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Review article

A comprehensive review of hydroxyapatite-based coatings adhesion on metallic biomaterials

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ABSTRACT

Metallic biomaterials have been employed in replacing and reconstructing the structural parts of the human physical structure due to their high mechanical properties, superior biocompatibility, and high corrosion resistance. The most common metallic biomaterials that have been used in implants include magnesium, stainless steel, cobalt-based alloy, titanium, and titanium-based alloy. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is one of the ceramic biomaterials considered as ideal materials for coating on metallic biomaterials as it possesses almost the closest similarity in chemical composition and excellent biocompatibility with natural bone tissue. Recently, the HAp-based coating has increasingly drawn attention to improve the adhesion quality in metallic biomaterials. This study comprehensively reviews the current progress in the adhesion qualities of HAp-based coatings on metallic biomaterials specifically for the biomedical application. It has been observed that a surface that meets the minimum unique characteristics will enhance the bonding force between the coating and metallic biomaterial as the substrate. Critical factors of coating/substrate materials, coating techniques, and coating thickness that determine the adhesion quality are thoroughly identified and discussed. The surface structure and microstructure of HAp-based coating are also reviewed to confirm the findings.

1. Introduction

Metallic biomaterials used for medical treatments can be traced back to around 20 years [1–3]. Around 70 – 80% of implant devices in the medwwwical field are made of metallic biomaterials [4–8]. Metallic biomaterials are extremely crucial for fracture fixation, bone repair, and failed tissue, especially failed hard tissue to improve patients' quality of life (QOL) [9–13]. This is due to their high strength, toughness, and durability [14–22]. The substantial demand for metallic biomaterials with excellent mechanical properties is increasing rapidly as the world population is getting progressively aging, and seniors would have a higher risk of hard tissue failure.

Representative practical metallic biomaterials can be categorised into the following groups; stainless steel (316L), cobalt-based alloys, and titanium-based alloys [23–27]. These biomaterials should own identical characteristics to human bones, including their Young's modulus value, which results in the lesser effect of stress shielding [28–31]. The most frequent designs for the implants are plates, rods, screws, and pins [32–34]. These metallic biocompatible implants are typically used in orthopaedic practices since they have approval by the United States Food and Drug Administration (FDA) [35–37]. Nevertheless, metals are typically synthetic materials, and their bio-functionality is at present inadequate, which means that metals are not credible as biomaterials. Hence, the biological and mechanical biocompatibility of metallic biomaterials requires much improvement [30,38–40]. The clinical applications of four classes of metallic biomaterial are summarised in Table 1.

One weakness of using metallic biomaterials is that they are usually artificial materials and have no bio-function [31,41,42,45,46]. The critical issue is related to adhesion strength between the metal substrate and coating layer. The coating spallation from the substrate results in adverse clinical responses to the implants and surrounding tissue [43,44]. Hydroxyapatite coating dissolves due to its poor crystallised structure, causing a decrease in adherence to the titanium surface and

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Table 1
Primary applications of metallic biocompatible implants [35].

	Primary utilisations	Reference
Stainless steels	1. Temporary devices (plates, screws, hip nails) 2. Total hip replacement	[38]
Co-based alloys	1. Total hip replacement (wrought alloys) 2. Dentistry castings	[38]
Ti-based alloys	1. Stem and cup of total hip replacements with CoCrMo or ceramic femoral heads 2. Other permanent devices (nails, pacemakers)	[40]
Mg	Biodegradable orthopaedic implants	[41,42]
NiTi	1. Orthodontic dental arch wires 2. Vascular stents 3. Vena cava filter 4. Catheter guide wires 5. Orthopaedic staples	[43,44]
Ta	1. Wire sutures for plastic surgery and neurosurgery 2. A radiographic marker	[44]

dramatic late implant failure [47,48]. In the past, uncoated 316L stainless steel revealed lower values of adhesion strength compared to coated specimens [49,50]. Therefore, surface modification is essential since bio-functions cannot be added during manufacturing processes such as casting, melting, forging, and heat treatment.

Hydroxyapatite (HAp-$Ca_{10}(PO_4)_6OH_2$) is the main inorganic component of bones and has been the most used biomaterial for over four decades in medicine and dentistry. However, previous researchers claimed that HAp ceramics are brittle and not suitable to be applied as implants for load-bearing applications [51–54]. Consequently, HAp was chosen as a coating on metallic biomaterials to improve their mechanical properties [55,56]. HAp-based ceramics were obtained from substituted apatite. Hence, it can be used as coatings for metallic implants to promote mechanical properties (low plasticity, fatigue and creep resistance) such as load-bearing ability and enhanced substrate–coating adhesion [57–60]. It has been proven that HAp coating allows for a controlled and rapid osseointegration [61,62]. Several researchers have mixed HAp with other elements/compounds to form HAp composites to achieve better mechanical properties [41,63–68]. Even so, it has been reported by Witte et al. that the development of a metal matrix composite made of AZ91 magnesium alloy had employed HAp particles as reinforcing fillers in the alloy matrix [69–73]. The mechanical properties of the composite can be primarily adjusted by altering the HAp mean particle size distribution, which resulted in the stabilisation of the degradation rate of the HAp particles' and further indicated fair degradation uniformity, both in artificial seawater and cell solutions. The porosity and uniformity of the Hydroxyapatite/Chitosan (HAp/CS) film prepared through the chemical electrodeposition method have been intensely studied to date. Most of the studies indicated that the adhesion strength of HAp/CS was much higher as compared to the single element of HAp film [74–78]. The composite coatings also demonstrated superior biocompatibility than the HAp coating due to the presence of calcium silicate ($CaSiO_3$) and influence of the porous structure [74,79,80]. Table 2 shows the minimum requirements for HAp coatings as described in the FDA procedures following ISO standards [81–83].

In fact, there are various coating deposition processes studied such as dip coating [61,84–92], sol-gel [93–99], electrophoretic deposition [100–107], electrochemical deposition [100,103,108–110], plasma spraying [49,111–117], high-velocity suspension flame spraying (HVSFS) [118–120], sputtering coating [83,121], hot isostatic pressing [122,123] and pulsed laser deposition [124–126]. Table 3 summarises the previous discussion on coating methods. However, this review only focuses on the most frequently applied coating techniques including sol-gel, dip coating, electrodeposition, and plasma spraying. The discussion includes coating/substrate materials, coating techniques, and coating thickness, and determines the adhesion quality based on these four coating methods. The surface structure and the microstructure of the HAp-based coatings were also included to confirm the findings.

Table 2
HAp coating requirements [83].

Essential	Requirement
Thickness	Not specific
Ca/P ratio	1.67–1.76
Phase purity	95% minimum
Crystallinity	62% minimum
Tensile strength	> 50.8 MPa
Shear strength	> 22 MPa
Density	2.98 g/cm^3
Heavy metals	< 50 ppm
Abrasion	Not specific

2. Importance of adhesion

The performance and durability of adhesives or coatings on substrates are greatly supported by two basic properties of cohesion and adhesion [128,129]. Adhesion is defined as an attraction between different surfaces, which refer to the force of the bond that holds substrates together in opposition to stress exerted to pull the substrates apart. Meanwhile, cohesion represents the internal strength of a material which is the attraction of particles within the adhesive or other materials that hold the adhesive together. Fig. 1 shows the illustrations of how the (a) adhesive and (b) cohesive strength occur between the adhesive and substrates.

Adhesion is divided into three basic types; (a) specific adhesion, (b) mechanical adhesion, and (c) effective adhesion [66,76,130–134]. Specific adhesion is the molecular attraction within contacting surface while mechanical adhesion occurs when adhesive flows into the microstructure of the surfaces to be bonded. In the meantime, sufficient adhesion occurs through the combination of specific and mechanical adhesion for the best possible joining strength. Bonding effectiveness can be determined from the combination of adhesion and cohesive strength. Adhesion bonding is considered failed once either the adhesive breaks apart or splits from the substrate. In addition, the adhesive and cohesive strengths of some adhesives are great enough that the cohesive force of the substrate fails before the adhesive bond forms [135–140].

2.1. Theoretical study of adhesion strength

Adhesion is considered as the bond strength which also implies the capacity of an adhesive or coating to stick to the surface and subsequently bond the two surfaces together. Adhesion strength is also classified as measurement or attachment of the adhesive or coating to the substrate. This phenomenon can occur via mechanical or chemical mechanisms, which is in reference to the ability of the adhesive to work its way into the insignificant pores on the surface of the substrate [129,130].

Once the surface is bonded to the adhesive, several aspects i.e. physical adsorption, mechanical interlocking, and chemical forces begin playing their roles, which influence on each other. Physical adsorption or wetting happens when the molecules in the wet coating make intimate contact with the substrate. Both the adhesive or coating causes the bonding of hydrogen atom with the substrate. Thus, interfacial bonding (electrostatic force) that holds the substances together cause the development of van der Waals forces between the molecules [130,141,142]. In between the coating and substrate, chemical bonds are formed. The mechanical interlocking occurs once the coating film penetrates the roughness on the substrate surface and dries. Schematic illustration of physical adsorption, chemical bonding, and mechanical

Table 3
Deposition of HAp coating via different techniques.

Approach	Coating thickness	Benefits	Weaknesses	References
Sol–gel	< 1 µm	Low processing temperatures; low cost; very thin and high purity coating; genuinely great adhesion	Some processes require controlled atmosphere processing; expensive raw materials	[93–99]
Dip coating	0.05–15 mm	Inexpensive; coatings applied quickly; can coat complex substrates; high surface uniformity	Involves great sintering temperatures; incompatibility of thermal expansion	[61,84–92]
Electrochemical deposition	0.05–0.5 mm	Inexpensive; able to coat complex substrate; high uniform coating thickness	Adhesion quality among coating and substrate is insufficient strong	[100,103,108–110]
Electrophoretic deposition	0.1–2.0 mm	Rapid deposition rates; able to coat complex substrates; uniform coating thickness	Involves high sintering temperatures; challenging to produce coatings without crack	[100–107]
Biomimetic coating	< 30 µm	Low processing temperatures; able to coat complex substrate; able to incorporate bone growth stimulating factors and to form bonelike apatite	Obliges replacement and a constant pH of simulated body fluid; time-consuming;	[111]
Plasma spraying	< 20 µm	Inexpensive method; rapid deposition process; fewer possibility of coating degradation	Non-uniformity in coating density; coating process causes modification of HAp structure; high-temperature procedure leads to phase transformation and grain growth of substance; relatively lower adhesion strength	[49,112–118]
Sputter coating	0.5–3 µm	Dense and uniform coating thickness; great adhesion strength	Time-consuming; line of sight technique; costly; produces amorphous coatings	[83,122]
High-velocity suspension flame spraying (HVSFS)	≤ 50 µm	Homogenous and dense coating, have hardness and elastic modulus values close to those of the corresponding bulk materials, high productivity and relatively low processing cost, including the fact that the coatings do not need any post-deposition heat treatment for consolidation	High-temperature procedure	[119–121]
Pulsed laser deposition	0.05–5 µm	Coating dense, porous, crystalline and amorphous	Line of sight technique; particle or splashing deposition; requires pre-treatment of surface; deficiency of coating uniformity	[125–127]
Hot isostatic pressing	0.2–2.0 mm	Coating dense; no shape or dimensional limitation	High cost; unable to coat complex shape substrate; requires high temperature; incompatibility of thermal expansion; elastic property differences	[123,124]

interlocking is shown in Fig. 2.

