency of the growth of the anodic film on the surface of AA2024-T351 alloy. This might be associated with the dissolution of intermetallic phases on the surface and near surface of the alloy.

Figure 8.1: Current density responses during anodizing of the as-received alloy and laser surface melting treated with 10, 25 and 50 pulses.

8.3 Characterization of the anodic films

It is well-known that the anodic oxide films produced on AA2024-T351 alloy in sulphuric acid reveal a lateral porosity. On the contrary, the anodic oxide films grown on pure aluminium has linear regular pores placed perpendicularly to the surface. Characterization of the anodic films was performed for specimens anodized time for 4 minutes and 20 minutes, respectively.

8.3.1 Anodized AA2024-T351 alloy without LSM pre-treatment

The structure of the oxide films formed as a result of anodizing the as-received AA2024-T351 alloy for 4 minutes in stirred 0.46 M sulphuric acid at room temperature with a constant voltage of 12 V was investigated by SEM and TEM, and
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

compared with the anodic film formed on the alloy with excimer LSM under different laser operating conditions.

Figure 8.2: High angle annular dark field micrographs of the cross section of the anodic film on the AA2024-T351 alloy anodized for 4 minutes. (a) Anodic film and matrix of the as-received alloy, (b) increased magnification of the anodic film/matrix interface reveals porous feature of the anodic film, scallop-shaped barrier layer and nanometre thick white layer (c) barrier layer at the film/matrix interface.

Figure 8.2 is HAADF micrographs showing the cross-sections of an anodic film formed on AA2024-T351 after anodizing for 4 minutes. Figure 8.2 (a) shows that the anodic film is approximately 300 nm in thick. It appears to be amorphous. The matrix of the AA2024-T351 alloy is displayed with intermetallic particles, as indicated by yellow arrows. Figure 8.2 (b) and (c) are higher magnification images of the anodic film, showing the barrier layer at the film/matrix interface that is scallop-shaped with a thickness of around 15 nm. Figure 8.3 (a) and (b) are TEM
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

micrographs displaying the anodic film with its typical array of cells and lateral porosity. The second phase particles as pointed by the red arrows are evident in the matrix. Figure 8.3 (c) demonstrates the anodic film formed on the as-received alloy containing a large void just at the interface of anodic film/matrix. The large void in the section could be the site of the intermetallic particle which either was partially dissolved through anodic oxidation or has fallen out during the sample preparation.

![Figure 8.3](image)

Figure 8.3: TEM micrographs of ultramicrotomed sections of the AA2024-T351 alloy after anodizing in 0.46 M sulphuric acid at 12 V for 4 minutes. (a-b) Anodic film formed on as-received 2024-T351 alloy matrix and (c) a large void at the metal/interface could be resulted from the fall out of IMP.

A cross-section of the sample anodized for 20 minutes was prepared by ultramicrotomy and characterised by TEM. Figure 8.4 displays the porous anodic morphology of the oxide film. The anodic film has significantly thickened with relatively uniform increased thickness up to 1.2 μm. The array of pores is apparent, with cracks perpendicular to the surface that may be the result of cutting. Fig 8.4 (b) displays the anodic film, with intermetallic particles in the underlying matrix. At higher magnification, Figure 8.4 (c) shows a squared-shape intermetallic particle with size around 100 nm. The barrier layer with scallop-shape appears to have thickness around 15 nm. A white, solute-rich band, about 3-4 nm thick is located
immediately beneath the anodic film/matrix interface. The band is formed by copper accumulation in the alloy as a result of oxide formation \[^2\].

Figure 8.4: High angle annular dark field micrographs of the cross section of the anodic film of AA2024-T351 alloy anodized for 20 minutes. (a) and (b) anodic film and matrix of the as-received alloy, (c) and (d) anodic film/alloy interface.

Further investigation by TEM reveals more detailed information on the features of the anodic film formed on the as-received AA2024-T351 alloy. Figure 8.5 (a) displays a uniform section of the amorphous anodic film, showing the porous structure and lateral porosity. The intermetallic particles are evident in the matrix. At higher magnifications, Figure 8.5 (b) and (c) show the porous feature of the amorphous anodic film. The film/matrix interface displays the barrier layer, of scallop shape, beneath the porous structure.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.5: TEM micrographs of ultramicrotomed section of AA2024-T351 alloy after anodizing in 0.46 M sulphuric acid at 12 V for 20 minutes; (a) uniform anodic film, (b) film with porous and fine granular features and (c) lateral porosity evident at increased magnification.

8.3.2 Anodized AA2024-T351 with LSM as pre-treatment

It is generally accepted that the morphology of the anodic film formed on AA2024-T351 alloy is considerably influenced by the presence of intermetallic particles on the surface of the matrix. The modification of the anodic film morphology is related to the growth rate of the film which differs on aluminium matrix from that on the intermetallic particles\(^{[1,3]}\). Therefore, laser surface melting that removes intermetallic particles from the surface of AA2024-T351 alloy affects the surface morphology of the anodic film formed by anodizing in the sulphuric acid.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

**LSM with 10 pulses**

SEM micrographs of the surface after LSM with 10 pulses followed by anodizing are shown in Figure 8.6 (a) and Figure 8.6 (b). Figure 8.6 (a) displays a thin anodic film, approximately 200 nm in thickness, formed on a 10 pulse laser-melted surface condition. From the observation of the cross section, the melted layer has a thickness of around 5 µm; solute bands are indicated by the green arrows. There are a few submicron second phase particles that are distributed in the middle region of the melted region. At higher magnification, Figure 8.6 (b) displays the anodic film with uniform thickness formed on the wavy melted layer. The anodic film formed on the 10 pulses laser melted layer is displayed in Figure 8.6 (c); at this location of the film has been lost, possibly due damage doing ultramicrotomy.

![SEM micrographs](image)

**Figure 8.6:** (a) and (b) SEM micrographs showing a typical anodic film formed on the melted layer produced under the 10 pulses LSM condition after anodizing in 0.46 M sulphuric acid at 12 V for 4 minutes. (c) TEM micrograph of cross-section of the anodic film.

Figure 8.7 reveals a thicker anodic film formed 20 minutes for on the laser-melted layer AA2024-T351 alloy treated with 10 laser pulses and anodized for 20 minutes, with a thickness of approximately 1.2 µm. At the anodic film/melted layer interface,
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

A refined microstructure is visible, where the large intermetallics have dissolved by LSM treatment.

Figure 8.7: SEM micrographs of a cross-section of the laser-melted alloy treated with 10 pulses followed by anodizing for 20 minutes. (a) Uniform anodic film formed on the melted layer. (b) At increased magnification.

During anodizing, pores just under the surface of the melted layer appear are covered by the anodic film. Figure 8.8 (a) displays a cross-section of the anodic oxide film formed on the melted layer. The melted layer appears to be free of intermetallic particles. At the melted layer/matrix interface, there are two large intermetallic particles each containing two distinguishable regions; the bright region is believed to be rich in copper and the darker region is rich in silicon. Figure 8.8 (b) shows the anodic film formed on a wavy surface of the melted layer and also around the inner surface of a pore, which is located about 4 µm beneath the surface. This suggests the existence of pathways that connecting the surface to the pores which allows the sulphuric acid to enter the pore and form the anodic film.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.8: SEM micrographs of a cross-section of the laser-melted alloy treated with 10 pulses and anodized for 20 minutes. (a) IMPs with two distinguished regions, the bright rich in copper and darker rich in silicon and (b) Anodic film formed around the inside of a pore.

