Surface Modification of Laser Metal Deposited Ti-6Al-4V +10%Mo for Biomedical Applications

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Abstract

The main goal of the project is to observe characteristic changes in laser metal deposited Ti-6Al-4V + 10% Mo at varying scan speeds. Laser metal deposition is an additive manufacturing technique that begins with two hoppers that hold the powdered metals. In the first hopper there is Ti-6Al-4V and the second hopper contains molybdenum. Ti-6Al-4V is a titanium alloy that contains 6 wt% aluminum and 4 wt% vanadium. When the molybdenum is added to the Titanium alloy the hardness, biocompatibility and corrosion resistance of the material are affected. The hoppers release the powder such that there is 90 wt% Ti-64 and 10 wt% Mo. The powders are deposited through a nozzle and a focused laser creates a melt pool of the two metal powders onto a substrate. A three dimensional design program is used to create the path that the laser follows, depositing layers of the metal, until the desired part is achieved. Five samples of the laser deposited Ti-6Al-4V +10% Mo were completed at the CSIR National Laser Center in Pretoria, South Africa. The five samples consist of scan speeds varied from 0.50 meters per minute up to 1.50 meters per minute, while the laser power remains at a constant 1700 Watts. The microstructure, micro hardness and corrosion resistance of the samples are the main focus in this project. Currently, Ti-64 is used in biomedical implants such as hip replacements. The results showed that the samples with the lower scan speeds have longer grain sizes, as the samples with the faster scan speeds have smaller grain sizes. The longer grain sizes create a stronger bond so the slower scan speeds of 0.50 and 0.75 m/min are ideal for biomedical applications. Additionally, the scan speeds of 0.75, 1.00 and 1.25 m/min have Vickers hardness values between 353 and 357. These high hardness values are not ideal because they could possibly cut into the surrounding bone of a hip replacement. On the other hand, the scan speeds of 0.50 and 1.50 m/min had average Vickers Hardness values of 322 and 324. The lower hardness value is ideal for biocompatible applications so that the implant does not cut into the surrounding bone. The corrosion resistance test first revealed that the surface of the samples are rough. This is important for osseointegration to occur. When the samples were removed from the 7-day corrosion test the grooves on the surface became deeper. All samples corroded to the same extent. Therefore, the scan speed of 0.50 m/min is considered ideal for biomedical applications.
In the future, a higher laser power should be used in order to successfully integrate the powdered metals by melting the molybdenum particles. Additionally scanning speeds lower than 0.50 m/min should be further researched.

1. Introduction

The purpose of this project is to research Ti-6Al-4V +10% Mo alloy when it is laser metal deposited onto a Ti-64 substrate at increasing scan speeds for application in biomedical implants. The Ti-64 +10% Mo alloy contains 80 wt% titanium, 6 wt% aluminum, 4 wt% vanadium and 10 wt% molybdenum. Three main studies where done in order to determine which scan speed is optimal for biomedical applications. First, the microstructure of the samples were observed and compared, then the Vickers hardness at each scan speed was determined and finally the corrosion resistance of each sample was considered as if it were implanted into the human body.

2. Background

2.1 Laser Metal Deposition

Laser Metal Deposition is an additive manufacturing technique that begins with a 3-dimensional model for a desired part. The model for this part is split up into thin horizontal layers. These layers are used to create a path for the laser to follow. Along that path, a focused laser creates a melt pool on a substrate. Powered metals are fed through two hoppers and then deposited onto the melt pool. As the deposit cools it becomes fusion bonded to the metallic substrate\(^1\). Simultaneously, Argon gas is used to shield the entire process from oxidation. The laser beam continues this process as it follows the path created. The paths are continued atop each other layer by layer, until the desired part is completed. A representation of this process is shown in Figure 1.

