Strontium-substituted hydroxyapatite coatings deposited via a co-deposition sputter technique

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A B S T R A C T

The bioactivity of hydroxyapatite (HA) coatings can be modified by the addition of different ions, such as silicon (Si), lithium (Li), magnesium (Mg), zinc (Zn) or strontium (Sr) into the HA lattice. Of the ions listed here, strontium substituted hydroxyapatite (SrHA) coatings have received a lot of interest recently as Sr has been shown to promote osteoblast proliferation and differentiation, and reduce osteoclast activity. In this study, SrHA coatings were deposited onto titanium substrates using radio frequency (RF) magnetron co-sputtering (and compared to those surfaces deposited from HA alone). FTIR, XPS, XRD, and SEM techniques were used to analyse the different coatings produced, whereby different combinations of pure HA and 13% Sr-substituted HA targets were investigated. The results highlight that Sr could be successfully incorporated into the HA lattice to form SrHA coatings. It was observed that as the Sr content of the SrHA sputtering targets in the study were increased (increasing Sr content), the deposition rate decreased. It was also shown that as the Sr content of the coatings increased, so did the degree of preferred 002 orientation of the coating (along with obvious changes in the surface morphology). This study has shown that RF magnetron sputtering (specifically co-sputtering), offers an appropriate methodology to control the surface properties of Sr-substituted HA, such as the crystallinity, stoichiometry, phase purity and surface morphology.

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1. Introduction

The nature of the initial interaction between calcium phosphate (CaP) thin films and osteoblasts can be mediated by the outermost surface properties of that material. As such, the phase, crystallinity, stoichiometry, composition and morphology of the CaP surfaces are seen as key parameters that must be accurately controlled in order to influence their potential biofunctionality with respect to osteoblasts. Hydroxyapatite [HA–Ca_{10}(PO_4)_{6}(OH)_{2}] has been extensively studied due to the structural and chemical similarities demonstrated with the main inorganic constituent of bone tissue and teeth. However, it is well documented that biological hydroxyapatite, which forms the mineral phases of calcified tissues (enamel, dentin and bone), differ from pure and synthetically produced HA. Biological apatite is comprised of a mixture of calcium phosphate phases, such as tricalcium phosphate (TCP), carbonated hydroxyapatite (CHA) and calcium-deficient hydroxyapatite (CDHA). In this regard, synthetic HA exhibits a Ca/P ratio of 1.67, whereas biological apatite deviates significantly from this value and are known to be calcium-deficient \((Ca_{10-x}(HPO_4)_x(OH)_{2-x})\), with a Ca/P ratio which can be as low as 1.5 [1]. Numerous impurities such as fluoride, magnesium, sodium, potassium, carbonate and chloride can also be found in naturally occurring bone. In addition to this trace amounts of elements such as strontium, barium, copper, zinc, and iron are commonly associated with biological apatite and may be seen as substituents in the apatite structure [2]. Therefore, one approach to control the osteoblastic response of HA coatings, both in vitro and in vivo, could involve the use of substituted HA, incorporating different ions, such as silicon (Si) [3], lithium (Li) [4] magnesium (Mg) [5], carbonate (CO_3) [6], zinc (Zn) [7], silver (Ag) [8], fluoride, (F) [9], chloride (Cl) [10], potassium (K) [11], copper (Cu) [12], sulphate (SO_4) [13], tantalum (Ta) [14], cerium [15] or strontium (Sr) [16] into the HA lattice, in order to mirror the complex chemistry of human bone. Many reports of the use of these substituted materials can be found in the literature, both as bone substitute materials and as coatings [17–19]. Of the different substitutions listed above, strontium substituted hydroxyapatite (SrHA) coatings have received a lot of interest recently as strontium (Sr) has been shown to have the dual benefit of promoting bone formation and reducing bone resorption, in vivo. Furthermore, it has been shown that strontium has the ability to enhance osteoblastic cell replication, to activate the Wnt/β-catenine signalling pathway that will therefore stimulate the formation of new bone through osteogenesis and differentiation into osteoblasts [20–23]. It has also been shown in a number of other studies [24,25] that strontium has the ability...
to inhibit the activity of osteoclasts. It has been reported that the optimum strontium concentration for enhanced osteoblast activity, including proliferation and differentiation could be observed when the substitution of strontium into HA was at a high level of 3–7% [26].

A number of different deposition methods have been investigated to deposit Sr-substituted HA surfaces, including Radio Frequency (RF) magnetron sputtering [16], plasma spraying [27], sol-gel methods [28], pulsed laser deposition [29], micro-arc oxidation [30] and co-blasting [17]. Of the methods highlighted here, RF magnetron sputtering has been shown to be particularly useful for the deposition of Ca-P coatings due to the ability of the technique to provide greater control of the coating’s properties, along with improved adhesion between the substrate and the coating [30–32]. Specifically, RF magnetron sputtering allows co-deposition of multiple target materials simultaneously and provides an alternative and simple method to produce Sr-substituted HA coatings [32]. A previous study by Ozeki et al. focused on the deposition of Sr-substituted HA coatings, albeit it using a single sputtering target of mixed composition (Sr-substituted HA powder) [16]. To date, however, to the best of the authors’ knowledge, there is no available information on the utilisation of co-sputter deposition as a method to deposit Sr-substituted HA surfaces using RF magnetron sputtering, with the primary objective of creating a surface with specific surface chemistry and morphology commensurate with enhanced biofunctionality.