**LSM with 25 pulses**

Anodizing was also conducted on the laser-melted surface treated with 25 pulses for 4 and 12 minutes, respectively. Results of characterisation of the anodic oxide films are presented in a series of micrographs using SEM, TEM/HAADF and TEM. Figure 8.9 (a) is an SEM micrograph, showing a cross-section of the anodic film, which is evident as a dark thin layer on top of the wavy morphology of the melted surface. The matrix appears in the lower part of the SEM micrograph with a typical distribution of intermetallics. Figure 8.9 (b) is an SEM micrograph of the anodic film at higher magnification, displaying an array of cells with lateral pores. The thickness of the anodic film is approximately 200 nm. There is a crack from the top of the film which might be caused during sample preparation. A copper enriched white layer is evident, just beneath the oxide film. The copper was accumulated during the anodizing process and appears with thickness around 2 nm or less. Figure 8.9 (c) and (d) are TEM images of the anodic film revealing the lateral porosity in the anodic film, which has a thickness of around 250 nm.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.9: (a) and (b) SEM micrographs of cross-sections of the anodic film formed on the laser surface treated with 25 pulses and anodized for 4 minutes. (c) and (d) cross-section of TEM micrographs of the anodic film.

Laser-melting of AA2024-T351 alloy treated with 25 pulses LSM condition followed by anodizing for 20 minutes, is evaluated and the results are presented in Figure 8.10. Figure 8.10 (a) displays a plan view of the anodic film formed on 25 pulses LSM condition melted layer of an approximate thickness of 5 µm. At increased magnification, Figure 8.10 (b) shows a uniform anodic film of thickness 1.1 µm. Figure 8.10 (c) is a TEM micrograph in the dark field of an ultramicrotomed section, showing features of the anodic film formed on the melted layer of refined microstructure. Figure 8.10 (d) is a TEM micrograph in the white field of an ultramicrotomed section, illustrating porous anodic film. The anodic film of an uniform thickness appears with cuts looking like cracks in the film that are caused by the diamond-knife cutting during sample preparation. Figure 8.10 (f) presents a TEM/HAADF image at higher magnification of the lower part of the anodic film and the film/ matrix interface. A point on the red line at film/melted layer interface is selected and marked 1 for EDX point analysis. The results showed the presence of Al, Si, O, Ni, Cu, Fe and Mn. The presence of Ni is due to the use of nickel grid that carried the sample.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.10: SEM, TEM micrographs and EDX analysis showing features of the anodic film formed on laser-melted surface treated with 25 pulses LSM condition followed by anodizing for 20 minutes; (a) thickness of 1.1 µm, (b) anodic film formed within the porosity near the surface, (c) anodic film at increased magnification, (d) porous anodic film, (e) anodic film features at higher magnification, (f) area 1 at the interface selected for EDX analysis and (g) EDX analysis of the selected area in (f).
EDX analysis was also carried out using a line scan on the near the bottom of the oxide film. Figure 8.11 (a) shows a TEM image with the selected line scan indicated by the red line and marked with two points on the line (marked 1 and 2). Figure 8.11 (b) displays the elemental profiles across the selected line. The line profile shows two consecutive peaks separated by a distance of 0.05 µm representing the position of the two nano-particles marked 1 and 2. The first particle contains aluminium, copper and magnesium which is likely to be S-phase (Al-Cu-Mg) and the second peak is rich in aluminium and copper with a low presence of magnesium suggest the presence of θ-phase. Further results of EDX analysis at these two locations are presented in Figure 8.11 (c) where the peaks indicate the presence of silicon, copper and nickel and lower values of manganese, iron and magnesium.

Figure 8.11: (a) TEM high-angle annular dark-fields (HAADF) of melted layer/film interface, (b) elemental profiles across the bands marked as Line 1 in red, (c) and (d) EDX analysis of two selected particle numbered 1 and 2.

**LSM with 50 pulses**

Figure 8.12 shows TEM micrographs of a series of cross-sections of the anodic film formed on the melted layer produced by 50 pulses laser conditions. Figure 8.12 (a) and Figure 8.12 (b) are the cross-section images by Ultra 55 SEM illustrating the
uniformity of the anodic film after anodizing for 4 minutes, formed on the wavy melted layer. Figure 8.12 (c) is a HAADF image illustrating the features of the anodic film as described above with a thickness around 200 nm and the barrier layer next to the film/melt interface. Figure 8.12 (d) shows a TEM image of an ultramicrotomed cross-section of the anodic film. The image clearly demonstrates a typical feature of periodic-packed arrays of pores within the anodic film. Figure 8.12 (e) and Figure 8.12 (f) show the anodic film at higher magnification, where a clear feature of the closed-packed array of columnar cells each containing a central pore. There are small void-like features in the anodic film as a result from radiation damage. In this part of the cross-section, the barrier layer appears to be about 20 nm thick.

Figure 8.13 (a) displays a HAADF image of the cross section of the anodic film formed for 4 minutes on laser-melted surface treated with 50 pulses. There is one pore that is about 50 nm in diameter in the melted layer. A red line on the selected area is the path for the elemental line scan. The results are presented in Figure 8.13 (b). The line scan displays peaks of copper, magnesium, manganese and iron as well as aluminium. Two points were selected and marked as 1 and 2 for the EDX analysis. The former represents the anodic film and the latter is the copper enrichment layer that has a thickness around 1-2 nm. Figure 8.13 (c) shows the chemical composition at the selected point in the porous film marked as 1. The chemical composition of the anodic film shows peaks of oxygen, aluminium and silicon. Figure 8.13 (d) shows the EDX results of copper-rich layer, indicating peaks of aluminium, silicon, oxygen, copper, manganese, iron and magnesium.
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Figure 8.12: SEM and TEM micrographs of ultramicrotomed sections of laser-melted alloy treated with 50 pulses followed by anodizing for 4 minutes. (a) SEM micrograph of a uniform anodic film, (b) SEM micrograph of the anodic film which covers the wavy surface melt, (c) HAADF TEM micrograph of the anodic film formed on the melted layer free of IMPs, (d) TEM micrograph of the anodic film, (e) TEM micrograph of the anodic film at increased magnification and (f) thickness of the barrier layer of the anodic film.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.13: (a) TEM high-angle annular dark-field (HAADF) micrograph of the anodic film on the laser-melted surface treated with 50 pulses followed by anodizing for 4 minutes. (b) Elemental profiles across the marked line 1 in red. (c) and (d) EDX analysis of the anodic film at point 1 and copper layer at point 2.

Figure 8.14 (a) illustrates the anodic film formed for 20 minutes on the laser-melted surface with 50 pulses LSM condition. The film thickness is roughly 1 µm. There are large voids within the amorphous porous structure of the anodic film. The solute bands are apparent in the melted layer. Figure 8.14 (b) is a TEM image of the film/melted layer interface at higher magnification, displaying the scallop shape of the barrier layer. Beneath the anodic film, the melted layer is free from intermetallic particles with nano-sized parallel solute bands. At higher magnification, the TEM micrograph in Figure 8.14 (c) displays nano-scaled solute bands in the shape of cellular bands. The results of EDX analysis along the red line marked with number 1 on the TEM micrograph is of presented in Figure 8.14 (e) where peaks indicate the presence of Al, Si, Cu, Mg, Mn, and Fe. Figure 8.14 (f) shows the EDX analysis for the particle at the bottom of the red line. Results show that the particle is enriched with silicon as well as copper, manganese and iron.
Figure 8.14: (a) HAADF TEM micrographs of the anodic film on the laser-melted surface treated with 50 pulses and anodized for 4 minutes. (b) Anodic film/melted layer interface. (c) and (d) HAADF TEM micrographs of the area just below the interface, (e) and (f) EDX analysis of the selected areas in (c) and (d).

