MECHANICAL ENGINEERING | RESEARCH ARTICLE

Flame spray coating of α-tricalcium phosphate on AISI 316L alloy

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Abstract: The use of hydroxyapatite derived from green mussel (Perna Viridis) shell wastes for implant coating was investigated in this study. The study looked into using a flame-spraying technique to deposit this low-cost hydroxyapatite on AISI 316 L alloy. A standardized pull-off test on a coating thickness of 56–70 µm and a porous layer yielded a coating strength of 4.12 MPa. A melted hydroxyapatite layer with uniformly dispersed particles was visible in the SEM micrograph. The chemical elements C, Ca, Fe, Ni, P, and O corresponding to calcium orthophosphate and the alloy were revealed by EDX analysis of the coating layer. The α-tricalcium phosphate (α-TCP) found on the coating was confirmed by XRD Rietveld analysis. When the alloy is used as an implant, this α-TCP layer coating appears to have the potential to improve biocompatibility.

Subjects: Mechanical Engineering Design; Biomedical Engineering; Manufacturing Engineering

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PUBLIC INTEREST STATEMENT
The use of hydroxyapatite derived from green mussel shells for flame spray coating on AISI 316L metallic implant materials was demonstrated in this study. The resulting uniform coating thickness ranged from 56 to 70 µm. Macroscopic and SEM morphology analyses revealed macro and micro-cracks caused by the specimen’s thinness and the substrate’s different thermal coefficients with developed α-TCP bioceramic. This bioceramic phase coated the surface with low XRD peak intensity and crystallinity, resulting in a low adhesion layer strength. The α-TCP phase on the coating layer is more likely to be biocompatible than the metallic implant when used for bone regeneration.
Keywords: AISI 316L alloy; α-Tricalcium phosphate; flame spray; hydroxyapatite; green mussel (perna viridis) shell; SEM method; biomaterial; XRD Rietveld analysis

1. Introduction
AISI 316 L alloy is an essential metallic biomaterial that may act as a part of human bone because of its excellent properties of mechanical strength, wear, and corrosion resistance (Nasab & Hassan, 2010). However, it has an exceptionally high elastic modulus, which may hinder bone regeneration. Besides, AISI 316 L and other alloys like CoCr and titanium-based metals are biologically inert within bone tissue, so they do not form a chemical bond with it (Hanawa, 1999). The nickel and chromium ions in AISI 316 L can be released over a long implantation period, making it toxic and carcinogenic (Brown & Simpson, 1981). This phenomenon also occurred in the titanium-based implant, which is still being debated by medical experts. The vanadium ion can be released into the body and cause cancer. This shortcoming of metallic implants can be addressed by flame spraying a hydroxyapatite/tricalcium phosphate (HA/TCP) coating on the metallic surface, resulting in a bioactive ceramic layer capable of bone regeneration in human cells (Jagadeeshanayaka et al., 2022). The resulting coated alloy, with its desirable mechanical properties and the osteoconductive properties of those bioactive ceramics, may optimize the host response to the implant.

Alloys can also be used to make fracture plates, bones, hip nails, pins, wires, joint caps, and screws, which can be used to fill the need for implants (Li et al., 2020). These components may work by holding bones in place and then improving bone tissue via osseointegration. For quick host cell recovery, metallic materials must be biocompatible with them (Niinomi, 2002; Priyadarshini et al., 2019). As previously reported, hydroxyapatite powder was applied to the surface of alloys providing improved biocompatibility, accelerated osseointegration, reduced the risk of wear and corrosion, and extended the service life of implants (Arcos & Vallet-Regi, 2020; Eliaz & Sridhar, 2008; Jiang et al., 2019). Additionally, the alloy surfaces coated with hydroxyapatite powder provided improved protection and accelerated healing. Indeed, hydroxyapatite has a crystal structure similar to that of human bone, allowing this biomaterial to achieve long-term osseointegration and improve prosthetic limb restoration (Niinomi, 2002; Priyadarshini et al., 2019). Specifically, hydroxyapatite has a high ability to adapt to human tissues due to its good response to the physical-chemical environment.

