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Spatial and depth-resolved studies of air plasma-sprayed hydroxyapatite coatings by means of diffraction techniques: Part I

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ABSTRACT

Hydroxyapatite coatings (HAp, $Ca_{10}(PO_4)_6OH_2$) were deposited by air plasma spraying onto Ti6Al4V substrates and investigated to determine the depth-dependent behaviour of phase composition, crystallinity, and residual stress using diffractometric techniques. Through-thickness characterisation was carried out by conventional X-ray and synchrotron radiations in reflection and transmission geometries. Results showed HAp together with its thermal decomposition products, tetracalcium phosphate (TTCP), tricalcium phosphate (TCP) and calcium oxide to be present throughout the coating thickness. Quantitative phase identification employing Rietveld refinement showed HAp and TTCP to be the two major phases, with the former decreasing with depth whilst the latter increases. The largest changes were observed adjacent to the coating-substrate interface region. Crystallinity investigation showed a similar trend, revealing a more crystalline near-surface region and increasing amorphisation toward the coating-substrate interface. Residual stress investigation revealed the normal components σ_{11} and σ_{33} to be tensile and compressive, respectively. The stresses relax and increase to respective minimum and maximum within the first 145 μm. With further penetration depth, both normal stress components became tensile.

1. Introduction

Hydroxyapatite (HAp), owing to its similarity to the mineral component of bone, has been extensively studied as a candidate material in biomedical applications, ranging from filling of bone cavities [1] and artificial eye components [2] to coatings for hip and dental implants for improved biological fixation [3]. However, the poor mechanical properties of hydroxyapatite limit its bulk utilisation in fully load-bearing applications. In such cases, the material is applied as a coating on metallic substrates such as Ti, Ti alloys and CoCrMo, thereby combining the excellent mechanical properties of the metal with the osseointegration ability of the bioactive, i.e., osteoconductive bioceramic material [4,5]. There is a plethora of coating techniques applied to depositing hydroxyapatite [6]. Although on an industrial scale thermal spraying is still the technique of choice to deposit hydroxyapatite powder on the metallic substrate (see, for example [7–12]), the high temperature of the plasma generally results in thermal decomposition of the material, leading to reduction in crystallinity [13] and introduction of undesirable thermal decomposition products [14], respectively. The latter include phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP), and sometimes calcium oxide. These phases are known to be susceptible to dissolution in simulated body fluids [15,16] and thus may compromise the mechanical stability and integrity of the coating. In addition, higher amounts of cytotoxic calcium oxide will impede osseointegration.

Although extensive investigations have been carried out on HAp coatings [6], the bulk of the work has focused on the near-surface region, i.e. the region in immediate contact with living tissue. For instance, coating investigation employing 8-keV conventional laboratory X-rays to study the effect of simulated body fluid on phase composition of plasma sprayed HAp [17] and residual stresses [10,18], mechanical properties of the coating [19], the effect of heat treatment on phase changes and crystallinity [20] have all been limited to about the first 20 μm of the coating. Probing the coatings with protons, e.g. in micro-PIXE for element distribution analysis [21] leads to an even shallower depth penetration. Depth profile investigations carried out thus far have been few and far between. Of those investigations, mainly destructive techniques such as layer removal methods were employed [22]. This of course has an inherent potential drawback in that sample preparation may affect some aspects of the results, in particular stress measurements. Other techniques also focussing on the coating surface include scanning

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electron microscopy for microstructure characterisation [23]. Although these studies provided crucial information albeit depth limited, their usefulness has been reduced by lack of quantification. In this work, results are presented of a comprehensive spatial and depth-resolved investigation of phase composition, crystallinity, and residual stress distribution of air plasma-sprayed HAp coating employing non-destructive X-ray and synchrotron radiations. The forthcoming part II of the study will present similar results extended to solid rod samples designed for fatigue tests.

2. Materials and methods

2.1. Sample preparation

Hydroxyapatite powder (CAPTAL 90, batch P215, Plasma Biotal Limited, Tideswell, Derbyshire, UK) with size distribution of 120 ± 20 μm was plasma-sprayed onto medical grade Ti6Al4V alloy supplied by Biomaterials Limited, North Yorkshire, UK. The substrates were 5 mm thick discs cut from a 20 mm diameter rod. Prior to spraying, they were grit-blasted with alumina particles of irregular shape with sizes ranging between 0.5 mm and 1 mm. Subsequently, the substrates were cleaned ultrasonically for 10 min at 40 °C, using a 10% Tickopur® solution in deionised water. Plasma spraying was performed without substrate cooling under atmospheric conditions, using a PT M-1000 (Plasmatechnik, Wohlen, Switzerland) system equipped with a Sulzer Metco F4 MB plasmatron. The powder was injected externally into the plasma, 90° to the direction of the plasma jet axis. Details of the coating parameters are reported in Table 1.