Figure 8.15 (a) shows a SEM image of a cross-section of an ultramicrotomed sample in which the anodic film displays a similar thickness of around 1 µm. Figure 8.15 (b) displays a larger area of the cross-section showing intermetallic particles at a distance of about 5 µm under the anodic film. Figure 8.15 (c) is a TEM image
showing the uniform thickness of the anodic film formed on the melted layer. The copper accumulation at the film/melted layer interface appears in white colour over a distance of 2 nm from the barrier layer. Figure 8.15 (d) is a TEM image of the film/melted layer interface showing the lower part of the anodic film and the upper part of the melted layer. In the latter, a discontinuous band of solutes of a nano-scale size is apparent parallel to the anodic film. A red line marked 1 was made for EDX analysis. Figure 8.15 (e) shows the results of EDX analysis at a point near the barrier layer where the presence of aluminium, silicon, and copper are evident.

Figure 8.15: (a) and (b) SEM micrographs, (c) HAADF TEM image of the anodic film on a laser-melted surface treated with 50 pulses followed by anodizing for 20 minutes, (d) Anodic film/melted layer interface and (e) EDX analysis of the selected areas in (d).

From comparing of the anodic films formed on the surfaces with and without laser treatment, it was seen that anodic film on the LSM surface was thinner thick than
that on the as-received alloy. The thickness of the anodic films decreased by increasing the number of laser pulses, as indicated in Table 8.1.

However, this seems to contradict the early suggestion made which was based on the relationship that was presented in Figure 8.1 indicating a decrease in the current density by increasing of the number of laser pulses. This relationship seems to suggest that the laser surface melting prior to anodizing should leads to an improved efficiency of anodic film growth which is believed to be associated with the dissolution of intermetallic phases on the surface and near surface of the alloy.

Reduction of the current density following LSM is possibly associated with the altered composition of the alloy surface, notably the enhanced concentration of the alloy elements in the solid solution. This will affect the composition of the anodic film formed during anodizing and hence, the current density achieved at the selected potential. Other features that may affect the current density are changes in the electrolyte composition in fissures and pores in the laser melted surface and associated potential drops due to the resistance of the electrolyte at such locations.

On the other hand, the barrier layer at the scalloped film/matrix interface has a thickness of around 15 nm. The band, of light appearance with thickness around 2 nm, immediately beneath the anodic film/matrix interface is a result of copper accumulation in the alloy through initial oxidation of aluminium. The anodic films exhibit similar features for all conditions with a characteristic of the influence of copper lateral porosity.

Table 8.1: Anodic oxide film thickness for various LSM conditions for variant and anodizing times.

<table>
<thead>
<tr>
<th>Anodising Condition: Anodised for 4 min</th>
<th>Thickness of anodic film, nm</th>
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</thead>
<tbody>
<tr>
<td>As-received surface</td>
<td>250-300</td>
</tr>
<tr>
<td>LSM with 10 pulses</td>
<td>200-250</td>
</tr>
<tr>
<td>LSM with 25 pulses</td>
<td>200-250</td>
</tr>
<tr>
<td>LSM with 50 pulses</td>
<td>190-220</td>
</tr>
<tr>
<td>Anodised for 20 min</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td>1200</td>
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<td></td>
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8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

8.4 Electrochemical investigation of anodized AA2024-T351

8.4.1 Potentiodynamic behaviour in deaerated 0.1 M NaCl solution

As-received alloy

Figure 8.16 compares the potentiodynamic polarization behaviour of the non-anodized AA2024-T351 alloy in deaerated 0.1 M NaCl solution with that of specimens that were anodized for 4, 12 and 20 minutes at 12 V in 0.46 M H₂SO₄ solution. The current density measured at passivation breakdown point is decreased compared to that of the as-received alloy. The values of current density for anodizing times of 4, 12 and 20 minutes are 6.0 × 10⁻⁸ A cm⁻², 3.0 × 10⁻⁸ A cm⁻² and 1.0 × 10⁻⁸ A cm⁻², respectively, compared with 3.0 × 10⁻⁵ A cm⁻² for the as-received alloy. This indicates that the current density has been decreased up to three orders of magnitude by the anodizing treatment. Further, the corrosion potentials of the anodized as-received alloy are shifted towards the positive direction with values of -0.70 V_SCE for 4 minutes, -0.76 V_SCE for 12 minutes and -0.72 V_SCE for 20 minutes of anodizing time compared with -0.92 V_SCE for the as-received alloy.

Figure 8.16: Polarization curves of AA2024-T351 alloy in de-aerated 0.1 M NaCl solution, anodized for different time periods at a fixed voltage of 12 V, in comparison with the as-received surface.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

**LSM with 10 pulses**

Figure 8.17 presents the polarization curves of AA2024-T351 alloy in deaerated 0.1 M NaCl solution, for 10 pulses laser-melted surface anodized for different times in comparison with both the as-received alloy and 10 pulses LSM condition without anodizing. It can be seen that the LSM has decreased the passive current densities, accompanied by significant shifts of the corrosion potential to the positive direction, compared with those anodized without LSM and the as-received alloy. Longer anodizing time leads to lower passivation current densities. Table 8.2 shows the polarisation parameters derived from Figure 8.17, indicating that the 10 pulses LSM condition decreases the passivation current density by three orders of magnitude compared to the as-received alloy, and two orders of magnitude compared to the 10 pulses LSM condition without anodizing.

![Figure 8.17: Anodic polarization curves of AA2024-T351 alloy in de-aerated 0.1 M NaCl solution, for 10 pulses laser-melted surfaces anodized for various times in comparison with both the as-received alloy and 10 pulses LSM alloy without anodizing.](image)
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Table 8.2 Anodic polarisation parameters from polarisation curves in Figure 8.17.

<table>
<thead>
<tr>
<th>Anodized time</th>
<th>( E_{\text{corr}} ) (V)</th>
<th>( E_{\text{pit}} ) (V)</th>
<th>( \Delta E ) (V)</th>
<th>Passive current density (A/cm(^2)) at ( E_{\text{pit}} ) point</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>-0.92</td>
<td>-0.51</td>
<td>0.41</td>
<td>3.0 ( \times ) 10(^{-5})</td>
</tr>
<tr>
<td>LSM</td>
<td>-1.09</td>
<td>-0.50</td>
<td>0.59</td>
<td>4.0 ( \times ) 10(^{-7})</td>
</tr>
<tr>
<td>4 minutes</td>
<td>-0.82</td>
<td>-0.49</td>
<td>0.33</td>
<td>4.0 ( \times ) 10(^{-8})</td>
</tr>
<tr>
<td>12 minutes</td>
<td>-0.74</td>
<td>-0.43</td>
<td>0.31</td>
<td>6.0 ( \times ) 10(^{-8})</td>
</tr>
<tr>
<td>20 minutes</td>
<td>-0.63</td>
<td>-0.50</td>
<td>0.13</td>
<td>2.0 ( \times ) 10(^{-8})</td>
</tr>
</tbody>
</table>

LSM with 25 pulses

Figure 8.18 shows the anodic polarization curves of AA2024-T351 alloy in deaerated 0.1 M NaCl solution for 25 pulses laser-melted surfaces anodized for varied times in comparison with both the LSM conditions and the as-received alloy without anodizing. Similar to the case of 10 pulses LSM condition, there is a substantial decrease in current density for the 25 pulses LSM condition, particularly for the 20 minutes anodized alloy compared to the as-received alloy. From Table 8.3, the passive current densities are decreased by three orders of magnitude compared with the as-received alloy and one order of magnitude compared with 25 pulses LSM condition. Such decreases in current densities are related to the decrease in the anodic activity caused by both LSM and the formation of the anodic film. The anodized samples show shifts in their corrosion potential toward more positive values. This could be associated with the reduction in the anodic activity caused by the presence of the anodic film. In addition, the 25 pulses LSM condition anodized for 20 minutes shows a more positive pitting potential of -0.38 V\(_{\text{SCE}}\).
Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.18: Anodic polarization curves of AA2024-T351 alloy in deaerated 0.1 M NaCl solution for the 25 pulses laser-melted surface condition, anodized for various times in comparison with both the LSM alloy and the as-received alloy without anodizing.