As an alternative to hydroxyapatite, α-tricalcium phosphate [α-TCP, α-(Ca,(P,OH)2)] has gained popularity as a powder precursor for various biomedical applications in bone repair and restoration (Awasthi et al., 2021; Carrodeguas & De Aza, 2011). TCP can be crystalline in two polymorphs: α-TCP and β-TCP. β-TCP is a more stable phase with extremely biocompatible. In fact, new bone grows in the space previously occupied by α-TCP as it resorbs. In this case, α-TCP can be made from polymorph β-TCP by heating non-crystalline powder with a specific composition at low temperatures or by thermal crystallization above the transformation temperature (Dorozhkin, 2014). Unlike hydroxyapatite, α-TCP material is osteoconductive but not osteoinductive. However, α-TCP is ideal for conditions in which implant material resorption is desired, followed by host bone replacement (Klein et al., 1991).

Because of its excellent biocompatibility, current research on derived-based TCP coatings has focused on surface modification that can improve biofunctionality to the base metal's surface and bulk properties. The flame spray coating method has been widely used in biomedical applications for depositing bioceramic on metallic substrates (Carrodeguas & De Aza, 2011; Dorozhkin, 2014; Gerald et al., 2020; Harun et al., 2018; Lai et al., 2015; Yao et al., 2019; Yugeswaran et al., 2015). This method has previously been used to coat TCP onto metal implant material, resulting in a compact morphology, low porosity, and good surface adhesion (Ferrer et al., 2019). However, this method has drawbacks, the most notable of which is poor long-term coating bonds with metallic substrates, resulting in coating layers of varying thickness and chemical and phase composition (Gadow et al., 2010; Khor et al., 1997; Saber-Samandari & Berndt, 2010; Saber-Samandari & Gross, 2009a).
Accordingly, TCP biomaterial coatings manufacturing strategy has concentrated on controlling variables such as time, heating temperature, and cooling rate. Furthermore, the main goal of using a flame spray for TCP coating is to discern how to control the processing parameters concerning layer coating microstructural development (Gross & Saber-Samandari, 2007). The method will eventually have a significant impact on biocompatibility and mechanical strength (Ferrer et al., 2019; Gadow et al., 2010; Gerald et al., 2020; Khor et al., 1997; Yusgeswaran et al., 2015).

In practice, the TCP coating method uses a flame spray feeding system relaying on the dry spray powder in conjunction with a gravity-assisted vibrating module that can be activated by high-pressure air thrust. Acetylene and oxygen gasses may generate enough heat at a certain speed and pressure to melt the powder particles. The most critical processing parameters are to control air pressure, acetylene, oxygen flow rate, standoff distance, and temperature. Thermal and kinetic energies may also influence the powder, melt and deposit it into the substrates, and produce high adhesive and cohesive bonds between successive layers (Amin et al., 2016; Zhang et al., 2020).

In terms of powder precursors required for the TCP coating, synthetic hydroxyapatite derived from green mussel (Perna Viridis) shell wastes is desirable as a raw material due to its positive impact on lower production costs and a protected environment. In addition, the synthetic hydroxyapatite powder is both non-immunogenic and non-toxic. It can be synthesized under controlled conditions using various traditional and hydrothermal methods to achieve the desired mechanical properties, Young’s modulus, optimal porosity, pore dimensions, interconnectivity, and biodegradability (Ninomi, 2002; Priyadarshini et al., 2019).

Despite containing similar calcium and phosphate ions, α-TCP and hydroxyapatite differ significantly in structure, density, and solubility, all of which influence the coating powder strategy. As a result, numerous studies have been carried out to assess the impact of various flame spray variables on the physical and mechanical properties of the layer coating, as well as its bioactivity (Amin et al., 2016; Gadow et al., 2010; Khor et al., 1997; Zhang et al., 2020). However, some questions about flame spraying-layer coating on surface metals remained unanswered. The processing parameters affecting the layer coating, particularly their phase evolution and the alteration of their physical and mechanical properties of alloy surfaces, necessitate a thorough microstructural examination. Hence, surface characterization and morphological analysis are important to understand the coating layer’s thermodynamic stability and biomineralization within the liquid-solid complex system. In this case, SEM/EDX (scanning electron microscopy/energy dispersive x-ray) and XRD (X-ray diffraction) methods are reliable for examining the biomineralization and morphological development of the coating layer.