Effective coating to the substrate can be classified from exhibiting of good adhesion strength. However, for the mechanisms to completely occur, they do not necessary to form good adhesion; in fact, the mechanisms merely depend on specific coating methods, type of substrate, and the way of approach. However, good adsorption is mainly required. The adhesion strength is given by the maximum tensile stress reading at the interface just until the adhesive layer or coating gets detached from the substrate. The value of adhesion strength depends highly on the coating thickness and solvent retention. Nevertheless, until now, there is a limitation of research discussing the property of adhesion [143].

2.2. Current issues of coating for metallic biomaterials

Poor adhesion strength between coating and substrate of metallic biomaterial leads to failure and unsuitable for load-bearing applications [144–146]. Previously, there were various deposition methods of bioactive coating by using HAp coating on metallic biomaterials; the methods were introduced over the years to improve adhesion strength to the metallic biomaterial substrates and its long-term trustworthiness [140,147–151]. The phenomenon (poor adhesion strength) between the coating and the metallic biocompatible substrate is in correlation to bond strength and overall considered a critical issue [152,153]. Once coating separation takes place—a consequence of poor adhesion strength—the surrounding tissues in the human body and the implant itself might be exposed to the adverse effects brought about by the detached particles.

Therefore, the purpose of introducing HAp as a coating on metallic biocompatible substrates is to maintain the mechanical behaviour of the metallic substrate, especially in load-bearing aptitude [127,154]. Additionally, HAp demonstrates biocompatibility behaviour, whereby its similar chemical composition to the human bone i.e. rich in calcium and phosphorus elements may give many benefits to the metallic implants to promote adhesion strength [61,97,155,156].

Blind et al. [157] reported the first clinical results of HAp coatings on titanium dental implants as excellent, even with poor bone quality. Nevertheless, mechanical failure started to occur at the interface of HAp and metallic substrate after an extended usage. Poor crystallised structure caused the HAp coating to dissolve and decrease adherence to the titanium surface. Therefore, it can be summarised that the stability of the HAp coating is the most important factor to determine the success of the implant. Besides, various HAp deposition techniques onto metallic biocompatible substrate could affect the coating properties, for instance, its adhesion strength and consistency [158–160].

3. Deposition techniques

3.1. Sol-gel preparation and dip coating

To date, a combination of sol–gel preparation and dip-coating methods have been extensively applied for coating purposes on metallic biomaterials. This method is one of the coating methods for the enhancement of adhesion strength [37,85,161]. CaP precursors, which are the most important solutes for sol preparation, are the combination of calcium and phosphorus. Normally, two solvents will be mixed together with CaP precursors. Most often water and ethanol are used as a solvent for the sol preparation [162–164]. The phosphorus precursor is commonly made of phosphorus pentoxide or triethyl phosphite. Sometimes, the precursor is mixed with the ethanol [165,166]. While in several sol preparations, the amount of water is dissolved in the solution to attain hydrolysis of the subsequent sol [167–172]. The selected calcium precursor is also added into the ethanol solution. Then hydrolysed phosphorus sol is also dissolved in a dropwise method [173,174]. Calcium nitrate is widely used for calcium precursor. The solution is mixed and refluxed at different reaction temperatures. In order to obtain the sol-gel suspension, the solvents are evaporated till the solution become

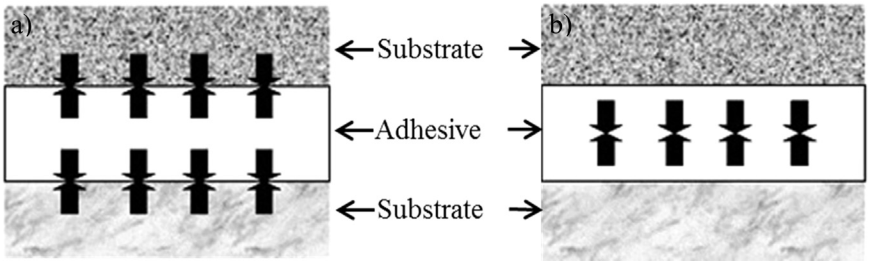

Fig. 1. The illustrations show how the (a) adhesive and (b) cohesive strength occur between the adhesive and substrates [137].

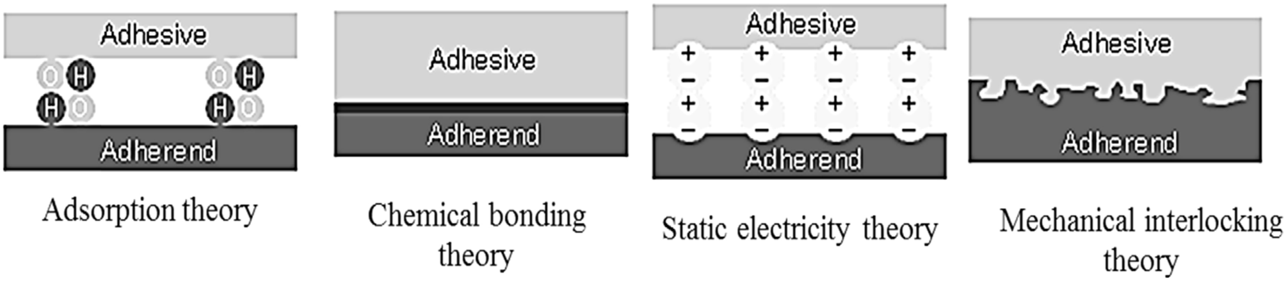

Fig. 2. Schematic illustration of physical adsorption, chemical bonding, and mechanical interlocking [137].

more viscous [175,176].

The effects from the chemical nature of the precursors and temperatures play an important role to produce the apatite phase. Fig. 3 shows the sol–gel process, which involves, (i) preparation of homogenous solution (CaP precursors mixed with reagents); (ii) polycondensation process, which changes the sol to a 'gel'; and (iii) a few processes of sol-gel slurry involving the aging, drying, and sintering/calcination [155,177,178]. Sol-gel process is popular owing to its easy procedures and being economical. Compared to biomimetic coatings process, this process is able to coat the material with complex or irregular shapes. Furthermore, the greatest benefit of sol-gel coatings compared to biomimetic coatings is in the strength of the coating and substrate adhesion, as proven in previous research [161,179–181]. A dense, thick, well-adhered apatite coating could be achieved in the biomimetic coating by carefully controlling the volume of modified simulated body fluid (m-SBF). In the biomimetic coating method, the m-SBF volume on the apatite coating highly affects the bone-like apatite coating. It is widely reported that the coating morphologies via biomimetic coating are more porous compared to other coating techniques. This is due to the bone-like apatite forming simultaneously in the SBF solution.

Dip coating is a method which includes three steps; (i) dipping, (ii) withdrawing, and (iii) drying as shown in Fig. 4. This technique offers various advantages such as low-cost set-up, process simplicity, uniformity of deposition, low processing temperature, and the ability to coat irregular shapes and patterns [182,183]. In dip coating process, the substrate is dipped and withdrawn from the solution at a fixed speed. Therefore, the coating thickness is in good control without producing waste. Several prototypes have been recommended to explain a homogeneous and uniform fluid layer formation by applying the dip coating method [184,185].

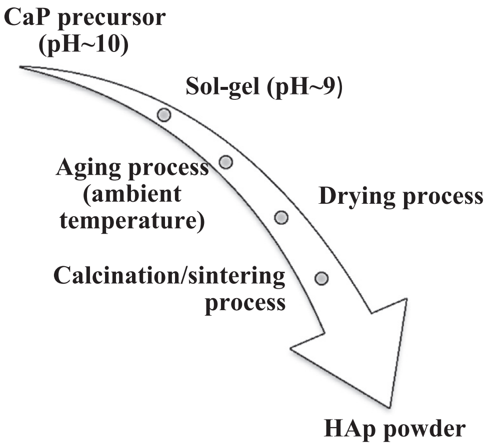

Fig. 3. Suggested flow for HAp preparation using sol-gel route.

In addition, the coating amount and layer thickness too can be controlled by adjusting the concentration of suspension and number of dips. Many studies investigated the significance of poly-(ε-caprolactone)(PCL) that applied different concentrations of 0, 10, 30, and 50 wt% on HAp coating behaviours. The coating deposition was dipped for five dipping times at a constant withdrawal speed of 200 mm/min [185,186]. The purpose of applying PCL to the HAP is to promote osseointegration by observing the pore formation on a surface level. The addition of 30% PCL on HAp onto Ti6Al4V substrate was revealed as a good grouping owing to a large thickness of the coating, which was around 184 µm. From the observation, there was no crack formation on the coating surface and the most significant results revealed that the adhesion between the coating and the substrate was improved. The nonappearance of cracks on the coating surface is reflected necessarily. This is as prevention from wear and corrosion of the substrate. Thus, the amount of released metal ions into bodily fluid could be protected [187–189].

