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Selective laser melted titanium alloys for hip implant applications: Surface modification with new method of polymer grafting

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ABSTRACT

A significant number of hip replacements (HR) fail permanently despite the success of the medical procedure, due to wear and progressive loss of osseointegration of implants. An ideal model should consist of materials with a high resistance to wear and with good biocompatibility. This study aims to develop a new method of grafting the surface of selective laser melted (SLM) titanium alloy (Ti-6Al-4V) with poly (2-methacryloyloxyethyl phosphorylcholine) (PMPC), to improve the surface properties and biocompatibility of the implant. PMPC was grafted onto the SLM fabricated Ti-6Al-4V, applying the following three techniques; ultraviolet (UV) irradiation, thermal heating both under normal atmosphere and UV irradiation under N_2 gas atmosphere. Scanning electron microscopy (SEM), 3D optical profiler, energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) were used to characterise the grafted surface. Results demonstrated that a continuous PMPC layer on the Ti-6Al-4V surface was achieved using the UV irradiation under N_2 gas atmosphere technique, due to the elimination of oxygen from the system. As indicated in the results, one of the advantages of this technique is the presence of phosphorylcholine, mostly on the surface, which reveals the existence of a strong chemical bond between the grafted layer (PMPC) and substrate (Ti-6Al-4V). The nano-scratch test revealed that the PMPC grafted surface improves the mechanical strength of the surface and thus, protects the underlying implant substrate from scratching under high loads.

1. Introduction

Hip replacement (HR) treatments have improved significantly over the last two decades, overcoming the challenge of higher revision surgery. The selection of implant materials is the key issue in minimising the revision rate. Titanium (Ti) and its alloys are extensively used as hip implants as they offer excellent mechanical strength, chemical inertness and high biocompatibility properties (Ramakrishnaiah et al., 2017; Ozan et al., 2017; Choudhury et al., 2016). Ti-6Al-4V alloy has received recent attention due to its relatively low Young's modulus compared to other metals, which helps to avoid the stress shielding effect after implantation (Ghosh and Abanteriba, 2016; Afrin et al.,). However, the elastic modulus of the alloy is still much higher than that of cortical bone, leading to aseptic loosening and premature implant failure (Fousová et al., 2017). To overcome this problem, the development of a new titanium β alloy is a noteworthy approach (Mussot-Hoinard et al., 2017). Although several studies have reported new systems with much lower stiffness, they are not identical to bone (Niinomi et al., 2012; Santos et al., 2016). Selective Laser Melting (SLM), an additive manufacturing technique, makes it possible to produce porous structures to minimise Young's modulus (Bartolomeu et al., 2017), an essential advantage for an implant. SLM provides controlled and interconnected pores which play an important role in creating strong bonds between the powder particles (Tan et al., 2017). This technique offers a rapid production rate with high utilisation of materials, and the macrostructure can be graded in a controlled manner (Bartolomeu et al., 2017). The SLM method facilitates the production of complex shapes over a short period with a uniform distribution of density, a homogeneous structure and minimal post-processing requirements. Hip implants can be produced directly from a CAD model using this technique (Wauthle et al., 2015), resulting in savings in cost and time. However, the widespread application of SLM is constrained due to limitations for long-term use of the product in a biological environment. Manufactured product using this technique has a high surface roughness resulted by few partially-melted particles on the surface. Consequently, the surface becomes more hydrophobic due to high surface roughness, leading to

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unfavourable protein adsorption (Dylla-Spears et al., 2017). Moreover, unmodified Ti-based materials can gradually stimulate the formation of a fibrous layer even after several years of implantation. Therefore, the fibrous layer interacts with the living tissue and leading to a progressive loss of osseointegration (Roos-Jansåker et al., 2003; Chouirfa et al., 2017). Sometimes implant surface itself creates a preferential site for bacterial adhesion and leads to inflammatory disease. The gradual loss of supporting bone due to inflammatory disease is one of the major reasons for implant failure. It is evident that untreated SLM fabricated titanium alloy surfaces are not able to establish strong chemical bonding with the surrounding biological tissues. Proper osseointegration of the joint not only enhance the hip replacement surgeries but also helps enormously to improve the quality of life for patients enlarging the lifetime of artificial hip implants. Hence, surface modifications are needed in order to obtain sufficient integration of the implant. Surface modifications help to achieve the desired properties by tailoring the physical/chemical properties of the surface. Surface modification techniques improve the wettability, biocompatibility and mechanical properties of the surface (Ghosh et al., 2016).

Most importantly, low friction and high wear resistance are desirable for artificial hip implants while the high roughness of 3D printed Ti-6Al-4V surface would have an adverse effect on the useful life of implants. Various surface modification techniques such as plasma treatment, heat treatment and surface coating are usually applied on SLM fabricated sample to improve the mechanical properties of the surface. Controlled surface modification on SLM manufactured sample is very complicated. As a result, commonly used mechanical methods such as sandblasting and grinding or physical methods such as thermal spraying and ion implantation might not be effective in a homogeneous surface treatment (Liu et al., 2004; Zavareh et al., 2014). However, chemical etching (CHE) and electrochemical polishing (ECP) could be applied to obtain a controlled and homogeneous roughness of the treated surface. Pyka et al. (2012) showed a significant reduction in surface roughness using a combination of CHE and ECP with HF-based solutions. Moreover, the HF-based solution helps to remove weakly attached partially-melted particles from the surfaces by chemical etching. Few studies on biochemical modification aim at in order to obtain faster osseointegration and bone adhesion (Kirmanidou et al., 2016; Puleo and Nanci, 1999). Surface modification incorporating bioactive biomolecules and/or biocompatible polymers could be the pertinent solution to enhance the osseointegration and wear resistance of SLM fabricated implant. However, polymer coating arises poor adhesion between the substrate and the coated materials. Thus, it could be easily delaminated and decrease the useful life of the implants.