The present work was undertaken in order to study the co-sputter deposition of Sr-substituted coatings from a custom designed RF magnetron sputtering facility utilising three sputtering targets (referred to as sources). In particular, the influence of different target compositions and configurations on the properties of the Sr-substituted sputter deposited coatings produced at a low discharge power level (150 W) were investigated. A low discharge power level was chosen for this study as the quality and consistency of the targets used could be guaranteed throughout the sputter deposition runs. All of the coatings produced were characterised after post-deposition annealing to 500 °C using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and stylus profilometry.

2. Materials and methods

2.1. Substrate preparation

For this study coupons of chemically pure titanium (cpTi), Titanium International Ltd (15 mm × 15 mm × 0.5 mm) were abraded using a succession of 800, and 1200 grade silicon carbide papers. The coupons were twice sonicated for ten minutes consecutively in acetone, isopropyl alcohol and distilled de-ionised water. The abraded coupons were then dried thoroughly in a convection oven at 70 °C for twelve hours.

2.2. Sputtering procedure

Sputtering targets, 76 mm in diameter and 5 mm thick, were produced by dry pressing hydroxyapatite [HA — (Plasma Biotap Caltal-R)] and 13% Biphasic Calcium Phosphate [SrHA — (Himed Inc. NY, USA)] powders (at a load of 40 kN for 10 min with a loading rate of 10 kN per minute). RF magnetron sputtering was performed using a cluster of three high vacuum Torus 3 M sputtering sources in a custom designed system (Kurt J. Lesker Ltd, USA) each operating with a 13.56 MHz RF generator and an impedance matching network (Huettinger, GmbH, Germany). The sources were all mounted at 65° to the substrate surface. For deposition from the sputtering targets onto the cpTi substrates, the RF power in the sputtering system was ramped up slowly to provide an initial break-in phase, thereby minimising any thermal shock effects. The break-in prior to deposition from the HA target was conducted at a ramp rate of 5 Watts (W) per minute (all with the source shutter closed). The base pressure was below 5 × 10⁻⁶ Pa, with an argon gas flow rate (BOC, 99.995%) of between 15–20 Sc cm and a throw distance of 100 mm. To produce the co-deposited coatings with different levels of Sr-substitution, targets combinations in the three source multi-target configuration were utilised as outlined in Table 1. The fragility of the HA and 13SrHA targets limited their power absorption capacity and consequently deposition was performed at 150 W for 5 h under the same atmospheric conditions as were used for the target break-in procedure. The power density for these HA targets was approximately 3.3 W cm⁻². After sputter deposition, the Ca-P coatings were thermally annealed in order to enhance their crystallinity. The samples were subjected to a ramp rate of 5 °C per minute to 500 °C (from room temperature) with a soak time of 2 h and a ramp rate of 5 °C per minute down to room temperature.

2.3. Characterisation of the Ca-P powders and coatings

Fourier Transform Infrared (FTIR) spectroscopy of the samples was carried out using a BIORAD FTS 3000MX Excalibur series instrument with a PIKE Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) accessory. Samples were analysed from 4000–400 cm⁻¹ in absorbance mode at a resolution of 4 cm⁻¹ with 20 scans per sample.

X-Ray Diffraction (XRD) of the samples was performed using a Bruker D8 Discover Diffractometer fitted with a Gobel Mirror. A Cu Kα X-Ray radiation (λ = 1.540 Å) source was employed with diffraction scans obtained at a tube voltage of 40 kV and a tube current of 40 mA. Each diffraction scan was recorded at 20 values from 20–50° with a step size of 0.04° and a scan dwell time for each increment of 30 s. For the grazing incidence angle XRD studies of Ca-P coatings on the cpTi substrates the tube angle was set to 0.75°.

X-Ray Photoelectron Spectroscopy (XPS) of the samples was undertaken using a Kratos Axis Ultra DLD spectrometer. Spectra were recorded by employing monochromated Al Kα X-Rays (hv = 1486.6 electron volts (eV)) operating at 5 kV and 15 mA (75 W). The base pressure was 1.33 × 10⁻⁷ Pa and the operating pressure was 6.66 × 10⁻⁷ Pa. A hybrid lens mode was employed during analysis (electrostatic and magnetic), with an analysis area of approximately 300 μm × 700 μm and a take-off angle (TOA) of 90° with respect to the sample surface. Wide energy survey scans (WESS) were obtained at a pass energy of 160 eV. High resolution spectra were recorded for O1s, Ca2p and P2p and C1s (incorporating the Sr3p peak) at a pass energy of 20 eV. The Kratos charge neutralisation system was used on all samples with a filament current of 1.95 A and a charge balance of between 3.3 and 3.6 V. Sample charging effects on the measured BE positions were corrected by setting the lowest BE component of the C1s spectral envelope to 285.0 eV, i.e. the value generally accepted for adventitious carbon surface contamination [34]. Photoelectron spectra were further processed by subtracting a linear background and using the peak area for the most intense spectral line of each of the detected elemental species to determine the % atomic concentration.

The deposition rate (and thickness) of the different Ca-P coatings were determined using a Dektak 8 stylus profilometer (Veeco Instruments Inc., USA). Measurements were taken across 10 step height positions on each sample created by masking titanium coated silicon substrates with aluminium foil prior to deposition in the sputtering system. A 12.5 μm diameter diamond tipped stylus was employed with scans lengths of 1000 μm at a load of 15 mg.