![Figure 1: Representation LMD Process\(^1\)](image)

2.2 Biomedical Applications

The Ti-6Al-4V alloy is commonly used to create biomedical implants such as total hip replacements. This is where the ball of the femur is removed and replaced with an artificial ball, known as a biomedical hip replacement\(^2\). Hip replacements must have a good balance between ductility and strength in order to withstand daily stresses of the human body movement. A lower Vickers hardness value is ideal because this will create a ductile material that is able to resist stress yielding, similar to the surrounding femur bone.

Currently hip replacements are being produced from various powder metallurgy forming techniques or wrought bar stock of Ti-6Al-4V with use of CNC machines\(^3\). Additionally, each hip replacement lasts for approximately 20 years. After the 20 year time period a repeat hip replacement is necessary. Due to the increase in age of the patient and the complexity of the surgery, this repeat hip replacement often results in a higher risk procedure and longer hospitalization\(^4\). If the corrosion resistance of the material could be improved upon, the need for repeat hip replacements would be eliminated.
2.3 Material Properties

Ti-6Al-4V has a low electrical conductivity which leads to a high corrosion resistance. Due to this high resistance to corrosion within the human body, titanium alloys have been used for biomedical applications since the early 1970’s\(^5\). The addition of molybdenum creates changes in the characterization of the alloy. Ti-64 has a melting point of 1604-1660 °C\(^7\), which is much lower than molybdenum at 2623 °C\(^8\). This results in unmelted molybdenum particles when integrating the two powdered metals together. Ti-64 has an average Vickers hardness value of 349\(^7\), while molybdenum has a lower Vickers hardness of 230\(^8\). It is expected that the addition of molybdenum will lower the Vickers hardness of the deposit and bring it slightly closer to the 45-50 Vickers hardness of the surrounding Femur bone for biomedical hip replacements\(^6\). Additionally, Ti-64 has an average modulus of elasticity of 113.8 GPa\(^7\) while molybdenum has an average modulus of elasticity of 330 GPa\(^8\), therefore it is expected that the addition of molybdenum will create a more ductile material. On the other hand, the density of Ti-64 is 4.42 g/cm\(^3\) and the density of molybdenum is 10.2 g/cm\(^3\). This higher density leads to the prediction that the addition of molybdenum would unfortunately create a heavier implant\(^7,8\).

3. Methodology

3.1 Sample Preparation

First, two hoppers were filled with two separate powered metals. One is filled with Ti-6Al-4V, while the other is filled with molybdenum. The control panel is adjusted such that the Ti-64 has a 3.6 rpm flow rate, while the molybdenum has a 0.4 rpm flow rate. This ensures that they alloy will be 90% Ti-64 and 10% molybdenum. Additionally, the laser was set to a laser power of 1700 watts with 6 tracks overlapping each other by 50%. The laser utilizes five different laser scanning speeds, starting at 0.50 m/min and increasing by 0.25 m/min increments, until it reaches 1.50 m/min as displayed in Table 1. This allows for five increasing scanning speeds to be observed. Figure 2 is an image of the five samples created. Visually it can be observed in that the slower scans produced a thick deposit, which gradually becomes thinner as the scan speeds increase.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Laser Power (W)</th>
<th>Scanning Speed (m/min)</th>
<th>Powder Flow Rate (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1700</td>
<td>0.50</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.75</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1.00</td>
<td>3.6</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>1.25</td>
<td>3.6</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1.50</td>
<td>3.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ti-64</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-64</td>
<td>3.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Figure 2: Laser Metal Deposited Samples
3.2 Cutting

A total of twelve samples were cut, two from each scanning speed and two from the substrate. The cutting was done using a Mecatome T300 cutting apparatus equipped with a Struers 20S25 cutting wheel, with all settings based on the Struers 2016 cutting handbook. Each sample was cut based on the red lines in Figure 3, resulting in each sample measuring approximately 10 by 10 by 7mm.