A research group in Japan recently introduced a new surface modification technique known as 'surface grafting' (Ishihara et al., 2015) which creates covalent bonding between the grafting material and the substrate. A method of direct grafting of Ti with sulphonate groups has recently been published by a polymer group in France (Chouirfa et al., 2016). Michiardi et al. (2010) also reported that a high number of osteoblasts were cultured on a Ti surface grafted with a phosphonic group polymer. Researchers reported that controlled protein adsorption and cell adhesion could protect hip implants from progressive loss of osseointegration (Karazisis et al., 2017; Migonney et al., 2013). The use of biocompatible poly (2-methacryloyloxyethyl phosphorylcholine) (PMPC) polymer on a highly cross-linked polyethylene (CLPE) during the grafting process has revealed a new area of research. The PMPC-grafted layer offers a phospholipid-like layer that mimics the articular cartilage of artificial hip joint (Moro et al., 2015, 2014). PMPC grafting offers the following benefits; it forms a hydrated lubricating layer; it possesses excellent biocompatibility and anti-bio fouling ability (Moro et al., 2010); it provides the unique surface properties of high lubricity, low friction, anti-protein adsorption and high cell adhesion resistance (Kyomoto et al., 2010a). However, there are limitations to the use of PMPC on CLPE. Moro et al. (2009) reported that water adsorption of PMPC-grafted CLPE surfaces mainly occurs at the CLPE liner. The use of CLPE may, therefore, have a negative effect on the performance of the PMPC grafting, reducing the productive life of the implant. Due to the significant improvement of 3D printed implants considering the mechanical properties, PMPC polymer grafting on 3D printed Ti-6Al-4V might offer a solution to inhibit biofilm formation and to improve the adhesion between metal implant and peri-implant tissues.

It is well known that a CLPE cup/liner is coupled with metallic or composite head materials in an artificial hip implant. The challenge remains to develop polymer grafting on 3D printed metal parts. However, the development of polymer grafting SLM fabricated Ti-6Al-4V has not been studied. The purpose of this study is to develop a new polymer grafting process to improve chemical bonding between the grafted layer and the substrate. Present study focussed on the characterisation of a polymer grafted layer to analyse the covalent bonding between the substrate and MPC polymer. In this work, a combination of several relevant surface characterisation techniques such as scanning electron microscopy (SEM), 3D optical profiler, energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) were performed to well-understand the production process of different polymer grafting techniques and finally it helped in optimising the grafting techniques.

2. Experimental

2.1. Materials

Rectangular Ti-6Al-4V implant with the dimensions of $8 \times 6 \times 3$ mm (XYZ) was fabricated using a SLM (SLM 250 GmbH, Germany) machine using Ti-6Al-4V powder (ASTM Grade 23, ELI, TLS Technik GmbH & Co., Bitterfeld-Wolfen, Germany) with an average particle size of 25–45 µm. The composition of Ti-6Al-4V powder is presented in Table 1.

The powder bed was preheated to 200 °C and all processing performed in an argon environment with less than 0.01% Oxygen, to prevent oxidation and degradation of the material during the process. All samples were fabricated at 0° inclination with respect to the building direction of the SLM process. The details of selected SLM processing parameters are shown in Table 2.

Samples were polished following standard grinding and polishing procedures and cleaned using acetone and ethanol. MPC monomer powder (product no: 730114-5G) and inhibitor removers (Product no.: 306312-12EA) were purchased from Sigma Aldrich.

2.2. Grafting procedure

Prior to the grafting process, all Ti-6Al-4V implants were cleaned in an acetone bath followed by cyclohexane and isopropanol bath. Kroll's reagent (2% hydrogen fluoride (HF) (Sigma), 10% nitric acid (HNO_3) (Sigma) and 88% distilled water (dH_2O)) was then used to remove the non-uniform oxide layer. The samples were cleaned five times with dH_2O to ensure the absence of HF and HNO_3. The washed samples were immersed in a Piranha solution (sulphuric acid (H_2SO_4)/hydrogen peroxide (H_2O_2) 10:20v:v) for the formation of peroxide radicals. In the first stage, samples were immersed in 10 mL H_2SO_4 (100%), then stirred for 1 min, followed by the addition of 20 mL H_2O_2 (30%) and a further 3 min of stirring. The color of the solution was altered due to an

Table 1
Composition of ELI Ti-6Al-4V powder.

Compositions of alloying elements (wt%)							
Ti	Al	V	Fe	C	N	O	H
balanced	6.47	4.08	0.17	0.008	0.009	0.1	0.002