<table>
<thead>
<tr>
<th>Target configuration</th>
<th>Coating thickness (nm)</th>
</tr>
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<tbody>
<tr>
<td>3HA</td>
<td>445 ± 16</td>
</tr>
<tr>
<td>2HA/15SrHA</td>
<td>341 ± 17</td>
</tr>
<tr>
<td>1HA/25SrHA</td>
<td>248 ± 14</td>
</tr>
<tr>
<td>35SrHA</td>
<td>204 ± 11</td>
</tr>
</tbody>
</table>

Table 1: Target configuration versus coating thickness.
3. Results

3.1. Characterisation of the Ca–P precursor powders

The properties of the HA and the Sr-substituted HA precursor powders were characterised using FTIR, XRD and XPS to determine the nature of the material prior to its use as a target for the sputter deposition of Ca–P coatings.

Fig. 1(a) shows a typical FTIR spectrum of the HA precursor powder in the range 4000–500 cm\(^{-1}\). Absorption bands characteristic of P–O stretching vibrations can be observed between 1080 and 950 cm\(^{-1}\) while O–P–O bending vibrations can be seen between 605 and 550 cm\(^{-1}\) [32]. The bands at 3570 and 632 cm\(^{-1}\) are indicative of O–H stretching and O–H librational bands, respectively [30,31]. In addition to these spectral modes, weak bands associated with carbonate (CO\(_3\)\(^{2-}\)) were observed at 1409, 1434, 1543 cm\(^{-1}\), along with an asymmetrical envelope centred at 869 cm\(^{-1}\) [6]. These results may indicate that this HA material has CO\(_3\)\(^{2-}\) substitution at both the OH\(^-\) (A-site) and PO\(_4\)\(^{3-}\) (B-site) positions [6,33].

Fig. 1(b) highlights the FTIR results for the SrHA precursor powder. Absorption bands characteristic of P–O stretching vibrations can be observed between 1100 and 950 cm\(^{-1}\) while O–P–O bending vibrations can be seen at 610 and 550 cm\(^{-1}\) [31–33]. The weak band at 3567 cm\(^{-1}\) is indicative of an O–H stretching vibration, however the peak expected for the O–H librations around 630 cm\(^{-1}\) is clearly absent. Peaks associated with carbonate (CO\(_3\)\(^{2-}\)) were also observed at 873, and between 1550–1400 cm\(^{-1}\) [6]. The peak observed at 873 cm\(^{-1}\) may also be associated with HPO\(_4\)\(^{2-}\) groups [34,35]. As with the HA powder, the FTIR results for the SrHA powder indicate that this HA material has significant CO\(_3\)\(^{2-}\) substitution in both the A and B sites [6]. It should be noted that the envelope relating to the P–O stretching bands between 960 and 1100 cm\(^{-1}\) for the SrHA powder has significantly lower peak resolution when compared to the HA powder. These observations would be consistent with Sr substituting for calcium (Ca) in the HA lattice [36,37].

The XRD pattern for the HA powder shown in Fig. 2(a) is equivalent to HA, with diffraction peaks observed at 2-theta (2\(\theta\)) values that correspond closely to those indicated for HA from the International Centre for Diffraction Data (ICDD) file #00-09-0432. The peak positions signify that the material contains only HA and no additional impurity phases. The XRD pattern for the SrHA powder is shown in Fig. 2(b). As expected for a Sr-substituted material, the peak positions are shifted to slightly lower 2-theta (2\(\theta\)) values and show significant broadening [36–38].

Fig. 3(a) shows a typical XPS wide energy survey-scan recorded as B.E. [0–600 eV] versus intensity in counts for the HA precursor powder. Peaks corresponding to Ca2s (438.8 eV), Ca2p\(_{3/2}\) (347.5 eV), Ca2p\(_{1/2}\) (351.1 eV), P2p (133.6 eV), P2s (191.1 eV), O1s (531.6 eV), O AugerKLL (764.0 eV) and Ca AugerKLL (963.8 eV) are clearly observed (and further reported in Table 2), and correspond closely to those reported in the literature for HA [31,32]. No other elemental species were detected at least at the detection limits of the instrument (–0.1 at.% concentration). The Ca/P ratio of the HA precursor powder, as determined by XPS was 1.67 ± 0.25 and matched the value for stoichiometric HA (1.67), as shown in Table 3. Fig. 3(b) shows a typical XPS wide energy survey-scan recorded as B.E. [0–600 eV] versus intensity in counts for the SrHA precursor powder. Peaks corresponding to Ca2s (438.8 eV), Ca2p\(_{3/2}\) (347.6 eV), Ca2p\(_{1/2}\) (351.0 eV), P2p (191.0 eV), O1s (531.6 eV), Sr3p\(_{3/2}\) (268.9 eV), Sr3p\(_{1/2}\) (280.1 eV), Ca3s (44.0 eV), O2s (23.0 eV) and Ca3p (25.0 eV) are all clearly evident (as reported in Table 2). The envelope for P2p and Sr3d peaks overlap significantly and can be seen around 133.6 eV. The spectral envelope observed at 133.6 eV consists of an overlap of the Sr3d and P2p peaks because the Sr3d\(_{3/2}\) (133 ± 0.5 eV), Sr3d\(_{5/2}\) (135 ± 0.5 eV) and the P2p (32–133 eV) lines are located so close together. All of these peaks observed correspond closely to those reported in the literature for Sr-substituted HA [39,40]. No other elemental species were detected here for the SrHA powder. The Ca/P ratio, Ca + Sr/P and Sr/Ca ratios of the SrHA powder, as determined by XPS was 1.33 ± 0.24, 2.02 ± 0.33 and 6.69 ± 0.28 respectively. The Sr/Ca + Sr ratio value for the SrHA powder (as shown in Table 3) was slightly below the value expected for this material [16].