![Figure 3: Cutting Outline of Samples](image)

3.3 Mounting

Cross-sections from each scan speed and the substrate were mounted in a PolyFast hot mounting resin with a carbon filler. Using a Struers CitoPress-I Pneumatic Hot Mounting Press, each sample was lowered into the apparatus with the cross-section facing down. The 20 mL of the PolyFast powder was added and the ram was tightened. First the mounting press heats the powder to 180°C while applying 250 bars of pressure for 3.5 minutes. Next, water is used for 1.5 minutes to cool the melted powder into a solid cylindrical shape with the cross-section exposed. This can be seen for each sample in Figure 4 below. This type of resin is designed for excellent edge retention in the samples after mounting. The mounting is necessary to increase ease of handling, both by hand and for use in grinding machines.

![Figure 4: Five Mounted Samples](image)

3.4 Grinding and Polishing

After mounting, each sample went through a three-step grinding and polishing process on a Struers Polishing Machine, as seen in Figure 5. First, each sample was rough grinded for ten minutes using a disk of Silicon Carbide Paper #320 at 250 rpm while under a pressure of 10 N force and lubricated by water to allow the grinding disk to spin smoothly under the samples. This rough grinding allowed for excess polyfast and uneven surfaces to be removed from the mounted samples. The second step was a fine grinding process in order to remove large imperfections on the sample. Each sample was grinded for 8 minutes with a MD Large Plate at 150 rpm while under a force of 10 N. The samples were lubricated with a Diapro suspension, which consists of diamond particles to achieve precise grinding. Finally, the third step was to polish the sample in order to remove all small scratches and imperfections. Each sample was polished with a MD Chem polishing disk at 150 rpm, under a force of 10 N while being lubricated with an OP-S suspension, which is a silica suspension for final polishing. The polishing step was repeated in 5 minute intervals until a mirror like finish on the sample was visible to the naked eye.

![Figure 5: Struers Grinding and Polishing Machine](image)
3.5 Microstructural Evaluation

According to the Struers Application Notes handbook, titanium can exist in two different forms. First, a closed packed hexagonal structure that is created at low temperatures is considered to be the $\alpha$ phase. The material can then undergo a change in structure when heated to 882°C. The rise in temperature creates the $\beta$ phase, a body centered cubic structure. Thus, this change in titanium allows for the allotropic material to consist of both $\alpha$ and $\beta$ phases.

3.5.1 Etching

According to the Struers Application Notes handbook on metallographic preparation of titanium, the most common chemical etchant for titanium alloys is Kroll’s reagent. The Kroll’s reagent was prepared by mixing 100mL of water, 1mL of Hydrofluoric Acid and 2mL of Nitric Acid. This reagent is used to color the $\beta$ phase dark within the grains of the alloy, allowing the distinction between the $\alpha$ and $\beta$ phases to be visible when under a microscope. The surface of each sample was submerged into Kroll’s reagent for 5 second intervals until the $\beta$ phase in the grains was visible under a light optic microscope.

3.5.2 Light Optic Microscope

In order to view the microstructures of each sample, the Olympus OM was used, as shown in Figure 6 below. The Olympus OM is a light refracting microscope that holds a mirror which reflects adjustable light rays onto the sample and then through the objective lenses. The objective lenses then magnify the image so it appears enlarged when viewed from the eyepiece. Images of each sample were observed at 50x, 100x, 200x and 500x magnifications. As the magnifications increase, the details in the microstructures become better defined.

![Figure 6: Olympus LOM](image)

3.5.3 Scanning Electron Microscopy

The scanning electron microscope (SEM), seen in Figure 7, was also used to view the microstructure of each sample. First, the samples were placed in the apparatus. Rather than using light rays, the SEM makes use of a focused electron beam. The beam interacts with the atoms on the surface of the sample, this interaction produces signals that visually display the surface of the sample.

