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, $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$) 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.

Keywords: Plasma-sprayed hydroxyapatite coatings, X-ray diffraction, Quantitative phase analysis, Degree of crystallinity, Residual stress.

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., osseoconductive 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 micrometres 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 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 Biotall Limited, Tideswell, Derbyshire, UK) with size distribution of $120 \pm 20 \mu\text{m}$ 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 $\Delta E/E$ 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.

The corresponding near-surface residual stress was investigated using a Bruker's D8 Discover equipped with a $\frac{1}{4}$ 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 $\psi = 0^\circ, 10^\circ, 20^\circ, 30^\circ, 40^\circ, 50^\circ, 60^\circ$ and 70° and six azimuth orientations, $\phi = 0^\circ, 45^\circ$ and 90° , and $\phi + 180 = 180^\circ, 225^\circ$ and 270° . The latter allowed measurement at negative tilt angles. Diffracted data was collected using a 2-D Vântec 500 gas detector. The HAp diffraction peak corresponding to the crystallographic plane (213) at $d = 1.841170 \text{ \AA}$ 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 $\frac{1}{2}S_2 = 11.5 \cdot 10^{-6} \text{ MPa}^{-1}$ 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 $\Delta E/E$ of 4×10^{-4} . High energy X-ray (100 keV, $\lambda = 0.123331 \text{ \AA}$) were utilised in the experiment.

The short wavelength allows covering the full diffraction range of both coating and substrate. A small beam spot of $35(\text{V}) \times 400(\text{H}) \mu\text{m}$, 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]. Figure 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 diamond blade. A sample slice was cut from the same batch but was not the same sample as measured with the 8 and 11 keV radiations. To minimise cutting-induced heating, the wheel was set at a low-speed of 150 rpm and the sample was continuously lubricated in emulsion. Figure 2 shows the geometry of the as-received sample and the piece cut for high-energy diffraction measurements. Stepwise measurements, with the incident beam at 90° , were carried out by moving the sample into the beam path in steps of $35 \mu\text{m}$, covering both the coating thickness and part of the substrate. The diffracted radiation was recorded using a 345-mm diameter 2-D MAR image plate detector (marXperts GmbH, Norderstedt, Germany; pixel size of $100 \times 100 \mu\text{m}^2$) located approximately 1m downstream from the sample as shown in Figure 3. The total time for read-out and erasure was 108 s. The sample was measured at three lateral points labelled x0, x4 and x8 along the edge of the cut slice (Figure 2c), separated by 4 mm.

Measurements were done with the 400 μm long side of the beam parallel to the coating surface with normal stresses σ_{11} and σ_{33} directions coinciding with coating-substrate interface line and the through-thickness direction respectively, as shown in Fig 4. Only one azimuth orientation was measured.

2.4 XRD crystallinity determination

The relative crystallinity of the coating was calculated as the ratio of the integrated intensity of all crystalline peaks I_c and the total integrated intensity I_t , i.e., the sum of amorphous ‘hump’ and crystalline peaks,

$$\% \text{crystallinity} = \frac{I_c}{I_t} \quad (1)$$

where $I_t = I_a + I_c$, with I_a integrated intensity of the amorphous hump and I_c integrated intensity of the crystalline phases. Although adopted from the procedure developed by Keller and Dollase [27], in which the mass fraction of ACP, x in a mixture of unknown proportions was obtained from the measured amorphous ‘hump’ area that was found to be a linear function of its proportion in the sample (see also [28]), no corrections on the measured intensity ratio values in the current study was done due to the unavailability of reference mixture data. The method also deviates from conventional ISO 13779-3 and ASTM F2024 standards

To confirm the accuracy of the amorphous content of the sample, the background contribution from the direct beam was subtracted from the diffraction data before crystallinity calculations. The background pattern intensity E was taken with a direct X-ray beam without the sample. The diffraction patterns of the sample were taken as a function of depth $S(z)$ and corrected according to

$$S_c(z) = S(z) - T(z) * E \quad (2)$$

where T is the sample transmission. This was measured as a function of depth, and at this energy (100 keV), the transmission was found to be ~ 1 .

