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Plasma sprayed hydroxyapatite coatings: Understanding process relationships using design of experiment analysis

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ABSTRACT

The biocompatibility and osteoconductivity of hydroxyapatite (HA) coatings have led to their use in a wide range of applications in dentistry and orthopaedics. One such application is for the uncemented fixation of implants, where coatings are commonly applied to titanium implants using a plasma thermal spraying process. The spraying process is affected by a large number of parameters leading to highly complex process–property–structure relationships. In a step forward from one-at-a-time analyses, this study used Design of Experiment (DOE) methodology to investigate the simultaneous effects of key plasma spray process parameters on hydroxyapatite coatings for biomedical applications. The effects of five plasma spray process parameters (current, gas flow rate, powder feed rate, spray distance and carrier gas flow rate) on the roughness, crystallinity and purity of hydroxyapatite coatings was determined using a fractional factorial design. The results of this study enabled identification of consistent and competing influences within the process and the identification of some first order interactions. In particular, the diffuse particle size of the HA feedstock powder was found to influence the responses observed within the parameter range investigated. The roughness of HA coatings was found to relate to the particle velocity and the degree of particle melting occurring, with higher coating roughness resulting when current was high, gas flow rate was low and powder feed rate was high. Highest coating crystallinity resulted at high current, low spray distance and low carrier gas flow rate. Under these conditions deposition of larger HA particles resulted leading to higher amounts of bulk crystalline material and the low spray distance increased the substrate temperature allowing amorphous material to recrystallise. Coating purity relates directly to thermal decomposition of the particles within the plasma jet with a high purity coating resulting at low particle temperatures *i.e.* at the lower ranges of powder feed rate, spray distance and carrier gas flow rate. This study thus brings greater clarity on the effects of plasma spray process parameters on the properties of resultant hydroxyapatite coatings.

1. Introduction

Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is a bioceramic with a composition similar to that of the mineral component of bone. It is biocompatible and osteoconductive, allowing the growth on bone cells on its surface [1,2,3,4,5]. As a result of its favourable biological properties it has been used successfully for many applications in dentistry and orthopaedics. One such application is as a coating applied to hip implants, where it provides implant fixation. The most commonly used method for the production of HA coatings is the atmospheric plasma spraying (APS) process [6,7]. This is a thermal spray process in which powder particles are melted in a plasma jet and propelled towards the substrate material. The process involves passing a readily ionised gas through an electric arc, formed between a cathode and an anode, resulting in the formation of a plasma jet. The plasma formed is unstable and quickly recombines releasing a large amount of thermal energy. Particles are fed into this high temperature jet, melted and propelled at high velocities towards the substrate. Temperatures involved can potentially be in excess of 15,000 °C depending on the selected process parameters [8,9,10]. The process has been used for many years to apply of a variety of coatings used to protect surfaces from severe harsh environments, such as, wear, corrosion and thermal effects.

Atmospheric (air) plasma spraying (APS) is a complicated process, affected by as many as 50 parameters, and for this reason the process–property–structure relationship is still not fully understood [11,12]. Clinically, HA coated implants have been found to remain functional *in vivo* for up to 15 years [13]. HA coatings are naturally resorbed in the body, releasing calcium and phosphorus ions needed to enable

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replacement of the coating by ingrowing bone tissue over time; however, delamination or rapid dissolution due to coating instability can lead to short-term implant failure [2,14,15]. The stability of HA coatings has been shown to be largely affected by its crystallinity and purity [3]. Highly amorphous coatings dissolve more quickly leading to the rapid weakening and disintegration of the coating [3,16]. Coatings with a high degree of crystallinity have lower dissolution rates and are thus more stable *in vivo* [11]. The production of HA coatings using APS has added complexities relating to the decomposition of HA at high temperatures leading to the formation of less stable calcium phosphate phases, such as α-tricalcium phosphate (α-TCP), β-tricalcium phosphate (β-TCP), tetracalcium phosphate (TTCP) and calcium oxide (CaO) [17–20]. Control over the phase purity of HA coatings is thus critically important. In terms of requirements for biomedical applications, ISO standards for hydroxyapatite coatings specify a requirement for a crystallinity of >45% and a purity of >95% [21]. In addition, early biological responses to HA coatings are influenced by the surface roughness of the coating which affects osteoblast cell attachment and thus bone growth on the coating once it is implanted into the body. Whereas fibroblasts and epithelial cells prefer smoother surfaces, osteoblasts attach and proliferation better on rough surfaces [22,23]. It is thus clear that in order to improve implant life, the tailoring of the properties of HA coatings is necessary [24,25]. This can only be achieved through a clearer understanding of the spraying process.

