Zirconia-Toughened Alumina Coated Ti6Al4V for Load-bearing Implants

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Abstract

Processing and characterization for zirconia toughened alumina (ZTA) coatings on Ti6Al4V (Ti64) alloy by directed energy deposition (DED)-based additive manufacturing (AM) is presented here. The objective of the study was to achieve a dense ZTA coating with the intent of providing an alternative to fully ceramic implants for articulating surfaces of total hip arthroplasty (THA). Preliminary work resulted in failed samples due to cracking, porosity, and delamination. After careful parameter optimization, a Ti64+5wt.%ZTA (5ZTA) composition produced a metallurgically sound and coherent coating with minimal porosity. Additionally, bulk structures were also feasible with the optimized coating parameters. Characterization of the 5ZTA composition displayed a 27.0% increase in hardness, 25% reduction in normalized wear rate, an increase in contact resistance during *in vitro* tribological testing along with a faster surface re-passivation post-tribological testing.

Keywords: Ti6Al4V; zirconia toughened alumina; load-bearing implants; surface modification; directed energy deposition.

1. Introduction

Studies have shown that current load-bearing implants for articulating surfaces fail prematurely due to several factors such as taper corrosion, dislocation, and/or fall events, or due to wear debris and poor biocompatibility [1–3]; one such failure mode is displayed in **Fig.1a**. Although CoCr alloys exhibit exceptional wear resistance and are used in articulating surfaces of load-bearing implants, Co and Cr ion release still occurs due to wear and galvanic corrosion from a mismatch in electrochemical potential between the CoCr femoral head and titanium hip stem. Additionally, wear induced degradation has shown negative physiological effects as a result of metal ion sensitivity [4]. Some manufacturers have addressed this mismatch issue with the use of all-ceramic femoral head and titanium neck sleeve – as is the case with the zirconia toughened alumina (ZTA) BIOLOX® delta and the BIOLOX® OPTION (CeramTec GmbH, Germany) femoral heads, respectively [5]. However, some catastrophic failure of these brittle implants has been reported even with a polymer liner after a fall event [6]. It is therefore the focus of the current study to move away from CoCr-based or all-ceramic femoral heads by replacement with harder ZTA-based coatings on Ti64 alloy. The concept, displayed in **Fig.1b**, would eliminate the use of CoCr alloy or full ceramic femoral heads, and the differences in electrochemical potential. The issue at hand is to establish a manufacturing process for ZTA-coated Ti64 structures.

2. Materials and Methods

<u>Fabrication of ZTA composite coatings on Ti64</u>: Ti64 and ZTA powders were sieved to a particle size range of 45-150μm. Powders were mixed into two weight percentages (wt.%) – Ti64+5wt.%ZTA (5ZTA) and Ti64+10wt.%ZTA (10ZTA). Samples were fabricated using a FormAlloy 5-axis DED-based AM unit, equipped with a 500W diode-pumped ytterbium 1070nm

wavelength fiber laser. Processing was carried out in an argon environment, with O_2 <30ppm. Initial and final processing parameters are displayed in **Table 1**.

Table 1. Processing parameters leading to the fabrication of a dense 5ZTA coating.

Composition	Slice (mm)	Power (W)		Translation Speed (mm/min)		Gas Flow Rate (L/min)		Powder Feeder Disc Speed (rpm)
		Contour	Infill	Contour	Infill	Shield	Carrier	
Pure ZTA	0.2	200		1200		13	8	0.3
5ZTA	0.3			1400	1200	14	10	0.3
10ZTA								
5ZTA	0.4	200	300	1600	1000	14	11	0.3
						20	14	0.5
	0.4	**200**	**300**	**1600**	**1000**	**20**	**14**	**0.7**