In this study, the hydroxyapatite powder from waste green mussel shells (Perna Peridis) was flame sprayed onto AISI 316 L substrates (Ismail et al., 2021). The roughness and coating thickness was measured, while the coating strength was examined using the standardized ASTM-D4541 pulling-off test. Moreover, SEM/EDX and XRD methods were used to investigate surface microstructural developments. In particular, the current study proposed an in-depth evaluation of the bond strength and microstructure of the layer on the surface alloy. The findings of the study are expected to contribute to a better understanding of the reuse of hydroxyapatite-based waste materials for coating onto the surface of alloys, followed by controlled homogeneous particle size and porosity.

2. Materials and method

2.1. Samples of coating preparation
The hydroxyapatite powders were prepared by the hydrothermal synthesis of green mussel waste, as previously reported (Ismail et al., 2021), and subsequently were used for subsequent flame spray coating on alloy surfaces. This hydrothermal process produced hydroxyapatite powder precursors with purity levels ranging from 90 to 97 wt. % and particle sizes ranging from 3 to
10 μm after 18 hours of synthesis at 160 °C. As substrates, AISI 316 L plates (Jiangsu Chenming Stainless Steel Co., Ltd., China) with dimensions of 50 mm long x 50 mm wide x 1 mm thick are chosen, as indicated by the designation SS-sample.

Following that, the sample was sandblasted prior to coating to provide clean and rough surfaces, which could improve coating strength onto metallic substrates. The substrates and powders were then weighted with a sensitivity of 10⁻² grams before the flame spray process on substrates containing 1 gram of hydroxyapatite powder was performed for 30 minutes. In the powder flame spray gun equipment, acetylene and oxygen gasses were used as combustion fuels (Metal Coat 5PM-II). This flame gun spray worked at a particle velocity of 300 m/s for ceramic coating, faster than the commonly used coating velocity of 100 m/s (Paulson et al., 2020; Singh et al., 2014). The gun spray was set to a 20-cm standoff distance and 0.5 bar air pressure during the coating process. The coated surface naturally cools in open atmospheric air. After the coating process, it was placed in a plastic container for further material characterization.

2.2. Surface roughness testing
The roughness of the coated surface layer was measured using a surface roughness tester (SJ-400 Mitutoyo). Ra and Rz are roughness values that correspond to the arithmetic mean, absolute deviation, and maximum average height of a profile within sampling, respectively (Panda et al., 2016).

2.3. Pull-off adhesion testing
The tensile pull-off technique described in ASTM D4541 was used in this study, which involved placing a test dolly on the surface and then pulling it away with a force perpendicular to the surface until the coated dolly could be removed from the substrate. (Figure 1). The data collected on pulling force and failure type were used to investigate the adhesion of the coated specimens. Pull-off tests were carried out on a 20 mm diameter dolly with a 1:1 epoxy-hardener ratio, as received for 18-h hardening (Fletcher, 2020). As the dolly was pressed onto the test plate surface, a hydraulic adhesion tester (DeFelsko Positest ATM) assisted in pull-off tests of the sample. The mechanical test was performed first, followed by the other mentioned tests. Because the ASTM-D4541 pull-off test surface area should be larger than the dolly and test plate used (in this case, a 20 mm diameter dolly and a 40 mm plate). Following the completion of the ASTM D4541 testing, the specimens were laser cut to a 10 × 10 mm size to fit the equipment holder for the micrography, EDX, and XRD analysis.

2.4. Characterization of surface coating materials
The SEM-EDX method (JSM-6510LA; JEOL Japan) was used to examine the morphology and chemical elements of the coating surface. The observed coating surface exhibited porosity, cracks, and uncoated, melted, and unmelted particles. Furthermore, the X-ray diffraction (XRD) method

Figure 1. Experimental set-up for specimens and dolly in the pull-off test.
(Shimadzu PV 7000, Japan) was used to collect XRD data over a 2θ-range of 10–90° by setting up 30 kV/30 mA, Cu-K radiation. A QualX computerized-based phase identification was employed to analyze the collected XRD data of the coated substrate (Altomare et al., 2015). Following that, the XRD Rietveld profile refinements using the program Fullprof-2k, version 3.30, validated the program’s suggested phase (Rodríguez-Carvajal, 2001). In this method, the profile refinements use the Crystallography Open Database’s crystal structure model (COD; Gražulis et al., 2009).