However, it should be noted that XPS is a surface analysis technique and can only obtain information from the top 10 nm of any sample.

From these findings it is clear that purity, crystallinity and stoichiometry of the HA powder was as expected and confirmed the presence of HA, which also contained low levels of CO\(_3\)\(^{2-}\) contamination. In comparison,
3.2. Characterisation of the Ca–P coatings

The coatings produced from the HA, and the different SrHA/HA target combinations were analysed using FTIR, XRD, XPS, stylus profilometry and SEM to assess the surface properties after thermal annealing at 500 °C. The as-deposited CaP and Sr substituted CaP coatings were not analysed in this study as previous work by the authors has shown that these surfaces are amorphous and require thermal annealing in order to produce crystalline coatings [31,32]. Therefore, all coatings that are described here are those that have been annealed to 500 °C. The thicknesses of the various different coatings are reported in Table 1. It is observed that as the number of Sr targets utilised in the deposition runs increases the deposition rate decreases significantly.

The FTIR spectrum of the coatings produced from the HA targets (3 HA) were indicative of crystalline HA, as shown in Fig. 4(a). Well resolved P–O stretching vibrations were observed as expected between 1100–950 cm⁻¹. O–P–O bending vibrations are also present between 620–560 cm⁻¹ [31,32]. Hydrogen phosphate bands (HPO₄²⁻) can also be observed at 1120 and 582 cm⁻¹ [32]. A very weak O–H librational band is observed around 630 cm⁻¹ as a weak shoulder, with a further peak associated with O–H groups observed at 3568 cm⁻¹. This peak may be associated with O–H stretching groups within the film [31,32]. The absence of strong OH functional groups, commonly observed at approximately 3632 cm⁻¹ and 3570 cm⁻¹, indicate a degree of dehydroxylation within the Ca–P crystal structure deposited from the HA targets under the conditions employed here. A further peak associated with O–H groups can be observed at 3541 cm⁻¹ and may be associated with loosely bound O–H groups, or disordered water molecules trapped within the coating [40,42]. No peaks indicative of CO₃²⁻ species were observed in the FTIR spectrum for the HA derived coatings. The peak positions in the FTIR spectra for the coatings derived from the 2HA/1SrHA target configuration were largely similar to those observed for the HA derived coating as shown in Fig. 4(b). Furthermore, the OH⁻ peak at around 3570 cm⁻¹ is still clearly present, along with the OH⁻ libration at 632 cm⁻¹. However, the OH⁻ libration is only present as a very weak shoulder in the coatings derived from the 2HA/1SrHA target configuration, which would be expected for a coating where Sr substitutes for Ca in the HA lattice [38,43]. Furthermore, weak CO₃²⁻ bands are observed between 1550–1400 cm⁻¹ and 890–820 cm⁻¹ [6,33]. However, this peak between 890–820 cm⁻¹ may also be due to the presence of HPO₄²⁻ and/or SrCO₃ [43]. The XRD pattern for the 2HA/1SrHA derived coating shown in Fig. 5(b), however, as expected for a Sr-substituted material, the peak positions are shifted to slightly lower 2-theta (2θ) values [44,45]. No significant peak broadening was observed for this particular coating. A similar effect (in relation to lower 2θ peak values) is again observed in Fig. 5(c) for the 2HA/1SrHA and 3SrHA derived coatings, as shown in Fig. 5(c) and (d), respectively. Furthermore, the intensity of the 002 peak appears to increase with increasing Sr content in the coatings. There is also a change in the relative peak intensities of the 211 and 112 peaks with increasing Sr content, as shown in Fig. 5. In the case of all the HA and SrHA derived coatings, no significant amorphous background hump was observed. In addition to this no other Ca–P phases were detected in the XRD pattern for any of the coatings.

The XPS results for the CaP coatings deposited from the HA targets, as highlighted in Figs. 6(a), 7(a)–(d) and Table 2, shows peaks
corresponding closely to those reported for HA in the literature and those obtained for the precursor powder used to produce the sputtering targets [31,32]. The Ca/P ratio for the HA derived coatings were 1.79 ± 0.13, as reported in Table 3. The Ca/P ratio of the HA derived coating is slightly higher than that expected for stoichiometric HA, however, it is line with expectations for coatings produced under the conditions employed here [34–36]. The peak positions reported for all the SrHA derived coatings were all in line with those expected for Sr-doped CaP materials, with clear evidence for the presence of Sr highlighted by the presence of the Sr3p3/2 and Sr3p1/2 peaks at approximately 269.0 and 280.0 eV, respectively [39,40]. These results are clearly shown in Figs. 6(b)–(d), 7(e)–(p) and Table 2. No other elemental species were detected for these coatings. The Ca/P and Ca + Sr/P ratios for the 2HA/1SrHA derived coatings were 1.38 ± 0.24 and 1.46 ± 0.17, respectively (as shown in Table 3). For the 1HA/2SrHA derived coatings, the Ca/P ratio is comparable to the 2HA/1SrHA (1.34 ± 0.24), however, the Ca + Sr/P increases significantly to 1.62 ± 0.45. For the 3SrHA derived coatings both the Ca/P and Ca + Sr/P ratios increase to 1.51 ± 0.11 and 1.95 ± 0.14, respectively (as shown in Table 3). If the Sr/Ca + Sr ratios are also compared for the different Sr-substituted coatings (as shown in Table 3), the ratios increase as the number of Sr targets in the deposition process increases. It is clear from the results highlighted here that with increasing Sr-content in the coatings.