Heat treatment of thin and loosely packed coated substrate is often required to densify the coating layer and increase the adhesion strength between the substrate and coating [188,190,191]. Fig. 5a and b show the cross-sectional images of pure HAp and 10% PCL on HAp composite coating, indicating the deposition of very thin and loosely packed coating, which requires a sintering process to improve the densification and adhesion to the substrate. High temperature is applied to cure the coated samples to increase the adhesion strength between coating and substrate and achieve apatite structures inside the applied coatings [192–194]. However, the curing temperatures are applied below the melting point of the materials to prevent upsetting the surface integrity of the substrates. Hence, various authors reported suitable curing of sol-gel coatings on Mg and its alloys in the range 25 – 400 °C [90,195–197]. It was indicated that the development of < 1 µm thickness of HA coating on 316L stainless steel was better as the samples were also exposed to annealed temperatures of around 375 – 400 °C [93]. The bonding strength of the as-produced coatings was about 44 MPa, which

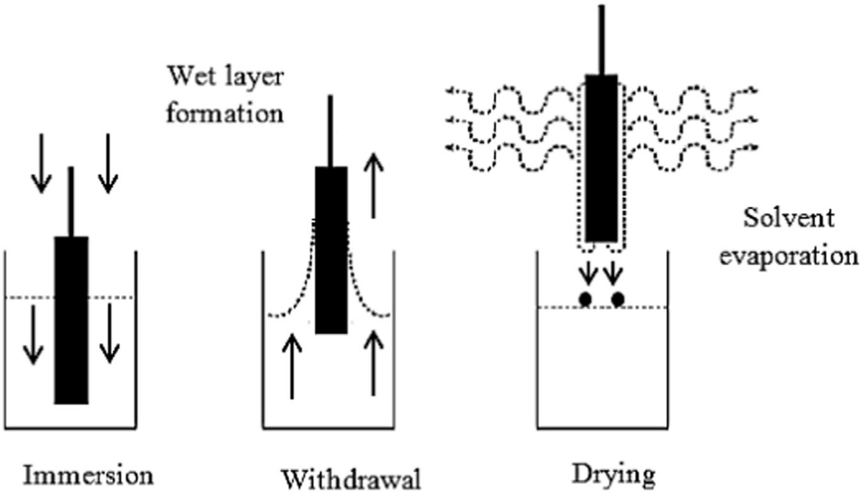

Fig. 4. Schematic diagram of dip coating technique.

relatively indicated good adhesion. For the presently investigated HAp/316L stainless steel system, the interlocking component of adhesion was maximised through surface roughening.

The combination of sol-gel and dip coating method was widely classified as uncomplicated, inexpensive, and a sustainable coating technique for coating biocompatible implants. In comparison to the spontaneous precipitation approaches, this technique can coat complex shapes or design efficiently, and also shortens the processing times; meanwhile relatively low temperatures were applied in this method to coat the HAp layers on metallic substrates. In addition, the adhesion strength between the coating and substrate is enhanced by sol-gel dip coating method, which is suitable for medical implants and industrial applications. Besides that, the sol-gel dip coating method is able to meet requirements in terms of thicker coating thickness compared to other methods (thickness in mm range) and be able to achieve Ca/P ratio in the range 1.67–1.76.

3.2. Electrochemical deposition

One of the commercial coating methods for biomedical applications is electrochemical deposition process [199,200]. Electrodeposition process is frequently conducted by anodic or cathodic systems. In this process, anodic deposition alone is inadequate to produce small feature size materials on the substrates. With regard to this, cathodic deposition has noteworthy advantages for modern and medical applications [201–203]. Through this method, two procedures are regularly applied for coating preparation, 1) the electrophoretic procedure (EPD), and 2) the electrolytic procedure (ELD). The EPD process describes the utilisation of suspensions of ceramic particles while the ELD process is the formation of metal salts from solutions. This electrochemical deposition is widely applied for coating on the titanium substrate. The subsequent filtrate is utilised as the electrolyte once the CaP proportion is dissolved in distilled water [204–206]. This procedure is regularly performed for watery arrangements like those utilised as a part of the wet substance deposition. Since the cathodic deposition has been prescribed, high

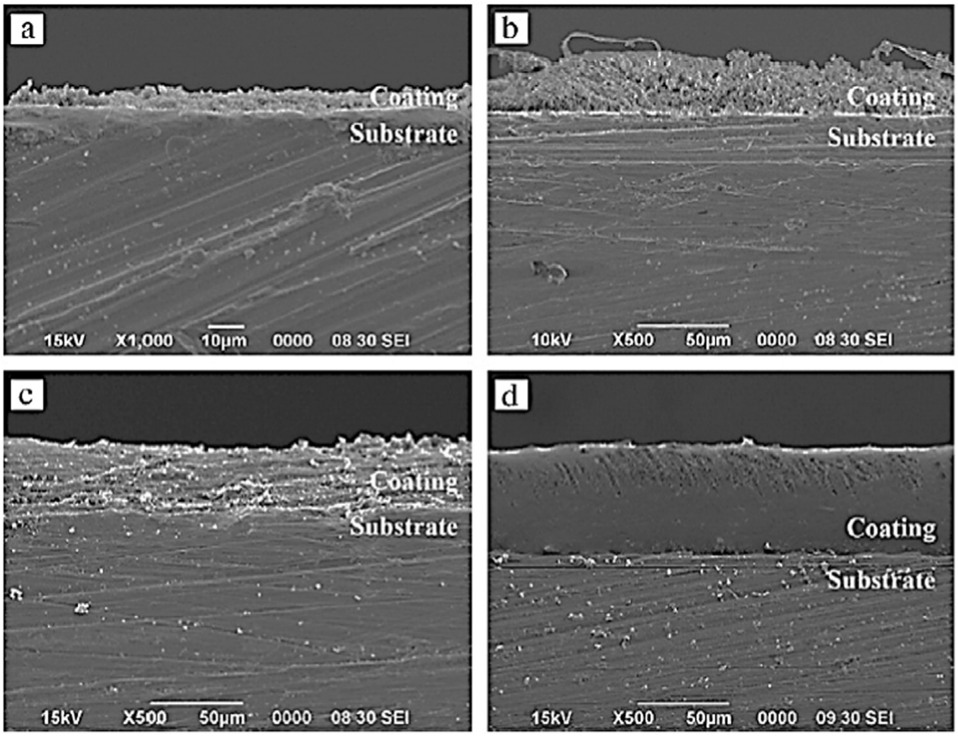

Fig. 5. A series of SEM images of the cross-section of (a) HAp, (b) 10% PCL/HAp, (c) 30% PCL/HAp, (d) 50% PCL/HAp [198].

anodic possibilities resulting from the reaction can influence the substrate surface adversely as proven by several numbers of works utilising this process [101,207,208]. Interestingly, graphite and platinum have also been utilised as the standard reference electrode for anodic material.

One of the favourable circumstances in HAp coating deposition process conducted through the electrochemical technique is the ability to form a uniform coating and quick coating process [209,210]. The procedure can be performed at moderately low temperature [211]. Electrophoresis process can produce impregnated ceramic particle towards a porous substrate and composite consolidation. Besides, a significant aspect of sintering behaviour greatly depends on the state of agglomeration of ceramic powders. The lower the sintering temperature, the more dense the (closely packed) fine particles which further leads to the formation of agglomerate-free structures [212]. The pre-sedimentation process can separate the aggregates [105]. In addition, defect areas could lead to higher rate of deposition, bringing about the uniformity of the deposit materials and better packing assembly of materials. The higher rate and better deposition layer are due to the insulating behaviour of the deposition.

Recently, many types of research have been conducted on the deposition of HAp onto metallic implant surface via electrochemical method [56,213]. The electrochemical deposition process can form a homogenous coating layer that enhances the adhesion strength between the coating layers and implant surface. Kuo et al. [214] conducted HAp coating on titanium by using the electrochemical method. The initial composition of a coating comprised b-tricalcium phosphate (b-TCP, $Ca_3(PO_4)_2$) and dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$, DCPD). The addition of 0.042 M $Ca(NO_3)_2$ and 0.025 M $NH_4H_2PO_4$ aqueous solutions into as-deposited coating was transformed to the HAp coating. The thickness of the HAp coating was approximately 18.6 µm with the adhesion strength of 106.3 MPa. The result was three times greater than the loading stress on the hip joint during gait (< 35 MPa). The finding was the strongest adhesion strength reported to date for HAp coated metallic biomaterials. As stated in Table 6, the bonding strength obtained by plasma spray was between 5 to 23 MPa, sol-gel dip coating was 42–45 MPa, and electrochemical method was reported in the range 5 – 17 MPa. Fig. 6 shows the cross-sectional area of SEM photo of HAp coating deposited at ten mA/cm2 for 30 min of the (a) uncovered thick under-layer coating, (b) demonstration of the EDS line-examining graph of the straight-line AB in Fig. 6(a).

The electrical current in electrochemical deposition is usually controlled by a potentiostat (fixed potential) and galvanostat (fixed current) [41,215]. Electrochemical deposition of HAp on metal substrates utilised customary strategies to diminish their debasement, unfortunately, it contains the abandons of the coating surfaces [30,42]. Hydroxide (OH-) particles are created at the substrate (cathode) surface with electric current crossing the electrodes as they were immersed in electrolyte during electrochemical deposition process [216,217]. The condition occurs due to the electrochemical response that is normally significant as the system insignificantly response towards the water, which leads to the significant accumulation of hydrogen gas [218,219]. The development of the hydrogen gas pockets on the surface of the substrate may rapidly occur and thus resulting in the decrease of the nucleation and presence of calcium phosphate. In this manner, it may prompt the arrangement of non-uniform coating [41,216]. The execution of HAp coating ought to tackle and enhance higher current thickness to counter the defects. A few modifications are recommended to adjust the direct current electrochemical deposition technique that should be more reasonable in the accompanying approach.

H_2O_2 was added to the electrolyte during the deposition process. H_2O_2 can replace the H_2O, thus bringing down the current deposition. The replacement of H_2O_2 will be able to modify the entire part of the system of electrochemical response [220]. The impacts of H_2 development might be evacuated due to the expansion of peroxide. Therefore, thick and uniform coating might be shaped [211]. Chandrasekar and Pushpavanam [221] presented a system with pulse electrodeposition, in which the power of hydrogen advancement response could be diminished during the coating deposition procedure. The ions are permitted to diffuse towards the substrate amid pulse electrodeposition and subsequently, the negatively charged layer will be discharged. This would add to even more dissemination of ions. Therefore, the hydrogen development is not enhanced with a time of coating. Besides, Blackwood et al. [220] analysed HAp coating on titanium substrate by applying galvanostatic pulse electrodeposition. The adhesion strength of HAp coatings and substrate surface is enhanced by periodic pulsed current densities in comparison to the constant current density.

