CHARACTERIZATION OF FUNCTIONALLY GRADED Ti6Al4V-Mo MATERIAL VIA LASER METAL DEPOSITION

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Abstract

This research assesses the material characteristics of several functionally graded Ti6Al4V samples with varying percentages of molybdenum. Ti6Al4V is a grade 5 titanium alloy which is widely used in both the aerospace and biomedical industries because of its superior properties, such as high strength and light weight. Molybdenum is a beta stabilizing element that is often combined with titanium alloys in order to offer even greater benefits including corrosion resistance and biocompatibility. Through the surface modification process known as Laser Metal Deposition, Ti6Al4V and Mo can be combined together in powdered form and parts can be made quickly and effectively. Several samples were made with varying percentages of molybdenum: 5%, 10%, and 15%, all of which have constant laser power and scanning speeds. Also, a functionally graded sample was produced, in which there are alternating layers of deposition of Ti6Al4V, 5% Mo, 10% Mo and 15%Mo. The properties of these alloys were compared to those of a pure Ti6Al4V sample. The properties that were compared are the microstructure, hardness, and corrosion resistance. This research showed that functionally graded materials have superior properties that can be taken advantage of for a variety of different applications, specifically within the biomedical industry.
1. Introduction

The Laser Metal Deposition (LMD) process is not yet a widely used process, despite the possible advantages it offers. One of these advantages is being able to make custom parts, which would be especially useful in personalizing implants for each body so that it is comfortable and fits that person well. Another advantage versus conventional manufacturing is that there would be less material waste. For most applications, a part is either cast or machined out of a block of metal. These manufacturing processes result in excess material waste that does not exist in LMD; only the material that will be in the final product is printed. A final advantage of this process is that it is quick and can be highly automated. This means that it could be a good process to be used in general manufacturing situations.

The main material that is currently used for biomedical applications such as hip and knee implants is titanium. This project is intended to keep all of the good characteristics that the titanium alloys offer, while improving some of the properties by implementing molybdenum metal. Some of the advantages of using this molybdenum are that it is more biocompatible and has properties, like modulus of elasticity for example, that are more similar to that of the human bone. The only main disadvantage of adding the molybdenum that can be seen at this point is that it would make the implant slightly heavier than if it were a pure titanium alloy, due to molybdenum’s higher density.

The goals of this research surrounded incorporating varying percentages of Molybdenum into the Ti6Al4V alloy by LMD for use in biomedical applications, such as hip replacements. In order to determine how well-suited each alloy was, each sample was put through multiple tests in order to determine its mechanical characteristics. The tests that were conducted were: microstructure analysis, micro hardness testing, and biocompatibility and corrosion resistance. By using these selected tests, it should become clear, based on the results acquired, which set of parameters is ideal for the intended use.

2. Background

2.1 Laser Metal Deposition

The process by which the two metal powders, Ti6Al4V and Mo, were incorporated is by the method of LMD. Figure 1 below depicts the process of LMD. It is here that the two metal powder streams can be seen coming down from the top and entering the field of the laser beam. The powders are then melted by the power of the laser and deposited onto the substrate, which is the piece of Ti6Al4V metal below. This process continues in a linear fashion along the substrate, by work of a robotic arm in order to get the correct shape and dimensions of the printed part.

![Figure 1: LMD Diagram](image)

The actual LMD setup used in this research can be seen below in Figure 2. The head of the machine, which is attached to the end effector of the robot, is the part that was depicted in Figure 1.
2.2 Ti6Al4V and Mo Properties

The materials used in this research included the titanium alloy, Ti6Al4V, and molybdenum. Titanium has a melting range from 1600-1660 degrees Celsius, compared to molybdenum which has a much higher melting temperature of 2623 degrees Celsius. The modulus of elasticity, or the tendency of the material to deform when forces are applied along an axis, of titanium is also significantly lower than that of molybdenum. Titanium is also less dense than molybdenum. Titanium, though, is a much harder material than molybdenum. It is hypothesized that, with these varying properties of the two different metals, that an alloy can be made that would have the optimum properties for use in the biomedical industry.

3. Methodology

3.1 The Laser

The laser used for this research was at the CSIR-NLC in Pretoria, South Africa. It was a 4.4kW Nd; YAG laser system. It is focused using a series of mirrors that reflect the laser beam into the precise location that it is wanted. The laser head is then positioned to a height that gives the laser beam a desired diameter for the particular sample. The laser was manipulated using an 8-axis Kuka robot arm that can be programmed to produce the desired part.

