

Corrosion Behavior of Additively Manufactured and Wrought Ti-6Al-4V Alloys in Phosphate Buffered Saline Solutions

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ABSTRACT

Additive manufacturing (AM) offers flexibility and customization along with economic advantages. In this study, additively manufactured and wrought UNS R56400 (Ti-6Al-4V) were exposed to phosphate-buffered saline (PBS) at various pH values, simulating a range of post-operative conditions. The corrosion behavior of these alloys was investigated per ASTM F2129-19a and ASTM G59-97, followed by potentiodynamic polarization scans. Microstructural characterization was conducted using scanning electron microscopy coupled with energy dispersive X-ray spectrometry.

Key words: Additive manufacturing, post-surgical conditions, pH, biomedical implant, Ti-64

INTRODUCTION

Titanium and its alloys have been a primary choice of material for metal implant fabrication due to their superior biocompatibility, strength, low density and corrosion resistance.¹⁻³ As a joint replacement material, these alloys experience varying modes of failure from mechanical loosening to inflammatory reactions.⁴ In particular, post-surgical conditions of the human body can provide an aggressive physiological environment for the implant alloy. For the first 10 to 15 days following surgery, the human body's inflammatory response results in a local in-vivo pH fluctuations in the tissue surrounding the implant.⁵ Hematomas and bacterial infections in the tissues surrounding the implant can lead to pH

fluctuations from as low as 3 and up to 9.^{5,6} Between 2012 and 2018, 8.2% of all knee surgeries in the United States needed revisions because of infection and inflammation.⁷

Additive manufacturing (AM) methods for metals open the possibility for rapid fabrication of implants with increased geometric design freedom (e.g. incorporating tailored porosity for bone growth, internal lattice features for mechanical optimization, etc.) which may be custom tailored to an individual's anatomical features.⁸ The AM process of interest in this paper, i.e., blown powder directed energy deposition (DED) involves the deposition of a metal powder into a melt pool on the substrate which is formed with a laser. The DED process is repeated layer-by-layer to form a 3D geometry, which inherently, possesses rapid cooling rates. This gives rise to the potential for increased porosity and surface roughness - factors that profoundly affect the resultant microstructure, residual stress state and corrosion behavior. To date, the bulk of materials research on AM alloys has focused primarily on microstructure and mechanical properties with only limited evaluation of corrosion behavior.⁹

The corrosion behavior of traditionally manufactured Ti-64 and related alloys in physiological solutions, e.g., PBS, Hank's and Ringer's solutions has been extensively studied.¹⁰⁻¹⁶ Corrosion studies of AM alloys are very limited. In one study, the corrosion resistance of selective laser melted (SLM) Ti-64 in Hank's solution was higher than wrought Ti-64.¹⁷ In a different study, SLM Ti-64 in PBS solution was more susceptible to formation of hydrated titanium oxide compared to the wrought alloy.¹⁸ However, given the range of AM processes, e.g., DED, SLM, etc., it is important to investigate the behavior of materials processed in specific ways. Additionally, there is very little work on the effect of pH on the corrosion behavior of metallic alloys. The study of DED Ti-64 in simulated physiological conditions would be a new contribution to the field. Therefore, the objective of this paper is to investigate the corrosion behavior of DED Ti-64 in PBS solution maintained at various pH values to simulate post-surgical conditions.