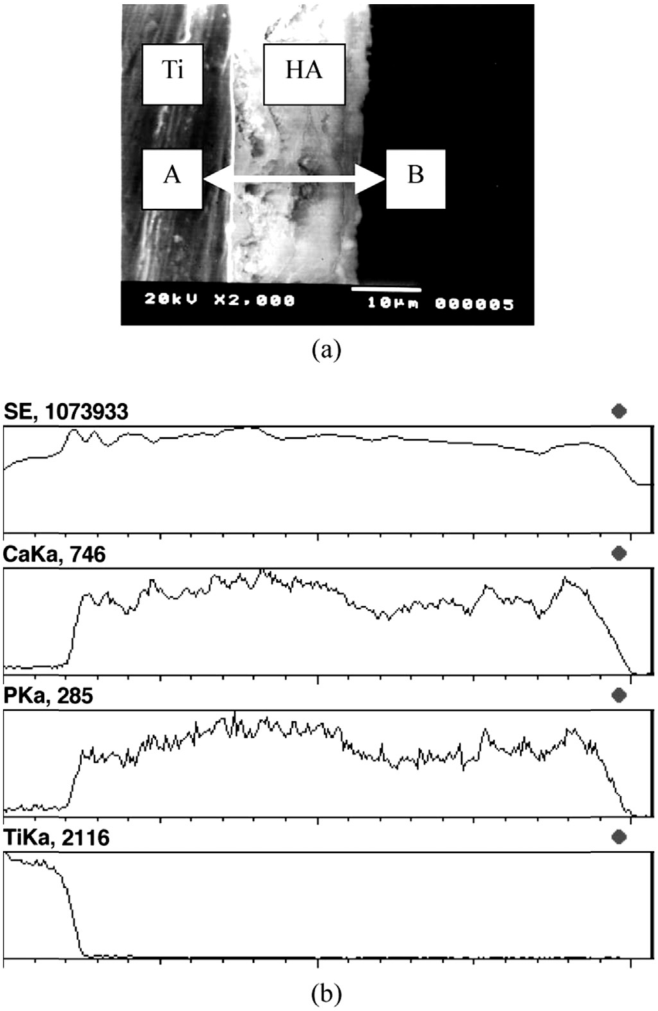

Fig. 6. (a) Cross-section view of HAp coated sample deposited at 10 mA/cm^2 and annealed for 1 h at 500 °C, and (b) line scanning pattern of line AB in (a) using EDS [214].

Additionally, the pulsed current is utilised to deposit HAp coating onto metal substrate 316 L stainless steel [222]. The ions become nearer to the cathode when the current is applied during the pulsed electrodeposition process and ions are evenly deposited. The ions from the bulk solution are diffused onto the surface of the cathode amid the relaxation time. This is one of the methods to promote the physical and chemical properties of coatings [223]. Gopi et al. [224] reported that the increment of pulse off time influenced coating and cell morphologies. It showed that the reinforcement of the proliferation of cells with the adhesion obtained was from 4 s pulse off time. The corrosion resistance in simulated body fluid also showed improvement.

Wang and Luo et al. [100] studied the effect of CoCrMo substrate with the thickness of 200 nm HAp coating on the substrate that can hold the coating quality of around 17.5 MPa, which was considered the base prerequisite for the minimum adhesion quality of HAp deposition

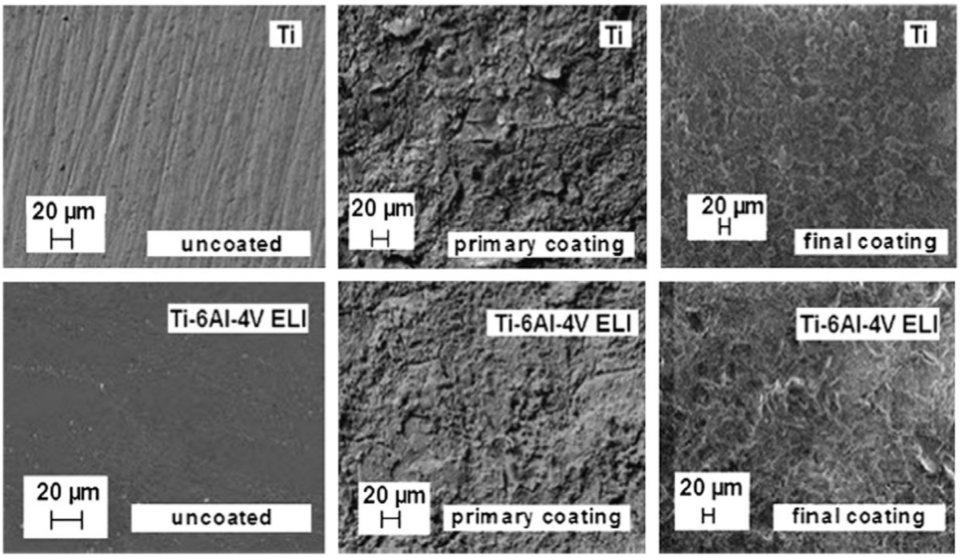

Fig. 7. SEM microstructure of uncoated substrates, primary and final coatings of Ti and Ti6Al4V alloy [216].

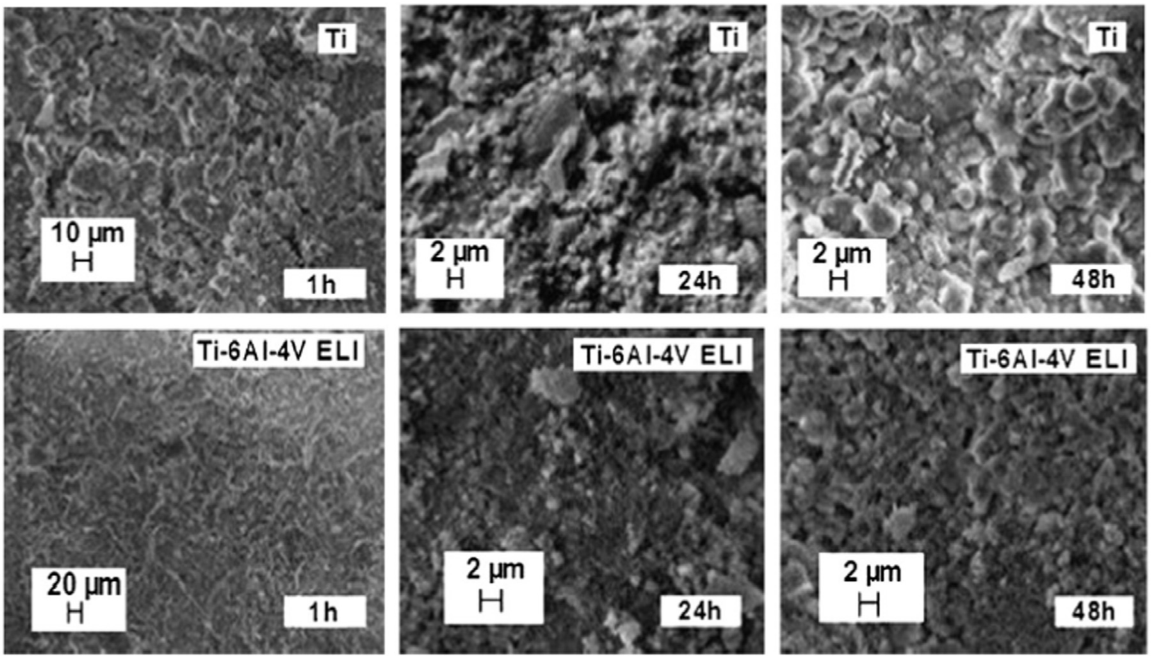

Fig. 8. SEM microstructure of the HAp coatings deposited on the Ti and Ti6Al4V alloy after 48 h immersion in Ringer's solution [216].

on metallic biomaterials [225]. Popa et al. [216], who had a comparative thought with Wang and Luo et al. [100] demonstrated that HAp coating on Ti and Ti6Al4V was more reasonable for cell adherence in contrast with brushite coating and uncoated material. This declaration was proven by the reinforced images of SEM microstructure in Fig. 7. In comparison, Fig. 8 shows the morphology of Ti and Ti6Al4V alloy coated with HAp coatings that are noticeably much denser and has lesser rugosity and a smaller amount of spallation regions after the immersion at consecutively three different periods of times, 1, 24, and 48 h. After 48 h immersion in Ringer's solution, the deposited coating layer ceaselessly disengaged the remaining pores with the size of approximately ~1 μm. It is believed that the immersion periods are crucial in order to produce a good structure for cell adhesion and proliferation. Fig. 9 demonstrates the XRD patterns of electrochemical deposition of CoCrMo elements after the submersion in the supersaturated calcification solution (SCS) for three different immersion times (2, 12, and 72 h). The expansion of inundation time ameliorates the morphologies of the coating.

Recently, an anodisation process has been introduced as pre-treatment for electrochemical deposition [226]. The purpose of anodisation is to support the developing mechanical interlocks flanked by the metal substrate and HAp coating [226–228]. Without post-treatment, homogenous and pure HAp coating is able to be achieved through the anodising process. It was stated by He et al. [229] that the Al coating on Ti substrate was with the anodisation and hydrothermal treatment. The results indicated the growth of CaP from the holes of anodised aluminium oxide (Al_2O_3) within the coating deposition. Besides, Yang et al. [230] conducted anodic oxidation treatment for bioactive Ti metal. Even though electrochemical and pre-treatment processes became vital, the studies on HAp coating deposited by an electrochemical method on the porous anodised Ti substrate was still in its progressing stage [205]. In addition, Zhao et al., [210] demonstrated the immersion of electrodeposited HAp coated on anodised titanium in a simulated body fluid (SBF) environment. Fig. 10 shows the XRD spectrum of the HAp deposition on anodised Ti substrate.

The immersion of HAp coated substrates in SBF solution that was

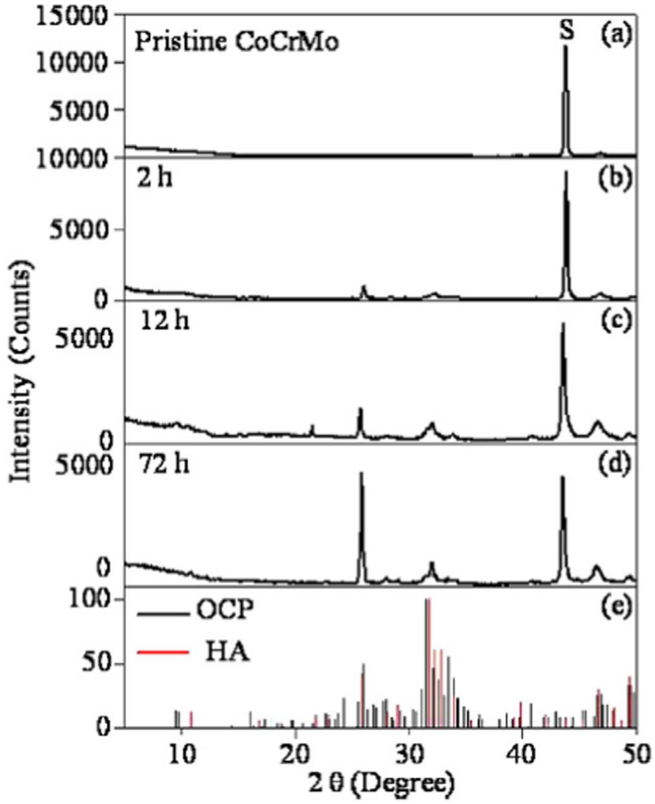

Fig. 9. XRD patterns of CoCrMo after immersion in Supersaturated Calcification Solution (SCS) at different soaking time and Octacalcium Phosphate (OCP) standard data [100].

