Laser Cladding of Ti-6Al-4V Alloy with Ti-Al2O3 Coating for Biomedical Applications

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Abstract. The indispensable properties of Ti-6Al-4V alloy coupled with poor tribological properties and delayed bioactivity make it a subject of interest to explore in biomedical application. A quite number of numerous coatings have been employed on titanium alloys, with aim to overcome the poor properties exhibited by this alloy. In this work, the possibility of laser cladding different ad-mixed powders (Ti - 5 wt.% Al2O3 and Ti - 8 wt.% Al2O3) on Ti-6Al-4V at various laser scan speed (0.6 and 0.8 m/min) were investigated. The microstructure, phase constituents and corrosion of the resultant coatings were characterized by scanning electron microscope (SEM), Optical microscope, X-Ray diffractometer (XRD) and potentiostat respectively. The electrochemical behaviour of the produced coatings was studied in a simulated body fluid (Hanks solution). The microstructural results show that a defect free coating is achieved at low scan speed and ad-mixed of Ti-5 wt. % Al2O3. Cladding of Ti - Al2O3 improved the corrosion resistance of Ti-6Al-4V alloy regardless of varying neither scan speed nor ad-mixed percentage. However, Ti-5 wt. % Al2O3 coating produced at low scan speed revealed the highest corrosion resistance among the coatings due to better quality coating layer. Henceforth, this coating may be suitable for biomedical applications.

1. Introduction
The human body biomechanical functions such as movement and body posture against gravity are made possible by musculoskeletal. Musculoskeletal is a biological system which is made of two sub-systems: the skeletal system and the muscular system [1]. However, in some circumstances tissue damage which could result from trauma or degenerative disease may be severe to a point that natural healing process would be inadequate [2]. With advances and innovations being made in the discipline of tissue engineering, it is possible to repair and restore the functions of a severely damaged bone tissue. In this regard, biomaterials known as scaffold would be required to bridge the gap and boost the osteogenic healing process [2]. A scaffold would serve a primary role of acting as an adhesion substrate for ingrowth cell, facilitates the delivery of drugs, provide temporary mechanical support to the newly grown tissue [3]. Hence, a material with unique characteristics such as biocompatibility, excellent corrosion resistance and low modulus is required to execute the aforementioned requirements expected from a scaffold. In this prospect, a material which satisfies almost all required properties and it is mostly used in biomedical applications is specifically titanium alloy (Ti-6Al-4V) [4-5]. Nevertheless, a scaffold made of Ti–6Al–4V is exposed to hostile corrosive body environment...
imposed by body fluid. This fluid emasculates the Ti–6Al–4V alloy capability to passivate and consequently leading dissolution of toxic ions like Al and V [6-7]. Moreover, the consequences of toxic ions lead to disruption of bioactivity behaviour between implant and tissues [8]. In case where articulation and movement occurs, and titanium alloy implant rubs against other materials such as bones; it would raise concerns. It has been reported that when titanium alloy slides against other hard or soft materials it suffers from wear [9]. Upon deterioration of protective oxide film due to wear, bare Ti6Al4V is subjected to rapid corrosion. This synergistic phenomenon is termed tribo-corrosion [10]. However, to overcome this setback and extend the life span of Ti–6Al–4V alloy incorporation of coatings with combination of excellent bioactivity, corrosion resistance, and biocompatibility is an effective method [11]. Fabrication of bioceramics like Ti and Al oxides (Al₂O₃) coatings may act as a barrier against diffusion of metallic ions from substrate into extracellular fluid [12]. However, because of their oxide nature, bioceramics are brittle and thus their application in load-bearing is restrained [13]. This challenge could be addressed by combining a metallic element with bioceramic and one metal which stands out to complement this combination is commercial pure titanium, as it exhibits characteristics such as corrosion resistance and good surface bioactivity [14]. Notably, the fabrication of Ti-Al₂O₃ composite on Ti-6Al-4V for biomedical application has been done by [12]. However, the authors used electrophoretic deposition technique. There are quite numerous techniques which could be employed to fabricate composites on titanium alloy. However, of all available surface treatments techniques, laser cladding has been proven to be a proficient method in fabricating (TiMMC) titanium metal matrix composites [15-16].

Zhang et al. [17] fabricated Al₂O₃/Ti-Al matrix intermetallic composite coatings on Ti–6Al–4V alloy using laser technique but emphasized more on mechanical properties of the coatings. Hence, this work is devoted to exploit the advantage of laser based coatings on the development of complex novel in-situ composite from admixed ratio of Ti-Al₂O₃ elemental powders that will mitigate the pressing issues related to Ti-6Al-4V alloy in biomedical applications. In addition, the influence of laser scan speeds on the electrochemical behaviour of Ti - 6Al - 4V in a simulated body fluid (Hanks solution) was investigated.

