

ELECTROCHEMICAL TESTING OF ADDITIVE MANUFACTURED Ti6Al4V AND NiTi MATERIALS IN A BIOLOGICAL FLUID ENVIRONMENT

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ABSTRACT

The use of additive manufacturing (AM) has seen a marked increase in the biomedical arena for hip and knee replacements, especially for older populations. The AM method is particularly attractive in the biomedical industry as it allows for patient specific designs in the case of unusual anatomy. AM also is well suited to manufacture highly complex parts and has the benefit of rapid prototyping and rapid manufacturing. However, as the increase in fabrication and use of these components have increased, there are still some underlying corrosion issues that have yet to be fully understood. This research looks at the electrochemical polarization behavior of AM fabricated UNS R56401 (Ti6Al4V) and NiTi (Nitinol) in a biological fluid. Different build orientations were evaluated as well as different post processing and different surface roughness. Cyclic polarization testing was performed per ASTM F2129¹ in a Phosphate Buffered Saline solution at 99 F. Surface roughness evaluations were performed prior to testing as well as Scanning Electron Microscopy prior to and after testing.

Key words: Additive Manufacturing, Ti6Al4V, NiTi, Electrochemical Testing, Biomedical.

INTRODUCTION

Additive Manufacturing (AM), also known as 3D printing, is a process by which a component is fabricated layer by layer.^{2,3} It boasts many benefits over conventional processing (casting) methods such as being able to fabricate complex components, flexibility to create drastically different components in the same build space, rapid prototyping, rapid manufacturing and ability to change the design without costly changes to the processing chain. The lure of these benefits has affected major industries such as aerospace, automotive, biomedical and to an increasing extent oil and gas industry, with the goal of producing final products from the AM machine in each of these sectors.

UNS R56401 (Ti6Al4V) is often used as an orthopedic material for hip replacements, femoral, knee joint constructions as well as for dental and mandible implants.⁴⁻¹⁰ It is suitable as a biomaterial due to

its high strength-to-weight ratio, high corrosion resistance, and biocompatibility.¹¹ Conventional manufacturing of these products are in standard sizes, which may not be optimally suited for each individual body. Improper sizing can lead to uneven stress distribution of the implant to the load bearing bone as well as contributing to micro-motion of the implant that would lead to lack of biocompatibility (cell adhesion and proliferation). At the same time, the goal of the final implantation is to maximize contact between bone and implant to ensure multiple points for cell adhesion. Thus, additive manufacturing of Ti6Al4V implants seem like an attractive processing step for successful implantation as it would allow to design and build for a specific patient anatomy.

Corrosion studies of AM fabricated Ti6Al4V have centered around differences in selective laser melting (SLM) and electron beam melting (EBM) methods^{12,13}, or looked at fine polishing only¹⁴, whereas others have looked at Ti6Al4V but in different types of environments.¹⁵ For Nitinol, limited research has been performed, and has focused on the effects of a polished (not as-fabricated) surface.¹⁶ But these efforts have not considered other factors that can affect the corrosion behavior of an AM build. One such factor is the orientation of an AM build. Although work is emerging on the impacts of sample orientation and location of the part on the build plate, a consideration must be given to the resulting surface structure and how it impacts the corrosion capabilities. Other factors such as powder size, AM build process parameters (laser power, and scan velocity), along with post processing steps of the AM products (such as stress relieving, HIP and surface finish) can lead to differences in material microstructure and surface characteristics.

This research will compare the corrosion behaviour of Ti6Al4V AM samples oriented at different angles on the build plate. Comparisons were made between the as-fabricated samples to polished samples and also to wrought Ti6Al4V ELI sample as a baseline. The corrosion behaviour of NiTi (Nitinol) samples in the three different orientations were also evaluated. Cyclic polarization testing was performed with optical and scanning electron microscopy (SEM) on the sample surfaces after exposure to identify surface corrosion characteristics.

EXPERIMENTAL PROCEDURE

A hollow hexagon shaped sample made of Ti6Al4V ELI (UNS R56401) powder was fabricated using a Renishaw[†] AM250 Selective Laser Melting (SLM) Powder Bed Fusion machine. The Ti6Al4V powder size was $-16/+45\mu\text{m}$. The sides of the hexagon represented different orientations on the build plate, with 1C orientation being perpendicular to the coater, 2C 30° from the coater and 3C a -30° from the coater (Figure 1).

The Nitinol AM sample was fabricated from $-20/+60\mu\text{m}$ powder. A cube sample was fabricated such that the different build surface faces could be tested. The X, Y, and Z surfaces were tested, with the Z axis representing the build direction as seen in Figure 2.

The surface roughness was performed both on the as-fabricated and polished sides using a Keyence[†] VR 3000 G2 machine. In addition, the surface structure of the samples was observed via SEM after cyclic polarization (CP) testing.

[†]Trade Name

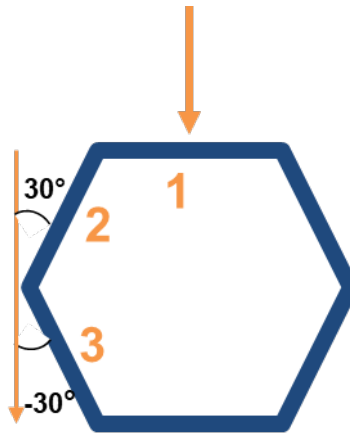


Figure 1: Diagram showing the Ti6Al4V AM coupon build. Arrow represents the direction of the coater.

