BIOCERAMIC HYDROXYAPATITE COATING FABRICATED ON TI-6AL-4V USING Nd:YAG LASER

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ABSTRACT

A method of synthesising a biocompatible HAP coating is presented. In the current study, Nd:YAG laser was used to directly melt pre-place HAP powder beds on Ti-6Al-4V. The processing parameters used were 750 W laser power, 5 mm/s scanning speed and 27° inclined beam plane. The coating was studied under white light and scanning electron microscope where it was possible to characterise the microstructures. The produced coating was characterised of mixed morphologies of HAP, short and elongated titanium needles at the surface while in the middle of the coating dendrite trunks without arms were observed. This observation is related to the heat inputs, dilution and melting of the substrate and powder during processing. The absence of the arms growing from the trunks indicated low heat inputs. In addition, the microstructure of the HAP after soaking in Hanks' solution indicated octagonal and hexagonal crystals of HAP. The hardness values indicated good metallurgical bonding at the interface. In conclusion, this study was successful in fabricating a desirable coating of HAP on Ti-6Al-4V for biomedical applications. This work highlights that even though laser power and scanning speed are predominantly influential parameter settings, it is also necessary to consider the angle at which the laser beam is scanned across the material.

INTRODUCTION

Materials used in replacing or repairing broken human bones or teeth range from metal alloys (e.g. cobalt chromium), polymers to ceramics. For example, literature details that the genesis of bio-metal that were used in fixing broken bones started with cobalt chromium alloy (CoCr) followed by stainless steel (SS) and most currently titanium alloys (e.g. Ti-6Al-4V). Reviewed literature indicated that CoCr was discontinued as materials of interest to be used in bone fixation since it was prone to corrosion and wear. Corrosion and wear of metal implants used in bone fixation led to the release of metal debris into the human blood system [1-2]. The debris is known to cause human long term disease such as Alzheimer's [3]. SS is preferred only to be used as screws, plates and bone pins, but not as long bones given their stiffness and mechanical strength. For long bone implants such as a hip, Ti-6Al-4V is preferred. Ti-6Al-4V has attractive mechanical properties that are desirable in the field of biomedical applications, but more so, it is proven to be a bio-inert metal that is biocompatible. Biocompatibility is the most required characteristics of the metal materials need to be used as scaffolds. However, Ti-6Al-4V lacks the biointegration property from which human natural tissues can grow around the implanted metal scaffolds [5]. Likewise, their prolonged used can lead to the leaching of alloying elements (Al and V) into the human blood system [6, 15].

Biointegration of fabricated scaffolds with the natural human tissues is the most endured field of study in tissue engineering. For the past two to three decades surface re-engineering of Ti-6Al-4V with HAP has become the most researched field for tissue engineering applications. A human natural bone consists primarily of about 43 % of hydroxyapatite (HAP). Favourably, HAP like other available calcium phosphate materials can be synthesised. The chemistry of synthesising calcium phosphate (CaP) materials is founded which makes it possible that the CaP material can be produced in bulk. Bulk HAP is weak in strength (brittle) and heat sensitive with a CaP ratio of 1.67. HAP is a bioactive ceramic material that is porous in nature and is the most biointegrable material of all the CaP materials. Surface re-engineering of Ti-6Al-4V material has been achieved by coating a thin film of HAP on them. This film is known to biointegrate scaffolds with the natural bone where at the interface, human natural tissues can start to grow inwards forming a network that is able to facilitate nutritional flow. Unfortunately, due to it being brittle it cannot be used as a stand-alone material for bulk supply [7-10]. Meanwhile, due to it being heat sensitive the choices from which a selection of an appropriate surface coating technique can be made are limited.

Several techniques have been used to coat HAP on Ti-6Al-4V for biomedical applications. Techniques such as ion beam, CVD, plasma, flame, HVOF, cold spraying and laser metal deposition have all been used successfully to deposit HAP coatings on Ti-6Al-4V [11].Plasma spraying technique is the most successful tool to fabricate HAP coatings on biometals given their high deposition rates and good metallurgical bonding. However, these techniques are known to produce HAP coatings that have decomposed phases of HAP due to high processing temperature. Nonetheless, in recent times, it has been shown that a post-curing stage that involves the use of laser to treat the plasma produced coatings that led to an improved high crystalline HAP rich coating. Even so, to the best of my knowledge, the process setting parameters necessary to achieve a desirable HAP coating with this post processing step are yet to be reported. In addition, there has never been a study that detailed a coating process that achieves a metallurgical fit coating with good content of HAP at the surface. Also, literature shows that "usually" the microstructures together with the mechanical properties of the fabricated HAP coatings are reported without results on their bioactivity being reported. This study will account for all the presented short-comings [11].