2. Experimental procedures

2.1. Materials

Ti-6Al-4V alloy of dimension (70 X 70 X 5 mm) acquired from VSMPOAVISMA Corporation were used as substrate in this work. The nominal chemical composition is as follows: 6.10 wt.% Al, 4.01 wt.% V, 0.15 wt.% Fe, 0.007 wt.% C, 0.12 wt.% O, 0.005 wt.% N, Ti, balance. Commercial pure titanium (99.9% purity) and alumina powders (99.9% purity) supplied by Sigma Aldrich, South Africa were chosen as coatings materials. These powders were mixed into the composition ratio of 95 wt.% Ti-5 wt.% Al₂O₃ and 92 wt.% Ti-8 wt.% Al₂O₃ using Turbula mixer at a mixing speed of 49 rpm for 6 h.

2.2. Laser deposition

Prior to laser cladding treatment, the surfaces of Ti6Al4V substrates were sandblasted and cleaned with acetone to remove contaminants from the surface and to enhance adsorption of the laser beam. Laser cladding was carried out using 4.4 kW continuous wave RofinSinar Nd:YAG equipped with an fiber optic beam delivery system. During laser deposition, composite powder was injected at a rate of 2 l/min into the melt pool formed by the laser beam during scanning of the substrate. Also, argon shielding gas was coaxially fed at 8 l/min. This was done in order to prevent oxidation as Ti has high affinity for oxygen. Moreover, to attain large clad surface area; multiple tracks were produced at 50% overlap. The laser spot diameter and power were kept constant at 2 mm and 900 W respectively, whereas, the scanning speed was varied between 0.6 and 0.8 m/min in order to distinguish the characteristics of clads obtained at various scan speeds.

2.3. Characterization of clad samples

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2.3.1. **Microstructure and phase analyses.** After laser deposition treatment, the produced clad samples were prepared for microstructural analysis following standard metallographic procedure. The microstructures of the coatings were examined using SEM/EDS (JEOL JSM 7600 F FESEM), meanwhile the resulted phases were characterized using XRD (Philips P1710 Panalytical) with Cu target Kα radiation. The phases present were scanned and identified by X’Pert High score plus software.

2.4. **Corrosion testing**

Prior to corrosion testing, specimens were prepared by sectioning them into 1 cm² and cold mounted in an epoxy resin. Grinding and polishing using 1200-grit SiC papers and diamond suspension respectively were carried to achieve a well polished laser coating surface. Upon testing, specimen was immersed into a cell filled with Hank’s solution (Sigma Aldrich) which resembles human body fluid. Electrochemical test was carried out using an Autolab potentiostat (PGSTAT30 computer controlled). An electrochemical cell setup was as follows: Hank’s solution as electrolyte at 25 °C; three electrodes connected, the working electrode (sample), counter electrode (graphite rod) and silver/silver chloride electrode as a reference electrode (SCE). The corrosion potential (Ecorr) was determined by scanning at the rate of 0.01 V s⁻¹ from a potential of −1.5 V to 1.5 V.

3. **Results and discussion**

3.1. **Microstructural evolution**

Figure 1 shows the SEM micrograph of Ti6Al4V substrate. It is observed that this alloy consists of two distinctive phase structures. The α-phase (darker phase) has an HCP structure whereas the β-phase (lighter phase) has a BCC structure. According to Adesina et al. [18], the α-phase is stabilized by Al whilst V stabilizes β-phase. Despite that these elements are crucial for stabilizing important phases, but their presence in this alloy poses human health risk if released into human system during service of this alloy in biomedical [16]. Henceforth, incorporation of composite such as Ti-Al₂O₃ coatings using laser may be valuable to suppress these toxic elements from being released.

Figure 2(a-d) shows the Optical micrographs of laser-clad coatings at varying scanning speeds of 0.6 and 0.8 m/min. Needle-like acicular structure known as α' martensite is observed in all the coatings microstructure. The observed martensitic structure transformed from α + β due to high cooling rate as a result of laser processing [14, 19]. However, one could question why the martensitic structure distribution between coatings produced at various scan speed and ad-mixed powder was inconsistent. Possible explanations for this occurrence may be attributed to that addition of Al₂O₃ in Ti microstructures matrix may have prohibited the continuous nucleation of martensitic network. The coating materials possess thermal conductivities and melting temperatures as listed: titanium (17 W/mK) [20], 1604-1660 °C [21]; Al₂O₃ (6.3–28.7 W/mK), 2054 °C (2327 K) [22]. Hence, the differences in thermal properties perhaps led to inhomogeneous temperature gradient and cooling rates. Cracks and pores observed in Figure 2(c-d) affects the quality of the coating layer. Defects such as gas and pores forms at high scan speed because of gas bubbles entrapped during solidification [14].