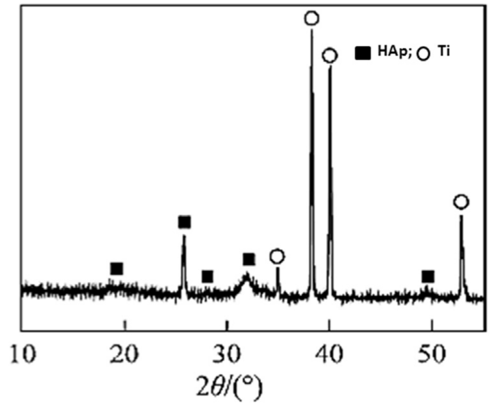

Fig. 10. The XRD spectrum of pure HAp deposited coating on anodised Ti surface substrate that shows a homogenous coating deposition [210].

Table 4
The n(Ca)/n(P) ratio and HAp coatings thickness after immersion in SBF solution [210].

	n(Ca)/n(P)	Thickness/μm
Before soaking	1.6156	16
Day 1	1.6698	16
Day 2	1.6723	19
Day 3	1.6722	32
Day 4	1.6727	76

left for four days showed good behaviour in terms of bioactivity and coating layer thickness. The immersion process encouraged the enhancement of the thickness coating as summarised in Table 4. The SBF solution mainly resembles and mimics the real human body fluid. The SBF solution reaction was conducted at 37 °C and buffered to the pH condition of around 7.2–7.4 using hydrochloric acid (HCl) and Tris (hydroxymethyl)aminomethane ($(HOCH_2)_3CNH_2$).

The in-vivo experiment was tested on rabbits and the results confirmed that the bonding strength between bone and implant was at a considerable stage but still not that noteworthy. This is related to the precipitation of apatite-like formation stored in the pores of an oxide layer with low porosity [231]. An electrolyte prepared from 0.75 M Ca acetate, 0.12 M NaEDTA, 0.025 M Ca biphosphate and NaOH with Ca/P ratio 1.3 had better mechanical stability. Besides that, CaP phase in the crystalline anatase and matrix of amorphous were totally dissolved [232,233]. The increment of the alkaline phosphatase's activity in osteosarcoma cells and a reduction in the proliferation proved that micro-arc oxidation enhanced the biocompatibility of Ti [233]. The in-vivo experiment indicated the triple enhancements in bone implant strength.

Nowadays, a few methods have been presented in order to enhance mechanical properties of the implants. One of the methods is through reinforcing materials such as Zirconia oxide (ZrO_2), carbon nanotubes (CNTs), and Titanium oxide (TiO_2) [234–239]. Other than that, several reports regarding the HAp-based coating showed that the enhancement in adhesion strength approaching 70% was greater compared to pure HAp coating [240]. HAp coating with the addition of single-walled nanotubes (SWNT) managed to get homogenous and high crystallinity and crack-free coatings formation. Additionally, the adhesion strength of the coating and substrate after introducing SWNT was improved from 15.3 to 25.7 MPa [240].

Yuan and Golden [160] introduced the 316 L stainless steel (SS) substrate with two layers of HAp coating deposited via electrodeposition. The coated substrates can be sintered either in vacuum (800 °C) or air (600 °C). In correlation to a single layer coating of HAp, the result of a double layer of HAp coating showed uniformity with good adhesion strength. Furthermore, the formation of the oxide layer as an intermediate layer between the substrate and coating helped to maintain the diffusion of harmful impurities from the substrate towards the coating surface in order to avoid the decomposition of HAp [102]. By applying high-temperature annealing or sintering in the formation of a uniform and denser CaP coating post-electrodeposition [241], a superior adhesion behaviour of the coated layer can be formed. Rath et al. [242] developed the TiO_2/HAp bilayer coating that showed significant enhancement in the adhesion strength (48 MPa) as well as corrosion resistance without compromising its biocompatibility compared to monolithic coating. The steep increase in the adhesion strength was believed to be due to mechanical interlocking and diffusion bonding at the interface. Therefore, the presence of dense TiO_2 interlayer in the bilayer coating was able to reduce the corrosion of current in Ringer's solution to a negligible value.

Albayrak et al. [243] reported the same technique used by Yuan and Golden [160]. Titanium oxide (TiO_2) was introduced as an oxide layer on the Ti6Al4V substrate prior to HAp coating. The coated substrates with the presence of TiO_2 had the thickness about 30 μm and were soaked for 1 min with different voltages at 10, 20, and 50 V. With the decreasing voltage value, the result showed an increment of adhesion strength. The comparison of the adhesion strength between electrodeposition methods is listed in Table 5.

In conclusion, HAp coatings conducted via electrochemical deposition technique were formed progressively by nucleation and growth processes that led to a uniform structure formation. A wide range of coating thickness can be formed by electrochemical deposition technique. In addition, the electrochemical deposition process can be performed at relatively low temperatures; it decreases the corrosion behaviour of the substrate through the coating. Consistently, sintering procedure enhances densification, bonding and adhesion behaviours of the coating. Nevertheless, the sintering process might lead to the HAp decomposition. In order to overcome the issue of HAp decomposition, an interlayer between substrate and coating was introduced. Therefore, the electrochemical deposition technique can be one of the most promising metal substrates for the future.

Table 5
Values of adhesion strength of HAp coatings deposited by electrodeposition process.

	Composition	Thickness (µm)	Adhesion Strength (MPa)	References
1	CoCrMo + HAp	0.2	17.5	[100]
2	Ti6Al4V + HAp (flake-shaped)	10	6.8	[235]
	Ti6Al4V + HAp (spherical)	10	10.7	
	Ti6Al4V + sHAp/ CNT-Ti	10	10.6	
	Ti6Al4V + HAp (needle-shaped)	10	8.5	
3	Ti + HAp (without oxidation)	3	5.0	[206]
	Ti + HAp (with oxidation)	3	7.3	
4	Ti + HAp	10	15.3, 106.3	[215,241]
	Ti + SWNTs/ HAp	10	25.7	
5	Ti6Al4V + HAp	30	13.8	[244]
	Ti6Al4V + TiO_2 (10 V)/ HAp	30	21.0	
	Ti6Al4V + TiO_2 (20 V)/ HAp	30	13.1	
	Ti6Al4V + TiO_2 (50 V)/ HAp	30	11.9	

3.3. *Thermal spraying*

Thermal spray field has gained quite an interest in numerous research fields since it is also considered a promising technique to achieve entirely new coating properties. Hence, it allows the allocation of new industrial application fields. Thermal spray method uses precursor solutions or suspensions as liquid feedstock to protect and enrich thermal barrier coatings or functional characteristics properties. Thermal spray process can be classed into three groups; flame, plasma arc, and electrical arc sprays. There are various methods for thermal spray processes such as atmospheric plasma spraying (APS), vacuum plasma spraying (VPS), liquid plasma spraying (LPS), suspension plasma spraying (SPS), high velocity oxy-fuel (HVOF), high-velocity suspension flame spraying (HVSFS), detonation gun spraying, and gas tunnel type plasma spraying (GTPS). All the thermal spray processes were introduced to deposit a bioactive HAp-based coating on metal [112,244–247].

3.3.1. *Plasma spraying*

Powder plasma spraying (PPS) is a widely used method to deposit biocompatible HAp coating [248–250]. The indirect method of plasma spray applies melting and spraying onto the surface by an electric arc. The process of this method involves heating the dry powder feedstock by thermal plasma jet. Then, the thermal plasma jet accelerates and impacts the feedstock towards the substrate. The powder feedstock is flattened in the form of lamellae.

Air or vacuum spraying is one of the plasma-assisted depositions, which is very popular compared to other methods. The coatings obtained from this method are capable having relatively good mechanical properties as shown in Fig. 11. The relative temperatures in the jet are 10,000 K [249], 12,000 K [251] or as high as 30,000 K [252], which intensely declines with the nozzle distance. Practically, all the materials are melted and propelled towards a substrate. Plasma spraying is an entrenched method for HAp coating on metallic implants. Indeed, several types of research have been conducted to observe the microstructure, phase transformation, and effects of post-treatment of the sprayed HAp properties for both in-vitro and in-vivo [253,254]. However, the limitation of the plasma-spraying technique includes variation in the adhesion strength of the coatings and substrates and changes in the HAp structure due to the coating process. Besides that, coating process by plasma-spraying method leads to poor adhesion of the coatings and metallic substrates [255,256].

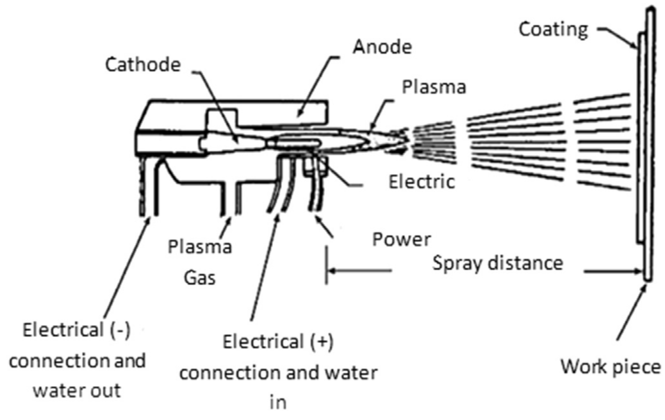

Fig. 11. Schematic illustration of plasma spraying technique [257].

The development of coated layer on titanium surface with apatite powder for 10 s was reported. The loosely absorbed powder was removed via ultrasonic cleaner [258,259]. Better apatite adhesion, strong adhesion between implant and bone, and enhanced osteoconductivity were detected. The adhesion strength between HAp coating and Ti and its alloys was discussed in [257]; however, it was also very obvious that by an increment of the immersion time in the simulated body fluid (SBF), the adhesion strength of HAp coating on Ti started to decrease [260,261].