Numerous studies have investigated the effects of varying process parameters on various properties of HA coatings [6,25–37]. Contradictions exist within the literature, for example, increased power or current was found by Tsui et al. [30] and Sun et al. [28] to lead to a decrease in the purity and crystallinity of HA coatings. However, Yang et al. [31] found crystallinity to increase with increasing spray current. Dyshlovenko et al. [38–39] and Cizek and Khor [40] report net power to have the greatest influence on crystallinity. One method that has been successfully used in order to establish the relationship between process parameters and the properties of a resultant coating is the Design of Experiment (DOE) technique. DOE studies of a variety of plasma sprayed coatings have been carried out, including alumina [11,41], titanium dioxide [42,43], zirconia [44,45], titanium nitride [46] and alumina–titania [11,47]. DOE experimental techniques have also been applied in the investigation of the complex process relationships involved in plasma sprayed hydroxyapatite coatings [39–40,48–53]. While these studies have brought about some clarity to the relationships between the spray process parameters and resultant HA coating properties, further understanding of these relationships is required. In this study, a Design of Experiment (DOE) methodology has been used in order to gain additional understanding of parameter interaction and desirable parameter ranges for plasma spraying of HA coatings. The specific objectives of the study were to assess the effects of varying five process parameters: current (A), gas flow rate (B), powder feed rate (C), spray distance (D) and carrier gas flow rate (E), on the crystallinity, purity and roughness of plasma sprayed hydroxyapatite coatings; key properties that influence coating stability and cellular response upon implantation.

2. Experimental methods

2.1. Materials

Titanium alloy, Ti6Al4V, was selected as the substrate material in this study as it is typically used in femoral implants as the receiving substrate for HA coatings. Discs, 10 mm in diameter with a thickness of 2 mm, were used. The discs were grit-blasted prior to spraying at a pressure of 5 bars and an angle of incidence of 75°, using pure white aluminium oxide (Al_2O_3) grit with a particle size of 500 μm (mesh 36), selected due to its biocompatibility. After grit blasting, loose grit particles were removed using high pressure air. The discs were then cleaned for 5 min in an ultrasonic cleaner. The average surface roughness (Ra) of the discs was determined, using the Surftest 402 surface profilometer, to be approximately 3.2 μm.

The HA powder used for the coating process was Captal 60–1 Thermal Spraying HA powder (Plasma Biotal Ltd., UK). This powder is reported by the manufacturer to have an average particle size of 45 μm. Particle size analysis was carried out using the Malvern Mastersizer particle size analyser to determine the particle size distribution. Powder morphology was examined using scanning electron microscopy (SEM) (LEO 440 Stereo Scan, Leica, UK), using a current of 150 pA, accelerating voltage of 15 KeV and a magnification range of 50–200×. The surface area of the powder was determined using Micromeritics GEMINI BET surface area analyser (Georgia, USA). Powder particle density was determined using the Helium Pycnometer (Micromeritics, Georgia, USA).

2.2. Experimental design

The experiment was designed using the statistical software, Design-Expert 7.0 (Stat-Ease Inc., Minneapolis, USA). A 1/4 fraction fractional factorial design (2^{5-2} design) was used to investigate the effect of various process parameters (factors) on the properties of HA coatings. Five factors were investigated, current (A), gas flow rate (B), powder feed rate (C), spray distance (D) and carrier gas flow rate (E). Two levels were selected for each parameter, based on parameters levels that are currently reported in literature (N1–N8) [26–31,39,50,54]. In addition, three centre point experiments were included to provide a measure of process stability and inherent variability while also checking for curvature (N9–N11). The parameter ranges selected are detailed in Table 1. The design consisted of 11 experiments, details of which are given in Table 2. The experiments were carried out in random order to ensure that systematic errors did not influence the results.

A polynomial equation was used to describe the relationship between the experimental factors and each response (Eq. 1):

$$Y = \beta_0 + \sum_{i=1}^{5} \beta_i X_i \quad (1)$$

where Y is the response, β_0 is the mean value of the response, βi represents the coefficient of the variable Xi.

The results obtained from the study were analysed using the Design Expert software. The main affects on each response were modelled using the backward selection method to eliminate insignificant terms (P-value ≤ 0.01). The analysis of variance (ANOVA) test was used to determine the statistical significance of the developed equations. Statistical measures, R^2, Adjusted R^2, Predicted R^2 and Adequate Precision, were used to determine the adequacy of the resultant equations. The most important of these measures is the R^2 value, which is a number between 0 and 1 and should be greater than 0.6 in order to indicate an adequate equation [55].

2.3. Plasma spraying

Plasma thermal spraying was carried out using a Sulzer Metco 9 MB plasmatron fitted with a 3 M7-GH nozzle (Sulzer Metco, Winterthur, Switzerland). High purity argon was used as both the plasma forming gas and the powder carrier gas. No secondary gas was used. A traverse

Table 1
Parameter ranges selected for the screening experiment.

	Low level (−1)	High level (+1)
A — Current (A)	450	750
B — Gas flow rate (slpm/scfh)	33/70	61.4/130
C — Powder feed rate (g/min)	10	20
D — Spray distance (mm)	80	120
E — Carrier gas flow rate (slpm/scfh)	4.7/10	9.4/20