Characterization of corrosion behaviour of laser beam formed titanium alloy

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Abstract. The application of Titanium and its alloys are found in various industries such as Aerospace, Human implant, Automotive, Chemical processing, Geothermal, and Armoury etc. The unique properties of Titanium have made it immune to all forms of environmental attacks such as the urban pollution, marine and industrial. However, it is believed that all manufacturing processes often influences the materials and mechanical properties of the processed material. This paper reports on the corrosion behaviour of Laser Beam Formed Titanium Alloy. Titanium sheets were laser formed using three constant parameters (laser power of 0.8 kW, the beam diameter of 12 mm and scan speed of 0.03 m/min) and varied parameter which is the number of scans – 3, 5 and 7. The corrosion behaviour was after that investigated in a 3.5% NaCl solution using the Potentiodynamic Polarization technique. The Potentiodynamic polarization curves were measured at a scan rate of 2 mV/s starting from 1000.0 mV concerning OCP to 1100 mV. The result revealed that the parent material had the most significant resistance to corrosion and the lowest corrosion rate per year. While for the Laser formed Titanium sheets, it was observed that as the number of scans increases the resistance to pitting was increased. However, the Titanium sheets samples formed at seven and five laser scans developed microcracks on the surface of the samples even though the resistance to corrosion is improved with the two sets of samples. These defects render the laser formed titanium sheets undesirable for intended applications.

1. Introduction

Laser Beam Forming (LBF) has been one of the accepted manufacturing processes, even though the process is still explored in its application to different industries. LBF was first employed in sheeting forming operation for the bending of sheet metals in 1985 [1]. A schematic of the LBF process is illustrated in Figure 1.
Figure 1. Schematic of Laser Beam Forming Process [2]

The irradiation patterns illustrated in Figure 1 is the methods employed to achieve a uniform deformation. The numbering system here is 1,2,5,6,9,10,11,12,7,8,3,4 support the cantilever system, which only develop a non-uniform profile. While 1,2,3,4,5,6,7,8,9,10,11,12 numbering system are employed in an open mold system whereby a uniform profile are developed. LBF process employs a source of focused or partially focused laser beam to irradiate the surface of the material consequently creating localized heating along the bend line [3]. The sharp thermal gradient developed in the material causes the material to bend towards the laser beam leading to permanent deformation.

The industrial application Titanium and its alloys in the aerospace, is because of its strength to weight ratio. This makes it unique from other materials such as steel and Aluminium that also finds application in the same industry. The corrosion resistance of Titanium and its high strength at elevated temperature has made Titanium and its alloys to be a preferred metal in the aerospace industry. Similarly, its inert nature to human body-biocompatibility and corrosion resistance has made Titanium especially Ti6Al4V ideal for medical implants of structures such as the hip joint and kneecap. Titanium is known to allow the bone to grow to adhere to the implant. Application of Titanium and its alloys in chemical and petrochemical industries has been because it increases the life of the equipment and facility. When compared with other metals the likes of copper, nickel and stainless steel, Titanium offers a better lifecycle. The unbeatable property of Titanium such as durability, strength, lightweight, resistance to heat and corrosion has also made application of Titanium and its alloys acceptable automotive industry for engine parts the camshafts, valves, springs, connecting rods and rock arms etc. [4].