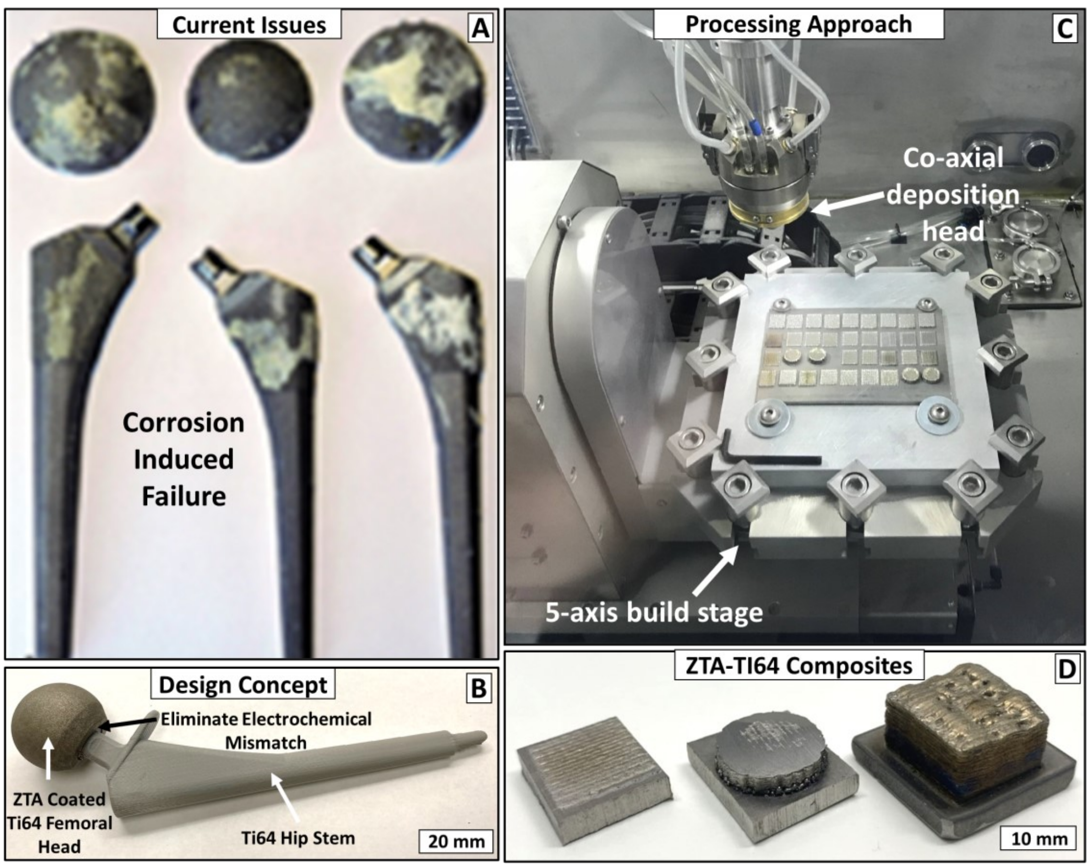

Figure 1. Images displaying: a) case study reporting failed hip implants due to taper corrosion [7], b) design concept for Ti64 femoral head and hip stem, the c) FormAlloy inert build environment and d) DED fabricated ZTA-Ti64 composites.

Microstructural characterization and hardness measurement: Fabricated structures were ground using SiC grinding paper up to 2000 grit, polished with 0.05µm Al_2O_3 suspension media, and then ultrasonically cleaned in ethanol. Microstructural analysis was conducted by sectioning the samples along the z-axis, grinding, polishing, cleaning, and then acid-etching with Krolls Reagent. Electron micrographs were collected using a field emission scanning electron microscope (FESEM, FEI-SIRION, Portland, OR). Vickers microhardness was measured using a Phase II Plus, Micro Vickers hardness tester (Upper Saddle River, NJ, USA). Six indents were done for each sample with a normal load of 200g and dwell time of 15s.

Contact resistance (CR) and open-circuit potential (OCP) characterization: *In vitro* tribological testing was performed using a single station Biotribometer (Ducom, India) following ASTM G133-05 standard [8]. The applied normal load was 5N, translation speed was 1200mm/min and amplitude of 10mm for a total sliding distance of 1000m in Dulbecco's Modified Eagle's Medium (DMEM, Sigma-Aldrich). OCP was recorded with the use of a modular line Metrohm Autolab potentiostat/galvanostat (Riverview, Florida, USA), with a 3-electrode corrosion-cell configuration; the reference electrode was a saturated Ag/AgCl/KCl, while the working electrode was the fabricated samples of varying compositions. CR and OCP were collected using the apparatus described in detail in our previously published reference 9 [9].