2.5 Theory of 2D XRD stress determination

The stress in a polycrystalline sample effects a change in the spacing of the diffracting lattice planes. Whereas in 1-D diffractometry this change is reflected by a shift of the corresponding diffraction peak position, in 2-D X-ray diffractometry (XRD²) the presence of residual stresses within the sample is reflected by the distortion of the corresponding Debye rings. The strain tensor ε_{ij} , determined in the sample coordinate system, and the distortion of the diffraction ring in a particular direction $(\eta, 2\theta)$ are related by the two-dimensional fundamental equation

$$f_{11} \cdot \varepsilon_{11} + f_{12} \cdot \varepsilon_{12} + f_{22} \cdot \varepsilon_{22} + f_{13} \cdot \varepsilon_{13} + f_{23} \cdot \varepsilon_{23} + f_{33} \cdot \varepsilon_{33} = \ln\left(\frac{\sin \theta_0}{\sin \theta}\right), \quad (3)$$

where f_{ij} are the strain coefficients, $\ln\left(\frac{\sin \theta_0}{\sin \theta}\right)$ is the diffraction cone distortion for a particular $(\eta, 2\theta)$ position, and θ_0 is the peak position for the stress-free material. Using Hooke's law and assuming isotropic conditions, the above equation can be expressed in terms of the stress tensor components as

$$p_{11} \sigma_{11} + p_{12} \sigma_{12} + p_{13} \sigma_{13} + p_{22} \sigma_{22} + p_{23} \sigma_{23} + p_{33} \sigma_{33} = \ln\left(\frac{\sin \theta_0}{\sin \theta}\right), \quad (4)$$

where p_{ij} are constants. This equation can be reduced further in the case of a biaxial stress state. The theory of stress determination employing XRD² has been well documented, see for example Refs. [29, 30].

2.6 Data analysis

Before the data could be analysed, the MAR image plate detector was calibrated for geometrical effects and distortions. This was done using a silicon standard sample measured under the same conditions as those of the sample to be investigated, and the data was analysed with the help of an automated MATLAB program [31]. The process was carried out in three steps:

a) The program first bins the data into radially symmetric multiple slices of required thickness with the 2-D data subsequently being transformed from polar coordinates to a rectangular coordinate system. A macro was written to carry out this step. A small step size increases the chance of observing deviatory strain, however, at the expense of an increase in processing time and a reduced number of grains contributing toward a given diffraction peak.

b) The reduced data are η -integrated for selected diffraction rings into a 1-D diffraction profile, and fitted with a mathematical function to determine peak positions. Figure 5 shows an example of η and 2θ integration of an image plate diffraction ring. In the case of a biaxial stress state, the peak position at $\eta = 0^\circ$ will be identical to $\eta = 180^\circ$, and similar for $\eta = 90^\circ$ and $\eta = 270^\circ$. In order to obtain the strain tensor components, the peaks were fitted as a function of detector azimuth. The fit assumes a linear d vs. $\sin^2 \psi$ behaviour as a starting assumption. This means that three-quarters of the values for a complete diffraction ring are not unique and therefore serve to improve the counting statistics.

c) Lastly, all peak positions calculated by the previous step are used to solve the 2-D fundamental equation (3) using least-square fitting. The error in peak positions calculated from the previous step is propagated to calculate the error of strain components as well as of the χ^2 goodness-of-fit tests. The latter is the normalized sum of the squares of the differences between the fit of the strain equation and the peaks positions. This error was calculated

assuming a Gaussian error distribution, which is a built-in function in the MATLAB fitting routine.

3. Results

3.1 SEM

Figure 6 shows scanning electron micrographs of the hydroxyapatite feedstock powder used for deposition. The micrograph shows the grains to be irregular in shape with closer examination revealing the grains to constitute a rather loose agglomerate of small crystallites, resulting in a porous microstructure (Figure 6b). Figure 7a shows a typical scanning electron micrograph of the surface of plasma-sprayed HAp coatings that is characterised by smooth glassy, i.e. amorphous regions, cracks running across the surface, and by solidified splats of fully or partially melted individual particles. In addition to the above-mentioned features, fine particles, pores and gaps, formed as a result of poor cohesive bonding between the splats, can be observed across the coating thickness as shown in Fig. 7b.