![Fig. 1. XPS Wide Energy Survey Scans (WESS) for (a) HA powder, (b) 13SrHA powder.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak positions—B.E. (eV)</th>
<th>Ca2p1/2/Ca2p1/2</th>
<th>P2p/Sr3d3/2/Sr3d3/2</th>
<th>Sr3p3/2/Sr3p3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA powder</td>
<td>285.0 531.3</td>
<td>347.4/350.9</td>
<td>133.4</td>
<td>–</td>
</tr>
<tr>
<td>13% SrHA powder</td>
<td>285.0 531.6</td>
<td>347.6/351.0</td>
<td>133.6</td>
<td>268.9/280.1</td>
</tr>
<tr>
<td>HA coating</td>
<td>285.0 531.2</td>
<td>347.4/351.0</td>
<td>133.5</td>
<td>–</td>
</tr>
<tr>
<td>2HA/1SrHA coating</td>
<td>285.0 531.5</td>
<td>347.6/351.1</td>
<td>133.6</td>
<td>269.6/279.9</td>
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<tr>
<td>11HA/2SrHA coating</td>
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<td>347.6/351.0</td>
<td>133.5</td>
<td>269.6/279.9</td>
</tr>
<tr>
<td>3SrHA coating</td>
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<td>347.4/350.8</td>
<td>133.4</td>
<td>269.7/279.8</td>
</tr>
</tbody>
</table>
sputtering targets there is an increase in Sr content of the sputter deposited coatings (albeit at lower levels than might have been expected), especially for the 1HA/2SrHA and 3SrHA derived coatings.

SEM was utilised here to determine the surface morphology of each of the different coatings produced. SEM analysis of the abraded cpTi substrate shows a surface that has random abrasion scratches running across its surface (not shown here). These abrasion scratches dominate the substrate surface and can range in width from 0.5 to 2.0 μm. Small hillocks, pits and fissures, which vary in size up to 2.0 μm, are also seen regularly across the surface, particularly between the polishing scratches. The corresponding SEM results for the CaP coating derived from HA targets on the cpTi substrate, as illustrated in Fig. 8(a) shows a relative tendency for the coatings to mimic the substrate topography and to conform to striations and defects produced by the abrasion of the substrate. Again, there is evidence from the SEM to suggest that there has been significant in-filling of the larger pits on the substrate surface, which is typical of previous studies utilising similar RF magnetron sputter deposited calcium phosphate coatings [38]. Furthermore, the SEM analysis of the HA derived coatings as shown in Fig. 8(a) indicates the presence of spherical features of around 150–300 nm in diameter. These spherical features are observed right across the entire surface of the coating, however, they do tend to be more evident around abrasion scratches and surface defects and have dimensions similar to those observed previously deposited on similar surfaces [31,32]. In comparison to this surface, the 2HA/1SrHA derived surface has a significantly reduced amount of spherical features, as can be seen in Fig. 8(b). These features are of similar dimensions and also tend to be found around abrasion scratches and surface defects. For the 1HA/2SrHA and 3SrHA derived coatings very few spherical features are observed on the surface, as illustrated in Fig. 8(c) and (d), respectively. It is evident from these SEM images that as the Sr content of the coatings increases the surface features observed become much less prominent across the SrHA surfaces.

4. Discussion

RF magnetron sputter co-deposition from HA and Sr-substituted HA targets in a tri-source sputtering system was utilised in this study in order to create a range of different SrHA coatings on titanium substrates with varying amounts of Sr. Before sputtering the HA and 13% Sr-substituted HA target materials (SrHA) were analysed using FTIR, XRD and XPS techniques. The purity, crystallinity and stoichiometry of these Sr-substituted HA powders were largely as expected and confirmed the presence of carbonated HA. From the FTIR, XRD and XPS results for the Sr-substituted HA powder (13% substituted HA) it is clear that the purity, crystallinity and stoichiometry of these Sr-substituted HA powders are much less prominent (or totally absent in the case of the OH stretching and librational bands in the FTIR spectra around 3570 cm$^{-1}$ and 632 cm$^{-1}$ becoming much less prominent (or totally absent in the case of the OH$^-$ librational band). Peak broadening, shifting and dehydroxylation are all indicative of Sr incorporation in the HA lattice [43]. The Sr-substituted HA powder also became more dehydroxylated as a result of the presence of Sr, with the OH$^-$ stretching and librational bands in the FTIR spectra around 3570 cm$^{-1}$ and 632 cm$^{-1}$ becoming much less prominent (or totally absent in the case of the OH$^-$ librational band). Peak broadening, shifting and dehydroxylation are all indicative of Sr incorporation in the HA lattice [36]. There is also a significant increase in the intensity of the CO$_3^{2-}$ peaks between 1550–1400 cm$^{-1}$ and at 870 cm$^{-1}$, indicating substitution of both the OH$^-$ and PO$_4^{3-}$ groups by...
Despite this, no significant HPO$_4^{2-}$ peaks were observed in the FTIR spectra for any of the precursor powders as might have been expected for a Sr-substituted CaP material [37].