3. Results and discussion

3.1. Adhesion and cohesion of the coating samples

Prior to the coating processes, the metal surface was sandblasted with glass beads with a size of 250–150 grids and an air pressure of 7 bar. The sandblasted samples were then preheated to maximize the splat adhesion to the substrate (Saber-Samandari et al., 2014, 2011), followed by a thermal spray with 1 g of hydroxyapatite powder. The specimens were then allowed to self-cool in open atmospheric air. Finally, the coated sample was weighed to determine the coating mass. Table 1 presents the measured mass of the sample before and after coating was employed. As a result, the mass losses for the sample were calculated as the difference between 1 g of initial hydroxyapatite powder and the mass of the coating, yielding a value of 52%. This result indicates that less powder was deposited onto the sample. This value may be increased by using artificial intelligence in the coating process, providing a more even and effective coating layer (Wei et al., 2001).

Further macro examination of the sample surface revealed cracks in the coating layer, which could be attributed to the thermal expansion coefficient (TEC) difference between the AISI 316 L substrate and hydroxyapatite powder. When the sample was cooled in the open air, cracks might

| Specimen     | Mass (g) | Before coating | After coating | Hydroxyapatite coat | Hydroxyapatite powder loss (%) |
|--------------|----------|----------------|---------------|---------------------|-------------------------------|
| SS-sample    |          | 18.29          | 18.77         | 0.48                | 52                            |

Figure 2. The layer coating detached due to the warping phenomenon.
form, causing the warping of the substrate (Amin et al., 2016). In this case, the TEC value of AISI 316 L is $20.5 \times 10^{-6}$ °C$^{-1}$, which is slightly higher than the TEC of hydroxyapatite powder ($13.4 \times 10^{-6}$ °C$^{-1}$; X Li et al., 2008). Due to the significant difference in TEC values, thermal shock appears to cause the AISI 316 L substrate to shrink faster than the coating layer. Additionally, a thin substrate with 1 mm thickness may increase the rate of expansion and shrinkage.

### 3.2. Roughness and bonding strength of the coating

Ra and Rz values determined the roughness of the coating. The coating's Ra and Rz values were 0.503 µm and 3.156 µm, respectively. This measured value was lower than the previous study, which used AISI 316 L and a titanium substrate (Singh et al., 2014). This value is likely insufficient for biomedical applications, owing to the small HA particle size of less than 10 µm, as other research found that a powder size of 20–30 µm gives a roughness of 4–6 µm (Gross & Babovic, 2002). To meet the requirements for biomedical applications, a higher surface roughness value must be achieved with a larger powder size. The adhesion strength and percentage of material detached from the sample as determined by ASTM D4541 pull-off tests are presented in Table 2. The lower adhesion values of the specimens compared to the standard strength (ISO 13779–2:2008) of 15 MPa (Unnamed 2008) may be related to the previously mentioned cracks and warping phenomenon (Figure 2). The surface quality of the bottom coatings may also influence variations in bond strength values. Furthermore, the absence of post-coating heat treatment may promote microcracks (Dorozhkin, 2015). Presumably, the bond strength of the coating with a larger area of active zones may contribute significantly to better adhesion (Guipont et al., 2010). Furthermore, the shape and size of grains (Levingstone, 2008) as well as surface roughness (Bose et al., 2015) may influence adhesion strength. Granular, nanosized, and coarse surfaces, in particular, may improve coating adhesion.

Instead, the adhesion strength of samples obtained in this study was significantly lower than the standard and previous test results on layer coating with other thermal spray methods (15–70 MPa; Furlong & Osborn, 1991; Juliadm et al., 2017; Saber-Samandari et al., 2018; Tucker, 2013; Vencl et al., 2011). Unlike previous research by Gadow et al. (Gadow et al., 2010), the layer coating obtained via high-velocity suspension flame spraying (HVSFS), atmospheric plasma spraying (APS), and high-velocity oxy-fuel spraying (HVOF) methods had bond strengths ranging from 10 to 25 MPa. More work should be done here by slowing down the velocity of the flame spray (Tucker, 2013).

### 3.3. Surface characteristics of the coating

The surface macrostructure and layer thickness of the specimens were examined using an optical microscope at magnifications of 10 and 30 times. ImageJ software was employed to obtain the desired color difference, area fraction, and dimension data from the micro-images of the particle coating. The thermal spray method appeared to have produced a coating layer product with different particle morphology, uniformity, and thickness due to the difficulty of adjusting the physicochemical parameters of the manual spraying process (Tucker, 2013). As a result, the surface of the specimen had a non-uniform physical appearance.