3.2 Phase analysis

Figure 8a-c show the diffraction patterns of the feedstock powder and coatings collected with 8, 11, and 100 keV radiations, respectively. Figure 8c is a superposition of the pattern collected at different depths below the coating surface including the near-surface regions of the substrate. As reported by other investigators (for example Refs. [32, 33], the high temperature of the plasma jet induces thermal decomposition of the starting HAp material, resulting in the formation of TTCP, TCP, and occasionally CaO. Phase identification results at the probed depths below the coating surface show these phases to be present (Fig. 8).

The two top patterns of Fig. 8c show Ti6Al4V to be the predominant phase at a depth of 245 μm indicating that probing extended to the substrate. Figure 9 shows the variation of the phase composition of the plasma-sprayed coatings with depth at the three measured points across the coatings thickness. The last two diffraction patterns in Fig. 9c were omitted due to difficulties with refinement achieving convergence. The results were corrected for amorphous contributions within the coating by subtracting amorphous content. As evident from the figure, HAp and TTCP are the two major phases with the former showing some concentration fluctuation in the near-surface region. Figure 10 shows the variation of the phase composition with depth averaged over the three lateral measuring points. The two major phases present show an opposite trend with depth, indicating a decrease of HAp from around ~75 wt% at the near-surface region to ~15 wt% at the coating-substrate interface region, a reduction of about 80%. The low data point of HAp at 35 μm can be considered an outlier. In contrast, with exception of the first two points the TTCP concentration increased from ~6 wt% to ~8 wt% (an increase of ~33%). Both β -TCP and CaO concentrations decreased strongly within the first 40 μm before remaining more or less constant to a depth of 180 μm , and then decreasing again.

3.3 Crystallinity

The feed stock powder was crystalline, with the manufacturer reporting a relative value of 100%. Figure 11a shows the variation of coating crystallinity with coating depth at the three measurement points chosen. As for HAp, the crystallinity shows some scatter within the first 40 μm that converges with depth below the surface. Figure 11b shows the averaged crystallinity over the three measured points across the spraying direction as a function of coating depth, obtained by conventional X-ray at 8 keV as well as 2nd generation synchrotron radiation at 11 keV and 3rd generation synchrotron radiation at 100 keV.

The data show a reduction in crystallinity with depth, with the near-surface region predominantly crystalline at ~93% and decreasing steadily with depth to ~ 53% at the coating-substrate interface region, a decrease by 43%. This is in accord with the notion that the molten hydroxyapatite particles impinging at the substrate surface will be quenched rapidly and solidify **predominately** as amorphous calcium phosphate (ACP), whereas later arriving particles cool more slowly owing to the limited thermal conductivity of the already deposited hydroxyapatite layer (see for example, Ref. [33]). The apparent increase in crystallinity at ~210 μm can be attributed to the underlying substrate peaks, as seen in the diffraction pattern in Fig. 8c.

By examining the data shown in Fig. 11, it is noteworthy to mention that there exists a significant difference between the crystallinity values measured with a conventional X-ray diffractometer and with synchrotron radiation. This may indeed signify that conventional diffractometer measurements prescribed by standards such as ASTM F2024, allowing the pattern to be acquired on an as-deposited coating, and ISO 13779-3 that requires that the coating be detached and ground into powder to account for through-thickness variations of crystallinity, should be taken with a grain of salt. It may well be that the "true" crystallinity is lower than conventional diffractometer measurements would suggest. This fact could have severe repercussion on the validity of quality control of biomedical implant coatings that impose minimum requirements on coating crystallinity as expressed in the ISO 13779-3 standard.

3.4 Residual stress analysis

Figure 12 show the $\sin^2\psi$ plots for the six azimuth angles collected with the 8 keV radiation.

The plots are generally linear with some curvature at low tilts. No clear indication of psi splitting is observed. Figure 13 reports the distribution of residual stress components and the stress amplitude ($\sigma_{11} - \sigma_{33}$) measured at the three lateral points chosen and their variation with depth below the coating surface. Since only one azimuth orientation was measured, only three stress components, i.e. σ_{11} , σ_{13} , σ_{33} could be determined. The stress amplitude ($\sigma_{11} - \sigma_{33}$) is a useful means to eliminate misalignment effects between different samples. The plots can generally be divided into two regions, I and II, above and below the central axis (around 140 μm), respectively. The three stress components at the different lateral points show agreement within error bars in region I, but significant scatter in region II, predominately at the coating-substrate interface region.