Table 8.3: Anodic polarisation parameters from polarisation curves in Figure 8.18

<table>
<thead>
<tr>
<th>Anodized time</th>
<th>E_{corr} (V)</th>
<th>E_{pit}(V)</th>
<th>ΔE(V)</th>
<th>Passive current density (A/cm²), at E_{pit} point</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>-0.91</td>
<td>-0.51</td>
<td>0.39</td>
<td>3.0 \times 10^{-5}</td>
</tr>
<tr>
<td>LSM</td>
<td>-1.05</td>
<td>-0.50</td>
<td>0.50</td>
<td>2.0 \times 10^{-7}</td>
</tr>
<tr>
<td>4 minutes</td>
<td>-0.70</td>
<td>-0.55</td>
<td>0.15</td>
<td>3.0 \times 10^{-8}</td>
</tr>
<tr>
<td>20 minutes</td>
<td>-0.59</td>
<td>-0.38</td>
<td>0.21</td>
<td>5.0 \times 10^{-9}</td>
</tr>
</tbody>
</table>

LSM with 50 pulses

As shown in Figure 8.19, the polarisation behaviours of the anodized AA2024-T351 with or without 50 pulses LSM as a pre-treatment are similar to those described for both the 10 and 25 pulses LSM conditions. However, the corrosion potential of the 50 pulses LSM condition with 20 minutes anodizing is more positive than the 25 pulses LSM condition with 20 minutes anodized. In addition, the passive current density is significantly decreased, as shown in Table 8.4. The passive current density of the anodized surface for 20 minutes with 50 pulses LSM condition is decreased by three orders of magnitude compared to the as-received. For the 50 pulse LSM condition, both the corrosion potential and the pitting potential are increased more.
than for the 25 pulses LSM condition. The general shift of the corrosion potentials might be associated with lower anodic activity, which is accompanied by a decrease in the current density that could be caused by a thicker anodic film.

![Figure 8.19: Anodic polarization curves of AA2024-T351 alloy in deaerated 0.1 M NaCl solution, for the 50 pulses laser-melted surface anodized for different times, in comparison with both the LSM alloy and the as-received alloy without anodizing.]

<table>
<thead>
<tr>
<th>Anodized time</th>
<th>( E_{\text{corr}}, \text{V} )</th>
<th>( E_{\text{pit}}, \text{V} )</th>
<th>( \Delta E, \text{V} )</th>
<th>Passive current density, ( (\text{A/cm}^2) ), at ( E_{\text{pit}}, \text{point} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>-0.92</td>
<td>-0.53</td>
<td>0.39</td>
<td>( 3.0 \times 10^{-9} )</td>
</tr>
<tr>
<td>LSM</td>
<td>-1.0</td>
<td>-0.51</td>
<td>0.49</td>
<td>( 9.0 \times 10^{-9} )</td>
</tr>
<tr>
<td>4 minutes</td>
<td>-0.74</td>
<td>-0.51</td>
<td>0.23</td>
<td>( 4.0 \times 10^{-8} )</td>
</tr>
<tr>
<td>20 minutes</td>
<td>-0.46</td>
<td>-0.31</td>
<td>0.15</td>
<td>( 6.0 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

8.4.2 Potentiodynamic behaviour in aerated 0.1 M NaCl solution

The anodic polarisation behaviour in aerated 0.1 M NaCl solution is presented in Figure 8.20, for the 50 pulses LSM condition anodized for different periods of time. It is observed that the surface anodized for 4 minutes shows a more pronounced passivation behaviour compared with the surface anodized for 12 minutes and 20 minutes, although the corrosion potential for both 12 and 20 minutes anodized surfaces are much more positive than that of the 4 minutes anodized surface.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.20: Anodic polarization curves of AA2024-T351 alloy in aerated 0.1 M NaCl solution for the 50 pulses laser-melted surface anodized for various times.

8.5 Immersion test in 0.1 M NaCl for 24 hours

8.5.1 Anodized AA2024-T351 alloy without LSM

The corrosion behaviour of the AA2024-T351 alloy anodized for 20 minutes without LSM was also investigated by an immersion test in 0.1 M NaCl solution for 24 hours. All the corroded samples were cut by ultramicrotomy using a diamond knife, for observations of cross-sections by SEM.

As shown in Figure 8.21, the top surface view reveals localised corrosion sites on the surface where pitting corrosion is evident. Such pitting corrosion may initiate defects in the anodic film formed due to the influences of various intermetallic particles. The defects may lead to the exposure of the intermetallics along with the surrounding matrix to the NaCl solution. From Figure 8.21, it can be seen that the pits cover a large area of the general surface. With higher magnification images (Figure 8.21 (b) and (d)), it can be seen that some pits contain almost completely dissolved of the particles and corrosion products are left within and at the periphery of the pits. Trenching is marked at the borders of the particles. These particles are more likely to be S-phase. During the immersion test, the presence of actively anodic intermetallic particles like Al2CuMg initiates corrosion and rapid dealloying while cathodic...
intermetallic particles such as \( \text{Al}_2\text{Cu} \) (\( \theta \)-phase) and also \( \text{Al-Cu-Fe-Mn-(Si)} \) stay almost intact. The reason is that the corrosion potential \( (E_{\text{corr}}) \) of the \( \text{S} \)-phase in \( \text{NaCl} \) solution is more negative than that of the AA2024-T351 alloy \(^{[4,5]} \) thus acting as anodes and leading to dissolution of these particles. At local anodes, the local surrounding corrosion front has a lower \( \text{pH} \), as a result of production of \( \text{Al}^{3+} \) ions \(^{[6]} \). The appearance of bubbles results from hydrogen evolution on the surface of the sample. During corrosion the following electrochemical reactions take place \(^{[7]} \);

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \\
\text{Al}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_2^+ + 2\text{H}^+ \\
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \\
\]

However, at the active particles, once dissolution of aluminium and magnesium take place, corrosion stops. Dealloyed \( \text{S} \)-phase particles leave a porous structure as shown in Figure 8.21.

In order to obtain more information on the composition of the corroded particles, an EDX line scan was conducted and the elemental line profiles are presented in Figure 8.21 (f). It shows that the two bright particles mainly contain copper, iron and manganese. This suggests that the particles are \( \text{Al-Cu-Fe-Mn} \) intermetallics. This kind of particle is unlikely to be attacked as described earlier. Trenching in the periphery of the particle is displayed in Figure 8.21 (d). This can be associated with cathodic activity of the particles. The copper rich particles are likely to have more noble corrosion potential than the \( \text{Al} \)-matrix. Intermetallic particles containing composition \( \text{Al-Cu-Fe-Mn-(Si)} \) are fairly inert. The trenching occurs at the border of the particles but takes a longer time to initiate than dealloying of \( \text{S} \)-phase \(^{[8]} \).
Figure 8.21: (a) SEM micrograph shows general view of the corroded surface of anodized AA2024-T351 alloy without LSM after immersion test in 0.1 M NaCl solution for 24 hours. (b) An increased magnification of the corroded area in (a) displays pitting, where parts of corrosion products pointed out by the red arrows. (c) Selected area to be magnified marked with dotted circle. (d) At higher magnification, trenching and dealloying are evident. (e) SEM image of selected area underwent line scan. (f) EDX elemental line profile.

