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Microstructures, hardness and bioactivity of hydroxyapatite coatings deposited by direct laser melting process

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ABSTRACT

Hydroxyapatite (HAP) coatings on bioinert metals such as Ti–6Al–4V are necessary for biomedical applications. Together, HAP and Ti–6Al–4V are biocompatible and bioactive. The challenges of depositing HAP on Ti–6Al–4V with traditional thermal spraying techniques are well founded. In this paper, HAP was coated on Ti–6Al–4V using direct laser melting (DLM) process. This process, unlike the traditional coating processes, is able to achieve coatings with good metallurgical bonding and little dilution. The microstructural and mechanical properties, chemical composition and bio-activities of the produced coatings were studied with optical microscopy, scanning electron microscope equipped with energy dispersive X-ray spectroscopy, and Vickers hardness machine, and by immersion test in Hanks' solution. The results showed that the choice of the laser power has much influence on the evolving microstructure, the mechanical properties and the retainment of HAP on the surface of the coating. Also, the choice of laser power of 750 W led to no dilution. The microhardness results inferred a strong intermetallic–ceramic interfacial bonding; which meant that the 750 W coating could survive long in service. Also, the coating was softer at the surface and stronger in the heat affected zones. Hence, this process parameter setting can be considered as an optimal setting. The soak tests revealed that the surface of the coating had unmelted crystals of HAP. The CaP ratio conducted on the soaked coating was 2.00 which corresponded to tetra calcium phosphate. This coating seems attractive for metallic implant applications.

1. Introduction

Artificial, osteo-applications require material implants with coatings which are bioactive, corrosion resistant and last long in-service [1,2]. In the past, coated cobalt–chromium alloys and stainless steel metals were used as load-bearing materials; however, artificial bone implants made from these metal alloys were characterised mainly of poor mechanical properties and in vitro corrosion side effects [3]. Currently, research makes use of titanium alloy (Ti–6Al–4V) for load bearing applications; with a particular focus on hip, long bones and teeth replacements. Ti–6Al–4V is the leading material for bone replacement since it is corrosion resistant, bio-compatible and has the required elastic modulus and good yield strength [4], but shows poor osteo-conductivity [5]. Nonetheless, Ti–6Al–4V implants which are left to serve long are known to cause health problems [3]. Geetha et al. [3] revealed that when left long in service, Ti–6Al–4V will release aluminium (Al) and vanadium (V) ions into the human body fluid system thereby becoming cyto-toxic. Both V and Al ions are associated with long term health problems [6] such as Alzheimer's, neuropathy and Osteomalacia [3].

To suppress Al and V ions from leaching into the human body fluids while correcting for the wear debris of this alloy, it is practised that their surface be modified via coating with a thin layer of a bio-active ceramic material [7]. Hydroxyapatite (HAP) is a preferred bio-active ceramic material; not only because it has a similar crystal structure as that of the human natural bone [5,8–12], but also because HAP coatings can induce osteo-conductivity between the metal implant and the human tissues in vivo [10,13–17]. Moreover, in clinical practices, HAP is a preferred coating material since it cannot be used as a load-bearing implant material due to its poor mechanical properties (low plasticity, fatigue, and creep resistance) [5,8–12,14,18,19]. Given the outstanding individual properties of both HAP and Ti–6Al–4V, it can be inferred that as associates, these materials can perform better when used as load bearing materials.

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In fact, several techniques have been used to modify the surface of this alloy by coating it with a thin layer of HAP [7,17,20]. The most prominent surface modification techniques that have been used, with or without positive success, include and are not limited to magnetron sputtering [13], pulse laser deposition [16,21], laser cladding [15,22], thermal spraying techniques [23], seeded hydrothermal deposition [8], cold spraying techniques [24,25], laser-engineered net shaping technique [10], laser assisted cold spraying [26] and direct laser melting [11,27,28]. Of all the said techniques, plasma spraying is the most commonly used. However, given the limitations with plasma coatings, research has been conducted on post surface treatment of plasma sprayed HAP coatings by high power lasers.

Thermal sprayed HAP coatings, including those produced by plasma spraying, are mainly presented with problems such as weak bonding, cracks, and phase transformation (low crystallinity) which reduce the life span of the coating in service. Sol–gel HAP coatings are characterised of lower adhesion strength, but improved phase composition when compared to plasma sprayed HAP coatings. The limiting factor in coating HAP onto Ti–6Al–4V using cold spray based techniques stems from the low plasticity of HAP particles which during spraying are unable to deform. Even so, a theoretical modelling study by Singh [29] gives a different view on the matter. Nevertheless, research continues to strive for a break-through in modifying the surface of Ti–6Al–4V with HAP. Surface coating of HAP on Ti–6Al–4V will eventually lead to a desirable coating that can be used to manufacture bone and teeth scaffolds that mimic the natural human bone.