Figure 14 shows the distribution of the average stress, determined using conventional $\text{CuK}\alpha$ X-ray and synchrotron radiations. The two independent stress components σ_{11} and σ_{13} are generally small and indicate tensile stress and clockwise direction of shear, respectively in both I and II regions that relax steadily in the former to a neutral axis around $\sim 110 \mu\text{m}$ followed by a steady increase in region II to a maximum of $\sim +46$ and $\sim +23$ MPa, respectively. The normal component σ_{33} indicates compressive stress that increases with depth to ~ -34 MPa in the same region. With further depth, the stress state changes from compressive to tensile, increasing with depth to a maximum of $+56$ MPa.

5. Discussion

5.1 Phase composition

The observed distribution of phases and the variation of crystallinity with depth can be explained in terms of the temperature gradient that exists during coating build-up. Plasma-sprayed coatings are composed of layers deposited splat-by-splat during each pass made by the torch. Hence, the entire coating is composed of a multitude of lamellae/splats deposited one after the other and on top of each other, respectively. Those hydroxylapatite particles that are fully melted during plasma spraying will solidify during cooling on the substrate surface. Considering that the first deposited layer heats up the substrate to a temperature T_1 , the second to a temperature T_2 , the n^{th} to a temperature T_n , the net effect will be the development of a phase composition commensurate with such a temperature gradient across the coating thickness. For the first lamella deposited on the pristine substrate, the cooling rate of a molten HAp particle on the comparatively cold metallic substrate is maximum. The large temperature difference between the impinging molten drops and the substrate leads to high cooling rates in excess of 10^6 K/s (for example Refs. [33, 34]). The nature of the resulting phases therefore depends on the cooling rate. As nucleation is impeded during rapid quenching, high cooling rates produce amorphous calcium phosphate (ACP). The phase compositions shown in Figs. 7 to 9 are consistent with previously reported work (see for example Refs. [13, 35, 36]). The data scatter observed within the first 35 μm among the three measured points can be attributed to a possible dissolution of coating material due to the emulsion lubricant used during cutting of the slice. The apparent increase in crystallinity beyond 175 μm shown in Fig. 11 is attributed to contribution from the overlapping substrate peaks.

Since each subsequent deposit heats up the previously deposited layer, the temperature difference as well as the cooling rate decrease continuously. On the one hand, the increasing temperature during deposition means less quenching of the subsequently arriving droplet, resulting in reduction in amorphicity, i.e. increased crystallinity as the coating thickens. On the other hand, the incoming droplet will “anneal” the previously quenched phases, provided the temperature is high enough. Under such condition, the always-present thermal decomposition products may reconstruct to form HAp. Reheating of powders consisting of thermal decomposition products quenched from 1500 °C produced direct reconstruction of HAp from TTCP at around 400°C whilst α -TCP transformed to β -TCP react with $\text{Ca}(\text{OH})_2$ to form more HAp [37, 38]. In addition, despite the high temperature encountered during plasma spraying, ACP still contains substantial amounts of protons and OH^- ions as revealed by electron energy loss spectroscopy (EELS; [33]). These residual ions are thought to act as a driving force for the (partial) crystallisation of ACP to hydroxylapatite during cooling [13].

A number of possible factors influencing the data can be attributed to the significant discrepancies among the TTCP concentrations obtained with the 8 keV and 11 keV, and the high-energy synchrotron radiation as shown in Fig 10b. As indicated in section 2.2, these factors include i) measurements carried out with conventional and synchrotron radiations were done on two samples from the same batch, ii) sample orientation using conventional X-ray radiation focused on the geometrical centre of the samples whilst that of the synchrotron radiation was slightly off-centre, and iii) the irradiated area using the former was at least 45 times larger than using the latter.