EXPERIMENTAL PROCEDURE

The alloys used in this study were (a) as-printed DED Ti-64, and (b) wrought Ti-64. Commercially available Ti-64 powder (nominally 45 - 106 μm) was utilized for the DED process. The as-printed Ti-64 alloy rods (nominally 5.08 cm long and 1.27 cm in diameter) were tested in the as-built condition, i.e., no post-print heat treatment was performed. The composition of the powder used for the DED Ti-64 is indicated in Table 1. The wrought alloy was supplied as round bar stock (nominally 1.27 cm in diameter) in the mill-annealed condition. The history of the wrought alloy was as follows: vacuum arc melted and re-melted, hot rolled, heated to 704°C (1300°F), held for 2 h, and air cooled. The composition of the wrought alloy was provided by the manufacturer (Table 2). To obtain test coupons, the as-printed DED Ti-64 cylinders were vertically sectioned, and then cut into smaller pieces, while the wrought Ti-64 coupons were cross-sectioned from the round bar stock. The coupons were metallographically prepared to a final polish of 0.05 μm , followed by successive ultrasonic cleaning of each coupon in deionized water, iso-propanol, and deionized water, and quick loading (within 3 minutes) into the corrosion test cell.

Table 1: Composition of DED Ti-64 feedstock powder

Alloy Powder	Weight Percent (wt%)							
	Ti	Al	V	Fe	O	C	N	H
Powder Ti-64	Bal.	5.5-6.5	3.5-4.5	max 0.40	max 0.20	max 0.01	max 0.05	<0.015

Table 2: Wrought Ti-64 alloy elemental composition

Alloy	Weight Percent (wt%)							
	Ti	Al	V	Fe	O	C	N	Y
Wrought Ti-64	Bal.	6.34-6.40	3.96-4.06	0.18-0.22	0.16-0.19	0.03	0.03	<0.001

Electrochemical tests were conducted following ASTM F2129-19a and ASTM G59-97 standards as a guide.^{19, 20} Phosphate-buffered saline (PBS) solution [nominally: 0.800 g/L NaCl, 0.020 g/L KCl, 0.115 g/L Na₂HPO₄ and 0.020 g/L KH₂PO₄] was prepared with 18.2 MΩ·cm ultrapure (Type I) water. The original pH of the as-prepared solution was 7.4 and was adjusted as needed with the addition of HCl to achieve lower pH values and NaOH to achieve a higher pH. The solution was deaerated using a nitrogen purge for 30 minutes prior and throughout the test. The PBS solution was also preheated to 37±1°C prior to exposure with the alloy's surface and the temperature was maintained constant throughout the test using a water jacket. A 250 mL three-electrode cell, in which the exposed working electrode with an area of 0.785 cm², was utilized to carry the electrolytic solution. The testing cell also contained a counter electrode, composed of platinum mesh, and a Saturated Calomel Electrode (SCE) [+241 mV vs. SHE] reference electrode. A schematic representation of the electrochemical cell set-up is demonstrated in Figure 1.

