Study of corrosion resistance in Ti 6Al 4V additive manufactured parts

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Abstract: Laser Directed Energy Deposition is an additive manufacturing process widely extended in industry, whose development is not free of challenges. The gaseous domain in which the process takes place, plays a major role in the resulting quality of the components, even bigger when the process involves a highly reactive materials like Ti 6Al 4V. Titanium alloys are extensively employed due to a combination of mechanical and chemical properties, being one of them their good corrosion resistance. The present work aims to provide an analysis of this corrosion resistance for LMD manufactured parts in comparison with raw material. For this purpose, a manufacturing methodology is described, using a local protective atmosphere to create the specimens, and a methodology for corrosion testing is presented. Results show similar corrosion resistance values for both raw and additively manufactured materials, therefore reinforcing the feasibility of manufacturing titanium parts by means of L-DED additive process.

Keywords: Additive manufacturing, Titanium, Laser directed energy deposition, Corrosion.

1. Introduction

Laser Directed Energy Deposition (L-DED) is an Additive Manufacturing (AM) process, which provides innovative solutions, optimization, and efficiency increase of several products and industrial applications [1]. A wide material selection can be processed by this technology, such as steel, titanium, and nickel-based alloys. Titanium and its alloys are widely used in the aerospace, automobile, and medical industries due to their low density, high specific strength, good corrosion resistance and biocompatibility [2]. However, titanium alloys present low thermal conductivities and thus difficulties during machining processes. Therefore, additive manufacturing results in a reliable solution to reduce subtractive steps creating near-net-shapes parts, at time, it brings new opportunities of creation, such as more complex geometry designs, functionally graded materials, coatings, and material waste reduction.

Powder Bed Fusion (PBF), on the other hand, is broadly used to manufacture titanium parts. The entire process is carried out in a completely inert atmosphere; hence an oxidation-free environment can be ensured [3]. However, part dimensions are usually more constrained as compared to other laser additive processes. The powder particles are required to be in a very specific and reduced size range, and below 40 µm, which increases its cost. Moreover, in most cases, a large percentage of the powder, which fills the processing volume is not used to build the parts and must be recycled for future manufacturing.
Laser Metal Deposition (LMD) or L-DED by powder injection, are often employed to create bigger parts for other applications, like repairing, surface coating, or even adding new features to a part created in another way. In general, mechanical properties obtained by the LMD process can be similar to other manufacturing technologies, being Ti 6Al 4V not an exception [4]. The required amount of powder is proportional to the parts size, and there is no need to fill the entire work volume, as it is in PBF. Additionally, the granulometry of the particles is considered to be acceptable from 40 µm to 150 µm approximately. Therefore, the powder injection process arouses a big interest as a manufacturing technology, leading to the research and development of new strategies and solutions to overcome the challenges it presents.

Despite all the advantages, titanium alloys present some difficulties when combined with laser additive technologies. The powders usually employed in this kind of processes are highly reactive and present a high risk of oxidation. Thus, an inert atmosphere must be ensured either by sealing the process volume and replacing the air with an inert gas, or by generating a local protective atmosphere [5,6]. The first solution is more extensively used, but it introduces a series of disadvantages such as high gas consumption, dimensional dependency on sealing environments, and large idle periods during the vacuum process.

In the second case, inert gas is injected directly into the processing area with the use of special nozzle designs. Nonetheless, new challenges come along with this solution, as other parameters must be considered, like heat evacuation, new geometry considerations, and surface temperature. The inert atmosphere generated is transient and it moves with the nozzle; consequently, surface oxidation must be avoided by controlling the heat evacuation and surface temperature. Moreover, the efficiency of the protective stream can be modified by geometric obstructions, hence an additive strategy must be considered to avoid such issues. Previous studies were carried out and aimed to develop a reliable solution in the generation of a local inert atmosphere for highly reactive materials [7]. However, even with a successful oxidation-free additive manufacture process, corrosion resistance must be evaluated to ensure the quality of the added material.

The present study evaluates the corrosion resistance of additively manufactured parts in titanium alloy (Ti 6Al 4V) by a L-DED process with powder injection and the local inert atmosphere solution mentioned before.

2. Methodology and Experiment Procedure

The AM experiments are carried out with a self-developed DED nozzle and a Yb:YAG fiber laser with a 1070 nm wavelength. The nozzle uses an additional protective gas flow to ensure the local inert atmosphere and to guarantee an oxidation-free titanium deposition. Both powder and substrate material are Ti 6Al 4V and their compositions are detailed in table 1 and table 2.

| Table 1. Chemical composition (wt %) of the Ti 6Al 4V substrate. |
|---------------------------------|---------|-------|-----|-----|----|----|-----|-----|
| Al    | V      | Fe    | O    | C   | N   | Y   | Ti  |
| 6.46 – 6.53 | 4.00 – 4.04 | 0.18 | 0.17 – 0.19 | 0.02 | <0.01 | <0.0009 | BAL |

| Table 2. Chemical composition (wt %) of the Ti 6Al 4V powder. |
|---------------------------------|---------|-------|-----|-----|----|-----|-----|
| Al    | V      | Fe    | O    | C   | N   | H   | Ti  |
| 6.4  | 3.9    | 0.22  | 0.07 | 0.01 | 0.009 | 0.001 | BAL |

Aiming to achieve the same area for all corrosion tests, a cylindrical geometry is proposed to be manufactured via the abovementioned powder injection L-DED process. Argon with 99.998% of purity is used as shielding, protective, and powder carrier gas.