The mechanical properties of HAp coating are mainly determined by the thickness of the coating. The thickness of HAp coating on the Ti6Al4V alloy by APS was about 150 µm thickness. This range of coating thickness significantly diminished fatigue strength while the range between 25 and 100 µm thickness did not show such an effect [262]. The reasons for the reduction in fatigue strength might be due to the intrinsic stresses that happened during spraying, coating cracks, while most significant stresses were discharged during spraying. The difference in the stiffness of the metal substrate and coating was also significant. It was reported that deposition of a coating by SPS obtained relatively thin coatings of 5 – 50 µm [263] compared to other results and could be achieved by using dry powder processing. The dry powder particles used for the SPS have diameters ranging from a few sub-micrometres to a few micrometres [264,265]. The thicknesses of APS coatings are in the range 200 – 300 µm and are quite porous in nature. The coating thickness can depend on the composition of the plasma gas i.e. $Ar/H_2/N_2/He$ (commonly used), the plasma gun input power, gas flow, powder feeding rates, the characteristics of feed materials, and spray stand-off distance which is frequently varied [266–268].

Furthermore, the structure and bonding properties of HAp coating on metallic biomaterials can be improved by subjecting them to a heat treatment process. Annealing of HAp coating was conducted for 90 h at 400 °C. The annealing process transformed a partial amorphous coating into a crystalline coating [262]. The mostly higher crystallinity of the coating was supposed to have good adhesion characteristics. Nevertheless, the colour and thickness of the coating changed and led to the decrement of fatigue strength. Annealing at a higher temperature such as at 700 °C for 1 h could enhance the coating purity, hydroxyl group, and crystallinity degree. However, the high spraying power values can cause a decrement of the adhesion strength between the coating and substrate due to the higher content of amorphous HAp [218]. Based on

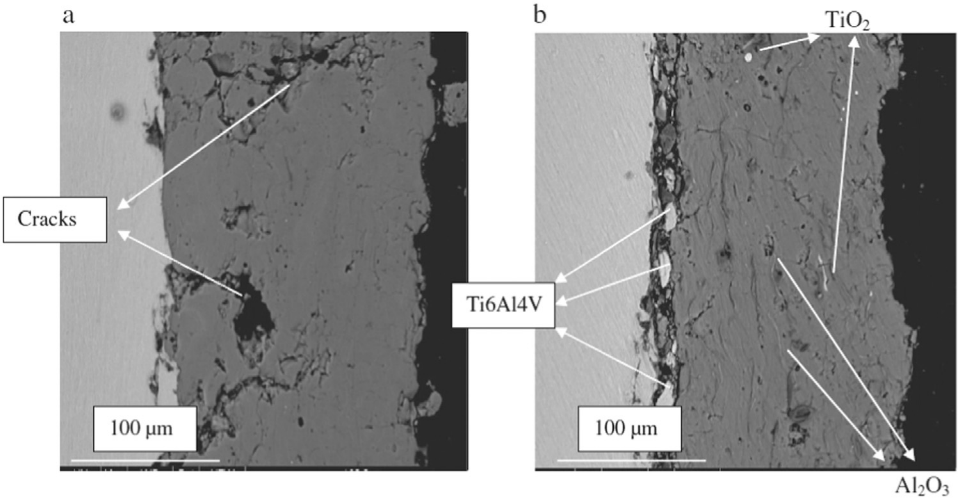

Fig. 12. The SEM cross-section view of plasma spray coatings on Ti6AL4V micrographs: (a) pure HAp coating on Ti6AL4V and (b) HAp reinforced by 10% (80 Al_2O_3–20 TiO_2) on Ti6AL4V [270].

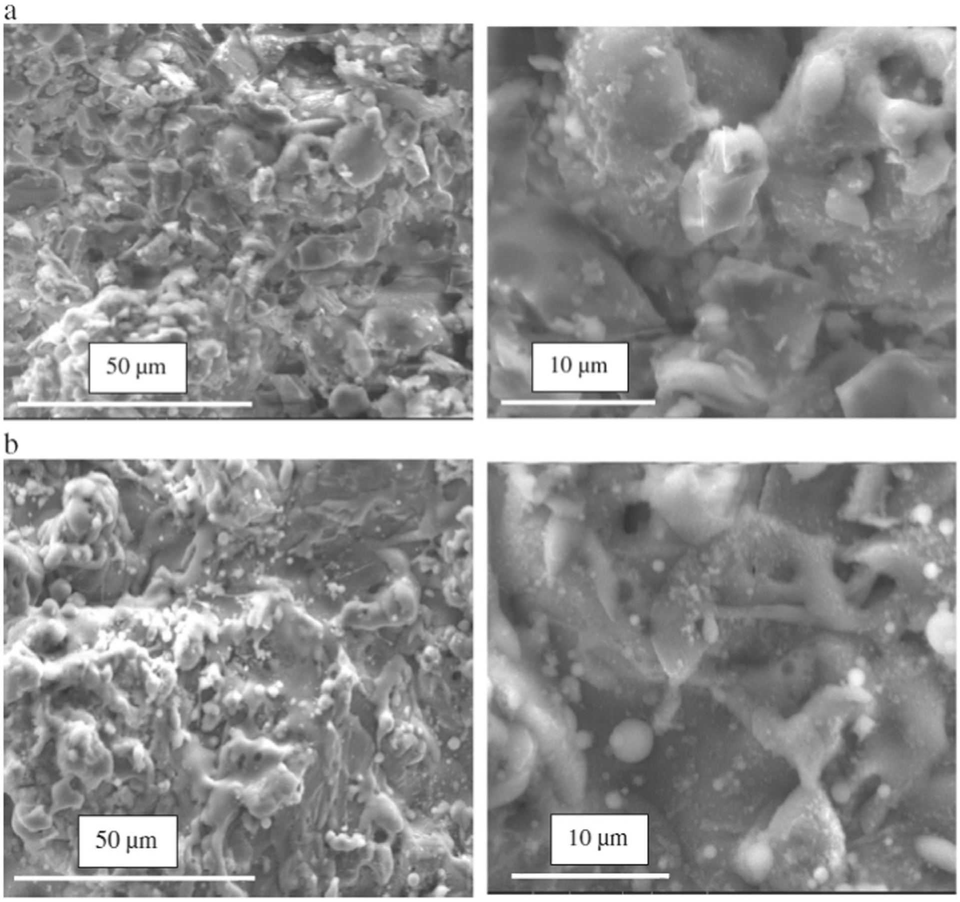

Fig. 13. The surface morphology of coatings (a) pure HAp coating on Ti6AL4V and (b) reinforced HAp on Ti6Al4V at different magnifications, 50 µm and 10 µm [270].

the observations in the annealing process of HAp coated at 1100 °C under vacuum condition, the secondary β phase was formed while hydroxyl groups are diminished. The higher the temperature of the annealing process, the higher the formation of the complex oxide of Ti and Ca, when the characteristic metallic Ti disappears [269].

The increment in adhesion strength can be achieved with the use of a coupling agent through chemical bonding [83]. By means to enhance adhesion property, the addition of Ti to the HAp helped improve the bonding strength of the coating significantly [159]. The bonding strength was increased from 14.5 to 17.3 MPa as the reinforced coating was between 20 and 60 wt% Ti. The increment in the Ti content could cause better adhesion of the coating layer to the substrate for further enhancement. Singh et al. [270] proposed such that HAp be reinforced with 10 wt% ($80Al_2O_3-20TiO_2$) on Ti6Al4V alloy. This solution enhanced the adhesion strength to above 32 MPa. Fig. 12(a) and (b) show that the coatings with and without the reinforcement of 10 wt% ($80Al_2O_3-20TiO_2$) had approximately the same thickness of around 150 µm. However, several cracks on the surface can be observed based on the cross-section area of the pure HAp coating shown in Fig. 12(a). Nonetheless, the coating with reinforcement was observed to be absent from the crack with more homogeneous surface as shown in Fig. 12(b). They agreed that it may be more promising for coatings to be composed of higher surface roughness from 5.53 to 7.31 µm as shown in Fig. 13(a) and (b) [270].

