Chapter 5

Hydroxyapatite-Based Coating on Biomedical Implant

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71063

Abstract

The use of metallic biomaterials for replacement of biomedical implants has been traced back from the nineteenth century. These metallic biomaterials have been declared as clinical success as their mechanical properties that satisfy the prerequisite of the human bone. Nevertheless, critical issues of the materials when they are utilised as implants; including the releasing toxic and harmful metal ions through wear and corrosion processes after longer implantation. Besides that, the bonding strength between bone and implants itself is considered weak due to the different components of human bone and metal implants. Hence, developing hydroxyapatite (HAp) coating on metallic biomaterials is expected to overcome the problems faced by biocompatible metallic biomaterials. As far as this, various commercial techniques have been introduced to develop the HAp coating on metallic biomaterials. The techniques are including plasma-spraying method, sol-gel dip-coating, electrochemical deposition and high-velocity suspension plasma-spraying. The formation of HAp coating on metallic biomaterials improved the corrosion resistance together promoting its load-bearing ability and enhanced substrate-coating adhesion.

Keywords: surface coating, biocompatible metals, coating techniques, biomedical applications

1. Introduction

Metals or also known as metallic biomaterials that have been used for medical treatments can be traced back around 20 years. Despite a significant number of metals that are able to be produced in modern industries, there are only three commonly biocompatible metals that are used as biomedical implant materials; stainless steel (316L), cobalt-based alloys, and titanium-based alloys [1–4]. These metallic biomaterials are typically used in orthopaedic practise since they have approval by the United States Food and Drug Administration (FDA) [4].

Since the biomaterials are employed in intimate contact with living tissues, it is important that the materials exhibited biocompatibility characteristics. The requirement of biocompatibility includes all features of bio-device functionalities during the interaction of tissues and cells with the implanted materials [5]. However, there are limitations of metallic biomaterials as an implant; weaknesses in bone-bonding ability and toxic ions released into the human body fluids after longer usage [6, 7]. Different chemical composition between the actual bone and the metal implant is one of the causes of ineffective in bone-bonding ability. Moreover, the metallic implants are also susceptible to corrosion degradation due to the surrounding aggressive body fluids [8].

Consequently, most of the researchers have introduced surface modification by applying bioactive ceramics such as hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$) as a bioactive coating on the metallic implants to the implant to enhance bone-bonding ability [9, 10]. The hydroxyapatite (HAp) is the primary inorganic ingredient of natural bones and has been the most widely used ceramic-based biomaterial for over four decades in medicine and dentistry. It has been proven by many researchers that HAp coating allows a controlled and rapid osseointegration between living bone and the surface of an implant [11, 12].

There are various commercial techniques to deposit the HAp coating on the metal-based biomaterials. In this chapter, four commercially HAp surface coating techniques including plasma spraying, sol-gel dip-coating, electrochemical deposition and high-velocity suspension plasma-spraying (HVSPS) are discussed. The discussion comprises biocompatibility, adhesion strength and corrosion behaviour studies about three aforementioned metallic biomaterials after the surface was coated by HAp.

2. Current issues of metallic biomaterials when applied as an implant

The selection of appropriate biomaterial to be classified as a metal implant material highly depends on its applications. The selected biomaterial should possess several essential characteristics such as excellent biocompatibility, osseointegration, high corrosion and wear resistance, suitable mechanical properties, ductility and high hardness.

2.1. Biocompatibility and osseointegration

The biocompatibility properties are defined as the ability of a material to be used in intimate contact physically and chemically with living tissues of a real bone without causing any adverse effects. Intuitively, it is necessary to confirm that there are no negative issues befell to metal implanted devices and surrounding living tissues since the materials are innately compatible with living cells and tissues [13].

Osseointegration denotes to a direct structural and functional connection between ordered, living bone and the surface of a load-carrying implant. It involves the process of new bone production and bone healing. Therefore, it is essential for an implant to have an appropriate surface to integrate well with surrounding bone. Surface chemistry, surface roughness and surface topography are the factors that vital for good osseointegration [14, 15].

2.2. Corrosion and metal ions release

Among critical issues and challenges of the medical implant are facing is the failure of an implant due to the corrosion aggressiveness. Consequently, a metal that performs well outside the human body may suffer a severe corrosivity reaction in the body as the environment is physically and chemically different from ambient. Due to that fact, all of the corrosion-resistant metallic implants reacted to an acidic environment and began to corrode when diagnosed for a long time in the human body. Most researchers have claimed that active implants corrosivity process rouse after 12–15 years of implantation period [6, 16].

3. Commercial techniques for hydroxyapatite-based coating onto metallic implant

The surface coating application offers the possibility of modifying the surface properties of implant devices to achieve improvements in biocompatibility, reliability, and performance. Therefore, most researchers have reported excellent studies of HAp coating onto various metallic implants specifically related to their biocompatibility and corrosion behaviour. Nowadays, different HAp deposition techniques have been carried out to overcome the biocompatibility, and corrosion issues arose from the metallic biomaterials [12, 17]. These deposition techniques include plasma spraying, sol-gel technique, electrochemical deposition and High-Velocity Suspension Plasma-spraying.