3. Results and discussion

Manufacturing and microstructural features of ZTA-coated Ti64: In the first approach, neat ZTA powder deposition was attempted on the Ti64 substrate. However, samples from such depositional passes exhibited delamination and cracking due to excessive residual stresses. In a follow-up approach, the ZTA amount was reduced to minimize thermally induced stresses and subsequent cracking. In this approach, two premixed powder compositions, 5ZTA and 10ZTA, were deposited on the Ti64 substrate. Their respective build parameters are shown in **Table 1**. The 10ZTA composition continued to be susceptible to thermally induced stresses resulting in observable cracks. However, the 5ZTA only displayed some residual porosity but no cracking which can be addressed by further process optimization; optimized samples are displayed in **Fig. 1c**. Therefore, the 5ZTA process build parameters were further optimized and the resultant samples were dense, crack-free, and exhibited coherent metallurgical bonding with the substrate. Additionally, bulk structures were also feasible with the same build parameters, both are displayed in **Fig. 1d**. The bulk structure provided proof of concept that the optimized parameters allow for a larger build, beyond a coating, without cracking or delamination. To further analyze the metallurgical bond these structures exhibited with the substrate, their microstructural features were characterized and acid-etched SEM micrographs are shown in **Fig. 2**. Upon close inspection of these etched cross-sections, minimal porosity was observed, microstructure was homogeneous, and no delamination or cracking occurred across the interface. Additionally, full integration of the ZTA particles was achieved in the Ti64 matrix as no particle-matrix separation was observed. Alternatively, a diffusion/reaction zone was observed as dissociation of the ZTA particle took place during fabrication of the coating. Such diffusion-based embedment leads to a stronger metallurgical bond when compared to other mechanically adhered particle-reinforced composites.

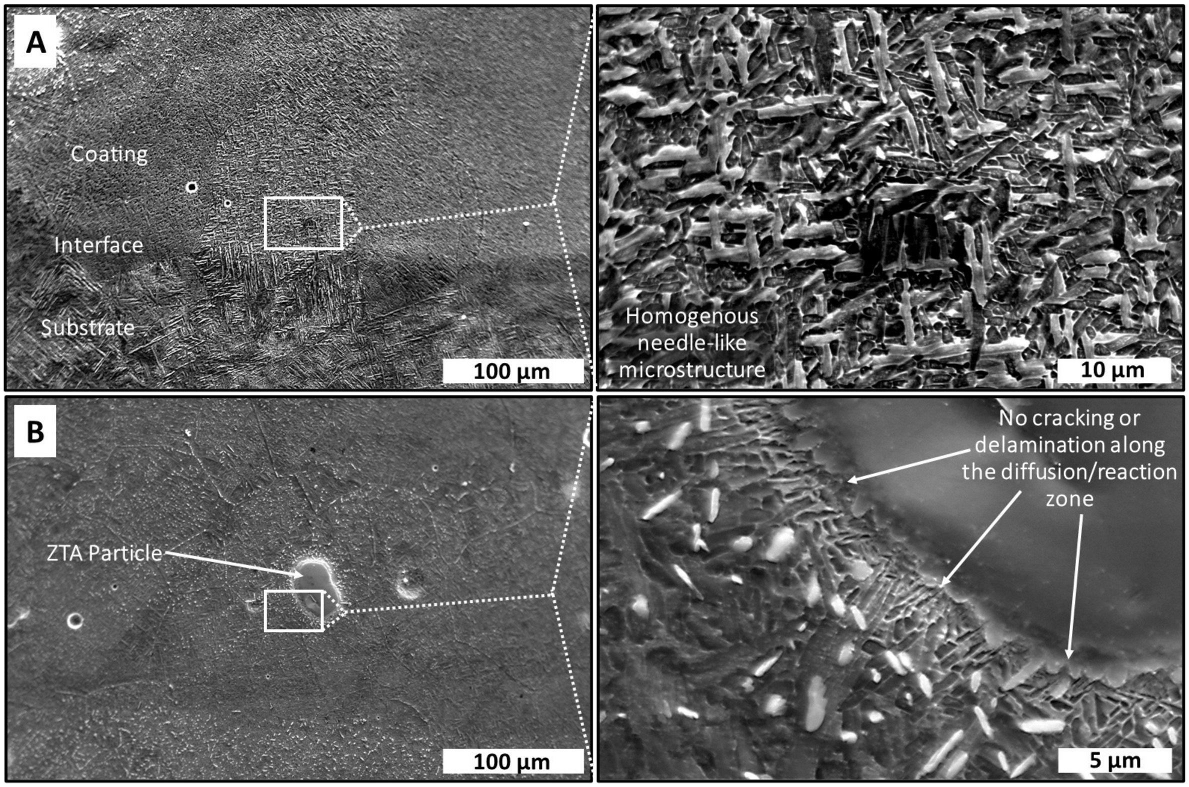

Figure 2. Electron micrographs of acid-etched 5ZTA displaying a) microstructural features and b) diffusion-embedded ZTA particle in the Ti64 matrix.