Another important aspect to consider pertains to coating thickness. In the present work, relatively thick coatings were deposited and investigated. It is well known that a thin HAp layer (<50 μm) yields better adhesion compared with thicker coatings [39], owing to reduced

residual coating stress [40]. However, this stress will be quickly relaxed in the course of bone integration. Thicker coatings ($\pm 150 \mu\text{m}$) show substantially reduced adhesion strength but may be required in some instances to ensure a more permanent bond to guarantee implant stability by a lasting biological effect. This is particularly evident when during an endoprosthetic replacement operation involving an exchange of the implant the cortical bone matter has been previously damaged, often in concurrence with an undesirable geometric configuration of the implant-supporting bone [41]. In this special case, a thin, quickly resorbed calcium phosphate coating will not be sufficient to sustain the required large-scale bone regeneration. Hence, thicker coatings will be required to stimulate bone reconstruction over longer times.

5.2 Residual stress profile in HAp coatings

The distribution of the stress observed in regions I and II of Fig. 14 can be attributed to a net sum of stresses originating from quenching (also known as intrinsic stress), differential thermal mismatch of the coating and substrate as expressed by the difference in the coefficient of thermal expansion (also known as thermal or cooling stress), and the stress arising from volume change associated with phase transformation. However, based on the slight change in the content of TTCP i.e. 6wt% to 8wt%, as shown in Fig 10b, it can be concluded that contribution of the latter to the final stress is minimal. With both the quenching and thermal stresses tensile due to, frozen-in splat contraction during cooling to substrate temperature upon deposition and the higher thermal coefficient of the deposit ($\alpha_{\text{HAp}} = 11.5 \times 10^{-6} \text{ K}^{-1}$) compared to that of the substrate ($\alpha_{\text{Ti6Al4V}} = 8.9 \times 10^{-6} \text{ K}^{-1}$) [42] respectively, the final stress state across the coating is expected to be tensile. However, with ceramic coating materials, the quenching stress, as predicted and reported by Tsui *et al* [43,44] and Kuroda *et al* [45], is expected to be small and constant over the coating thickness. The stress distribution shown in

Figs 13 and 14 are therefore mainly related to the contribution of thermal stress with the maximum magnitude that can be accommodated without coating failure given by,

$$\sigma_{th} = \left[\frac{E}{1-\nu} \right] (\alpha_c - \alpha_s) \Delta T, \quad (5)$$

where E is Young's modulus, ν is Poisson's ratio, α_c and α_s are the thermal expansion coefficients of coating and substrates, respectively and ΔT is the temperature difference between the final and initial states. Note that depending on the sign of $(\alpha_c - \alpha_s)$, the thermal stress can be tensile or compressive.

The observed σ_{11} stress distribution in the current study, see Fig. 14a, is consistent with the above argument as well as Finite Element Analysis computational results obtained by Cofino *et al.* [46]. Although the 8 keV obtained stress value is slightly higher, it is integrated within the trend. The higher value can be attributed to the fact that being near-surface, the magnitude is not affected by the deposition of subsequent layer(s) hence more tensile. On the other hand the observed σ_{33} stress distribution, see Fig. 14c, is consistent with synchrotron measurement findings reported in the same study [46], which showed, in general, a compressive stress state across region I and part of region II, turning tensile with increasing depth below the surface. Given that the top surface of the sample is a free surface and restraint of the through-thickness deformation is not expected; the significant σ_{33} values in Fig. 14c can therefore not only be attributed to Poisson effect; various other factors also contribute. These include effects of thermal gradient across coating thickness during deposition [47], a possible gradient in quenching stress due to e.g. different interlamellar bonding, intralamellar microcracking, and open gaps well as different mechanical strengths of the intralamellar materials. This is evident from the heterogeneous microstructure observed across the coating thickness, see Fig. 7b. The possible discrepancies and differences relating to the non linear distribution of stress components, Figs 13 and 14, as opposed to the linear through-thickness stress distribution predicted by the analytical model of Tsui *et al.* [44], based on constant quenching stress

assumption, can be attributed to the presence of amorphous calcium phosphate and the observed non uniform microstructure amongst other. The results obtained in this study also show consistency with findings of Tsui *et al* [43] who, using curvature technique, reported tensile stress of around 40 MPa for HA coated Ti-6Al-4V substrate sprayed at 36 kW and are comparable with ultimate tensile strength of HAp coatings, which ranges between 40 and 60 MPa [48].