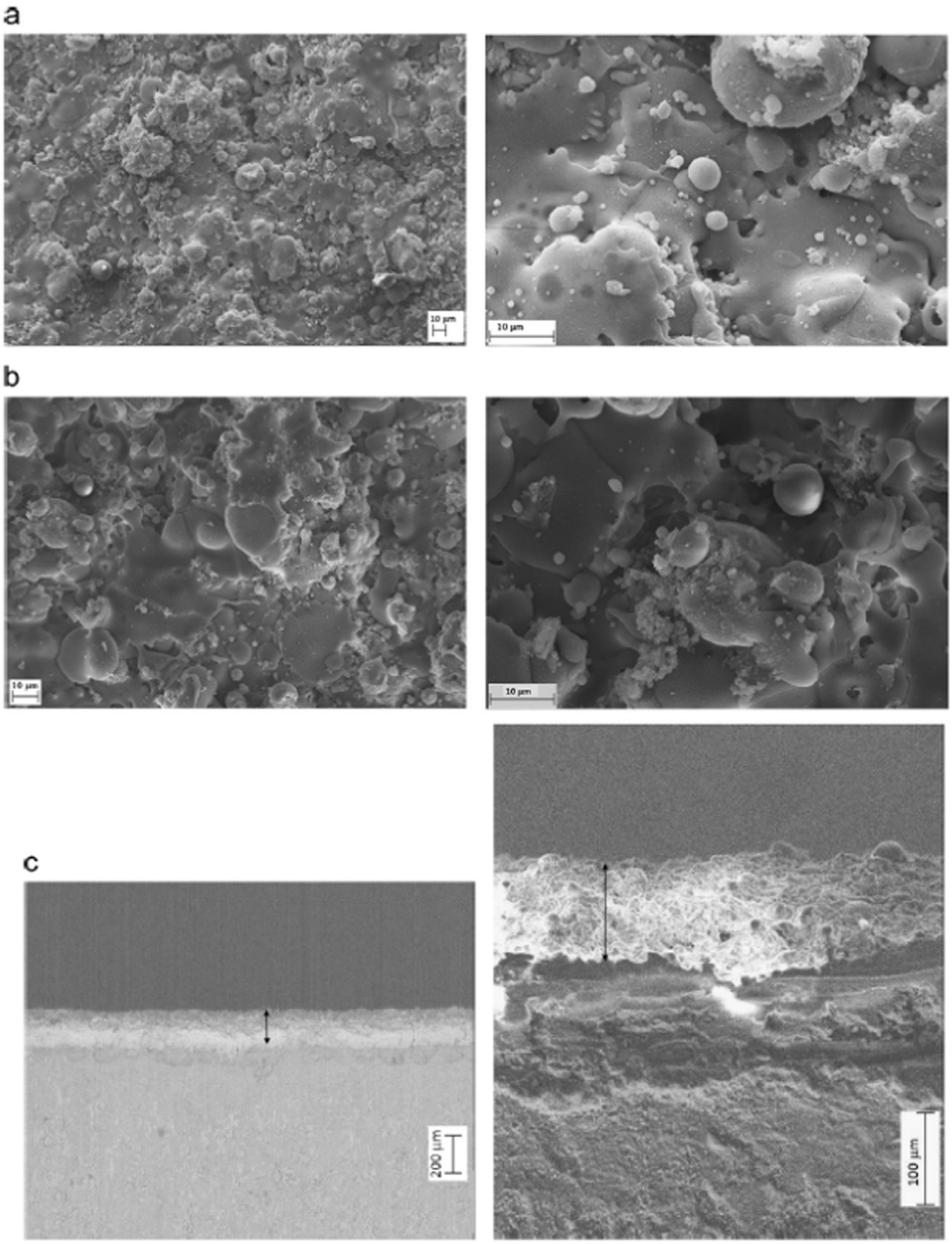

Fig. 14. The surface morphology of HAp/Si coating on magnesium plates (a) before, (b) after heat treatment, and (c) cross-section view [72].

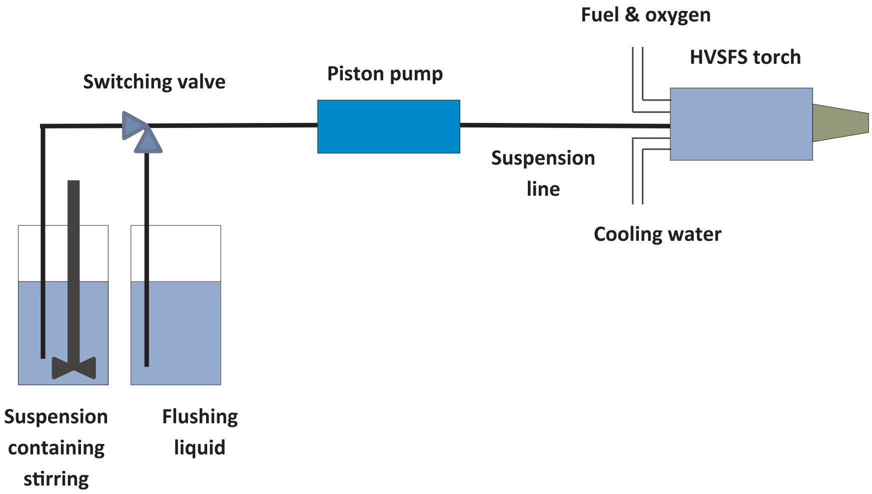

Fig. 15. Schematic diagram for HVSFS.

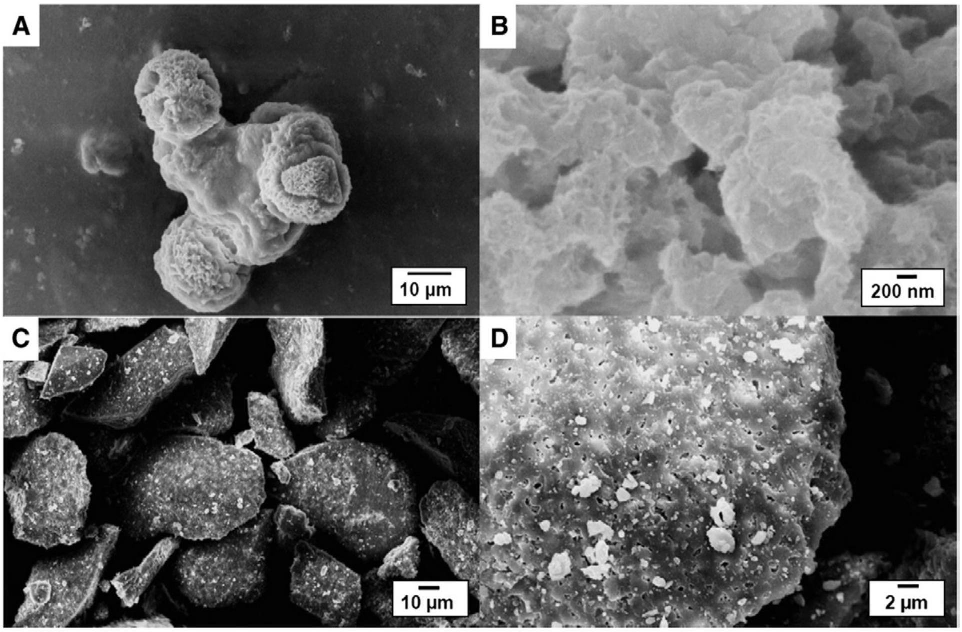

Fig. 16. The micrograph of HAp particles obtained from the dried water-based suspension (A, B) and crushed particles of the dry spray powder (C, D) [244].

The rough surface of the metal substrate exhibited better adhesion strength compared to a smooth surface of the metal substrate [41,141]. It was proved that the solid and roughen surface upon the post-heat treatment not only could reduce the microcracks and pores in the coating but also release residual stress between the coating and substrate [193]. The SEM images of the coatings before and after heat treatment (Fig. 14(a),(b),(c)) are showed as in the results from Bogya et al. [72].

3.3.2. *High-velocity suspension flame spraying (HVSFS)*

Currently, the high-velocity oxygen-fuel (HVOF) flame spraying method has been intensively introduced. The method gives promising results in terms of allowing the formation of suspension spraying layer [271–273]. By introducing the axial powder injection, the new high-velocity suspension flame spraying (HVSFS) method is typically able to resolve the injection complications [274–276]. With regards to this, the highest velocity of the particle would be able to produce better coating protection with low porosity. This innovative suspension thermal spray technique has ideally become the most in-demand technique in depositing a thin layer of coating on the substrate [277,278]. In comparison to other methods such as electrophoretic coatings for pure HAp, the coating does not require any heat treatment or post-deposition for consolidation. Furthermore, the method features relatively low processing costs with high and efficient productivity [279,280].

As compared to conventional dry powders, the suspension based feedstock could incite more flexibility in creating new composite materials by altering the material compositions which are controlling the primary particle morphology [281–284]. Furthermore, a fine powder particle either in micro- or nano-size could be synthesised by the thermal spray community. The method enables direct delivery of the particles into gas or plasma jets as shown in Fig. 15. The direct processing of fine particles dispersed in liquid solvent significantly yields smaller lamella size of the coating layer that depends on the standard parameters of spray powder processing [120,276].

Nevertheless, the atmospheric plasma spraying (APS) also yields several drawbacks although the process involves low-cost setup, robust productivity, and adequate heat input transferred toward the substrate. The drawbacks are mainly found in chemical and structural modifications of crystalline bioactive ceramics, for instance, the failure to apply a thin coating of HAp layer below 50 µm [284]. In this case, HAp starts to decompose to tricalcium phosphate and tetracalcium phosphate when the processing temperature increases. On another note, the formation of CaO is a result of thermal degradation [118,285]. Instead, the acceptable thin coating layer is necessary to promote the osseo-conductive or osseo-inductive aspects on the coated area. Unfortunately, the long-term mechanical stability and adhesion tend to incur damage due to a high thickness of coating. Other than that, it is certainly the reason for encouraging related deposition stresses, which weaken the adhesion and cause long-term de-bonding between the substrate and the coating. It affects the harmful metal ions being released into the surrounding tissues which causes failure of the implants [118,286].

The HVSFS technique could produce high-quality and low-thickness coatings, especially when the layer thickness is below 50 µm [244,274]. The development of the system does indeed fill in the gap between conventional thermal spraying and thin-film technologies (PVD, CVD). The thinner coatings produced from this technique usually contain less residual stress with a minimised risk of delamination [287,288]. The coated properties, especially the ones involving bonding strength between the substrate and coated layer produced from HVSFS techniques tend to be affected seriously due to the effect of processing parameters such as gas flow, air-fuel ratio spray distance, and electric arc current. As reported by Gadow et al. [244], bio-ceramic coatings could be based on dry spray HAp powder used for HVOF, and APS nanoscale HAp suspension (water-based) for HVSFS. As shown in SEM microstructure in Fig. 16, the dispersed particles of the two suspensions contain aggregated nano-sized (< 50 nm) of primary particles. The HAp nanoparticles appear to be intensely cohesive and constantly agglomerated in the suspension as shown in Fig. 16 (A and B).

By introducing different suspension solution mediums such as diethylene glycol (DEG) as a substitute for water suspension, the result of the adhesion strength of the HAp coatings is enhanced and supposed to be superior [244]. The DEG-based solution enhances the adhesion strength as compared to the water-based suspension. In fact, DEG based suspension offers many advanced properties such as low interlayer porosity with denser coatings as shown in Fig. 17. The resulting condition is due to the higher adhesion strength. The highest adhesion strength is around $25\ \mathrm{N/mm^2}$ as reported for HVSFS-HAp coating [244]. G. Bolelli et al. [118] demonstrated that the HVSFS deposited HAp coating is made possible with the addition of TiO_2 onto commercially pure Ti. The TiO_2 layer acts as a thermal insulating layer, which slows down heat extraction from the deposited material to the substrate. The HVSFS deposited HAp coatings are typically dense with