CR, OCP, normalized wear rate, and microhardness measurements: Throughout *in vitro* tribological testing, CR and OCP were recorded for the two compositions, and the data is displayed in **Fig. 3a** and **3b.** An increase in CR during tribological testing is indicative of surface passivation, which is articulation induced. Throughout testing, 5ZTA displayed higher CR values; initially ~12ohms, then averaging ~13ohms during articulation and finally ~30ohms towards the end of testing. The control Ti64 initially displayed ~4ohms then ~<1ohm during initial articulation, and finally increased to ~5 ohms as testing progressed. The results indicate that both compositions had their naturally formed passivation layer removed due to articulation and both have the tendency of producing mechanically assisted passive constituents on the surface; however, 5ZTA is most prone to exhibit this characteristic, more so, after a period of articulation. Upon interpretation of the collected OCP data, a drop in potential was observed for both compositions during articulation; most commonly due to the removal of the naturally formed passivation layer and exposure of the metal with the DMEM media [10]. Upon articulation, the Ti64 control surface becomes more negative (anodic) initially and then stabilized at ~-750mV. The 5ZTA composition decreased to -500 mV and displayed less fluctuation throughout *in vitro* tribological testing. Once articulation is ceased, both compositions begin to re-passivate, however the 5ZTA composition passivates quicker. The reduced OCP fluctuation and decrease in ΔE for 5ZTA goes hand-in-hand with the increased CR data, i.e., a more chemically stable surface is present. Additionally, the positive shift in OCP after articulation is referred to as a cathodic shift and allows for cathodic protection when in contact with the physiological environment [11]. In this fashion, the material is more chemically stable and less susceptible to react with the surrounding host tissue. Considering the implementation of the current study for load-bearing implants, characteristics during and after articulation are of most importance. Mechanical properties were also observed to improve for 5ZTA; hardness increased from 393.3±6.5 to 499.4±10.8$HV_{0.2}$, while the wear rate dropped from 3.03±0.13 to 2.28±0.8 mm^3/Nm. When compared to Ti64 that is an increase of 27.0% in hardness and a 25% reduction in wear rate.