![Figure 7: Scanning Electron Microscopy Set-Up](image)

3.5.4 Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS) is part of the Scanning Electron Microscopy. The difference is that EDS takes the signals from the focused electron beam and gathers information on the surface composition. Thus, EDS can be used to determine exact percentages of different elements within the sample.
3.7 Vickers Hardness Testing

Hardness is a measurement of a material’s ability to resist deformation when a load is applied. The Vickers hardness test uses a diamond indenter in the shape of square based pyramid with an angle of 136° between opposite faces. The diamond indenter is used to penetrate the sample at a force of 500kg, or 4.9 N for 15 seconds. The first indent was made on the top of the deposition of the sample, from there the following indents were made 200 micrometers apart until there where a total of 20 indents. The Vickers hardness apparatus is shown in Figure 8. The diameter of each diagonal across the base of the pyramidal indentation are measured in millimeters and labeled as \(d_1\) and \(d_2\). The Vickers hardness is calculated by using equations 1 and 2 below, where \(F\) is the force in kg, \(D\) is the average diameter in millimeters and \(VH\) is the Vickers hardness measurement.

\[
VH = \frac{1.8544F}{D} \quad (1)
\]

\[
D = \frac{d_1 + d_2}{2} \quad (2)
\]

3.8 Corrosion Resistance Testing

In order to observe the corrosiveness of the samples, the remaining five unmounted samples were placed into a jar and submerged into a Hanks Balanced Salt Solution. Basically, Hank’s Solution imitates natural body fluid. The jar was then sealed with a rubber cork to protect the Hank’s Solution from any condensation, as shown in Figure 9. The jar was then placed into a Memmert water bath system as shown in Figure 10. The water bath was held at constant 37.0°C, the temperature of the human body, for seven consecutive days. The samples are then reviewed using the Scanning Electron Microscope to identify any corrosion that has occurred on the surface.
4. Results and Discussion

4.1. Light Optic Microscope (LOM) Observations

At a magnification of 50x, sample 3 was observed to reveal a clear image where the deposited Ti-6Al-4V + 10% Mo is visible atop of the Ti-64 substrate. Figure 11 shows that the deposit is homogenous throughout the sample, including visible black spots which are looked at closer in section 4.2. The interface is a clear line that shows where the deposit comes into contact with the substrate and creates bond. Additionally, the area where the heat produced by the laser alters the substrate is labeled as the heat affected zone in Figure 11. When sample 4 was observed under the LOM long columnar grains became apparent. There is a clear distinction between the α and β grains. The β grains were colored dark from the etching, allowing for the lighter α grains to also become visible, as shown in Figure 12 below. Figure 12 also shows one deposited track laying atop the previous track to the left, emphasizing the 50% overlap between the tracks.

As the magnification was increased, the grains become detailed enough to allow for measurement. The columnar grains from sample 1 with the slowest scan speed and sample 5 with the fastest scan speed were measured in micrometers, as shown in Figures 13 and 14 respectively.

First, Figure 13 shows smaller grains near the top of the image. The small grain size is due to the rapid cooling at the top of the sample, while the middle of the deposit cools slowly. It is clear to see that the grains in sample 1 are much longer than the grains in sample 5. In order to compare the grain sizes, the average grain sizes of each sample are represented in Figure 15 below.
Samples 1 and 2 have similar grain sizes at 471 and 479 micrometers long at scan speeds of 0.50 m/min and 0.75 m/min respectively. After sample 2 the grain sizes begin to decrease while the scan speeds increase, reaching a grain size of about 306 micrometers at a scan speed of 1.50 m/min. Thus, the grain sizes have an inverse relationship with the scanning speeds. This inverse relationship can be linked to the fact that the slower scanning speeds produced a thick deposit, allowing for longer columnar grains to form. Since the longer grains have more contact with each other, a stronger bond is created\textsuperscript{11}. Therefore, samples 1 and 2 with lower scan speeds are ideal for biomedical applications.

4.2 Scanning Electron Microscopy Observations

A dark spot in sample 3 was viewed under the scanning electron microscope at a magnification of 1000x as shown in Figure 16 below. Towards the top of the image there are white thin lines visible; these are the grain boundaries in the microstructure. In the center of the image the dark spot is revealed to actually be a large white circular spot. It is hypothesized that this spot is an unmelted molybdenum particle, this is looked into further by the energy dispersive spectroscopy. Below the white particle is a thick white line which is the interface where the deposit makes contact with the substrate. Finally, the bottom of the image shows some of the heat affected zone (HAZ) in the substrate.