Typically, Sr substitution for Ca in the HA lattice results in an increase in both CO$_3^{2-}$ and HPO$_4^{2-}$ groups (especially CO$_3^{2-}$ groups) due to the increased lattice strain caused by the larger Sr ions [36,40]. The XRD results for the Sr-substituted powder also highlighted that due to the incorporation of Sr into the HA lattice, the peak positions shifted to slightly lower 2-theta ($2\theta$) values. The peaks also exhibited significant broadening with increasing Sr content as can be observed in Fig. 2. This would be in...
Fig. 7. High resolution XPS spectra for (a–d) HA coating, (e–h) 1Sr 2HA coating, (i–l) 2Sr 1HA coating and (m–p) 3Sr coating.

Fig. 8. SEM images for (a) HA coating (b) 1Sr/2HA coating, (c) 2Sr/1HA coating and (d) 3Sr derived coatings.
line with expectations and is due to substitutional strain in the lattice [35, 36,46]. The XRD results also highlighted that no other CaP phases were detected in any of the Sr-substituted powders. The XRD results for the Sr-substituted HA powders corroborated those results highlighted from the XPS and FTIR analyses confirming that the SrHA powders contain appreciable levels of Sr, with Sr substituting for Ca in the HA lattice. This usually results in structural disorder along the c-axis. It is well documented that a lack of hydroxylation within the HA lattice affects the degree of atomic ordering in HA [45,47]. Interestingly, for the Sr-substituted HA powder used here to produce the sputtering targets, no pronounced 002 preferred orientation was observed in the diffraction pattern. Previous studies on Sr-substitutedapatites have shown that as the Sr content in HA increases, so does c-axis orientation [36]. A typical random crystal-lite orientation was observed for all of the Sr-substituted powders used to produce the sputtering targets in this body of work.

After sputtering these different materials onto the cpTi substrates distinct changes were observed in their surfaces properties as determined using FTIR, XPS, XRD, stylus profilometry and SEM analyses. The surface Ca/P ratio of the thin films deposited from three HA targets was determined to be 1.79 ± 0.13, which is slightly higher than that expected for stoichiometric HA [36,37]. This value is in line with the expectation of coatings produced under the conditions employed here [31,32]. Furthermore, no Sr is detected on the surface of these coatings (as confirmed by the XPS results). The coatings produced from the three HA targets also show the expected 002 preferred c-axis orientation, as determined by XRD analyses. Typically, 002 preferred orientation in HA coatings results in an elevated Ca/P ratio, which is in line with the Ca/P ratio determined here [48]. To add to this, the FTIR results highlight that these coatings produced from the HA precursor powders contain no trace of CO₃²⁻ within the lattice (as might have been expected) but do show evidence of significant HPO₄²⁻ functional groups due to the strong peaks around 1120 and 580 cm⁻¹ (as shown in Fig. 4(a)). The HA derived coatings are also slightly dehydroxylated. In this case, the OH⁻ libration is only observed as a shoulder around 630 cm⁻¹. Typically, it is expected that if HA is dehydroxylated then the charge balance within the crystal structure must therefore be provided by other means. HA is understood to undergo carbonate (CO₃²⁻) substitution within the crystal lattice at multiple sites [45,46]. The FTIR results obtained here cannot confirm the presence (or absence) of CO₃²⁻ groups in the lattice of any of the samples due to the observed specular reflectance in the spectra above 1200 cm⁻¹, therefore a direct determination of CO₃²⁻ substitution cannot be made. However, the XPS analyses do suggest the presence of CO₃²⁻ on the surface of the coatings due to the peak observed around 288–290 eV in the C1s envelope (as shown in Fig. 7(c)). This would suggest incorporation of low levels of CO₃²⁻ substitution in these HA derived coatings. It is assumed that the HA derived coating deposited here is not a calcium deficient hydroxyapatite (CDHA) material [Ca₁₀₋ₓ(PO₄)ₓ₋ₓ(OH)₂₋ₓ] − x, which would result in a material that has a Ca/P ratio less than 1.67 [45]. The presence of a Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ(OH)₂₋ₓ₋ₓ−x species in the HA derived coating is more likely. The slightly elevated Ca/P ratio observed here in the XPS results may also be a consequence of calcium enrichment of the uppermost surface of the HA derived coatings, as has been observed in coatings produced previously under similar conditions [31,32]. This has been described previously, whereby when such surfaces are thermally processed at high temperatures (above 500 °C), weakly bound PO₄³⁻ species are lost as a consequence of thermal processing.