Figure 8.22 shows the cross-sectional view of the corroded sample after the immersion test. The anodic film in Figure 8.22 (a) appears as a thin, dark grey layer on the top. A number of black spots near at the film/matrix interface are evident in the matrix. At higher magnification, localised corrosion attack is evident, in the form of pitting. The corroded areas display some large pits approximately 7 µm in size with irregular shapes as shown in Figure 8.22 (b). The pit shape is probably
associated with dealloyed and/or dissolved S-phase intermetallic particles which were exposed to the 0.1 M NaCl solution. The anodic film is found to contain some cracks and is punctured by pits. The cracks are most likely to be related to the hydration of the anodic film after the immersion test. The pits appear as voids in the lower part of the anodic film, propagating into the matrix. These voids are the sites of the intermetallic particles as evident in Figure 8.22 (c) and Figure 8.22 (d). The latter figure displays a deep pitting in the matrix. Some remnants of the dissolved particles on the bottom of the pit are evident. Figure 8.22 (e)-(l) clearly shows the effect of the presence of intermetallic particles in the anodic oxide film affecting the corrosion resistance. The pitting corrosion results in the formation of voids, partially corroded intermetallic particles caused by dealloying and dissolved intermetallic particles that lead to the formation of trenches causing irregularity of the anodic film. Figure 8.22 (g) displays a different shape of intermetallic particle with size of 3 µm wide and 0.5 µm embed in the upper part of the anodic film as shown at higher magnification in Figure 8.22 (h).
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.22: BSE micrographs of AA2024-T351 alloy anodized without LSM after an immersion test in 0.1 M NaCl solution for 24 hours. (a) plan view of corrosion attack, (b) at increased magnification, irregular shaped pits are apparent, (c) cracks are indicated by yellow arrows and pits are pointed by red arrows, (d) penetration of a pit in the matrix, (e) defects in the anodic film caused by corroded IMP, (f) defect in (e) at increased magnification, (g) IMP in associated with defect of the anodic film, (h) higher magnification of (g) shows the IMP is partially consumed during the anodizing process, (k) void at the arrow with appearance of contamination during sample preparation all over the matrix and (i) a void in the anodic film as a result of fall out of IMP at the surface.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

A large void is present in the anodic film as indicated by the red arrow in Figure 8.22 (k). From the above observations, it can be seen that pitting corrosion is evident, and the pits penetrate deeply into the matrix. Clearly, the presence of the intermetallic particles results in formation of defects in the anodic film leading to less protection against corrosion. On the other hand, some regions of the anodic film have less attack when these large intermetallic particles are not present as shown in Figure 8.23.

![BSE micrograph](image)

Figure 8.23: BSE micrograph of part of anodic oxide film formed on the as-received AA2024-T351 alloy.

**8.5.2 Anodized AA2024-T351 alloy with 25 pulses LSM**

BSE micrographs of cross-sections of the anodized AA2024-T351 alloy with 25 pulses LSM after an immersion test in 0.1 M NaCl solution for 24 hours are shown in Figure 8.24. No evidence of pitting corrosion in the melted layer is evident in either Figure 8.24 (a) or Figure 8.24 (b). The 7 µm thick melted layer appears free of both pits and intermetallics, with solute bands at matrix interface. However, further observation of the sample in Figure 8.24 (c) reveals a few black spots that are likely to be the result of pitting corrosion and a few cracks as indicated by the yellow arrows in Figure 8.24 (d). In addition, thick solute bands resulted from partially melted particles at the interface of melted layer/matrix are evident but no corrosion is found. There are no pits in the melted layer or voids in the anodic film. However, it is noticed that there appears a horizontal crack parallel to the surface within the anodic film.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.24: SEM/BSE micrographs of cross-sections of the anodized AA2024-T351 alloy with 25 pulses LSM after an immersion test in 0.1 M NaCl solution for 24 hours. (a) Intact melted layer and matrix, (b) image of (a) at higher magnification, (c) undamaged melted layer and (d) at higher magnification, showing cracks in the anodic film, with no corrosion of the effect on the melted layer and the matrix.

8.5.3 Anodized AA2024-T351 alloy with 50 pulses LSM

Similar to the above observation for the 25 pulses LSM, the anodized AA2024-T351 alloy with 50 pulses LSM presents almost no evidence of localised corrosion, as shown in Figure 8.25, except for a few spots at the interface of film/melted layer as indicated by the yellow arrows. Inspection at higher magnification shows an exfoliation of the anodic film, leaving trails of scallop-like marks with thickness around 300 nm at the top of the melted layer. The rest of the melted layer appears intact. Figure 8.25 (e) and 8.25 (f) show no pitting corrosion.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.25: SEM/BSE micrographs of cross sections of the anodized AA2024-T351 alloy with 50 pulses LSM after an immersion test in 0.1 M NaCl solution for 24 hours; (a) cross section of a large area of the sample, (b) corrosion-free melted layer, (c) cracks in the anodic film with corrosion-free melted layer, (d) cracks in the anodic film at higher magnification, (e) another portion of undamaged melted layer and (f) corrosion-free edge of the melted layer.

From the above observations, it can be seen that the presence of the intermetallic particles results in a less protective anodic film. In particular, particles containing iron slow down the oxidation rate compared with both aluminium and copper during the anodizing process that may act as initiation sites for localised corrosion attack. Chloride ions on the anodic oxide film defects, chloride ions penetrate through these weak points on the oxide film to the alloy surface causing severe pitting corrosion as described above. On the contrary, the results showed that in the absence of large intermetallics the anodic film presents better corrosion resistance.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Since the LSM with 25 and 50 pulses prior to anodizing is produced a relatively uniform surface layer with a melt depth from 5 μm to about 10 μm, and complete dissolution/removal of the intermetallic particles, the formed anodic films on the LSM surface display much improved resistance to corrosion.

8.6 Immersion test in EXCO solution for 6 hours

The exfoliation and intergranular corrosion behaviours were investigated in a relatively severe EXCO solution in order to evaluate the sensitivity of anodized AA2024-T351 alloy both with and without LSM. The EXCO test is based on ASTM G34-01 standard \[^9\]. All samples in this chapter are anodized and sealed in hot water for 30 minutes.

8.6.1 Anodized AA2024-T351 alloy without LSM

The EXCO immersion test was conducted for 6 hours on the AA2024-T351 alloy without LSM anodized for 4 and 20 minutes, respectively. The cross-sections of the anodized sample for 4 minutes are displayed in Figure 8.26 (a) and Figure 8.26 (b), showing severe intergranular corrosion without appreciable attack on the grain interior. Figure 8.26 (c) demonstrates detachment of some grains from the matrix as shown in the top part of the cross section. The presence of large intermetallic particles on the surface causes defects in the oxide film, forming a site to initiate localized corrosion as shown in Figure 8.26 (d).
Figure 8.26: SEM/BSE micrographs of cross sections of the anodized AA2024-T351 alloy (anodized for 4 minutes) without LSM after EXCO immersion test for 6 hours; (a)-(b) severe intergranular corrosion in the matrix, (c) detachments of grains and (d) large IMP just beneath the anodic film.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.27: SEM/BSE micrographs of cross-sections of the anodized AA2024-T351 alloy (anodized for 20 minutes) without LSM after EXCO immersion test for 6 hours; (a)-(b) severe IGC occurred in the matrix and (c) grain detachment in the matrix.