Furthermore, compared to the color image, the surface image of the layer processed with ImageJ software provided the percentage of particle uniformity on the layer. A bright white color on the specimen surface indicates a layer coating, whereas dark colors indicate uncoated parts, cracks, porosity, or charred coating. Figure 3 shows the surface morphology of the coated

### Table 2. Adhesion strength, and the material detached from specimens after pulling-off tests

| Specimens | Adhesion/Cohesion | Tensile adhesion Strength (MPa) | Material release (%) |
|-----------|-------------------|--------------------------------|----------------------|
| SS-sample | Adhesion          | 4.15                           | 77                   |
specimens, image processing results, and percentage of particle uniformity of the coating results. The surface morphology images in the sample appeared to be uniform, with a white color value of 90.0%, indicating a relatively uniform coating particle.

3.4. Coating layer thickness measurement
The thickness of the layer coating was measured with an optical microscope and processed with ImageJ software. The substrate and the attached layer coating could be distinguished in the presence of boundaries and color differences. The thickness of each specimen was measured at five different points by drawing a straight line from the beginning of the border between the layer and the substrate to the outermost part of the layer. After obtaining the thickness at five different locations, the average thickness was calculated. Figure 4 shows the image processing results and the measured layer thickness. The non-uniform obtained value of the measurement results may correspond to the level of uniformity of the coating results. Furthermore, the layer coating thickness on the sample was relatively constant between 65 and 69 µm. These thickness values, ranging from 50 to 200 µm, meet the criteria for biomedical applications (Latka et al., 2020; Wang et al., 1993). A thinner coating is now recommended to overcome residual stresses and reduce coating costs, which could be around 50 m (Gross et al., 2010; Juliadmi et al., 2017).

3.5. Coating microstructure developments
Figure 5 depicts the surface layer coating morphology on AISI 316 L implants. All surface coatings appeared to have the spherical morphology of the layer coating, including the presence of particles resulting from melting and un-melting powders, porosity, micro-cracks, nanoparticles, and uncoated metal (Saber-Samandari & Gross, 2009b). These characteristics were identical to those found in previous studies on the surface morphology of hydroxyapatite obtained by thermal spray on the AISI 316 L and titanium substrate (Latka et al., 2020; Liu et al., 2018).

Figure 3. The as sprayed (a) and calculated coating uniformity (90%) (b).

Figure 4. The image processing and measured layer coating thickness with the standard deviation represented by the number in parenthesis.

Average Thickness
65.22 (8.84) µm
Furthermore, the sample contains microcracks that may be associated with the warping phenomenon. This condition resulted in material release in the sample, which reduced the coating’s adhesiveness (Gross et al., 2010). Low adhesion can be caused by numerous unmelted particles with a lower surface area than the melted particles sticking to the substrate. Heat treatment with a controlled cooling rate after coating can reduce the micro-cracks phenomenon (Saber-Samandari & Gross, 2009b). Nanoparticles were discovered in the sample layers, with small agglomerates visible colonizing multiple sites. These nanostructures on metal layers have the potential to improve the mechanical and biomechanical properties of specimens (Arcos & Vallet-Regi, 2020). The calcium orthophosphate particles in the unmelted phase had a spherical shape, whereas the particles in the melting phase had an irregular shape. Layer porosity on the specimen surface revealed holes or voids as in the previous study (Saber-Samandari et al., 2018). The ImageJ software was used to calculate the melted, unmelted, and porosity (Figure 6).

In the current study, the percentage of melting phase in the sample was relatively high, which did not correspond to adhesion strength values. These findings confirmed that the bond strength value of the coating not only corresponds to a percentage of the melting phase but can also be caused by warping and the thinness of the substrate (1 mm) (Saber-Samandari et al., 2018). Furthermore, layer thickness can have an effect on bond strength values. The thicker the layer coating, the lower the bond strength value (Overgaard, 2009; Wang et al., 1993). The sample contains 1.8 percent porosity, which is required for bone tissue to grow, thereby strengthening and accelerating bone healing (osseointegration; Overgaard, 2009).