In comparison, the XPS results for the 2HA/1SrHA derived coatings were in line with expectations for a Sr-substituted HA material. Peaks for SrPO₄ and Sr₃P₂O₇ can be clearly observed around 269.6 and 279.9 eV in addition to the expected peaks for a CaP material [31,32, 39]. Figs. 6(b) and 7(e)–(h) show representative wide energy survey scans (WESS) and high resolution spectra for the 2HA/1SrHA derived coatings. The Ca/P ratios (and corresponding Ca + Sr/P ratio) for the 2HA/1SrHA coatings were 1.38 ± 0.24 and 1.46 ± 0.17, respectively, as reported in Table 3. Although the Ca/P ratio does not change significantly for the 1HA/2SrHA coatings, the Sr + Ca/P does increase to 1.62 ± 0.45. For the 3SrHA both the Ca/P and the Sr + Ca/P ratio both increase, as highlighted in Table 3. Furthermore, if the Sr/Ca + Sr ratios of the Sr-substituted coatings are also compared to one another (as shown in Table 3), it is evident that the Sr levels within the coatings increase slightly as the number of targets utilised in the deposition process increases. These results would be in line with expectations when compared to a previous study by Ozeki et al., whereby SrHA coatings were deposited from a single Sr doped HA target [16]. Furthermore, the Sr content of the coatings deposited in that study were lower than that of the original precursor target material and the same trend is observed in this study. Interestingly, as the number of Sr targets in the deposition process increased, the deposition rate appears to decrease significantly, as highlighted in Table 1. This reduced deposition rate with increasing Sr content of the sputtering targets observed in our study would be consistent with expectations, however it does contradict the previous results of Ozeki et al. [16]. These results also highlight the fact that under the conditions employed here, the deposition rate of SrHA materials is lower than that observed for the HA derived coating set. Therefore, the sputter yield for Sr atoms (Atomic Weight (AW) − 88) does not appear to be as high as the Ca (AW − 40) or P atoms (AW − 31). Typically, it would be expected that the Sr atoms undergo less scatter in the plasma due to their atomic weight, however, given the relatively low sputtering power employed in this study it is less likely that all of the Sr atoms have the required energy or momentum to reach the substrate surface (in line with the number of SrHA targets used in the deposition process) [35]. Despite this it should be pointed out that although both studies have considered sputter depositing coatings from HA targets with different amounts of Sr content, the conditions employed in both studies were distinctly different. Specifically, Ozeki et al. [16] employed a single sputtering source (mounted axially to the substrate) whereas in this study, three sputtering sources were employed, each mounted at a 65° angle to the substrates’ surface. Furthermore, the study reported here has employed a co-deposition process with the number of SrHA and HA targets varying between the different deposition runs, as outlined in Table 1. It is therefore possible, that the experimental conditions employed during deposition in this study may have had a significant impact on the dynamics of the sputtering process, and as a consequence, the Sr content and deposition rate for the different coatings produced [32].

Considering all of the results obtained here, this could suggest a formula such as Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ(OH)₂₋ₓ₋ₓ−x for the 2HA/1SrHA and 1HA/2SrHA coatings. The presence of CO₃²⁻, which is not within the formula described here, could be explained by the presence of low levels of SrCO₃ [43]. Weak bands, possibly associated with SrCO₃ were observed between 890–820 cm⁻¹ in the FTIR spectra for all of the SrHA coatings (as shown in Fig. 4(b)–(d)). Alternatively, the presence of small amounts of carbonated CaP materials (such as Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ(OH)₂₋ₓ₋ₓ−x − y(PO₄)₂₋x₋y(PO₄)(OH)₂₋ₙ) in combination with Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ−y(PO₄)(OH)₂₋ₙ (or labile HPO₄ groups) cannot be entirely ruled out for both the 2HA/1SrHA and 1HA/2SrHA derived surfaces. Although the presence of SrCO₃ could be inferred from the FTIR results no SrCO₃ peaks were detected in the corresponding XRD patterns or XPS spectra (at least within the detection limits of the technique) [37]. Therefore, the 2HA/1SrHA and 1HA/2SrHA derived surfaces may be better explained by the formula Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ(OH)₂₋ₓ₋ₓ−x or a combination of Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ−x−y(PO₄)(OH)₂₋ₙ−x with Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ−x−y(PO₄)(OH)₂₋ₙ−x is less as this allows for both a Ca/P and Sr + Ca/P lower than 1.67. The extremely high Ca + Sr/P ratio observed for the 3SrHA derived coatings in this study were perhaps unexpected, when compared to those for the 2HA/1SrHA (1.46 ± 0.17) and the 1HA/2SrHA (1.62 ± 0.45) derived coatings. The formula Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ−x−y(PO₄)(OH)₂₋ₙ−x or a combination of Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ−x−y(PO₄)(OH)₂₋ₙ−x with Ca₁₀₋ₓ₋ₓ₋ₓ₋ₓ(PO₄)ₓ₋ₓ₋ₓ₋ₓ−x−y(PO₄)(OH)₂₋ₙ−x can’t explain the high Ca /Sr/P ratio (1.95 ± 0.14) of the 3SrHA derived coatings.
coatings in isolation. It is likely that this higher than expected Ca + Sr/P ratio could be due to Ca enrichment of the uppermost surface of the 3SrHA coating, with the higher amount of Sr present in the sample likely to be a contributory factor also.

The corresponding XRD results for all of the Sr-substituted coatings highlight that they have peak positions that are shifted to slightly lower 2-theta (2θ) values with increasing Sr content, as can be observed in Fig. 5. In addition the XRD results also show that the SrHA derived surfaces all exhibit a preferred 002 c-axis orientation. The intensity of the 002 peak (and therefore the 002 c-axis orientation) also appears to increase relative to the other peaks (namely the 211 peak) with increasing Sr content in the coatings (commensurate with the number of Sr containing targets in the process increasing). There is also a change in the relative peak intensities of the 211 and 112 peaks with increasing Sr content, as shown in Fig. 5(b) to (d) for the SrHA surfaces. These observations would be in line with previous studies on Sr-substituted HA, whereby it has been shown that as the Sr content in HA increases, so does c-axis orientation [36]. Interestingly, no other Ca-P phases were detected in the XRD pattern for any of the Sr-doped annealed coatings in this study, whereas a study undertaken by Ozeki et al. highlighted the presence of additional unwanted CaP phases after sputtering from Sr-doped HA targets [55]. As highlighted previously, the coatings produced here were deposited using distinctly different experimental conditions, and as such it might be expected that different results were observed between the two studies. In comparison, the SEM results here indicate that as the Sr content of the HA coatings produced here increases, the morphology of the resultant coatings changes, which would be in line with expectations [26,48]. In the results observed here, as shown in Fig. 8, the presence of increased levels of Sr, particularly for the 1HA/2SrHA and 3SrHA coatings appears to inhibit the formation of the regularly distributed spherical features more readily observed for the HA and 2HA/1SrHA derived surfaces.