Further, the results of increased thickness of the anodic oxide film via 20 minutes anodizing after the EXCO immersion test are shown in Figure 8.27. Figure 8.27 (a) and (b) present a similar degree of intergranular corrosion of the matrix to the observation for 4 minutes anodized sample as described above. At higher magnification, detachment and removal of grains are evident in Figure 8.27 (c). It appears that the increased anodic film has no effect on corrosion resistance.

8.6.2 Anodized AA2024-T351 alloy with 10 pulses LSM

Figure 8.28 (a-b) shows the intergranular corrosion of the anodized AA2024-T351 alloy after 10 pulses LSM, with less severity than that in anodized alloy without LSM. The melted layer with its typical wavy shape and 5-7 µm thickness is attacked along the melted layer/matrix interface, resulting in exhibiting delamination that has been described in EXCO test of laser-melted AA2024 alloy in Chapter 7.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.28: SEM/BSE micrographs of cross-sections of 4 minutes anodized AA2024-T351 alloy with 10 pulses LSM after EXCO immersion test for 6 hours; (a) delamination and IGC of the matrix and (b) delamination of the melted layer with deep penetration of IGC to the matrix.

By increasing the anodizing time from 4 to 20 minutes, the AA2024-T351 alloy with 10 pulses LSM condition suffered from corrosion as shown in Figure 8.29. Figure 8.29 (a) shows that intergranular corrosion is only evident at the melted layer/matrix interface while the cross-sections of Figure 8.29 (b) and Figure 8.29 (c) reveal intergranular attack in the matrix as well as along the interface between the melted layer and the matrix. At higher magnification, the attack is apparent at the interface with branches penetrating into the matrix as indicated by the red arrow in Figure 8.29 (d). Further increase in magnification, an exfoliation of the melted layer is marked at the interface is revealed in the BSE image of Figure 8.29 (f)
Figure 8.29: SEM micrographs of cross-sections for 20 minutes anodized AA2024-T351 alloy with 10 pulses LSM after EXCO an immersion test for 6 hours; (a) less severe IGC attack, (b) IGC of the matrix, black spots are contamination, (c) delamination of the melted layer and penetration of IGC, (d) corrosion of solute bands at the interface, (e) delamination of melted layer with very fine paths of IGC in the matrix and (f) detachment of the melted layer from the matrix.

Figure 8.30 displays corrosion product at a site of detachment of the melted layer. A long crack, shown by the yellow arrows is evident in the anodic oxide film. The anodized AA2024-T351 with 10 pulses LSM suffers from corrosion, leading to the delamination of the melted layer.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.30: SEM micrograph of cross-section of 20 minutes anodized AA2024-T351 alloy with 10 pulses LSM after EXCO immersion test for 6 hours shows cracks in the anodic film and the detachment of the melted layer with corrosion product.

8.6.3 Anodized AA2024-T351 alloy with 25 pulses LSM

At low magnification, Figure 8.31 (a) shows a general view of the 4 minutes anodized sample after an EXCO immersion test for 6 hours. The matrix shows no evidence of intergranular corrosion. There are some scattered grey spots as a result of contamination. Figure 8.31 (b) verifies the intactness of both the matrix and the melted layer. The Figure also shows few pores in the melted layer. Figure 8.31 (c) confirms the absence of intergranular corrosion and Figure 8.31 (d) illustrates the contamination. At higher magnification of the melted layer (Figure 8.31 (e)) the presence of an anodic film inside the pores and the solute bands are not attacked by corrosion. After 6 hours of EXCO immersion test, this part of the sample resisted corrosion, reflecting the improved performance from anodizing the LSM-treated specimen.

Figure 8.31 (a) shows an intergranular corrosion is evident in this region. The intergranular corrosion is at the melted layer/matrix interface and the matrix. A large intermetallic particle is present at the thinnest part of the melted layer (valley) which could form defects within the anodic film. At increased magnification, Figure 8.32 (b) verifies the intermetallic is intact. Figure 8.32 (c) and (d) also reveal signs of delamination at the interface between the melted layer and the matrix.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.31: SEM micrographs of the cross-section of 4 minutes anodized AA2024-T351 alloy with 25 pulses LSM after a EXCO immersion test for 6 hours; (a) at low magnification, in the direction of the red arrow showing a large wide area of the sample, at higher magnification, (b) and (c) show undamaged melted layer, (d) dark gray spots due to contamination and (e) pores with anodic film formed on the interior surface, with no corrosion.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.32: SEM micrographs of cross-section in direction of the yellow arrow in Figure 8.31 (a); (a) melted layer delamination, and IGC through the matrix, (b) higher magnification of the red area in (a) displays a large IMP near the surface with IGC in the matrix, (c) scattered large pits in the matrix with limited IGC and (d) large irregular shaped pit at the melted layer/matrix interface.

Observation of the corrosion attack for the 20 minutes anodized alloy treated with 25 pulses LSM is displayed in Figure 8.33. Figure 8.33 (a) shows a 500 µm wide range view of the cross-section. Most of the region appears free of intergranular corrosion. However, at the far right, limited intergranular corrosion is evident at the melted layer/matrix interface which penetrates slightly into the matrix as shown by the red arrows. At higher magnification, features of the melted layer, the matrix and the effect of IGC over this area which was exposed to EXCO immersion test for 6 hours, are depicted in micrographs of Figure 8.33 (b) to (g). Figure 8.33 (b) displays corrosion at the solute bands while the matrix is unaffected. Figure 8.33 (c) illustrates the melted layer and matrix with no evidence of IGC. However, there exist some contaminations on parts of the melted layer as result of sample preparation. Figure 8.33 (d) shows the presence of the anodic film on the melted layer where both the melted layer and the matrix are undamaged. Figure 8.33 (e) demonstrates that
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Pores within the top part of the melted layer can be also covered with anodic film which enhances the resistance to corrosion. Figure 8.33 (f) shows severe IGC accompanied by delamination at the melted layer/matrix interface where corrosion products are evident at the interface between the melted layer and matrix.

Result of investigation of the rest of the cross-section is shows in Figure 8.34 (a). At higher magnification, the circled region, Figure 8.34 (b) shows another site of delamination at the interface parallel to the melted layer is evident. In addition, intergranular corrosion emerges in the matrix just below the delaminated area. Furthermore, Figure 8.34 (c) shows the presence of a large pit at the interface between the melted layer and the matrix which was a site of an intermetallic and underwent dealloying. Therefore, from the results for the 25 pulses laser condition compared with the results the 10 pulses LSM condition, it can be seen that the performance of the anodic film against the corrosion resistance is increased for the 25 pulses LSM condition.
Figure 8.33: SEM micrographs of cross-sections of 20 minutes anodized AA2024-T351 alloy with 25 pulses LSM after EXCO immersion test for 6 hours; (a) at low magnification, a large wide view of specimen shows no corrosion attack, apart from the far top right; limited corrosion attack pointed by two red arrows, (b) increased magnification of (a), showing undamaged melted layer, (c) anodic film within the melted layer, (d) melted layer and matrix free of IGC, (e) pores at the top part of the melted layer covered with anodic film and intact melted layer, (f) initiation of the interface delamination, (g) interfacial delamination with limited IGC in the matrix.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

Figure 8.34: SEM micrographs of cross-sections of 20 minutes anodized AA2024-T351 alloy with 25 pulses LSM after EXCO immersion test for 6 hours. (a) overall 3-D view of specimen after EXCO immersion test, (b) increased magnification of damage area in red circle shows pit, interfacial delamination and IGC in the matrix and (c) Further magnification, shows crack at the melted, fall out of the IMP accompanied by exfoliation of melted layer.