Laser enabled material deposition techniques like Laser engineered net shaping (or (LENS) are current and are available for use in rapid prototyping and manufacturing. Laser cladding techniques are traditional methods of surface engineering, but still survive due to its ease in operation and flexibility, particularly when high power lasers are used. In this paper, Nd:YAG laser (a solid state laser) was used to directly melt HAP powder beds on Ti-

6Al-4V substrates. Laser beams are highly controllable, coherent and are able to achieve strong metallurgical bonding between HAP and the base metal. In the past, CO2 lasers were used for the purpose of producing durable HAP coatings where they were able to preserve the crystallinity of the HAP (CaP 1.67). But, given that Nd:YAG has higher absorption ratio compared to CO2 lasers, it is understood that it is best suited for such applications [12]. Even so, concerns with traditional coating techniques seem to overshadow direct laser melting (DLM) techniques. Requirements with DLM are in controlling the processing parameters such that dilution must be avoided. Dilution occurs when both the pre-placed layer and the substrate are both melted in which case during rapid cooling and solidification the two materials reacts and form various phases. In this paper, Nd:YAG laser was used to melt the pre-place HAP onto Ti-6Al-4V. The choice of the processing parameters like the scanning speed, beam angle and laser power seem to be the parameters that need optimising where it is shown here that dilution was minimised to an extent that the produced HAP coating was well bonded, crack-free and retained the initial HAP (CAP) composition.

MATARIALS AND METHODS

Materials

The HAP 90 powder was supplied by Plasma BIOTAL, United Kingdom and was used as a starting material. The powder was fine and due to this; it was deposited onto the Ti-6Al-4V substrate by first converting it into a powder bed. The powder beds were produced by mixing the powder with polyvinyl alcohol (PVA). Once placed on the Ti-6Al-4V the HAP:PVA slurry was allowed to dry over night before processing. The initial CaP ratio, determined by mapping with the electron dispersive microscope (EDS) component of the scanning electron microscope, of this powder was 1.80 before processing. The Ti-6Al-4V substrates used were 70 x70 x 5 mm^3 in dimension. Before preplacing the beds, the substrates were sand-blasted and cleaned with acetone. The 044 Rofin, Nd:YAG laser with maximum power output of 4.4 kW was used to melt the preplace powder beds. For this work, 750 W laser power was used. The coating was produced by directly scanning across the bed a 5 mm spot diameter beam that was inclined at 27°. The Kuka robot arm was used to control the laser spot.

Bioactivity test

The produced coatings were prepared by mounting with a polyfast resin using a hot mounting press. The mounted samples were then polished and etched with Kroll's reagent for 20-30s to reveal the titanium microstructure which could be easily discriminated from HAP before characterisation. The best coating was taken for soaking in the Hanks' solution where it was possible to perform the bioactivity test using the immersion method. The balanced Hanks' solution was supplied by gibco life technologies, Johannesburg, South Africa. The coating was immersed in the Hanks' solution that was contained in the Petri dish which was suspended in a water bath that allowed for the temperature to range between 37.5- and 38°C. The coating were only soaked for 48 hours when the change in the microstructure occurred. The microstructures of the soaked sample were studied with JOEL scanning electron microscope (SEM).

Methods

The produced coating was mounted with polyfast resin using a hot mounting press and etched with Kroll's reagent. Optical analyses were conducted using the Olympus optical microscope (OM) fitted with a SZ 30 camera and JEOL scanning electron microscope equipped with Energy Dispersive X-ray spectroscopy (SEM-EDS), JSM-6510. The coating that underwent bioactivity test by soaking in Hank's solution was analysed under a white light using OM for microstructural identification. Further microstructural analyses and elemental composition were conducted on the *in vitro* sample using the Auriga, CrossBeam Focal Ion Beam (FIB) Workstation with GEMINI FESEM column equipped with The Oxford X-Max instrument with 20 mm square window, Aztec Software. Microhardness of the coating was

conducted by indenting the sample across the phase (top to bottom) using Matsuzawa Seiki Micro Hardness Tester.

RESULTS

Coating

Figure 1 presents the HAP coating that was produced by directly melting HAP pre-placed powder bed on the Ti-6Al-4V substrate using 750 W laser power.