3.2 Research Parameters

The parameters that define this research can be seen in the tables below. The controlled parameters are the laser power, scanning speed and gas flow rate, while the variable is the percentage of molybdenum used. This is true for both the first and second sets of experiments that were completed during the course of this research.
3.2.1 First Set

The first set of samples was produced using the parameters laid out in Table 1. One cladding, containing 6 tracks with 50% overlap, was produced for each percentage of molybdenum: 5, 10, and 15%, respectively.

Table 1: First Set Parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser power (W)</th>
<th>Scanning speed (m/min)</th>
<th>Powder flow rate (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V + 5% Mo</td>
<td>1700</td>
<td>0.5</td>
<td>Ti6Al4V 3.8, Mo 0.2</td>
</tr>
<tr>
<td>Ti6Al4V + 10% Mo</td>
<td></td>
<td></td>
<td>Ti6Al4V 3.6, Mo 0.4</td>
</tr>
<tr>
<td>Ti6Al4V + 15% Mo</td>
<td></td>
<td></td>
<td>Ti6Al4V 3.4, Mo 0.6</td>
</tr>
</tbody>
</table>

3.2.1 Second Set

The second sample was produced using the parameters depicted in Table 2. One sample was produced which was functionally graded with layers of 10 tracks and 50% overlap. The layers, going up from the substrate, were as follows: Ti6Al4V, 5% Mo, 10% Mo, 15% Mo.

Table 2: Second Set Parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser power (W)</th>
<th>Scanning speed (m/min)</th>
<th>Powder flow rate (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V</td>
<td>1700</td>
<td>0.5</td>
<td>Ti6Al4V 4, Mo 0</td>
</tr>
<tr>
<td>Ti6Al4V + 5% Mo</td>
<td></td>
<td></td>
<td>Ti6Al4V 3.8, Mo 0.2</td>
</tr>
<tr>
<td>Ti6Al4V + 10% Mo</td>
<td></td>
<td></td>
<td>Ti6Al4V 3.6, Mo 0.4</td>
</tr>
<tr>
<td>Ti6Al4V + 15% Mo</td>
<td></td>
<td></td>
<td>Ti6Al4V 3.4, Mo 0.6</td>
</tr>
</tbody>
</table>

Once the samples were produced via LMD, they were then photographed in order to document their original characteristics. This can be seen in Figures 4 and 5 below.

Figure 4: First Set (5%, 10%, 15% Mo)  
Figure 5: Second Set – Functionally Graded
3.3 Preparation of the Samples

In order to be able to analyze the samples, they first need to be prepared using the following process that involves cutting, mounting, grinding and polishing, and etching of the sample. Each of these steps is described in detail in sections 3.3.1-3.3.4.

3.3.1 Cutting

Before cutting, each sample was measured to have approximately 10 mm long sections. These cut samples were used for microstructure and hardness testing. Then, a second, slightly smaller rectangular piece was cut from each sample, with the exception of the functionally graded sample. These second samples were used for the corrosion resistance and biocompatibility tests. These sections were cut using a Mecatome T300 cutting machine with a 20S25 Silicon Carbide wet abrasion cutting blade.

3.3.2 Mounting

Once the sections of the samples were cut, one of each sample (the ones to be used for microstructure and hardness testing) were mounted. This is for ease in handling the samples and also for use in the grinding and polishing phase to hold the samples in place. The samples were mounted using a Struers CitoPress-1 Pneumatic Hot Mounting Press. First, the sample was placed cross-section down, as this is the area to be analyzed, and one scoop of PolyFast polymer mounting powder was added to the loading cylinder. Then, the ram was put in place and tightened in order to secure the sample. The machine was then turned on, mounting each sample using the process of heating the loading cylinder to 180°C with increased pressure for 3½ minutes. After this, the samples were cooled using water flowing through the machine for 1½ minutes.

3.3.3 Grinding and Polishing

After mounting, the samples had an almost dirty look, due to the PolyFast powder and the process of hot mounting itself. In order to get rid of the excess powder and any scratches that may have occurred during the cutting phase or through handling, each sample must be grinded and polished. This consists of a rough grinding, fine grinding, and polishing stages. The rough grinding stage used Silicon Carbide paper and water as a lubricant. The SiC paper had large, rough grits that removed the excess PolyFast along with major scratches on the surface of the sample. The next stage, fine grinding, used a pad that distributed the DiaPro liquid, which is a water based diamond suspension containing 9µm diamond particles. These fine particles made the DiaPro work as both a lubricant and as the grits that grinded away finer scratches on the sample surface. The final stage, polishing, was done using a pad that felt almost like velvet. It was very soft and would not harm the surface. The lubricant used here was an OP-S Suspension that worked very well to remove even the tiniest of scratches on the sample. After rinsing in water, the samples appeared mirror-like. This means that the samples were done with the polishing stage.