Several studies into the forming of Titanium and its alloy has been conducted to address different areas of investigation which ranges from the forming process in comparison to other forming techniques [1], [5], its sustainability as a manufacturing process [3], effects of processing parameters on its mechanical behaviour and material properties [6]-[9]. Studies into the corrosion behaviour of laser beam formed Titanium alloy is scares in the literature [2], [10]. The study of Vijay et al. [11] gave a good insight into the fundamental corrosion mechanisms involved in titanium alloys. Corrosion may be in different form and characterized by a relatively uniform attack that occurs on the surface of the metal. Corrosion may be in a general form, crevice and Electrochemical Corrosion. Most corrosion in metals occurs through the electrochemical reactions at the interface between the metal and the electrolytic solution. The rate of reaction is determined by the equilibrium between the electrochemical opposing reaction [12]. In an electrochemical reaction, the first reaction occurs when the metal oxidizes releasing electron into the metal. While in a cathodic reaction electrons are removed from the metal. The flow of electrons is characteristics of electrochemical corrosion, which balances the electrons. The schematic of the Anodic and Cathodic reaction, and Corrosion current are shown in Figure 2 (a) and (b) respectively.
The vertical axis is the potential while the horizontal axis is the absolute current. The straight line represents the theoretical current for the anodic and cathodic reactions. The curved line, on the other hand, is the sum of the anodic and cathodic current is known as the total current. The point where the current changes from anodic and cathodic and vice versa is the sharp point on the curved line. The corrosion potential \( E_{corr} \) is the equilibrium potential assumed by the metal in the absence of electrical connections. The value of either the anodic or cathodic current at the corrosion potential is known as the corrosion current \( I_{corr} \). The corrosion current cannot be measured directly and is found by extrapolating the linear portions of a log current vs potential plot. The place where they intersect can be used to determine corrosion current and corrosion potential.

The corrosion current determined by the Tafel analysis can be used to determine the corrosion rate per year.

\[
CR = K1 \left( \frac{I_{corr}}{\rho} \right) \text{EW}
\]

Where:
- \( K1 = 3.27 \times 10^{-3} \) (mm g/1A cm yr)
- \( \rho \) = Density (g/cm\(^3\))
- \( \text{EW} \) = Equivalent Weight = 15.84 for Ti6Al4V

2. Experimental Methodology

2.1. Materials

The Titanium alloy of 1mm was used for the laser forming process, with a sample dimension of 90 x 30 x 1 mm\(^3\). The samples were formed with two sets of process parameters: constant Laser power (800 W), Spot size (12 mm) and scan speed (0.03 m/min) and variable number scans - 3, 5 and 7. Samples were formed using a 4.4 kW laser system; an open mould was employed to allow a full deformation of the formed samples.

2.2. Microstructural Evolution

The formed samples were sectioned, mounted in hot polyfast resin, grounded and polished to characterise the microstructural evolution. The resulting microstructures were characterised through the optical microscopy and SEM. The metallographic samples were prepared based on the ASTM standard E3, 2011, hot mounted in polyfast resin, ground and polished, and etched by immersing the samples in Kroll’s reagent to reveal the grain structure of the microstructure.
2.3. Corrosion Analysis

The formed samples were sectioned into 10 x 6mm2, attach the insulated copper wire to one face with a conducting tape and mounted in epoxy resin. The mounted samples were then grounded and polished to characterise the microstructural. The corrosion analysis was conducted using the Potentiodynamic polarization technique according to the ASTM G 3-89 and ASTM 5-94. The Electrochemical setup consist of a 200ml covered Pyrex TM glass conical flask suitable for the conventional three-electrode system is shown in Figure 3. Four holes were made on the cover of the cell for the reference electrode, the working electrode, the counter electrode and the temperature measurement.

The samples being tested is set as the working electrode, Platinum rods as the counter electrodes and Silver/Silver Chloride 3M KCl electrode as the reference electrode (SSE). The corrosion behaviour was investigated using 3.5% NaCl solution and all electrochemical tests were conducted at room temperature. The samples were immersed in the electrolyte before the Potentiodynamic cyclic polarization was measured to allow stabilization at the Open Circuit Potential (OCP). The Potentiodynamic polarization curves were measured at a scan rate of 2mV/s starting from -1000.0 mV to 1100 mV.