### 3.6. Surface chemistry of the coating

Regardless of the coating product’s actual chemical compounds, the elemental chemical compositions (wt.%) of the layer coating samples were analyzed by SEM/EDX, and the results are shown in Figure 7. Cations, on the other hand, can form oxide compounds (oxides and phosphates). The
layer coating results revealed the atomic and mass percentages of C, Ca, P, and O atoms. Several atoms were identified on the specimen’s surface, including the atoms that comprise the AISI 316 L substrate metal, namely iron (Fe), chromium (Cr), and nickel (Ni).

The weight percentages of O, P, and Ca atoms suggested that Ca-orthophosphate ceramics could form on the specimen surface. Furthermore, the presence of carbon atoms (C) suggests that the calcium carbonate phase may exist as amorphous calcium carbonate (ACC) in the layer coating (Jeon et al., 2020). However, the presence of other metal atoms corresponded to the chemical composition of the substrate as well as the presence of porosity (Wang et al., 1993). Furthermore, using the percentage values of Ca and P atoms from the EDX data, the predicted Ca/P molar ratio was 1.4. This ratio may correspond to coexisting amorphous calcium phosphates (ACP) with molar ratios ranging from 1.2 to 2.2 (Dorozhkin, 2015). Furthermore, the low Ca/P value could be attributed to the thermal transformation of a powder precursor of calcium-deficient hydroxyapatite (CDHA) with a Ca/P molar ratio of 1.5. Indeed, the standard Ca/P molar ratio of 1.67 may be suitable for the hydroxyapatite phase for good biocompatibility (Kang et al., 2013; Łatka et al., 2020). As a result, increasing the Ca/P molar ratio on the sample after coating necessitates heating or hydrolyzing (Rocha et al., 2018).

3.7. Calcium orthophosphate evolution of the coating

The XRD spectra of the sample were matched for phase identification with the JCPDS database using the software program QualX (Altomare et al., 2015). Search match procedures involved determining the background, subtracting background, searching for spectrum peaks, and presenting data with 2D stack plots. Based on reference data from JCPDS card#9-348, α-TCP phases were observed following the search-match procedures (Figure 8a). The XRD- Rietveld method also confirmed that the crystal solid obtained on the sample revealed a primarily crystalline phase of α-TCP (Figure 8b). This finding was also supported by detailed XRD crystal structure analyses, which revealed that the α-TCP crystal structure agreed very well with those found in the literature (Table 3; Mathew et al., 1977).

On the sample, the XRD patterns revealed a glass-crystalline transition (Figure 8a). Apparently, a prominent, broad hump (background) mixed with the convincing Bragg peaks of the crystalline α-TCP phases at the broad peaks between 25 and 40°. In this case, ACP phase growth in the 2θ-range may be linked to a specific short-range order structure. Furthermore, rather than pure phase transitions, this process may result in changes in phase compositions (amorphous and crystalline phases). To improve the crystalline layer coating, a post-heat treatment at temperatures above 600°C is required.

The coating layer’s crystallinity index (Ic) could be determined using the Origin software’s spectrum analyzer feature. Equation (1) can be used to calculate the area integral under the XRD spectrum:
Figure 8. X-ray diffractograms of a) 316 L alloy and SS-samples, and b) the XRD Rietveld refinement plot showing I (obs) observed and I (calc) calculated intensity. SS stands for stainless steel, and α-TCP stands for α-tricalcium phosphate.

Table 3. Structural data of α-TCP from coating layer of the SS-sample

| Property | Structure model (Levingstone, 2008) | The coating layer |
|----------|----------------------------------|-------------------|
| Symmetry group | Monoclinic | Monoclinic |
| Space group | P 1 21/a 1 | P 1 21/a 1 |
| A (Å) | 12.8939 | 12.89388 (496)* |
| B (Å) | 27.3640 | 27.36403 (778) |
| C (Å) | 15.1574 | 15.15756 (408) |
| α° | 90 | 90 |
| β° | 126.1288 | 126.12897 |
| γ° | 90 | 90 |
| ATZ | 7444.382 | 7444.382 |
| V (Å³) | 4.31 | 4319.551 |

* The standard deviation is represented by the number in parenthesis

\[ I_c = \left( \frac{A_{crys}}{A_{crys} + A_{am}} \right) \times 100\% \]  \hspace{1cm} (1)