3.3.4 Etching

In order to be able to see the microstructures and determine the grain boundaries of the samples, they needed to be etched. Although several chemical etchants exist that work well for titanium alloys, for this research Kroll’s Reagent was used. It was made by mixing 100 ml of water, 2 ml of hydrofluoric acid, and 3 ml of nitric acid. Each sample was submerged for 5-15 seconds, until the microstructure could be seen. This required quite a bit of trial and error so that each sample would be etched enough in order to see its microstructure, but not to over etch the sample so that it burns. This was extremely difficult for the functionally graded sample, due to the fact that the varying alloys became fully etched at different amounts of time in the etchant. The result was the top layer, 15% Mo, not being etched and the 5% Mo layer burning due to over etching in a matter of seconds. Because of this, this sample in particular was re-polished and etched over and over again.

3.4 Microstructure Testing

The microstructures of the samples were examined in two ways: with the light optic microscope and the scanning electron microscope (SEM). It is essential to use both of these techniques to be able to obtain varying views of each sample. Each of these methods are described in farther detail in sections 3.4.1 and 3.4.2.
3.4.1 Light Optic Microscope

The Light Optic Microscope was used in examination of the microstructure of the samples. This microscope is relatively simple and can produce magnifications of 50x, 100x, 200x, 500x, and even 1000x. Although these magnifications are relatively low and the microscope is fairly simple, very detailed and precise images can be obtained from it.

3.4.2 Scanning Electron Microscope

The Scanning Electron Microscope, or SEM, was used in addition to the Light Optic Microscope. The SEM works by scanning a highly focused electron beam over the surface of the sample to create the image. The electrons in the beam interact with the surface of the sample, which produces various signals that are used to gather information about the samples topography. SEM can produce up to 3000x magnification of the samples. [6]

3.5 Hardness Testing

In order to test the hardness of each sample, the Vickers Hardness testing method was used. The Vickers method, also known as the microhardness method, is based on an optical measurement system. It uses a light load, 4.9 Newtons or 500 grams force, with a diamond indenter to make a very small indentation. This indentation is measured both horizontally and vertically and these values are used in order to compute a Vickers Hardness number using the Vickers Hardness equation. [7] In order to not affect the hardness of the sample, each sample was re-polished in order to remove the etchant that was used to examine the microstructures.

3.6 Corrosion Testing

The corrosion resistance of the samples was necessary for this research. This is because the main application of these alloys would ultimately be for biomedical devices that would be placed inside the human body. It could be detrimental if the implant easily corroded and released harmful chemicals into the body. In order to try to mimic the conditions of being inside the human body, the unmounted samples were placed into the Hank’s Solution – a chemical solution made in order to simulate bodily fluids. This container of the Hank’s Solution and the samples were placed in a water bath that was set at body temperature, 37°C. The samples remained like this for one week and were then removed and examined under SEM in order to determine if any corrosion had occurred.

4. Results and Discussion

4.1 Microstructure

The main point of interest when using the light optical microscope was looking at the deposit and also the interface between the deposit and the substrate. The grains in this section are elongated, while they are fairly small and circular at the very top of the deposit. This can be attributed to the rate of cooling during the LMD process. The next layer, the Heat Affected Zone (HAZ), is just as its name suggests: this is the area of the substrate that was affected by the heat and power of the laser during the LMD process. The final layer is the unaffected substrate, where the deposit was printed. These different areas can be seen below in Figure 6.

![Figure 6: 10% Mo Sample at 50x Magnification](image)
The elongated grains in the deposit were measured for each sample (5%, 10% and 15% Mo) and compared. The average grain size for each sample was calculated and the results can be seen in Table 3 below.

Table 3: Average Grain Sizes

<table>
<thead>
<tr>
<th>% Mo</th>
<th>Average Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>451.6632</td>
</tr>
<tr>
<td>10</td>
<td>279.7058</td>
</tr>
<tr>
<td>15</td>
<td>139.0304</td>
</tr>
</tbody>
</table>

From these results it can be seen that, as the percentage of molybdenum increases, the average grain size in the sample decreases. This is a very interesting observation and could be taken advantage of for several applications. This can be more easily seen in Figure 7, which is a graph of the percentage of molybdenum versus the average grain size in that sample.