6. Conclusions

Depth-resolved studies employing both conventional X-rays and synchrotron radiations were carried out on air plasma-sprayed HAp coatings.

- a) Phase identification results showed thermal decomposition products to be present throughout the coating thickness. Quantitative Rietveld analyses showed the distribution trend with depth of the two major phases, HAp and TTCP, to be opposite. The amount of hydroxyapatite decreased from ~53wt% at the near-surface region to ~15 wt% adjacent to the coating-substrate interface region, whereas the amount of tetracalcium phosphate increased from ~6 wt% to 8 wt% in the same range with significant changes occurring in the first 60 μm .
- b) The crystallinity distribution shows a trend similar to HAp, decreasing from 93% in the near-surface region to 53% at the coating-substrate interface region.
- c) The stress components σ_{11} and σ_{13} are tensile and indicate clockwise direction of shear, respectively and relax to zero within the first 110 μm , but increase with further depth steadily to reach maxima at $\sim +20$ and $\sim +10$ MPa, respectively. In contrast, σ_{33} is compressive and first increases to ~ -30 MPa slightly deeper in the coating, but

changes further in depth to tensile, reaching a maximum of +15 MPa at the coating surface.

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Tables

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

Figures

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

Figure 2: Geometry and dimensions of the sprayed HAp coating a) original disc, b) cut slice and c) cut slice indicating measured points.

Figure 3: Schematic diagram illustrating high-energy X-ray diffraction measurements in transmission geometry; the axes triad indicates the three directions.

Figure 4: Schematic diagram illustrating the orientation of the X-ray beam in relation to the sample and the normal stress directions.

Figure 5: a) Typical 2-dimensional diffraction pattern illustrating η and 2θ -integration, b) converted conventional 1-D pattern.

Figure 6: Scanning electron micrographs of hydroxyapatite feedstock powder taken at different magnification.

Figure 7: Scanning electron micrograph of a typical as-sprayed HAp coating: a) top surface, b) cross-section.

Figure 8: Diffraction patterns of HAp coatings, superposed with feedstock powder, plotted in d-spacing: a) 8 keV conventional X-ray, b) 11 keV 2nd generation synchrotron radiation, and c) representative 100 keV 3rd generation synchrotron radiation of the different lateral points; the marked spacing indicates measurement points below the surface. The patterns show the presence of HAp (o), tetracalcium phosphate (#), tricalcium phosphate (•) and CaO (*).

Figure 9: Variation of phase composition in wt% with depth measured at the three lateral points perpendicular to the spraying direction: a) HAp, b) TTCP, c) β -TCP, and d) CaO.

Figure 10: Variation of phase composition (spatial average of Fig. 9 superposed with conventional X-ray, 2nd and 3rd generation synchrotron data) of HAp coatings with depth: a) HAp, b) TTCP, c) TCP and d) CaO.

Figure 11: Crystallinity variation in HAp coating: a) at the three lateral points perpendicular to the spraying direction and b) averaged spatially resolved data obtained by conventional X-ray (8 keV), 2nd and 3rd generation synchrotron radiations (11 and 100 keV).

Figure 12: $\text{Sin}^2\psi$ plots for the different azimuth angles collected with 8 keV radiations.

Figure 13: Variation of residual stress tensor components with depth at the three lateral points perpendicular to the spray direction: a) σ_{11} , b) σ_{13} , c) σ_{33} and d) stress amplitude $\sigma_{11} - \sigma_{33}$. The dotted lines show the change from compressive (region I) to tensile (region II) mode beyond 120-140 μm .

Figure 14: Variation of residual stress tensor components, averaged over the lateral points perpendicular to the spray direction, with depth at the three: a) σ_{11} , b) σ_{13} , c) σ_{33} and d) stress amplitude $\sigma_{11} - \sigma_{33}$. The dotted lines indicate the change from compressive (region I) to tensile (region II) mode beyond about 120 μm .

Table 1:

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	0.1m/s
Traverse speed	0.017 m/s

Figure(s)

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 6

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Figure 11

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Figure 13

Figure 14