8.6.4 Anodized AA2024-T351 alloy with 50 pulses LSM

A cross-section of 400 µm width of the sample is shown in Figure 8.35 (a). No evidence of intergranular corrosion can be detected. Further investigation was done by increased magnification where both Figure 8.35 (b) and Figure 8.35 (c) show no corrosion in the melted layer. However, Figure 8.35 (d) displays the melted layer and the matrix with a very thin line at the interface as indicated by the yellow arrow with a length of 20 µm indicating the initiation of intergranular corrosion. Figure 8.35 (e) reveals the effect of corrosion on the solute bands that resulted from incomplete dissolution of the melted intermetallic particles. Figure 8.35 (f) and Figure 8.35 (g) show the intergranular path passing by a partially corroded intermetallic particle at the interface. Hence, results of Figure 8.35 indicate an improved corrosion protection
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy using 50 pulses compared with 10 or 25 pulses LSM laser conditions, in particular, a limitation of the intergranular corrosion at the melted layer/matrix.

Figure 8.35: SEM micrographs of cross-sections of 20 minutes anodized AA2024-T351 alloy treated with 50 pulses LSM after EXCO immersion test for 6 hours; (a) at low magnification, showing a wide area view, (b) and (c) two successive cross-section areas at higher magnification of (a), both melted layer and matrix are intact, (d) initiation of interface delamination of the melted layer (at yellow arrow), (e) corroding solute bands in the melted layer, (f) partially corroded IMP at the interface and (g) at increased magnification, initiation of trenching at the top of IMP and partially corroded solute bands.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

![Figure 8.36: (a) noodle-like corrosion product in a pit at the melted layer/matrix interface, (b) initiation of interface delamination with no IGC attack of the matrix and (c) and (d) corrosion-free melted layer and matrix.](image)

**8.7 Conclusions**

- The anodic films formed on AA2024-T351 alloy with LSM have a typical closed packed array of columnar cells, each with a pore in the centre forming the film skeleton of lateral pores. The thickness of the anodic oxide film on the 50 pulses LSM surface is less than those treated with 10 and 25 pulses, the as-received alloy surface. This can be related to the reduction of the current density following LSM which altered the composition of the alloy surface, notably the enhanced concentration of the alloy elements in the solid solution. This will affect the composition of the anodic oxide film formed during anodizing and hence, the current density achieved at the selected potential. Other features that may offer an increase in current density are changes in the electrolyte composition in fissures and pores in the laser melted surface and associated potential drops due to the resistance of the electrolyte at such locations.
8. Evaluation of laser surface melting as a pre-treatment method prior to anodizing AA2024-T351 alloy

- Polarization curves of the anodic films formed on AA2024-T351 alloy with LSM, particularly for 25 and 50 pulses, display significant shifts in pitting potential to more positive values, accompanied by a decrease in the passive current density. This implies anodizing after LSM in particular for 25 and 50 pulses significantly enhances the corrosion resistance.

- The anodic film formed on AA2024-T351 alloy without LSM suffered from severe pitting corrosion in the immersion test in 0.1 M NaCl solution for 24 hours. Cross-sectional examination showed defects in the anodic film related to the presence of intermetallic particles, mainly for the particles enriched with iron which are not totally oxidized during the anodizing process due to their low oxidizing rate compared to aluminium and copper. This is expected to cause defects in the oxide film that result in less corrosion protection generated by the anodic films as the surface exposed to an aggressive solution.

- The anodic films formed on AA2024-T351 alloy surface with LSM by 25 and 50 pulses increased the pitting potentials in NaCl solution also exhibited significantly improved corrosion resistance in 0.1 M NaCl solution immersion test. Neither pitting nor intergranular corrosion was observed. The anodizing on a surface with refined microstructures extensively improved the corrosion resistance of the alloy.

- The EXCO test showed that the anodized surface after LSM treatment demonstrated much less delimitation and intergranular corrosion in the matrix than both the anodized alloy without LSM treatment as well as the laser-melted surface without anodizing.

- Delamination of the melted layer was not observed in the EXCO test for 20 minutes anodized previously surface treated with 50 pulses LSM. A lower degree of intergranular corrosion was found only in very limited areas where there were heavy solutes and large intermetallic particles at the interface. After six hours of EXCO test, the matrix was almost intact and free from pitting and intergranular corrosion.
8.8 References


9. ASTM G01.05 committee, ASTM G34-01 standard testing method for exfoliation corrosion susceptibility in 2XXX and 7XXX series aluminium alloys (EXCO test), USA: ASTM International.
Chapter 9

Conclusions and future work

9.1 Conclusions

9.1.1 Original microstructure of AA2024-T351 alloy

The original microstructure of AA2024-T351 alloy has been characterized in detail, in terms of intermetallic phases and grain orientation. Surface potential measurement of various intermetallic particles has been also conducted. The obtained results are in good agreement with the literature.

- The main intermetallic particles of the AA2024-T351 have been identified, including spherical-shaped $\text{Al}_2\text{MgCu}$ ($S$-phase) particles, round shaped $\text{Al}_2\text{Cu}$ ($\theta$-phase) particles and irregular shaped $\text{Al-Cu-Mn-Fe-(Si)}$ particles.
- $\theta$-phase particles, $\text{Al}_2\text{Cu}$, are of dimensions typically between 1 and 2 $\mu$m, $S$-phase particles, $\text{Al}_2\text{MgCu}$, with typical size of 0.5 to 4 $\mu$m have the highest population of the alloy amongst all the particles.
- Small sized dispersoid particles of submicron size were observed by TEM on samples prepared by twin-jet electropolishing method that contained Al, Cu and Mg.
- EBSD mapping showed the grain orientations of the AA2024-T351 alloy. Results of EDX line scans indicated the presence of $\text{Al}_2\text{MgCu}$, $\text{Al}_2\text{Cu}$ and $\text{Al}_{20}\text{Cu}_3\text{Mn}_3$ in laths and rod like shapes lined at the grain boundaries. SKPFM revealed $\text{Al}_2\text{MgCu}$ ($S$-phase) were anodic with respect to the matrix, with a potential in a range of -125 to -150 mV where the matrix was taken as reference with value of zero. Cathodic $\text{Al-Cu-Mn-Fe-(Si)}$ particles displayed potentials up to 300 mV with respect to the matrix.
9. Conclusions and Future Work

9.1.2 Microstructural characteristics of laser-melted AA2024-T351 alloy

- **Surface morphology:** LSM with a fluence of 7 Jcm\(^{-2}\) resulted in the formation of ripples on the alloy surface. The distance between the ripples decreased with increasing in the number of pulses at the fixed fluence, increasing the number of pulses (10, 25 and 50 pulses) resulted in increase in surface roughness and increase in surface area.

- **Overlapping effect:** Overlapping using an overlap ratio of 20 % to cover a large area leads to re-melting and re-heating of previously melted track. Increasing the number of pulses (10, 25 and 50 pulses) increases in the areas of re-heated zones.

- **Melted depth:** LSM resulted in a thin melted layer with a typical melt depth in the range of 5 to 10 µm. By increasing the number of pulses (10, 25 and 50 pulses) at fixed laser fluence, the depth of melted layers is increased.