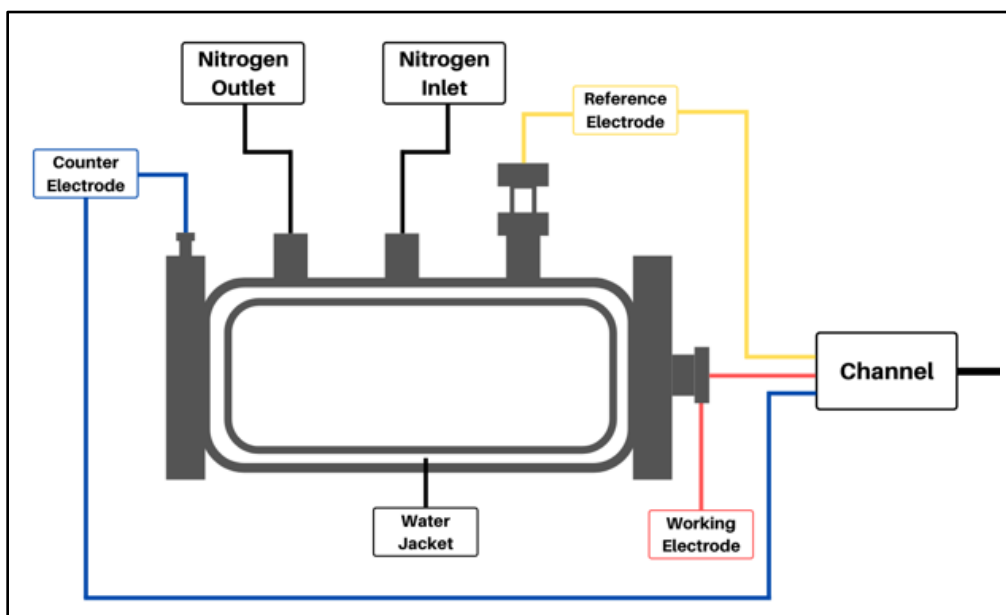


Figure 1: Schematic representation of the electrochemical cell set-up

The ASTM F2129-19a test started with a 1 h open circuit potential (OCP) measurement, followed by a cyclic potentiodynamic scan (CPP) in which the applied voltage swept from 0 mV vs. OCP to 800 mV vs. SCE then reversed back to 600 mV vs. SCE with a sweeping rate of 0.167 mV/s throughout the full scan. The modified ASTM G59-97 test also started with a 1 h OCP measurement, followed by a linear polarization resistance test (LPR) with a voltage range of ±30 mV vs. OCP with a constant scan rate of 0.167 mV/s. The LPR test was followed by a Tafel test in which the voltage applied ranged from -400 to +400 mV vs OCP at a scan rate of 0.167 mV/s. Multiple electrochemical test replicates were conducted to verify the findings.

RESULTS

Figures 2a and 2b demonstrate the microstructures of the wrought and DED Ti-64 alloys. The backscattered electron image of the wrought Ti-64 alloy reveals the alpha (α) + beta (β) microstructure while the DED Ti-64 in Figure 2b reveals a very fine microstructure. The rates of solidification associated with the DED processes can affect the alloy microstructure and in particular, the size of the alpha colonies in the Ti-64 alloys.⁸ The alpha phase thickness is inversely proportional to the cooling rate, i.e., faster cooling rates decrease the size and thickness of alpha phase.²¹ This is consistent with the fine scale of the microstructure for the DED Ti-64 seen in Figure 2b. The as-printed DED microstructure

shows different microstructures as seen in Figure 3. The non-uniformity in the microstructure of as-printed Ti-64 has been reported by others.^{22, 23} These differences in microstructure are likely to have an effect on the properties of the materials, e.g., mechanical properties, corrosion behavior, etc.