Surface modification using lasers seems attractive given that they have high coherence and are directional; in which case they offer precise modification and treatment on specific area without harming the entire serviced part [30]. Thermal and thermo-chemical processes are two known distinct processes where lasers are used to modify surfaces. The former process relates to the melting of the surface while leaving its initial properties unchanged. The latter process relates to material being added onto a treated surface in order to change their initial properties or just leading to the inter-metallic bonding between the clad and the substrate with little dilution being experienced [10,31,32]. The thermo-chemical process includes laser alloying and laser cladding. In this study, another form of laser cladding called direct laser melting is investigated [33,34]. Laser cladding is used to produce surface coatings with thickness that ranges from 0.3 to 1 mm. Coatings produced by laser cladding are achieved by either injecting solid powder particles that flow considerably into a laser generated melt pool whereby a fusion layer with good metallurgical bonding is produced or by preplaced methods. Preplaced methods are applied to powders which are resistant to flowing or too fine. HAP powder is normally supplied in a fine particle size distribution range. In this state, the HAP powder has poor flowability characteristics whence it can simply be processed into a coating by first preplacing it with binders onto the Ti–6Al–4V substrate before directly melting it with coherent, high power laser like Nd:YAG.

Nag et al. [12] indicated that direct laser melting process of HAP onto Ti–6Al–4V is by far more successful than any other coating techniques since the achieved metallurgical bonding is far better than those achieved with tradition coating techniques. Despite this, Nag et al. argue that HAP coatings achieved by direct laser melting process lack a highly concentrated content of HAP at the top of the clad with retained chemical properties that are similar to the precursor HAP powder. This means that even though direct laser melting is seen as a successful tool in producing HAP coatings on Ti–6Al–4V, the produced coating has little or reduced content of HAP with reduced crystallinity. This is very concerning since HAP coatings produced by traditional coating methods suffer from the same results. These observations are attributed to the occurring reaction between the pre-placed and the substrate that occurs during dilution and rapid solidification process. To tackle this problem different researches have been conducted detailing the effects of laser scanning speed, laser power and powder feed rates [12,28]. Most recently, studies on the effects of different binders and their effects on the resulting microstructures of HAP coatings produced by direct laser melting process were reported followed by their bio-activity studies [11,28]. Kusinski et al. [33] showed the required intermediate metal–powder region desirable in laser cladding; which speak to the bonding ability of the coating and the substrate. Roy et al. [10] explained that HAP laser processed coatings that possess characteristics such as high content of HAP at the surface and low dilution have the potential to reduce the interfacial bonding problems (metal–ceramic region) while prolonging the life expectance of the coating in vitro. Roy et al. [10] is in agreement with Nag et al. [12] as they both believed that by controlling dilution effects, the resulting coating will have good content of HAP on the surface with little decomposition of the precursor-preplace HAP powder.

Nag et al. [12] studied the microstructure of Ca–P on Ti–6Al–4V produced by direct laser melting process without reporting on their mechanical properties and bio-activity. Chien et al. [11] and [22] investigated the microstructures, binder effects, laser output power, laser traverse speed and hardness of the coatings during laser cladding. Chien et al. [28] subsequently characterised the bioactivity of the optimised samples from their previous work reported in Ref [22]. The latter authors reported hardness of about 1000 Hv when PVA was used as a binder at 740 W laser power. In Refs [10] and [35], hardness of about 702 Hv and 260 Hv using LENS and laser surface engineering process independently is reported. These values differ from that of pure HAP which is 535 Hv [21]. Cheng et al. [35] highlighted that there is little published information on the hardness of laser coated HAP. Even so, the available information does not relate hardness to the quality of the coating.

Laser melting processes such as laser cladding and direct laser melting, which are unlike traditional deposition techniques, can produce coatings with good metallurgical bonding. The mechanical properties, microstructures, and bioactivity of laser melted HAP powder beds on Ti–6Al–4V are yet to be widely reported in open literature. In addition, optimised process parameters that lead to the retainment of bulk quantity of HAP at the surface of the coating during direct laser melting are still to be established. This paper reports on the microstructures, microhardness and bioactivity of HAP coatings fabricated on Ti–6Al–4V by direct laser melting process. In addition, this work has compared different coatings of HAP produced on Ti–6Al–4V with different laser powers using direct laser melting process, and reported the process parameters that led to the retainment of HAP on the surface of the coating.

2. Materials and method

2.1. Sample preparation

PVA granules with specifications of 0.001% chlorine, 0.2% water and pH range of 5–7, supplied by Merck KGaA, 64271 Darmstadt, Germany, were mixed with deionised water and heated to 100 °C while magnetically being stirred for 3–4 h to create a thick colourless paste which was mixed with the hydroxyapatite powder, CAPTAL 90, supplied by Plasma BIOTAL, United Kingdom to create a slurry which was pre-placed, as a powder bed, on the Ti–6Al–4V substrate which was initially sandblasted and chemically cleaned with ethanol. The HAP elemental analysis conducted by SEM-EDS, in weight %, concluded that this powder had Ca/P ratio of 1.80 before processing. The Ti–6Al–4V substrates had dimensions of $70 \times 70 \times 5$ mm^3. The preplaced HAP powder beds were left to dry in a fume cupboard overnight before processing and their thickness was measured to being 0.9 mm.

2.2. Direct laser melting process

The already prepared pre-placed HAP powder beds were used to carry out direct laser melting process. The prepared powder beds were directly melted with a laser source of 044 Rofin, Nd:YAG utilising 750 W and 1.0 kW laser powers. The laser spot of 5 mm width, now