When these results are taken in combination with the FTIR, XPS and XRD results for the Sr-doped coatings, it is obvious that with increasing Sr content (and an increasing degree of preferred 002 orientation), there are observable differences in the surface morphology (specifically with respect to the size and distribution of surface features). This would be in line with the observations of Capuccini et al. [26], Kim et al. [48], Oliveria et al. [38], and Wei et al. [39]. Other studies, which have specifically studied Sr-substitutedapatite coatings, have contradicted these findings (as a consequence of Sr doping), in that they did not observe any significant difference in the surface morphology between such Sr-substituted surfaces and those produced from pure HA [49]. Again, significantly different experimental methods may explain these observable differences.

Previous work by others has highlighted that a preferred 002 orientation can be beneficial and enhance the cellular response in vitro [48]. Further to this, it has also been reported that with standard CaP materials (namely HA), the bioactivity attributed to Ca-P materials originates due to the actions of free Ca ions [50]. This suggests that the 3SrHA coatings produced here, with the high Sr + Ca/P and Sr + Ca/Ca ratios may provide appropriate surfaces to enhance the cellular response. However, SrHA coatings with increased levels of Sr content, such as the 3SrHA derived coatings may be more prone to dissolution in physiological conditions when compared to the other coatings produced here. This is largely due to the increased ionic radius of Sr (which substitutes for Ca in the lattice) [29,42,43]. This typically results in an increase in the lattice parameters (a and c), with the CaII site thought to be the preferred site for Sr substitution [18]. This degradation behaviour of the SrHA material is a consequence of a number of different factors; however, the degree of Sr substitution is obviously seen as highly significant given the effect it has on the organization of the HA lattice [16,26]. It is therefore obvious that by controlling the deposition parameters, most notably, the choice and arrangement of the sputtering targets (as utilised in this study), the Sr content, stoichiometry and surface morphology of the coatings can be controlled. Consequently, this can help regulate the micro-environment in close proximity to the biomaterial's surface and play a vital role in the success, or otherwise of the SrHA biocomposite, both in vitro and more importantly in vivo. In general, the effect of Sr-substitution in HA has also been well documented as having a positive effect, both in vitro and in vivo through enhancing osteoblast activity (proliferation), differentiation and reducing osteoclast activity [37]. Furthermore, Sr has also been implicated in antimicrobial activity as well [17]. With respect to the surfaces created here, all of the SrHA coatings appear to be of high quality with Sr clearly substituting for Ca within the HA lattice (to varying levels). All of the SrHA coatings appear to contain low levels of both CO\textsuperscript{3-} and HPO\textsubscript{4}\textsuperscript{2-}, with all of them, apart from the 3SrHA having a higher than expected Sr + Ca/P ratio. This would suggest that the SrHA derived coatings produced here exhibit a range of properties that would be commensurate with those expected to deliver significant benefits, both in vitro and in vivo, when compared to pure HA [16].

5. Conclusion

The aim of this particular work was to study the feasibility of using co-sputter deposition for creating Sr-substituted HA (SrHA) coatings from a three source RF magnetron sputtering system. In particular, the influence of different target configurations on the properties of the Sr-substituted sputter deposited coatings produced at a low discharge power level (150 W) were investigated. The results presented herein demonstrate that co-deposition sputtering can be used to produce Sr-substituted HA coatings. The results also indicate that all of the different SrHA coatings produced contain low levels of CO\textsuperscript{3-} and HPO\textsubscript{4}\textsuperscript{2-}. When 1 or 2SrHA targets were utilised (referred to as 2HA/1SrHA or 1HA/2SrHA coatings, respectively), the Ca/P and Sr + Ca/P ratios were lower than that expected (1.67). This could be explained by the formula Ca\textsubscript{10−Z}−X−Y −Z(Sr)\textsubscript{Y} (HPO\textsubscript{4})\textsubscript{X} (PO\textsubscript{4})\textsubscript{6−X−Y} (PO\textsubscript{4})\textsubscript{6−Z} −X −Z(CO\textsubscript{3})\textsubscript{Z} (OH)\textsubscript{2} −X −Z which allows for the lower stoichiometries observed. However, the coatings deposited when 3SrHA targets were utilised (referred to as 3SrHA) produced coatings with a much higher Sr + Ca/P ratio which cannot be explained by the same formula. The higher stoichiometry observed here is most likely due to Ca enrichment of the surface along with the presence of additional Sr ions. The presence of SrCO\textsubscript{3} cannot be ruled out for any of these coatings, however, they would only be present to very low concentrations on the surface of the coatings as indicated by the results obtained here. It was also observed that as the number of SrHA targets in the deposition runs increased (from 0 to 3), the deposition rate decreased. However, all of the coatings produced did not appear to contain any other impurity CaP phases, with XRD data showing peaks corresponding to that of ICDD #09-0432 for HA, albeit shifted to lower 2θ values due to the incorporation of Sr into the HA lattice for Ca. In addition to this, as the Sr content in the coatings increased the degree of preferred 002 orientation seemed to increase, producing a range of different morphologies as a consequence. RF magnetron sputtering employing a co-deposition approach, therefore offers a means to control the attendant surface properties of Sr-substituted HA, such as the crystallinity, stoichiometry, phase purity and surface morphology. However, these surfaces would need to be investigated by rigorous in vitro and in vivo testing to provide further evidence of their potential clinical utility.

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