![Figure 7: Percentage of Molybdenum versus Grain Size Graph](image)

Similar results were found in the functionally graded sample. Figure 8 shows the entire functionally graded sample under SEM at 30x magnification and each of the sub-pictures came from the Light Optic Microscope at 500x magnification. The differences in the grains of the layers can easily be seen in this Figure 8.

![Figure 8: Functionally Graded Sample](image)

From this figure, it can be seen that there is good interfacial bonding between the layers. The majority of the layers are characterized by columnar grains, which can be seen in the individual pictures of each layer. These columnar bonds are strong and, the longer they are, the stronger they are. This becomes important when deciding which alloy
to use for a particular purpose. In some applications, stronger grain bonds may be needed, while in others they may not be necessary.

4.2 Hardness

The Vickers Hardness Machine was used in order to test 8-12 different points in the deposition layer(s) of each sample. These hardness values were then averaged in order to try to see a trend in the obtained values. The average Vickers Hardness values for the single layer deposition samples can be seen in Figure 9 below.

![Figure 9: Single Layer Deposition Vickers Hardness Profile](image)

This microhardness profile shows an inconsistent trend in its results. This was not expected, but could be a result of the complex laser-material interaction, along with a variance in the thermal profile during the deposition itself. It could also be attributed to humidity or temperature in the room, uneven cooling rates, early oxidation, etc.

For the functionally graded sample, the same procedure took place and the microhardness profile can be seen in Figure 10 below.

![Figure 10: Functionally Graded Sample Vickers Hardness Profile](image)

The microhardness profile of the functionally graded sample shows that the 5%, 10%, and 15% Mo layers are significantly less hard than the printed Ti6Al4V and substrate layers. This is probably due to the laser-material interaction resulting in a softening of the deposit formed. This lower hardness in the sample is a good characteristic, as it increases biocompatibility because it is softer than the substrate, bringing it closer to the hardness property of bone, allowing greater integration to happen. This lower hardness also increases toughness and ductility [8], which again are desirable properties for use in the biomedical industry.

After the hardness of each sample was examined, the layers with the same percentages of Molybdenum were compared, between the single layer deposition samples and the functionally graded sample. A visual representation of this can be seen in Figure 11 below.
As can be seen in Figure 11, the functionally graded sample has enhanced properties when compared to the single layer deposit because it has a fairly homogeneous hardness that is much lower than the single deposit. Again, this lower hardness increases the biocompatibility of the sample. The functionally graded sample also shows epitaxial growth, with not much difference in the hardness from layer to layer. This is another positive characteristic of the functionally graded material when considered for the biomedical industry.

4.3 Corrosion Resistance and Biocompatibility

After being immersed in the 37°C (body temperature) Hank’s solution for one week, the samples were extracted and evaluated under SEM. Before they were submerged, they were also examined under SEM in order to compare the before and after images to see if any changes occurred. The before and after images can be seen in Figures 12 and 13, respectively, below.

After examining these results, it can be concluded that no significant changes can be seen. This is probably due to the short amount of time that they were inserted for. This does show that the samples were not extremely corrosive, but the samples would need to be inserted in the Hank’s Solution for a longer period of time in order to see any significant changes in the surface morphology.

Although the corrosion resistance test did not produce any significant results, looking at the surfaces of the samples reveals a few things. First, the surface appears spongy and rough. This will actually enhance the integration into the human body, because when it comes into contact with the bodily tissues, the tissues will very easily grow onto and around the material. Therefore, it is revealed that the surface morphology shows that the samples would be biocompatible.
5. Conclusions

Through this research, many aspects of laser metal deposited samples, both single layer and functionally graded, were examined and tested for possible future use in the biomedical industry for applications such as hip and knee replacements. The results obtained in this research can help to find an alloy that has the optimum properties for these uses.

It was found that as the percentage of Molybdenum increases, the grains get significantly smaller through examination of the microstructure of the single layer deposit samples. It was also shown that the Vickers Hardness of the single layer deposit samples shows an inconsistent trend due to the complex laser-material interaction and could also be due to a variety of other, uncontrollable factors. In contrast, the Vickers Hardness profile of the functionally graded material shows this sample to have enhanced properties with fairly homogeneous hardness with respect to the layers that incorporated the Molybdenum powder. Finally, the corrosion resistance test has shown that the samples are not extremely corrosive, but further tests would need to be conducted in order to get a more thorough result.

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7. References