2.2. Near-surface coating characterisation

For coating characterisation, X-ray diffractometry available at NECSA's X-ray laboratory was employed. Phase identification measurements were carried out using a Bruker D8 ADVANCE diffractometer equipped with a theta-theta goniometer. Beam optics included a Goebel mirror on the primary side and Soller slits on the secondary side. Measurements were carried out at the geometrical centre of the as-received sample's top surface. A copper tube operated in line focus mode was used for analysis and the diffracted data were collected using a compound silicon strip technology-based 1-D Lynx Eye detector. Qualitative and quantitative phase identification was carried out using the manufacturer's proprietary Eva v13 software (BRUKER AXS, Diffrac^{plus} Basic Evaluation Package Release 2007) and TOPAS v4.2 software (TOPAS-ACADEMIC v4.2, Coelho Software, Brisbane, Australia, 2007). The latter was also used for crystallinity evaluation. Additional phase identification measurements were carried out at the 2nd generation Laboratório Nacional de Luz Síncrotron (LNLS) facility, Campinas, Brazil. Measurements were done, on the same sample with the same orientation, using 11 keV synchrotron radiation at the D10A-XRD2 beamline. The beam source was a 4°-bending magnet with energy resolution ΔE/E of 1.3×10^{-4} [24]. Data acquisition was done with a 0-D-scintillation detector. The beam size at the sample surface was 0.6 mm height by 1 mm width.

Table 1
Plasma spray parameters (slpm = standard litres per minute).

Parameter	Value
Primary plasma gas (Ar)	45 slpm
Secondary plasma gas (H_2)	6.5 slpm
Carrier gas (Ar)	5 slpm
Relative powder feed rate	20% of maximum
Relative hopper stirrer rotation rate	40% of maximum
Stand-off distance	90 mm
Plasma power	30 kW
Horizontal speed	0.1 m/s
Traverse speed	0.017 m/s

The corresponding near-surface residual stress was investigated using Bruker's D8 Discover equipped with a 1/4 Eulerian cradle with the primary side optics including a graphite monochromator and a 0.8 mm collimator. Measurements were done using a copper tube operated in point focus mode, employing the Ψ-tilting method. Sample was measured in side inclination geometry with sample rotation axis in the diffractometer plane. For a full stress tensor determination, measurements were done at eight tilting angles $\psi = 0°, 10°, 20°, 30°, 40°, 50°, 60°$ and 70° and six azimuth orientations, $\phi = 0°, 45°$and 90°, and $\phi + 180 = 180°, 225°$ and 270°. The latter allowed measurement at negative tilt angles. Diffracted data was collected using a 2-D Våntec 500 gas detector. The HAp diffraction peak corresponding to the crystallographic plane (213) at d = 1.841170 Å was used to measure residual strain. Assuming validity of the Kroner-Eshelby grain interaction model, the X-ray elastic constants (XECs) $S_1 = -2.48$ and $\frac{1}{2}S_2 = 11.5 \cdot 10^{-6}$ MPa^{-1} were used for stress determination. The XECs were calculated using reported literature single crystal constants for hydroxyapatite [25]. Data was analysed with LEPTOS v6 software.

2.3. Bulk characterisation

For through-thickness characterisation of the coating down to the coating-substrate interface, diffraction measurements in transmission geometry were carried out at the 3rd generation Advanced Photon Source's X-ray Operation and Research 6-ID-D beamline at Argonne National Laboratory (ANL), using high energy (70–130 keV) X-rays. The beamline was an undulator monochromatic radiation source with an energy resolution ΔE/E of 4×10^{-4}. High energy X-ray (100 keV, λ = 0.123331 Å) were utilised in the experiment.

The short wavelength allows covering the full diffraction range of both coating and substrate. A small beam spot of 35(V) × 400 (H) μm, obtained by slits manipulation, was used in probing the samples. Prior to the experiment, a thin slice of the original sample was prepared. This was required to minimize intensity attenuation and possible stress relaxation, to optimise detector resolution, and to ensure the presence of sufficient material required for satisfactory statistics. Although intensity attenuation was not a critical factor considering the penetration power of the radiation, a thick slice would compromise detector resolution [26]. Fig. 1 shows the attenuation lengths of the synchrotron radiation in HAp and Ti6Al4V alloy as a function of the photon incidence energy. It is evident that at 80 keV ($8 \cdot 10^4$ eV), the radiation significantly penetrates both materials with little attenuation. Taking into account the above-mentioned factors, a compromise thickness of 6 mm was selected. The slice was cut using an ISOMET cutter, equipped with a

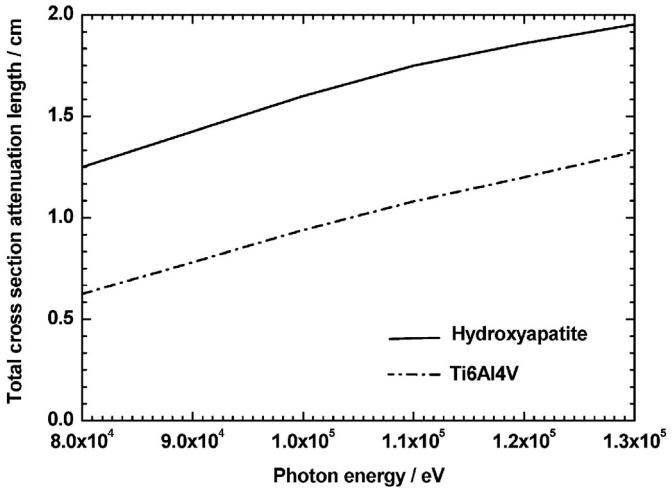

Fig. 1. Total cross-section attenuation length as a function of incidence energy: a) HAp coating, b) Ti6Al4V alloy.