3. Results and Discussion

3.1. Evolved Microstructure

The microstructure of the cross-section of the three LBF samples scanned at three, five and seven scans are shown in Figure 4 (a), (b) and (c) respectively. LBF process can be described as a heat treatment process because the heat was generated from the laser beam resulting into laser-material interaction. Martensitic -α grain structure was developed during laser scan of three. The laser heat produces strain hardening which strengthens the material surface.
Similarly, for LBF samples scanned at five laser scan, the average grain size at the cross section was observed smaller than average grain sizes of samples scanned three times. This is due to the increased number of scans causing an increase in the thermal strain produced in the material and hence, an increase in strain hardening of the material. It should also be noted that the average grain size for the samples irradiated seven scans was smaller than the average grain size of the samples irradiated with three scans. LBF samples with seven number of scans continued to exhibit the martensite microstructure. As was the case with previous samples, an increase in the number of scans led to a decrease in the grain size at the cross-sectional area.

3.2. Corrosion Testing

The corrosion behaviour was investigated using 3.5% NaCl solution and all electrochemical tests were conducted at room temperature, with the mounted LBF samples immersed in the electrolyte.

The cyclic polarization scan was conducted to determine pitting in the LBF samples at a different number of scans. A total of fourteen samples were laser formed, four per LBF samples and two samples for the parent material. The Cyclic polarization graph of the filtered plot is shown in Figure 5. Pitting’s are detected and determined by the direction the hysteresis occurs, which are either in the clockwise or anti-clockwise.

Figure 4. (a), (b) and (c) LBF samples: (a) Three scans, (b) Five scans and (c) Seven scans
The cyclic polarization shows that the hysteresis is in the anti-clockwise direction for all the four samples. This means that the parent material and the LBF samples scanned at three, five and seven are not susceptible to pitting corrosion [13]. However local and crevice corrosion may still occur. The width of the loop indicates the crevice corrosion and the wider the loop, the greater the crevice corrosion. The result of the corrosion potential ($E_{corr}$) and current ($I_{corr}$) are presented in Table 1.

| Sample     | $E_{corr}$ (mV) | $I_{corr}$ (A/cm$^2$) |
|------------|-----------------|-----------------------|
| Parent Material | -325            | 1.42 x 10^{-7}        |
| 3 Scans    | -650            | 6.3 x 10^{-6}         |
| 5 scans    | -600            | 6.3 x 10^{-6}         |
| 7 Scans    | -350            | 1.99 x 10^{-7}        |

The analysis from the Tafel plot shows that the pitting potential for LBF sample with scan seven was better (-350mV) when compared to LBF samples with five scans (-600mV) and three scans (-650mV). While the parent material had the lowest breakdown potential of -325mV. With the higher value of the corrosion potential for LBF sample at seven scans, it is implied that the LBF sample with the lowest number of scan tends to corrode more than the other LBF samples [14]. However, the rate of corrosion is determined by the corrosion current density. The $I_{corr}$ values give the direct measure of the corrosion rate. It was observed from Table 1, that the corrosion current for LBF sample with scan 3 and 5 are identical while the seven scan sample has lower corrosion than the samples with three and five. The corrosion rate for the four samples is determined using Equation (1) and presented in Table 2. It was observed that the corrosion rate decreases with increased number of scan while an improvement in corrosion resistance as the number of scans increases.

| Sample     | Corrosion rate (μm per year) |
|------------|------------------------------|
| Parent material | 1.66                        |
| 3 scans    | 73.66                        |
3.3. SEM Analysis

The corrosion samples were observed under the SEM, and the photos are shown in Figure 6. The surface morphology shows that the three LBF samples corroded uniformly, in line with the cyclic polarization scans and no pitting found on the surface of the corroded samples.

![Surface morphology of corrosion samples under SEM](image)

Figure 6. Surface morphology of the corrosion samples under the SEM for (a) three scans, (b) five scans and (c) seven scans

4. Conclusion

The corrosion tests showed that Titanium alloy is immune to pitting both in its unformed state and after undergoing the laser beam forming process. The breakdown potential of the parent material is the greatest, followed by the seven-scan sample which has a very similar breakdown potential to the parent material. The three and five scan LBF samples had the lowest breakdown potential which indicated the greatest potential for corrosion to occur. The corrosion rate per year was also the lowest for the parent material. However, the seven-scan sample had a similar corrosion rate. The Laser Beam Formed samples irradiated with 3 and 5 scans had a much higher corrosion rate compared to the parent material.
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