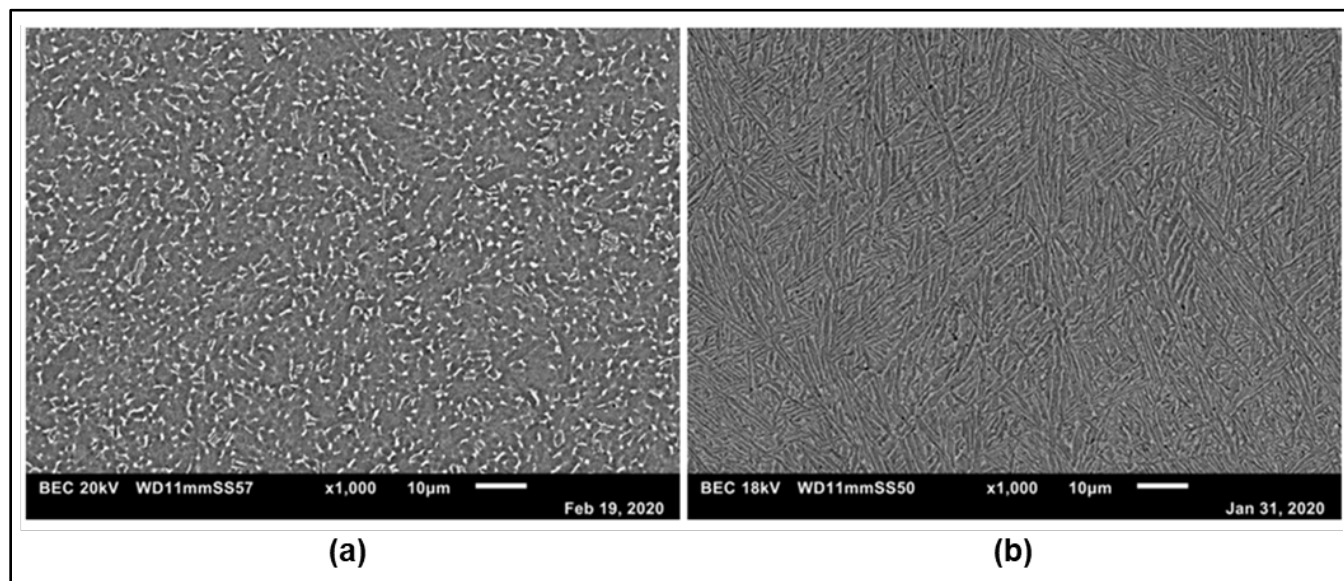


Figure 2: Backscattered electron images of a) wrought Ti-64 and b) DED Ti-64

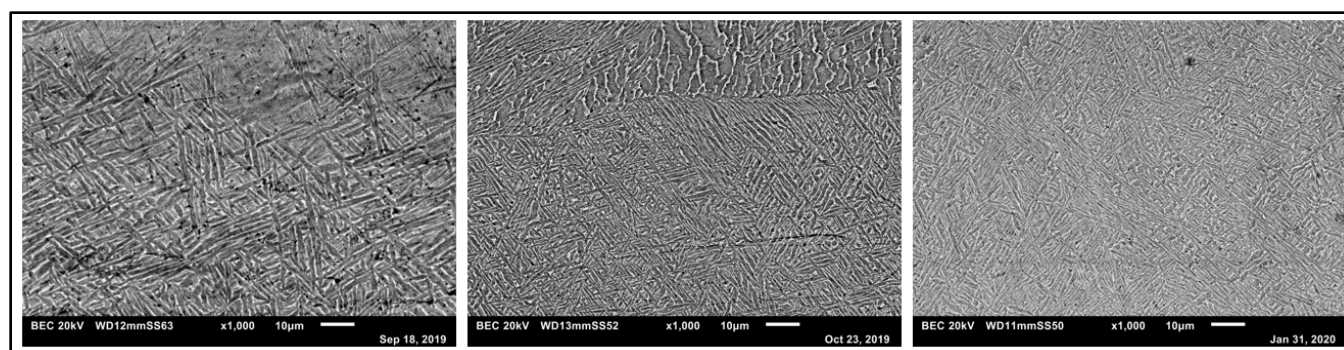


Figure 3: Backscattered electron images of DED Ti-64 showing the variation in microstructure

Backscattered electron images (BEI) of DED Ti-64 and the corresponding elemental maps obtained by energy dispersive X-ray spectrometry (EDS) are presented below in Figure 4. The image reveals the microstructure of the as-printed DED Ti-64 with uniform distribution of Al and V in the titanium matrix. The observed microstructure is similar to that of a Ti-64 alloy printed by directed energy deposition.²⁴ In Ti-64 alloys, the Al, an alpha stabilizer tends to segregate in the alpha phase.²¹ On the other hand, the V element, being a beta stabilizer, tends to partition to the beta phase.²¹ In particular, studies indicate that an extended enrichment of alpha phase with Al and beta phase with V can result in preferential localized corrosion attack on the beta phase.²¹

Figure 5 shows the cyclic potentiodynamic polarization curves guided by the ASTM F2129-19a standard. These plots indicate that both DED and wrought Ti-64 alloys form passive films as demonstrated by the small increase in current density for a large change in applied potential during the forward scan. The applied potential which marks the onset of this behavior - attributed to the formation of a protective oxide film - is termed the passivation potential. In the case of titanium alloys, this protective oxide film is titanium dioxide (TiO_2). The latter is the thermodynamically stable phase for the relevant pH range and passivation