- **Microstructure and intermetallic particles:** LSM resulted in dissolution of the intermetallics and dispersoids present in the as-received alloy, within the melted layers. LSM also resulted in formation of solute bands. There are two typical types of bands. The first is the formation of discontinuous, thin bands within the melted layers; the second is the relatively thick bands at the interface between the melted layer and the substrate. The second one is typically copper-rich bands.

- **Potential mapping:** laser-melted layers exhibited a uniform surface potential, with potentials from +25 to -10 mV with respect to the matrix.

- **Residual stress:** The melted layers revealed tensile residual stress compared with the compressive stress of -20.5 \(\pm 15.7\) MPa in the X-direction and -27.7 \(\pm 16.3\) MPa in the Y-direction for the ground surface of AA2024-T351 alloy. The maximum values obtained for the laser tracks in the X-direction and in Y-direction are 98.6 \(\pm 22.5\) MPa and 115.9 \(\pm 25.3\) MPa, respectively which occurred for 25 laser pulses.

- **Hardness:** The hardness of the melted layer increased slightly with respect to the matrix as a result of refinement of the microstructure and due to the extensive solid solubility that might lead to solution hardening.
9. Conclusions and Future Work

9.1.3 Corrosion behaviour of AA2024-T351 alloy before and after LSM

The corrosion behaviour of AA2024-T351 alloy before and after LSM was evaluated by potentiodynamic polarization in deaerated and aerated 0.1 M NaCl solution, immersion tests in 0.1 M NaCl solution for 24 hours and in EXCO solution for different periods of time.

- **Polarisation behaviour**: Excimer LSM of AA2024-T351 alloy improved the localised corrosion resistance, by reducing the passive current density up to two orders of magnitude and almost three orders of magnitude for deaerated and aerated 0.1 M NaCl solution, respectively. The higher the number of laser pulses, the better the corrosion performance. This improvement of corrosion resistance is attributed to the significant decrease in the cathodic activities of the surface as a result of the removal of intermetallic particles and increase in the copper content in the aluminium solid solution. In contrast to the as-received alloy, the pits as well as corrosion products were reduced significantly for the laser-treated alloy. This suggests that the refined microstructure and the extended solid solubility of copper reduce the number of pits on the surface, since copper in the solid solution increases corrosion resistance.

- **Immersion test in 0.1 M NaCl solution**: The results have demonstrated a decrease in both the number of pits and the amount of corrosion products due to LSM. However, the overlapped regions, particularly the re-heated regions, had more pits and corrosion products than other regions.

- **Immersion in EXCO solution**: The AA2024-T351 alloy displayed severe intergranular corrosion during an EXCO test for 6 hours, causing detachment of grains. The laser-melted alloy, with the increase of the number of laser pulses, revealed a significant decrease in the degree of intergranular corrosion attack. Different degrees of delamination of the laser-melted layers were observed, suggesting that the presence of copper-rich bands, particularly at the melted layer/matrix alloy interface, favours the formation of micro-galvanic corrosion.

9.1.4 Effect of LSM on anodising of AA2024-T351 alloy

In order to investigate the effect of LSM on anodising of AA2024-T351 alloy and further enhance the corrosion resistance of the laser-melted surface, anodising in 0.46 M H₂SO₄ solution at a fixed voltage of 12 V was applied to the laser-melted
surface of AA2024-T351 alloy, and to the as-received alloy condition for the purpose of comparison.

- **Microstructure:** The anodic film formed on AA2024-T351 alloy treated with LSM has a typical film skeleton of lateral porosities. The thickness of the anodic oxide film on a 50 pulses LSM treated surface was less than those treated with 10, 25 pulses and the as-received alloy surface. This can be related to the reduction of the current density following LSM which altered the composition of the alloy surface, notably the enhanced concentration of the alloy elements in the solid solution. This affected the composition of the anodic oxide film formed during anodizing and hence the current density achieved at the selected potential.

- **Corrosion behaviours:**
  
  1) **Polarisation behaviour:** Polarisation curves of the anodic films formed on AA2024-T351 alloy with LSM, particularly for 25 pulses and 50 pulses, displayed significant shifts in pitting potential to more positive values, accompanied by a decrease in passive current density. The shift of the pitting potential to more positive potential values of the anodised 25 and 50 pulses conditions of the treated AA2024-T351 alloy has not been show before.

  2) **Immersion in 0.1 M NaCl solution:** The anodized surface of as-received AA2024-T351 suffered from severe pitting corrosion in the immersion test in 0.1 M NaCl solution for 24 hours. Cross sectional examination showed defects in the anodic film related to the presence of intermetallic particles, mainly for the particles enriched with iron which were not totally oxidized during the anodizing process due to their relatively low oxidation rate. This is expected to cause defects in the oxide film that result in less corrosion protection of the alloy. The anodic films formed on AA2024-T351 surface with LSM by 25 and 50 pulses increased the pitting potentials in NaCl solution and also exhibited significantly improved corrosion resistance in 0.1 M NaCl solution immersion test. Neither pitting nor intergranular corrosion was observed. Hence, the formed anodic films on the surface with refined microstructure and extended solid solubility have extensively improved corrosion resistance of the alloy.
9. Conclusions and Future Work

3) **EXCO test**: The EXCO test showed that the anodized surface with LSM demonstrated much less degree of delamination than the anodized surface without LSM and the laser-melted surface without anodizing, accompanied by less of intergranular corrosion in the matrix. Delamination of the melted layer was not observed in the EXCO test with a 50 pulses LSM and 20 minutes-anodized surface. A lower degree of intergranular corrosion was found only in small isolated areas, where the rest of the matrix was almost intact and free from pitting and intergranular corrosion.

In summary, the main finding/contributions of the present work are that 1) an improved understanding of the microstructural characteristics of AA2024-T351 alloy after excimer laser melting, including the refinement/dissolution of the intermetallic particles and the formation of copper-rich bands within the melted layers, particularly at the interface between the melted layer and the aluminium-matrix; 2) establishment of correlation of laser operating conditions with the microstructural characteristics, in terms of surface morphology, crack and porosity formation, melted layer depth, dissolution of large intermetallic particles, overlap effects and residual stress; 3) the improvement of corrosion resistance after laser treatment as evident from polarization behaviour and immersion tests; 4) an improved understanding of the corrosion mechanisms involved in laser-melted AA2024-T351 alloy, particularly the discovery and discussion of the delamination phenomena is of significance for excimer laser surface melting of a wide range of metallic alloys; 5) application of the excimer LSM as a pre-treatment technique prior to anodizing of AA2024-T351 alloy to achieve significant improvement of the corrosion protection of the alloy. This has opened up a new research area of utilizing excimer laser surface treatment as a pre-treatment technique for a wide range of industrial applications.

9.2 **Suggestions for Future work**

This study has shown that excimer LSM of AA2024-T351 alloy led to the significant corrosion resistance against localized corrosion. Future work might be suggested as follows:
9. Conclusions and Future Work

- As the presence of defects such as porosity in overlapped regions for higher number of laser pulses at the laser fluence of 7 J cm\(^2\), there might be a possibility of elimination of such defects by increasing the number of laser pulses but decreasing the laser fluence.

- Pits were found more in the laser re-heated region. Although it is unlikely to eliminate the re-heating, it might be possible to reduce the effect by selecting laser operating conditions. A mathematic modelling of the thermal fields during laser processing might be useful to minimize the reheating effects.

- More TEM work is required on the distribution of precipitate of solute bands in the melted layer in particular at the interface between the melted layer and the matrix to identify the role of these bands in the corrosion process.

- Further improvement of corrosion protection by the anodic oxide films could be achieved by using different anodizing solutions and varied laser operating conditions.