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Toward 3D printed bioactive titanium scaffolds with bimodal pore size distribution for bone ingrowth

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Abstract

Inkjet 3D printing as a versatile rapid manufacturing method was utilized for making titanium scaffolds with customized pores and geometry. A suitable binder/powder/solvent system was employed to make titanium printable and the parts were subjected to a firing process for strengthening. Mechanical stiffness of the part was tailored by varying printing and sintering parameters to meet that of the bone. Since titanium is inherently bioinert, the bioactivity of the parts was enhanced by surface modification of internal channels by electrochemical deposition of hydroxyapatite or hydrothermal treatment to form titania on the surface.

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1. Introduction

Additive manufacturing (AM) is a collection of techniques for mouldless free form fabrication of 3D components by computer controlled sequential delivery of energy and/or material to specified points in space to produce the component [1-3]. Although additive manufacturing is a well-known technology for concept modeling and visualization, utilizing of this technology for manufacturing functional parts is currently a very new topic. New technologies provide this opportunity to rapidly manufacture functional parts, with the same or even superior properties to that of bulk products. Currently, AM techniques for metals are paving the path toward applications in the near-net shape fabrication of complex geometries with tailored mechanical properties for biomedical, automation and aerospace sectors [3-5]. Biomedical sector is looking for some unique advantages in additive manufacturing techniques, such as customizing shape and geometry of implants, manipulating with pore size and its geometrical distribution, modifying mechanical properties by creating porous structures and patient oriented designs [3,6-9].

Metals have so far shown the greatest potential to be the basis of implants for long-term load-bearing orthopaedic applications, owing to their excellent mechanical strength and resilience when compared to alternative biomaterials, such as polymers and ceramics. Particularly, titanium and its alloys have been widely used in orthopaedic and dental devices because of their excellent mechanical properties and biocompatibility. In order to perform like natural bone, bone implants should match the mechanical properties of natural bone. The mismatch of the mechanical properties could result in "stress shielding" when the mechanical properties of the implant is in excess of the properties of bone.

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Bone tissue scaffolds must provide initial sufficient mechanical strength and stiffness to oppose contraction forces, and later for the remodelling of tissue. In regenerating load-bearing bone tissues, additional issues relating to the scaffolds' mechanical properties have to be resolved [10].

With the advent of electron beam melting (EBM), direct metal laser sintering (DMLS), selective laser melting (SLM), selective laser sintering (SLS), laser engineered net shaping (LENS) and laser aided additive manufacturing (LAAM) processes direct replication of metallic structures has become a reality [10]. Creating pores in the CAD design is one of the strategies to manipulate the stiffness of implants. The range of materials used with these advanced manufacturing technologies has also increased over time, broadening the spectrum of applications [5,10-12].

Currently stainless steel, titanium and its alloys have been successfully manufactured using the above techniques. Although these technologies are capable to make precise components with properties close to that of bulk material, the high capital cost of the equipment prevents these technologies to find an appropriate position in small and medium manufacturing industries. Inkjet 3D printing is one of the rapid manufacturing techniques which can provide some unique advantages over other AM technologies for metals [1]. In this technique instead of using laser or electron beam to melt the powder, an ink cartridge, print a binder layer by layer on top of a powder bed. The parts can be subsequently sintered in a furnace to obtain necessary strength. Much lower capital cost of the equipment and capability to control sintering process via the subsequent thermal cycle are some advantages of the inkjet 3DP method. Although precision of the parts out of inkjet 3DP is not as good as SLM or EBM, for biomedical applications the precision of the parts is not that critical. So, inkjet 3DP is a suitable technique for low cost rapid manufacturing of metallic components for biomedical applications.

Although titanium is a biocompatible material, it is not considered as bioactive and in case of bone tissue engineering or implant stabilization titanium material has no or little effect on fast growing and good attachment of cells to the implant. Surface modification technologies can alleviate this problem and promote bone adhesion and cell ingrowth [13]. Currently, most surface modification techniques such as HA coating, or biomimmetic coatings are done on plane substrates using techniques such as plasma spraying, Sol-gel, electrochemical deposition, hydrothermal treatment and electrophoretic deposition.

Although titanium can be rapidly manufactured using additive manufacturing techniques, modifying the surface or internal channels of scaffold or porous material can be utilized in order to push the technology one step further.

In this work, a feasibility study on manufacturing of titanium scaffolds using inkjet 3D printing method is presented. By optimization of process, porous titanium parts with mechanical properties close to that of bone are obtained. The surface and internal channels of scaffold is coated by TiO_2 and HA by using a hydrothermal treatment and electrochemical deposition respectively.

2. Experimental

2.1. 3D printing of titanium

A schematic of 3D printing process for manufacturing functional components has been shown in Fig.1. The process starts with preparation of powder material. In this stage, Titanium powder with spherical shape and certain particle size is dry mixed with PVA, a water soluble polymer. The mixing is carried out using a ball mill mixer or vibratory mill for 8-10 hr. Zirconia balls with diameter of 20 mm are used to facilitate the mixing process. After preparation of powder mixture, the parts were created using a ZPrinter 310 Plus. A view of the machine has been shown in Fig.1. The CAD files were created using an Autocad or SolidWorks software package and converted to an STL file to feed into machine using the company software. The depositing binder used was Deionized water which is dispersed through a printhead provided by HP. In 3D printing process, a print head travels over a bed of loose powder upon which it prints the cross-sectional data. The powder is distributed accurately and evenly across the build platform by using a feed piston and platform, which rises incrementally for each layer. The layer thickness we used in this research was adjusted to 0.1 mm. A roller mechanism spreads powder fed from the feed piston onto the build platform. This process repeats until the whole model built up completely. After printing completed, the samples are left overnight in powder bed in order to get enough strength. Then the parts are taken out and put in an oven at 50-70°C for at least 1 hr. The samples are taken out for de-powdering. The samples are put in a tube furnace for debinding and sintering in Argon environment at a temperature between 1000 to 1350°C for 2 hours. Debinding and sintering profile has been shown in Fig.1.

Using the above techniques, titanium scaffolds with interconnected porosity were prepared and characterized using scanning electron microscopy and mercury porosimetry. Young's modulus of the scaffolds was measured in the compression mode using printed cylinders or cubical scaffolds.