Where \( A_{crys} \) is the peak area of the crystalline phase, and \( A_{am} \) is the amorphous peak area under the spectrum (Rocha et al., 2018). The XRD spectrum was used in the analysis of the crystallinity index for the XRD spectrum for 2θ angle from 10° to 43° without smoothing where the peaks of the calcium orthophosphate phase dominated. As a result, the sample’s crystallinity was 38.28%. The coating layer of the specimen appeared to be primarily composed of amorphous phases, which could promote high resorptability (Gerald et al., 2020; Khor et al., 1997). This result was consistent with the findings of Khor et al., (Khor et al., 1997) who discovered that using a small powder size for thermal spray could result in amorphous HA, TCP, and CaO phases. The literature also corresponds to the coating’s roughness value, which can be classified as smooth with only 0.503 μm of layer roughness (Gerald et al., 2020). This amorphous phase can be reduced by post-coating heat treatment (Zhang et al., 2020).
3.8. The significant finding of the study

The surface of a non-biodegradable metal orthopedic implant must be bioactive for osseointegration (direct bonding with bone). A coating technique can be used in this case to deposit a bone-like α-TCP (calcium orthophosphate) on the metallic implant surfaces, making the implants more bioactive and resulting in osseointegration. While not a major issue for coating metals, high-temperature flame spray processes are appropriate for coating high melting point alloys, which are increasingly used in orthopedic implants. Coating such materials with bone-like α-TCP can also improve their bioactivity in vitro and in vivo. This experimental coating produced a thinner calcium orthophosphate layer (average 65.22 μm) with high particle uniformity (over 90%) and a low adhesive tensile strength of 4.15 MPa. These findings suggested that when used on implants, the current coating technique may improve osseointegration.

Alternatively, α-TCP is a ceramic widely used in orthopedic and dental cements that can be synthesized by solid-state reactions occurring at high temperatures, making temperature and cooling rate control in the flame spray method essential to avoid the formation of secondary phases such as beta tricalcium phosphate (β-TCP). The majority of recent research on the synthesis of α-TCP has focused on the thermal transformation of a powder precursor of ACP (amorphous calcium phosphate) or CDHA (calcium-deficient hydroxyapatite) with a Ca/P molar ratio of 1.5 (Arcos & Vallet-Regi, 2020; Carrodeguas & De Aza, 2011), or through a solid-state reaction of a high-temperature mixture of solid precursors, self-propagating high-temperature synthesis (Overgaard, 2009), and combustion synthesis (Burkes et al., 2008; Jeon et al., 2020; Mathew et al., 1977). Significantly, this experimental flame spray coating demonstrated that hydroxyapatite begins to decompose to α-TCP after about 30 minutes at temperatures up to 1150 °C, whereas thermal decomposition of hydroxyapatite was followed by water dehydration. This finding is consistent with previous peer-reviewed journal research (Hanawa, 1999; Yugeswaran et al., 2015). As a result, the following equation (Eq. 2) has been proposed for the hydroxyapatite decomposition reaction at temperatures greater than 1150 °C (Arcos & Vallet-Regi, 2020):

$$\text{Ca}_9(\text{HPO}_4)_2(\text{OH})(s) \rightarrow 3\alpha - \text{Ca}_3(\text{PO}_4)_2(s) + \text{H}_2\text{O}(g) \quad (2)$$

Because the investigated bioceramics are widely regarded as bioactive, the formation of α-TCP in vitro and in vivo should imply that they have good osteoconduction ability. As a result, it is necessary to reconsider whether α-TCP formation is the most appropriate criterion for assessing the bioactivity of orthopedic materials. However, more research on α-TCP specimens implanted on cancellous bone in rabbit tibia is needed to demonstrate osteoconduction. In addition, priority should be given to the compositional aspects of various powder precursors and strategies for improving coating kinetics.

4. Conclusions

The current study demonstrated that coating metallic biomaterial substrates with α-TCP is feasible. The resulting coating’s average thickness appears to have met the standard for biomedical implant use (>50 μm). Furthermore, SEM analysis revealed that the surface coating contained particles that were uniformly distributed, allowing for faster tissue growth and osseointegration. To meet the desired biomedical standard, the surface roughness and adhesion strength of the coating must be improved. The discovery of α-TCP phases with high amorphous phases, which produce a high resorbability coating, was validated by EDX and XRD Rietveld analysis. The hydroxyapatite powders derived from green mussel shells could be used for implant coating and could be improved with further post-heat treatment, powder size, and spraying process modification in terms of effectiveness, thickness, crystal, and morphology.
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