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Calcium phosphate coatings: Morphology, micro-structure and mechanical properties

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Abstract

Many biomedical implant coating systems consist of micro-deposited calcium phosphate droplets thermally sprayed onto a commercially pure Ti (CP Ti) substrate. In this study, the morphology of solidified droplet “splats” was examined using Scanning Electron Microscopy (SEM). The topography of splats sprayed onto substrates at room temperature (25 °C) and preheated to 100 °C and 300 °C was investigated. The splat shape was found to be strongly dependent on substrate preheating temperature. A homogeneous deposit density of amorphous calcium phosphate in splats deposited onto the cold substrate was confirmed by micro-Raman spectroscopy, whereas a very early stage of re-crystallization was detected using Transmission Electron Microscopy (TEM) for splats deposited onto 300 °C preheated substrates.

TEM in conjunction with Focused Ion Beam (FIB) revealed the splats' ultra micro-structure. Correlation of Atomic Force Microscopy (AFM) with these results enabled links between different types of micro-structures and true splat contacts with the substrates to be shown. Splats deposited onto the substrate at 300 °C showed generally well-adherent interfaces. The established presence of a thin layer of native oxide on this polished and preheated surface could serve to enhance the splat-substrate adhesion.

Nano-indentation revealed that splats deposited onto the substrates at room temperature and 100 °C have similar hardness and elastic modulus values; however, preheating the substrate up to 300 °C improved these micro-mechanical properties.

These combined findings promote further understanding of the extrinsic properties of the bulk calcium phosphate coating.

Keywords: C. Mechanical properties; Calcium phosphate; Morphology; Microstructure

1. Introduction

Thermal spray coatings are formed from individual molten particles that spread and solidify to create single solidified droplets as they impact on a substrate. The flattened and hardened particles take various shapes and are called “splats”. They represent the building blocks of a whole coating. Coating characteristics are dictated by the manufacturing process, but enhanced understanding of the desirable characteristics requires consideration of the geometrical form, micro-structure and micro-mechanical properties. It is the first layer of splats which determines the coating-substrate adhesion, while the coating cohesion is determined by the nature of the inter-splat contact. Although research has been directed towards bulk coatings, a recent emphasis has examined individual splats as a means to obtaining a deeper understanding of coating properties [1–4].

Splat morphology has an important effect on coating quality and is a function of process parameters such as particle size, impact velocity [5], and substrate condition [6]. It is also related to the substrate temperature [7,8]. Preheating the substrate prior to thermal spraying can prevent splashing and also reduce the gas that may become trapped between the splat and the substrate. The first analytical model of particle flattening was developed in 1983 [9] and succeeding work has been either experimental [10] or numerical modeling [11]

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in nature. Most studies on the effect of substrate temperature on the morphology of single splats have investigated High Velocity Oxy-Fuel (HVOF) or plasma spraying [12,13]. Little work has been done on splats generated by other thermal spray processes such as flame spraying, in which powders are injected into a flame torch of lower temperature and velocity than that of the HVOF and plasma spraying methods.

The first part of the current study examines the effect of substrate preheating on splat morphology of calcium phosphate coatings produced by the flame spraying method. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a biocompatible material resembling the mineral component of bone and teeth, and finds application in forming functional coatings on biomedical implant devices. In this study, hydroxyapatite powder particles are deposited onto commercially pure titanium (CP Ti) substrates at room temperature, 100 °C and 300 °C. The aim is to establish the minimum temperature where a disk splat is formed without any splashing, i.e., the “transition temperature”, as first defined by Fukumoto et al. [14]. Disk splats produce nearly fully dense coating, while splashed splats produce highly porous coating and are desirable for cell proliferation [15].

Research on the micro-structure of single splats of molten calcium phosphate is limited. The coating obtained mainly comprises hydroxyapatite, but other crystalline and amorphous calcium phosphate phases are also present. The micro-structure of thermally-sprayed hydroxyapatite splats and the formation mechanism of micro-pores within the splats has been investigated using TEM [16]. In the present study, attention is given to the effect of preheating the substrate with regard to the splat micro-structure.

The primary interest of many studies, however, has been the bonding of the coatings to substrates, which is determined by the strength of the bond between the first splat and the coated surface. As a fundamental approach to determining coating reliability, the third aim of this study is to consider the bonding between individual splats and the substrates. Exposing the interface using a conventional cross-section preparation technique is a complicated task. The FIB apparatus offers the possibility of preparing such cross-sections. Only a few reports on FIB-assisted cross-sectioning of a splat are available to date [17–19].

Measurements of mechanical properties such as hardness and elastic modulus have been performed to understand and improve the coating quality for long-term stability of an implant material. This study examines the micro-mechanical properties of splats using nano-indentation techniques. Nano-indentation methods have been successfully developed for testing single solidified micro-sized deposits [3,4,20].

2. Experimental procedures

2.1. Substrate preparation

The commercially pure titanium (CP Ti) substrates were surface finished by grinding with a semi-automatic polisher using SiC papers (800, 1200 and 2500 grit), followed by mirror polishing on a Dur surface instrument (Struers, Denmark) with 3 μm and 1 μm diamond suspensions. The flat surface was cleaned in an ultrasonic bath with isopropyl alcohol to remove any remaining residue.

2.2. Feedstock powders and coating production

Hydroxyapatite powder (CAM implants, Netherlands) was sieved to a particle size of 30 ± 10 μm. Characterization has been documented in a different paper that has used the same powder [21]. This powder was delivered from the powder feeder (Metco 3MP, Sulzer Metco, Wohlen, Switzerland) into a flame spray torch (Metco 5P, Sulzer Metco, Wohlen, Switzerland) operated with acetylene and oxygen, with air as a carrier gas at a rate of 3 g/min. This relatively low powder feed rate allowed the particle flux to be controlled so that the likelihood of producing individual, non-overlapping particles was enhanced. A typical production feed rate of 25 g/min would produce similar particle morphologies; however, individual characteristics would be confounded due to mutual interactions. The polished substrates were positioned 13 cm from the torch and the powder sprayed onto the CP Ti, with the surface at room temperature or preheated to 100 °C and 300 °C before coatings, to produce flattened solidified droplets with a round shape and minimal splashes. Details of reference samples (i.e. amorphous calcium phosphate and sintered hydroxyapatite) have been documented in an early study [4].

2.3. Micro-Raman spectroscopy

Micro-Raman provides a capability to identify the bonding within calcium phosphates and distinguish between different crystalline phases. This is crucial with thermally sprayed hydroxyapatite powders that can undergo phase decomposition or form an amorphous phase under rapid cooling conditions. The micro-deposit was located with a 100 × objective in the optical microscope and analysis was conducted using a Raman Renishaw RM1000 micro-spectrometer (Renishaw, UK) with an excitation wavelength of 514 nm and a spectral resolution of 1 cm^{-1}. Spectra were recorded within the range of 800–1100 cm^{-1} to show the most intense peak for calcium phosphates.

2.4. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

The calcium phosphate splat surface was observed using a conventional SEM (ZEISS SUPRA 40VP). The sample was gold coated using a DYNAVAC CS300 coating unit before being mounted on pin-type aluminum SEM mounts with double-sided conducting carbon tape. AFM (MFP-3D, Asylum Research) was performed to determine the topography of deposited droplets.