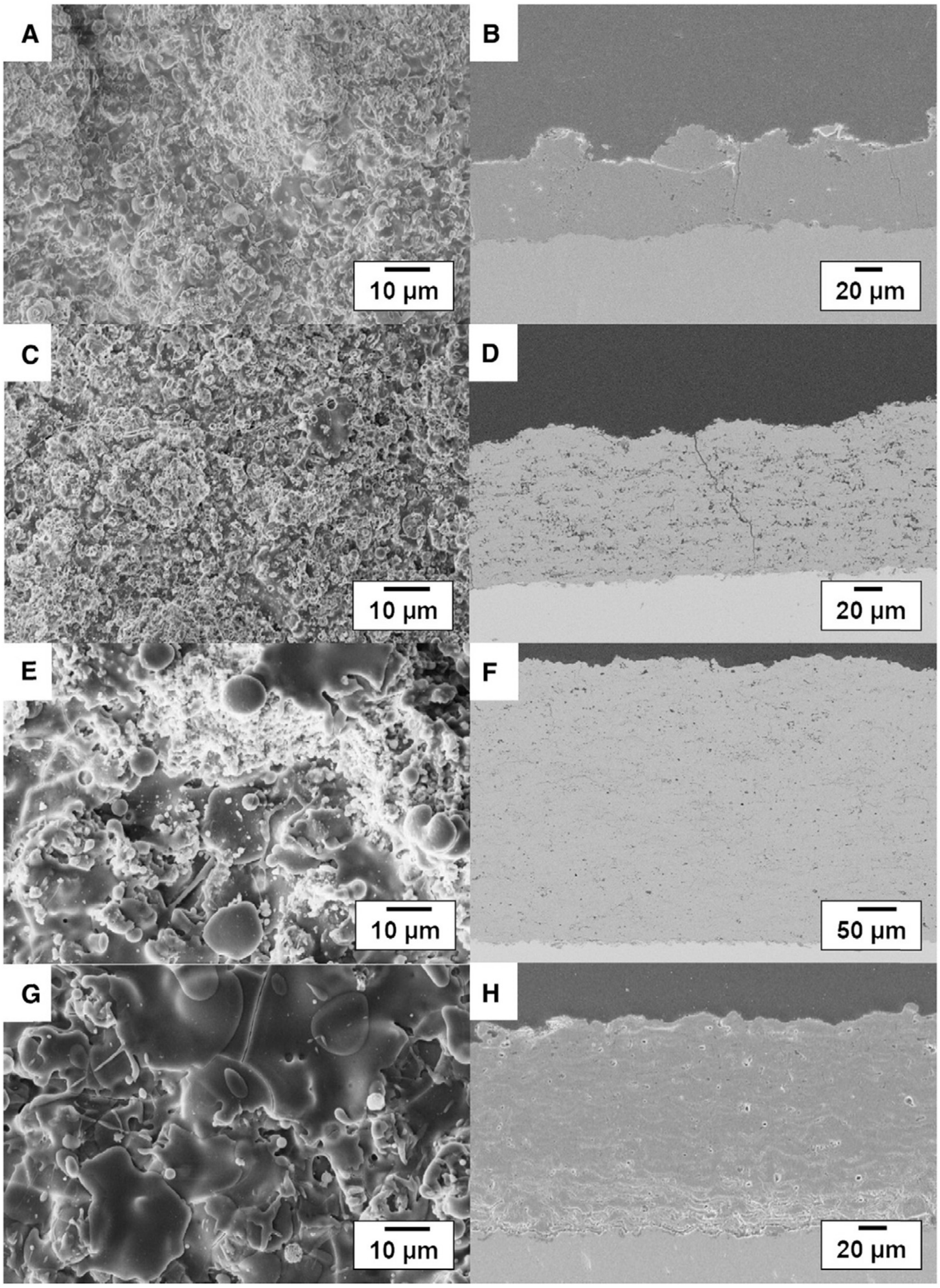

Fig. 17. SEM micrographs: (A) Surface of a DEG based HVSFS-HAp coating, (B) A cross-section of a DEG based HVSFS-HAp coating, (C) The surface of a water-based HVSFS-HAp coating, (D) A cross-section of a water-based HVSFS-HAp coating, (E) The surface of an HVOF-HAp coating, (F) A cross-section of an HVOF-HAp coating, (G) The surface of an APS-HAp coating, and (H) Cross-section of an APS-HAp coating [244].

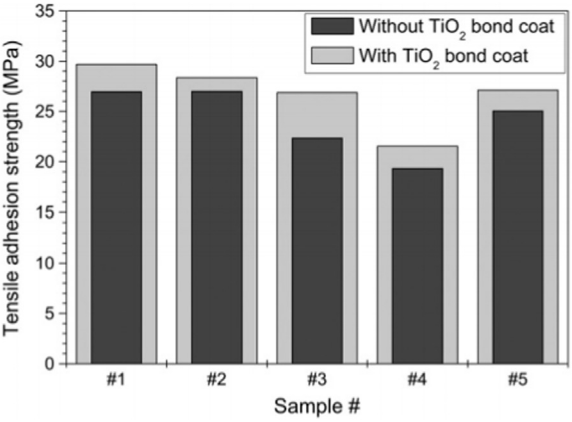

Fig. 18. Adhesion strength of the HVSFS-deposited HAp coatings [119].

27–37 µm in thickness and some transverse microcracks. Even its crystallinity characteristic is of between 10 to 70%, depending on the deposition parameters and amount of a TiO_2 concentration. The adhesion strength between the metal substrate and HAp coating was enhanced due to the presence of TiO_2 layer as shown in Fig. 18.

APS, HVOF, and HVSFS methods are widely applied for HAp coating processes especially the ones that involves Ti metal as substrates [250,289,290]. The processing parameters such as gas flow, air-fuel ratio, electric arc current, and spray distance are the main factors in determining the coating property performance in terms of the adhesion strength between the substrate and coating of these thermal spraying techniques [291,292]. The increment of the flow rate of oxygen enhances the behaviour of the coating composite. Besides that, the fuel flow rate also plays an important role in influencing the coating performance. Enhancing oxygen flow rate along with fuel flow rate leads to stronger adhesion strength. Other than that, reducing the spray distance also brings to stronger adhesion strength [246]. The mechanical

Table 6
Comparison of adhesion strength values of HAp coating and metal substrate with different deposition techniques.

Technique	Material	Adhesion strength (MPa)	References
Sol-gel dip coating	316 L stainless steel + HAp + heat treated	~42–45	[93,180]
	Ti + HAp + heat treated	~ 22–35	
	Ti + TiO_2 + HAp + heat treated	~22–55	
Electrochemical deposition	CoCrMo + HAp	17.5	[100,207,242,245]
	Ti + HAp	15.3	
	Ti + HAp	5.0	
	Ti + HAp + oxidation	7.3	
Atmospheric plasma spray (APS)	Ti + HAp	~5–23	[261]
High-velocity oxy fuel (HVOF)	Ti6Al4V + HAp	~24 ± 8	[292]
High-velocity suspension flame spray (HVSFS)	Ti + HAp	~26	[246]
	Ti + TiO_2 + HAp	~30	

properties and microstructure of the subsequent HVSFS coatings are influenced by the types of dispersion mediums to set the HAp in comparison to other processing parameters.

The adhesion strength between HAp coating and metal substrates reported for thermal spraying deposition method involving APS, HVOF, and HVSFS are above conventional electrochemical method. As plasma spray is the leading deposition method for the application of calcium phosphates, further optimisation of parameters is essential for increased adherence, crystallinity, and reduction of amorphous material and residual stress. The APS and HVOF methods are limited to conventional dry spray powder with a particle size greater than 5 µm because fluidisation of the powder becomes more challenging with the decreasing particle size, while HVSFS uses two different suspensions—water-based and DEG based suspensions. Both suspensions contained nano-sized HAp particles. Comparing these three methods (APS, HVOF, and HVSFS), the HVSFS method was preferable as it was able to enhance adhesion strength between the HAp coating and metal substrates. The bond strength of the deposited HAp coatings is dependent on the spray process and parameters. Applying suspension in HVSFS method increases the adhesion strength compared to the conventional dry spray powder in the APS and HVOF methods.

Table 6 shows numerous values of adhesion strength obtained by three different HAp deposition techniques onto the metallic biomaterials; sol-gel dip coating, electrochemical deposition, and thermal spray. According to the information in Table 6, it was stated that sol-gel dip coating and thermal spraying deposition methods were able to enhance adhesion strength of the HAp coating and metal substrates compared to electrochemical deposition. In the current research, the thermal spraying method especially APS was declared as a commercial method to develop HAp coating due to its capability in improving adhesion behaviour. The HVOF and HVSFS methods were newer modifications developed from the APS method. It was proven that these new methods are enhancing adhesion strength of the coating. Other than that, sol-gel dip coating method is one of the easier methods to develop HAp coating to metal substrates. It is also able to improve adhesion strength since the values of adhesion strength reported in Table 6 for this method is near the thermal spraying method. Based on the researcher's review, the sol-gel dip coating method could be the best method to coat HAp on the metal substrates and replace the thermal spraying method as a commercial method in order to improve the quality of adhesion strength and also coating phase purity. Previously, there were several cases of the coating via thermal spraying method reported due to the high temperature during coating deposition process. Therefore, the sol-gel dip coating can be conducted at room temperature to avoid the decomposition of HAp at high temperature (more than 800 °C).

Due to the high demand and increasing research in biomedical metallic implants, there have been various HAp emerging deposition methods introduced in these recent years such as aerosol deposition, liquid precursor plasma spraying (LPPS), radiofrequency magnetron sputtering, and electrohydrodynamic spray deposition (EHDSD). Most of the researchers worked hard in trying to introduce new deposition methods as they believed it might influence the adherence of the coating onto the metal substrates. Nevertheless, regardless of the coating deposition methods, coating characteristics are also highly influenced by the process variables, among others, that each method should optimise. The task is to select and justify the properties to be included in the optimisation exercise. Apart from the deposition methods discussed in the present review, there are others that have been used to deposit nano-HAp coating onto metal substrates and undergone surface modification or a nanostructured coating, other than HAp. Examples of such methods are electrodeposition in the presence of a static magnetic field and planetary ball milling.

4. Conclusion

The adhesion qualities of HAp coating on metallic biomaterials have been reviewed in detail. Four common techniques of deposition, namely sol–gel, dip coating, electrochemical deposition, and thermal spraying were evaluated and the coating parameters that affect the adhesion strength of the coating were discussed. A summary of adhesion strength based on deposition techniques is as listed in Table 6. The variation of the coating methods, types of coated materials, deposition techniques, and other influencing factors used in the coatings may affect the coating thickness, resulting in different crystallinity of the coatings, phase, and chemical composition, and microstructure or morphology. To date, the standard uniformity in addition to the oxide layer and composite coatings of HAp layer is proposed to improve the adhesion strength between the coating layer and substrate. Based on this review, the HAp-composite coatings have a significant potential to improve the mechanical and biochemical properties as compared to pure HAp coatings. The introduction of oxide interlayers such as TiO_2 or ZrO_2 onto the substrate prior to the coating processes can enhance the adhesion strength. Finally, the post- and pre-heat treatments such as etching and sandblasting have also shown positive effects, and definitely, the hope to further fortify bonding strength shines brighter.

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