The process parameters are based on previous works and set to 700 W of laser power, with a spot of 1.6 mm of diameter, a feed rate of 800 mm/minute, and a powder mass flow of 3 gr./minute. The different gas flows are set to 15.0, 4.5, and 10.0 l/minute as shielding, carrier, and protective gas flows,
respectively. The inert atmosphere is generated by the combination of these three streams, at the exit of the nozzle, but mainly by the last one. A simplified scheme is presented in figure 1(a).

A zigzag pattern is employed as show on figure 1(b), changing the starting point and angle for every layer, to ensure a more homogeneous piece. The process is monitored with a two-colour pyrometer to ensure a constant temperature and to avoid overheated parts.

Additive manufactured parts and bulk material are machined and then sliced to prepare the samples to obtain the Potentiodynamic polarization curves after polishing. Electrochemical tests were performed (Open Circuit Potential (OCP) and Potentiodynamic polarization called Tafel curves) in VSP-300 Biologic potentiostat. A three-electrode configuration was used: a working electrode (1 cm² of the sample) exposed to a volume of 250 mL of quiescent electrolyte (3.5 wt.% NaCl), a platinum mesh as a counter electrode and a saturated calomel electrode (SCE, saturated KCl) as reference electrode. OCP was monitored during 3h before carrying out the polarization test using a scan rate of 0.167 mV/s from -0.3 V to 3.0 V Vs. OCP.

3. Results and Discussion
The result of the additive manufacturing and successive machining process, dismissing the very first and the top superior layers, is a set of three cylinders with a diameter of 25 mm, and a height of 45 mm, figure 2. The entire process is carried out aiming to obtain a constant value of the testing area to ensure the repeatability of further experiments. The diameter was selected to maximize the tested area considering the maximum dimension allowed in metallographic mounting press available.

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Figure 1. (a) Additive process scheme. (b) Pattern strategy.

Figure 2. Cylinders additively manufactured.
Six additive specimens are obtained from these cylinders by cutting 5 mm-thick cross-sectional layers while, a reference anode to compare with is machined from a Ti 6Al 4V billet. The samples are prepared in resin by means of a mounting press to leave only the circular faces exposed. The specimens are tested by immersing one side in a NaCl solution for 180 minutes until stabilization, while measurements of the open circuit potential (OCP) are taken in the opposite face. Figure 3 shows two example curves for an additively manufactured and bulk-material samples, and plotted versus time.

![Figure 3](image)

**Figure 3.** (a) OCP curve for bulk sample. (b) OCP curve for additively manufactured sample.

Potential differences are applied on the specimens to obtain the Tafel curves. Additive manufactured samples show a similar behaviour against corrosion when compared to the bulk material samples used as reference. Figure 4(a) and 4(b) present two different Tafel curves, where these results can be observed, and figure 4(c) shows how an additively manufactured sample has a slightly superior corrosion resistance.

The results obtained can be summed up in an average OCP and potential corrosion of 0.265 V and 0.270 V respectively for the reference sample, while for the AM specimens, these values are -0.138 V and -0.215 V. The higher result obtained for the AM material reach an OCP of -0.350 V and a potential corrosion of -0.358 V.

4. Conclusions
The corrosion resistance of the deposited Ti 6Al 4V alloy has been analysed and compared with a reference specimen. DED tests have been carried out with temperature monitoring and an extra protective gas flow to ensure a process free of oxidation. It has been concluded that the implementation of a local inert atmosphere is a reliable solution for cases, where it is not possible to accomplish a complete inert environment. The strategy used to create the samples for testing results in massive titanium cylinders without pores nor cracks.

Results show that additively manufactured titanium alloy presents a similar corrosion resistance to the reference material and no oxidation resulting from the deposition process is present. Therefore, the additive manufacturing process and the use of a local inert atmosphere combine their advantages and provide an alternative manufacturing process for the Ti 6Al 4V alloy, widely used in industry.

The study sets the basis for new tests aimed at improving the corrosion resistance of components manufactured by this technology. Additive manufacturing by L-DED allows not only the creation of new components, but also their repair or the creation of coatings. Future works aim to evaluate the corrosion resistance of the coatings of titanium alloys, or even the improvement of this resistance by integrating or mixing materials in the manufacturing process. Being, this last option a particularly advantageous aspect of the L-DED process.
Figure 4. (a) Tafel curve for bulk sample. (b) Tafel curve for additively manufactured sample. (c) Tafel curve for AM sample with higher corrosion resistance.

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