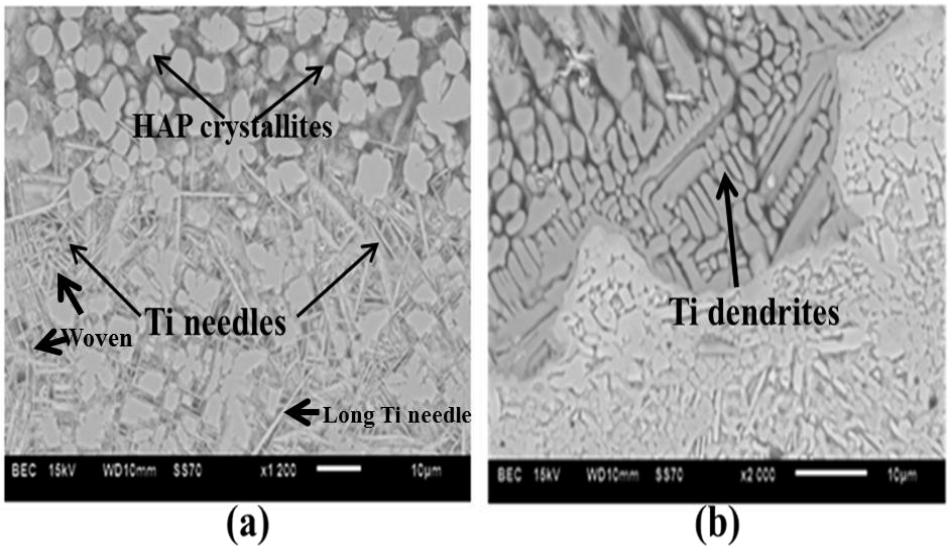

Figure 1: HAP melted using 750 W laser power: (a) Mixed HAP crystallites morphology, and (b) formed dendrites structures

Figure 1 represents the HAP coating that was produced by the process as discussed above. Figure 1 (a) presents the macrograph taken from the top surface of the coating. The characteristics of this coating include mixed morphologies (e.g. hexagonal, octagonal, randomly shaped and leaf-like) of HAP crystallites grown on top of the coating, titanium needles (both long and short). These mixed morphology of HAP crystallites are grown first (top half) on the coating then inter-twinned with the observe titanium needles. It was observed that the long needles point out of the micrograph while the short needles formed a woven, sieve-like structure. The observed woven structures are necessary for the re-enforcement of the strength of the coating while the elongated needles could be like pillars where they support or suspend the HAP crystallites which seem to be sitting on-top of them.

Figure 1(b) reports on the interface between the substrate and the coating. This micrograph is characteristic of titanium dendrites (mainly branches with developed arms). There is a relationship between the effect of laser power and the development of titanium dendrites. Already these dendrites suggest that the heat input during melting was considerable enough to form a good metallurgical bonding, but not melt the material such that dilution was induced. A highly heat affected titanium dendrite will definitely grow arms which will develop into stems from which secondary arms will grow [13]. These results concur with those reported in Ref [13]. With noting is the lack of dilution that can be deduced from Figure 1 (b). A morphology that presents dilution is typically characterised of two phase material infused within each other; an observation which could not be made from Figure 1 (b). The latter observation and the observation of the dendritic structures obviously conclude that the chosen laser power and scan speed can be considered optimum to avert from high inputs heating energy to be generated during processing. Although, these parameters have been used elsewhere without success [3] which therefore means the

incline beam plane had a critical role to play in the development of the reported coating. No other study has been presented that reported this effect on parameter settings.

Microhardness SEM images

Figure 2 presents the indentations taken from the top to the bottom of the coating.