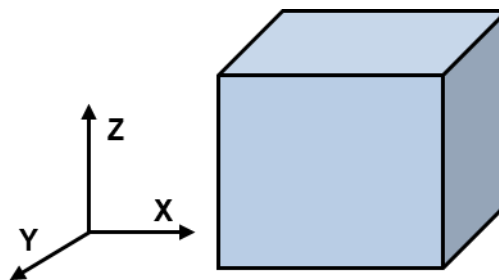


Figure 2: Diagram showing the Nitinol AM coupon build. Samples tested in the three different orientations.

Cyclic Potentiodynamic Polarization Testing was performed per ASTM F2129¹. The test solution was phosphate buffered saline (pH 7.4) previously deaerated overnight with Nitrogen. Testing was conducted at 37°C (99 F) under a flow of Nitrogen gas. An Ag/AgCl electrode was used as the reference electrode while a Pt mesh acted as the counter electrode. The scan rate was 0.167 mV/sec. Since this was preliminary testing, only one scan rate was selected. After a minimum of one hour at the open circuit potential (E_{oc}), the sample went through a forward scan and reversed at 2.5V until the E_{oc} was reached. For the Ti6Al4V samples, duplicate measurements were performed on the as-fabricated outer diameter (Outside or OD) side while a single scan was performed on the inner diameter (ID) side of the sample that was polished to a 1200 grit finish. A wrought Ti6Al4V sample that was also polished to 1200 grit was utilized for comparison. Polarization scans were also performed on all three NiTi directions (X, Y, and Z) in the as-fabricated and polished conditions.

RESULTS

Ti6Al4V

The results of the surface roughness (Ra) measurements are presented in Table 1 for the Ti6Al4V samples. The Ra values were very similar for the as-fabricated samples oriented differently to the coater (90°, 30°, and -30°) with values ranging from 7 to 14 μm . It should also be noted that the as-fabricated OD and ID sides also had very similar surface roughness values. The polished samples, on the other hand, all had Ra values less than 1 μm , which in most cases was more than an order of magnitude lower than the as-fabricated samples.

Figure 3 shows the SEM micrographs of the surface morphology of the three different Ti6Al4V orientations in the as-fabricated state. The samples displayed typical surface condition of an AM sample prepared by powder bed fusion in that powders are partially melted on to the sample surface, along with river patterns indicative of the melt by SLM.

Table 1
Surface Roughness Measurements for Ti6Al4V Samples

Material / Orientation	Surface Condition	Avg Ra, μm	Avg Rp, μm	Avg Rv, μm
Ti6Al4V – 1C (90°)	As Fabricated – OD	10	57	27
	As Fabricated – ID	13	71	39
	Polished – ID	0.90		
Ti6Al4V – 2C (30°)	As Fabricated – OD	7	47	22
	As Fabricated – ID	7	39	24
	Polished – ID	0.97		
Ti6Al4V – 3C (-30°)	As Fabricated – OD	9	44	35
	As Fabricated – ID	14	79	28
	Polished – ID	0.79		
Ti6Al4V – Wrought	Polished	0.68		

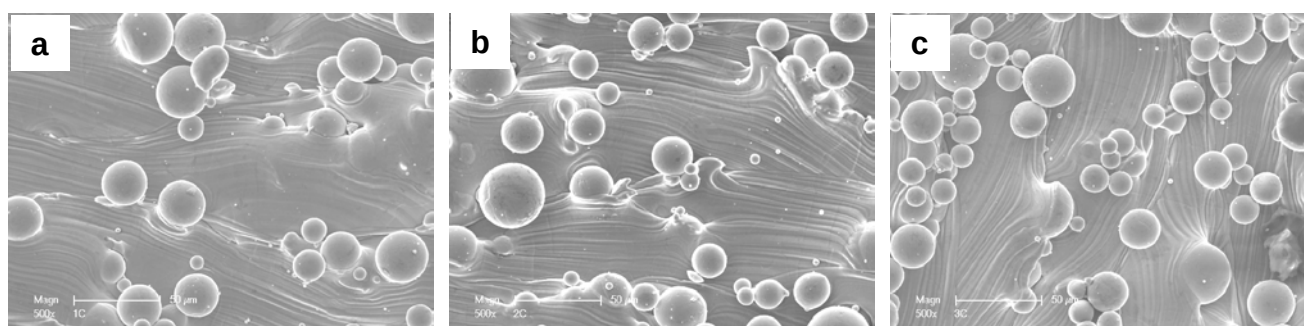


Figure 3: SEM photographs showing surface structure of as-fabricated Ti6Al4V samples prior to testing in the a) 1C (90°), b) 2C (30°) and c) 3C (-30°) directions at 500x.

Cyclic polarization testing on the Ti6Al4V AM samples in the as-fabricated state showed open circuit potentials (E_{oc}) in the range of -0.178 V to 0.144 V (as seen in Table 2 and Figure 4). The pitting potential (E_{pit}) was very similar for all as-fabricated samples with potentials between 2.09 V to 2.31 V. Pitting was verified visually after exposure (Figure 4b). The repassivation potential (E_{rp}) was approximately 1.5 V for all sample orientations. There was some variation in the passive currents of the samples. In addition, most samples also displayed a disruption in the passive region in the curve, indicating only pseudo-passive behavior (Figure 4a). The polished AM samples seen in Figure 5a, had much lower passive currents and were much more stable (ie. no passive disruption) than the as-fabricated state. The pitting potential was only reached by one of the samples prior to the reverse scan indicating that the polished samples would have a higher pitting potential. Similarly, the wrought Ti6Al4V sample had the same low passive currents as the polished AM samples. The pitting potential was not reached on these samples as well before the reverse scan, also indicating higher pitting potentials than the as-fabricated Ti6Al4V (Figure 5).