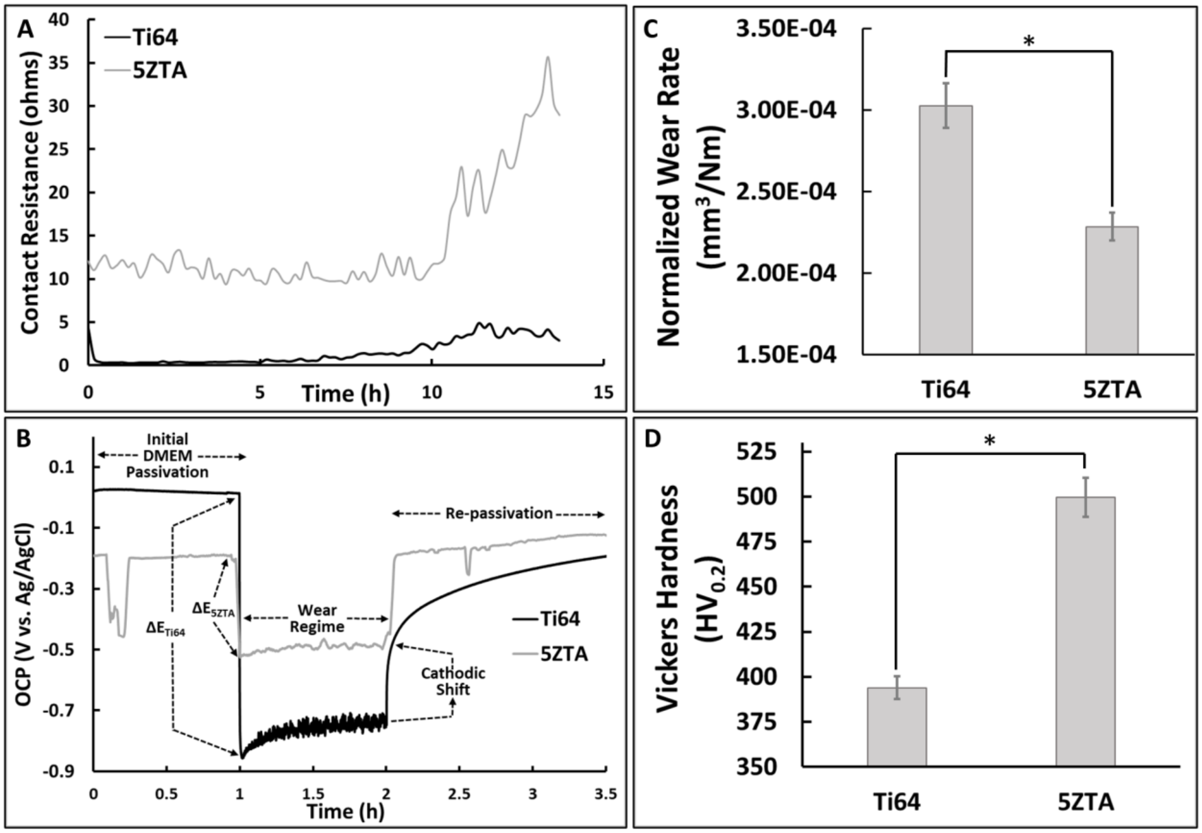

Figure 3. *In vitro* tribological data for Ti64 and 5ZTA, where a) displays the instantaneous contact resistance, b) displays the open-circuit potential, c) normalized wear rate, and d) displays Vickers surface hardness. (*) Displayed statistical significance was at $\alpha=0.05$ and p-value < 0.0005.

4. Conclusions

Processing and characterization for zirconia toughened alumina (ZTA) coatings on Ti64 alloy by DED-based AM is presented here. Microstructural characterization revealed dense and metallurgically sound ZTA coatings on Ti64. *In vitro* tribological testing resulted in an observed increase in CR and a 25% reduction in wear rate. Hardness was increased by 27.0% and OCP analysis resulted in observable cathodic shift and faster repassivation after articulation. It is hypothesized that this work will influence the bio-manufacturing industry by laying the groundwork for an alternative to CoCr or all ceramic-based femoral head.

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6. Declaration of Interest

None

7. References

[1] V.E. Ozden, N. Saglam, G. Dikmen, I.R. Tozun, Oxidized zirconium on ceramic; Catastrophic coupling, Orthop. Traumatol. Surg. Res. 103 (2017) 137–140. https://doi.org/10.1016/j.otsr.2016.10.004.

[2] J.L. Gilbert, S. Sivan, Y. Liu, S.B. Kocagöz, C.M. Arnholt, S.M. Kurtz, Direct in vivo inflammatory cell-induced corrosion of CoCrMo alloy orthopedic implant surfaces, J. Biomed. Mater. Res. - Part A. 103 (2015) 211–223. https://doi.org/10.1002/jbm.a.35165.

[3] M.E. Moussa, C.I. Esposito, M.E. Elpers, T.M. Wright, D.E. Padgett, Hip Dislocation Increases Roughness of Oxidized Zirconium Femoral Heads in Total Hip Arthroplasty: An Analysis of 59 Retrievals, J. Arthroplasty. 30 (2015) 713–717. https://doi.org/10.1016/j.arth.2014.10.036.

[4] N. Hallab, K. Merritt, J.J. Jacobs, Metal sensitivity in patients with orthopaedic implants, J. Bone Jt. Surg. 83 (2001) 428–436. https://doi.org/10.1111/j.1600-0536.2011.01886.x.

[5] B.J. McEntire, R. Lakshminarayanan, R. Bock, Alumina-Zirconia Ceramic Implants and Related Materials, Apparatus, and Methods, US 9,353,010 B2, 2016.

https://doi.org/10.1002/bm.a.31230.K-H.

[6] C.S. Rankin, P.G. Robinson, N. Beattie, P. Gaston, Fracture of a BIOLOX Delta Ceramic Femoral Head: A Case Report and Update of the Literature, JBJS Case Connect. 9 (2019) 1–5. https://doi.org/10.2106/JBJS.CC.18.00336.

[7] M.M. Morlock, D. Bünte, H. Ettema, C.C. Verheyen, Å. Hamberg, J. Gilbert, Primary hip replacement stem taper fracture due to corrosion in 3 patients, Acta Orthop. 87 (2016) 189–192. https://doi.org/10.3109/17453674.2015.1128780.

[8] A. International, G133 – 05: Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear, Annu. B. ASTM Stand. 05 (2016) 1–10. https://doi.org/10.1520/G0133-05R10.2.

[9] J.D. Avila, Z. Alrawahi, S. Bose, A. Bandyopadhyay, Additively Manufactured Ti6Al4V-Si-Hydroxyapatite composites for articulating surfaces of load-bearing implants, Addit. Manuf. 34 (2020) 101241. https://doi.org/10.1016/j.addma.2020.101241.

[10] N. Eliaz, Corrosion of metallic biomaterials: A review, Materials (Basel). 12 (2019) 1–91. https://doi.org/10.3390/ma12030407.

[11] G.W. Stachowiak, A.W. Batchelor, Engineering Tribology, Elsevier, New York, 1993. http://www.ncbi.nlm.nih.gov/pubmed/22068761.