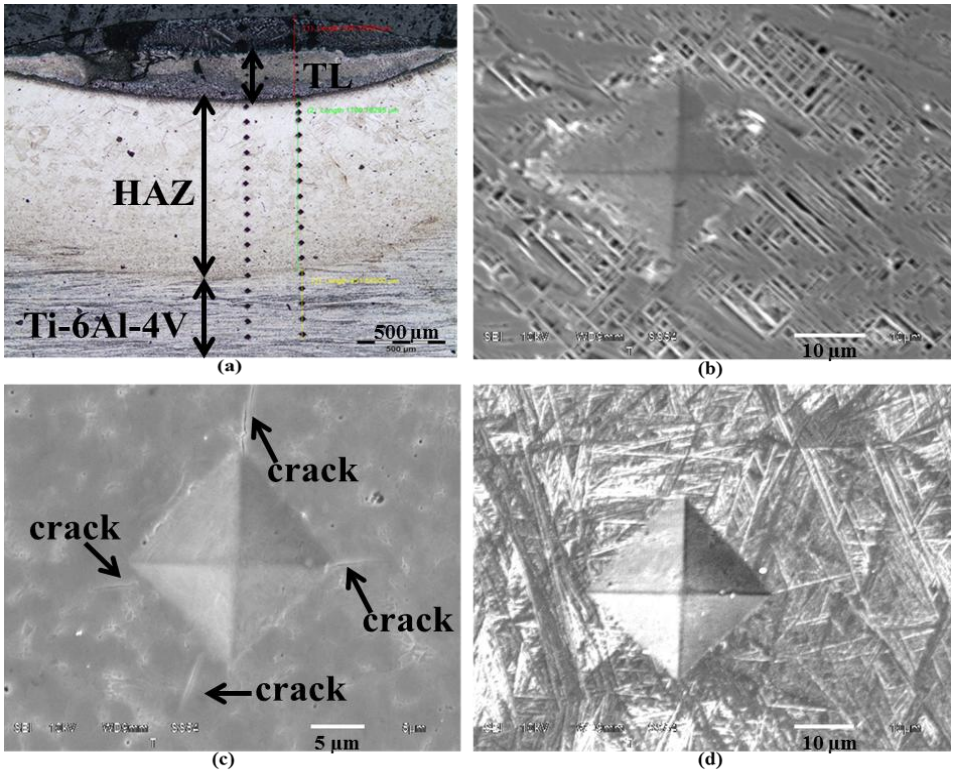

Figure 2: Vickers' micro-indentation on the: (a) Actual coating, (b) Top of the coating (c) Middle of the coating, and (d) Heat affected zone

Figure 2 (a) illustrates all the regions that exist post laser processing. These regions are the top surfaces (crust/clad); transition layer (interface between the crust and the substrate); heat affected zone (HAZ) which relates to the heat input and dilution; and the substrates (Ti-6Al-4V). Typically, a complete indent looks like a pyramid. A bigger pyramid is indicative of a soft surface while a small indent is indicative of a hard surface. In this study three areas of interest were indented. The three areas are the clad, transition layer (TL) and heat affected zone (HAZ). The interface is normally indented to predict the bonding ability of the coating to the substrate. Figure 2 (b) shows a conspicuous indent for metals and ceramic materials. It seems as if though the indenting pin was sliding across the surface where it was unable to scratch the surface or wear it off. However, the indent is big enough to conclude that the top surface of the coating was made-up of soft materials which were low in hardness. Figure 2 (c) was taken at the interface (TL region). The indent is big enough to show that the material was soft. Meanwhile, the pyramid shows signs of cracking at the edges. This cracking concludes the presence of HAP phase which is brittle in nature. The indents shown by Figure 2 (d) were taken in the HAZ region. The indent is small compared to the other indents. In fact the indent on the coating is bigger than the indent taken on the TL which is bigger that the indent taken in the HAZ region. This observation shows that the hardness of the coating increased inwards towards the coating. It would therefore be expected that the clad is softer than the TL which is softer than the HAZ. These results are within the considerations of the laser material processed microstructures

where it is always anticipated that the HAZ has to have the highest hardness. The average hardness results indicated that the clad, TL, HAZ and Ti-6Al-4V have hardness values of about 166 Hv, 706 Hv, 945 Hv and 355 Hv respectively. These values confirm the observation made, but more importantly they show definitively that the TL has a hardness value twice that of the substrate which suggested good metallurgical bonding.

In summary, the microstructures of the coating presented here indicate a coating that is rich in HAP content on the surface. The observed HAP crystallites are of mixed morphologies. In addition, two sets of dendrites were observed where the short dendrite made a woven structure and the elongated dendrites were sticking out of the micrograph like pillars. The microhardness indents show biggest, bigger and small pyramid for the clad, TL and HAZ respectively. The microhardness values correspond to this observation and it is not perplexing since it is known that woven and pillar dendrites act as support strength of the coating. This coating retained all the mechanical requirements for biomedical application and it was evaluated for bioactivity by soaking in the Hanks' balanced solution as presented in section 3.3, Figure 3.

Hanks' solution test

Figure 3 presents the coating after it was left to soak in Hanks' solution for 48 hours.