3.2. **Phase constituents**

The XRD of coatings produced at varied laser scan speed and composite ad-mixed is displayed in Figure 3. As seen from this Figure, all the coatings reveal TiO₂ phase with high intensity. This phase formed probably because supplied heat by laser and quantity of O from air were adequate to prompt oxidation. Moreover, phases such as several types of aluminium oxides and titanium aluminate oxides were detected in all the coatings. The formation of these phases can also be witnessed in the other studies done by [12, 22, 23]. The penetration of O into the molten pool thus to form TiO₂ led to the establishment of the TiO₂-Al₂O₃ system. As a result of thermodynamically and kinetics mechanisms, TiO₂-Al₂O₃ system spontaneously favoured the formation of titanium aluminate oxides [23]. However, addition of more Al₂O₃ quantity possibly altered the formation of these phases regardless of varying laser scan speed. According to de Morais et al. [24] vanadium is highly toxic either in elemental and oxides state. Thus, the presence of V related phase in coatings (Ti-5 wt.% Al₂O₃ – 0.6 m/min and 0.8
m/min, Ti-8 wt.% Al$_2$O$_3$ – 0.8 m/min) would pose harmful effects if these coatings are considered for scaffold treatment. However, it could be noted that the absence of V related phases was achieved at the coating of Ti-5 wt. % Al$_2$O$_3$ deposited at 0.6 m/min scan speed. With this observation, the harmful effect of vanadium is thereby mitigated.

![Figure 1. SEM micrographs of Ti-6Al-4V alloy.](image1)

![Figure 2. Optical micrographs of the coatings: (a) Ti-5 wt.% Al$_2$O$_3$– 0.6 m/min, (b) Ti-5 wt.% Al$_2$O$_3$– 0.8 m/min, (c) Ti-8 wt.% Al$_2$O$_3$– 0.6 m/min, Ti-8 wt.% Al$_2$O$_3$– 0.8 m/min.](image2)
3.3. Corrosion behaviour

Figure 4 shows the results of the electrochemical behaviour of the produced coatings and substrate. As it could be seen from Figure 4, that the potential and current density of the laser cladded coatings are superior compared with the Ti6Al4V alloy substrate. This implies that the fabricated coatings are vital in protecting the surface of the substrate from exposure to the electrolyte. As reported by Popoola et al. [16] the laser coating film on the surface acts as a cathode, which prohibits the movement of ions. However, the Ti-5 wt.% Al2O3 coating produced at 0.6 m/min exhibit the highest corrosion resistance among other coatings. According to Mokgalaka et al. [25] in certain environmental conditions, protective oxide film consisting of titanium dioxide (TiO2) predominantly and also including aluminium oxide (Al2O3) is responsible for corrosion resistance. With relevance to this evidence, phases such as TiO2 and Al2O3 coupled with titanium aluminate oxides phases observed in this work may be deemed responsible for achievement of superior corrosion resistance. Moreover, addition of more Al2O3 quantity (Ti-8 wt.% Al2O3) was supposed to yield better results. However, Al2O3 is porous thus this material creates a site for electrolyte accumulation and diffusion [12,26]. Thus, this is a reason addition of Ti-8 wt.% Al2O3 yielded inferior corrosion resistance than Ti-5 wt.% Al2O3. Also, Obadele et al. [14] observed that cracks and pores formed due to laser cladding at high scan speed such result in high corrosion density. This observation is also witnessed in this work.

![Figure 3. XRD of the coatings.](image)

![Figure 4. Potentiodynamic curves of the substrate and coatings.](image)
4. Conclusion

Laser cladding coating of Ti-6Al-4V with Ti-Al$_2$O$_3$ is plausible. However, a defect free coating is achieved at coating of Ti-5 wt.% Al$_2$O$_3$ produced at laser scan speed of 0.6 m/min. The presence of martensitic structure coupled with TiO$_2$, Al$_2$O$_3$ and titanium aluminide oxides phases led to optimum corrosion resistance for the aforementioned coating. Henceforth, this coating could be considered for coating biomedical implants such as scaffold since it does not pose risk of vanadium dissolution into humans.

5. References

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