![Figure 16: Sample 3 SEM](image)

4.3 Energy Dispersive Spectroscopy Observations

In order to verify the white spots as molybdenum particles, a grouping of the particles in Sample 4 were observed. The energy dispersive spectroscopy was set to determine the elements in the darker area displayed as spectrum 2 in Figure 17. Table 2 shows the percentage of each element found in that dark area. The weight percentage match the expectation of Ti-6Al-4V +10% Mo fairly well.

![Figure 17: Sample 4 EDS Dark Area](image)

<table>
<thead>
<tr>
<th>Table 2: EDS Dark Area Weight Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>Mo</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

The EDS was then shifted to the white particles displayed as spectrum 3 in Figure 18, to verify the predication. Based on Table 3, the light area consists of 99.72 wt% molybdenum and only 0.28 wt% titanium. This confirms the hypothesis that the white areas are unmelted molybdenum particles.
These unmelted molybdenum particles are likely to produce imperfections in a hip replacement. In order to fully melt these particles, the laser power could be increased, producing more hearths, melting the particles and successfully integrating the two powered metals together.

4.4 Vickers Hardness

Generally, a balance must be achieved between materials being too hard, in which they would become brittle and break, and being too ductile, in which they will not maintain the original shape when affected by an outside force. The average Vickers hardness of the deposit from each sample is shown in Figure 19 below. Samples 2-3 show similar high values ranging from 353 to 357 for Vickers Hardness. Sample 1 with the slowest scan speed of 0.50 m/min and sample 5 with the highest scan speed of 1.50 m/min both have the lowest hardness values of 322 and 324 respectively. The difference between the averaged values is approximately 32. While this difference is large enough to recognize, it would take a difference of at least 40 to see a significant impact when implementing the hip replacement. Based on the slight changes that will be seen, the lower hardness values are ideal because they are slightly closer to that of natural bone. The higher hardness value indicate that the implant is more likely to cut into that surrounding bone.

4.5 Corrosion Resistance

An image of the sample 1 with a scan speed of 0.50m/min before being placed in the Hank’s solution is shown in Figure 20 below. The surface appears to be rough and spongy; this roughness is essential for osseointegration, which allows the body cells to attach and grow onto the implant. Figure 21 shows sample 1 after the 7-day corrosion resistance test was completed. It can be observed that the grooves had grown deeper and some of the material has been pulled out. This proves that some corrosion has occurred, however the change in weight was unmeasurable. Since the change in weight was insignificant a predications cannot be made but, it can be said that there was not extreme corrosion after seven days. Each of the 5 samples appear to have corroded to the same extent. In order to predict the corrosion resistance further, the test would have to be continued for a longer period of time with measurements of the change in weight recorded.
5. Conclusion

Characteristics of laser metal deposited Ti-6Al-4V +10% Mo at varying scan speeds were considered. In conclusion, scanning speeds of laser metal deposited Ti-64+ 10% Mo have an inverse relationship with grain size, as seen in Figure 15. The longer grain sizes create a stronger bond, determining that samples 1 and 2 with a scan speeds of 0.50 m/min and 0.75 m/min have the ideal grain structure for biomedical applications. Furthermore, samples 1 and 5 with scan speeds of 0.50 m/min and 1.50 m/min respectively, have low Vickers hardness values of 322 and 324. This is lower than the values for samples 2, 3 and 4, as seen in Figure 19. The lower hardness values are ideal for biomedical applications because the material with higher hardness values will tend to cut into the surrounding bone. Each sample revealed a similar amount of corrosion after being immersed in the Hank’s solution for seven days. Unfortunately, the difference in weight loss was unmeasurable. In the future, the corrosion resistance test should continue over a longer period time while weight loss is measured, a higher laser power should be used in order to create the heat needed to fully melt the molybdenum particles and finally lower scan speeds should be considered.

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7. References