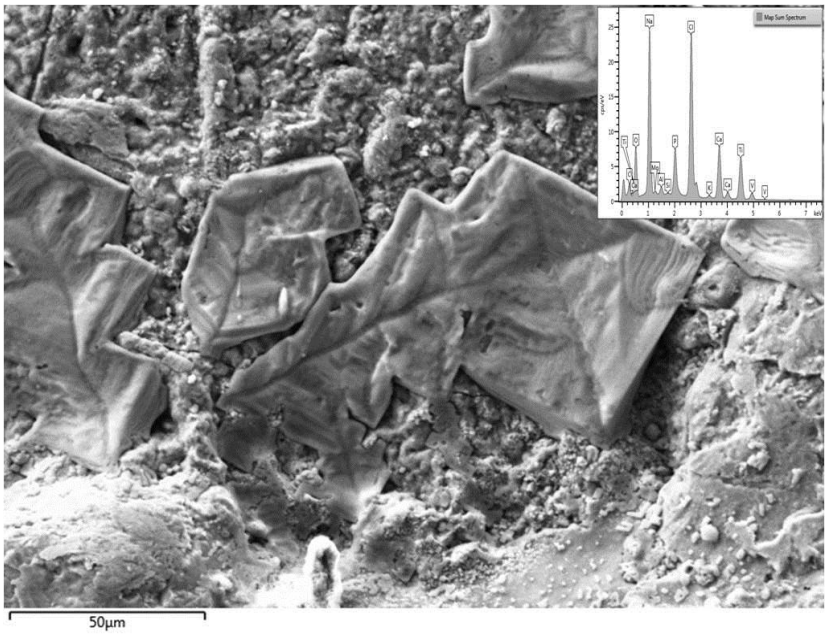

Figure 3: Crystal forming during soaking of the coating in Hanks' solution

Figure 3 shows that during soaking, semi-melted crystals of HAP are formed. These crystals, initially called HAP crystallites, are indeed mixed in morphology. From Figure 3 we can only observed a hexagonal structure and an octagonal structure. The observed crystals were sitting on top of the coating. Crystallographically, HAP is hexagonal in structure while tetra-calcium phosphate (TTCP) is monoclinic in structure. Abundant literature is available on the information supporting the existence of both HAP and TTCP in tooth and bone. Also, information relating to the structural arrangement of these two calcium phosphate materials shows that their epitaxy are so similar that sometimes impossible to grow one without the other. Their X-ray diffraction lattice parameters are available in literature and support this observation [16]. The semi-melted crystals could suggest a hexagonal melted crystal, but the SEM-EDS mapping results (attached at the far right corner of Figure 4) suggests that this crystals had CaP ratio of 2.00. The feedstock powder used had a CaP ratio

of 1.80. CaP ratio of 2.00, according to Markovic et al [14], corresponds to TTCP calcium phosphate materials. The initial HAP powder had CaP ratio of 1.80 instead of 1.67 for pure HAP, it can be said that the powder was a mixture of these two calcium phosphate materials. The average CaP of both HAP and TTCP empirically equals 1.84. In this case, it can be said without doubt that the selected processing parameters did retain the initial composition of the material.

SUMMARY

A direct laser melting process was successfully achieved by melting a polyvinyl alcohol bonded HAP pre-place powder bed on Ti-6Al-4V using Nd:YAG laser as a heating source. The selected parameters indicated that in addition to the chosen laser power and scanning speed, the inclined beam plane is also necessary when fabricating the HAP coating that is desirable for biomedical applications. This study produced a coating that was well bonded and crack-free with no dilution. The microstructures of the coating revealed a coating rich in HAP on the surface. The microhardness indents showed a soft clad (Figure 2 (a)) that is well bonded (Figure 2(c): TL hardness value). These strengths correlated well with the initial proposition that indicated that the observed woven structure made by the short titanium needles and the elongated titanium needles were only there to support the HAP that was sitting on top of them. The microstructure of the coating before bioactivity test indicated mixed morphology of HAP crystallites. The bioactivity test confirmed this observation where it was possible to see that the HAP crystals were partially melted and where dominated by hexagonal and octagonal crystals.

CONCLUSIONS

This study was successful in synthesising the HAP coating on Ti-6Al-4V substrate using Nd:YAG laser. The process parameter setting should include 750 W laser power (Nd:YAG laser), 5 mm/s scanning speed and an inclined beam plane of 27° if one is to successfully produce a coating that is rich in HAP with reserved composition post processing.

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