3.1. Plasma-spraying technique

Plasma spray is one of the popularly used methods used to deposit biocompatible HAp coating onto metallic implants [18, 19]. In these recent years, this approach is highly utilised for dental and orthopaedic implants. The indirect method of plasma spray applies melting and spraying onto the surface by a method an electric arc. The process 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. Plasma spraying can be carried out under vacuum, controlled atmospheres, or in an ambient atmosphere. Air or vacuum spraying is one of the plasma-assisted depositions, which is very popular compared to other methods. The coatings applied by plasma spray can have relatively good mechanical properties. The relative temperatures in the jet are 10,000 K, 12,000 K or as high as 30,000 K, intensely declining with the nozzle's distance [20]. Practically all the materials are melted and propelled towards a substrate.

Development of the coated layer on a titanium (Ti) alloy surface with hydroxyapatite powder for 10 s shows better apatite adhesion, strong adhesion between implant and bone, and enhanced osteoconductivity [21]. The properties of HAp coating are mainly determined by the thickness of the coating layer. The thickness of HAp coating obtained on the Ti6Al4V alloy by the air plasma spray (APS) was about 150 μm thickness. This range of coating's thickness significantly diminishes the fatigue strength while the range between 25 and 100 μm thickness does not show such effect [22]. The reasons for the reduction in fatigue strength might

be due to the intrinsic stresses that happened during spraying, coating cracks, and most significantly stresses discharged during spraying. The difference in the stiffness of the metal substrate and coating is also significant.

The coating deposition by a suspension plasma spray (SPS) obtained a relatively thin coating layer 5–50 μm as compared to other plasma-spray techniques and only could be achieved by dry powder processing [23]. The dry powder particles used for the SPS having diameters ranging from a few submicrometer to a few micrometres [24]. The thicknesses of APS coatings are in the range 200–300 μm and quite porous. The coating thickness depends on the composition of plasma gas used which is $Ar/H_2/N_2/He$, plasma gun input power, gas flow rate, powder feeding rate and characteristics of feed materials, and spray stand-off distance, which are frequently varied [25, 26].

Furthermore, the structure and bonding properties of HAp coating on metallic biomaterials can be improved by using heat treatment process. Annealing process transformed a partial amorphous coating into a crystalline layer [22]. The mostly higher crystallinity of the coating layer was supposed to have excellent adhesion characteristics. 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 lowering of the adhesion strength between the coating and substrate due to the higher content of amorphous HAp [27]. Based on the observations of the annealing process of HAp coated at 1100°C under vacuum condition, the secondary β phase formed while hydroxyl groups are diminished. The higher the temperature of the annealing process, the greater the formation of the compound oxide of Ti and Ca with the characteristic metallic Ti disappeared [28].

An introduction a coupling agent through chemical bonding can enhance adhesion strength between the HAp coating and metallic implants [29]. The addition of Ti to the HAp improved the bonding strength of the coating significantly [30]. The bonding strength was increased from 14.5 to 17.3 MPa as the composition of 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. According to Ref. [31] proposed HAp reinforced with 10 wt% ($80Al_2O_3$-$20TiO_2$) on the Ti6Al4V alloy. This solution enhances the adhesion strength to above 32 MPa.

3.2. Sol-gel dip-coating method

Recently, a combination of sol-gel preparation and dip-coating method are extensively employed for a coating on a metallic biomaterial. The method is one of the coating methods used for enhancement of adhesion strength [32, 33]. A calcium phosphate (CaP) precursors are the most important solutes for sol preparation. The CaP precursor is the combination of calcium (calcium nitrate) and phosphorus (phosphorus pentoxide or triethyl phosphate). Normally, there are two solvents will be mixed with the CaP precursors. Most often water and ethanol are used as a solvent for the sol preparation [34, 35].

The dip-coating is a method which includes three steps: (i) dipping, (ii) withdrawing, and (iii) drying. 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 [36, 37]. The substrate is dipped and withdrawn from the solution at a fixed speed. Therefore, the coating's thickness is in good control without producing waste [38, 39].

Additionally, the coating amount and the layer thickness can also be controlled by altering the frequency of suspension and the number of dippings. HAp coating via sol-gel dip-coating technique can obtain homogenous coating and the coating thickness in the range 0.05–15 mm [33, 40]. The coating thickness varies according to the viscosity of the sol-gel used [12]. A lower annealing temperature used for sol-gel dip-coating process can produce adhesive thin coating layer without severe cracking. An extremely high temperature (6000–10,000°C) is applied in plasma-spray deposition can decompose the HAp properties into tricalcium phosphate, tetra-calcium phosphate, calcium oxide (CaO), and others amorphous phases [41, 42]. When increasing annealing temperature from 375 to 500°C, the adhesion strength between HAp coating and the substrate increases [43, 44].

Latterly, several modifications of sol-gel dip-coating method are developed to enhance the quality of coating surface. A poly ε-caprolactone (PCL) was applied to HAp to promote osseointegration by observing the pores formation on a surface level [45]. The addition of PCL on HAp onto Ti6Al4V substrate was reported as a good grouping owing to a large thickness of the coating, around 184 μm. There was no crack formation on the coating surfaces, and the most significant results revealed that the adhesion between the coating and the substrate was improved. The absence of cracks on the coating surface was reflected necessarily. This is an effective prevention of wear and corrosion for the substrate. Hence, the amount of releasing metal ions into surrounding (body fluid) can be minimised as the coated metal exhibit better corrosion resistance [46–48].

Heat treatment of thin and loosely packed coated substrate is often required to densify the coating layer and to increase the adhesion strength between the substrate and coating [47, 49, 50]. The high temperature is applied to cure the coated substrates to improve the adhesion strength between coating and substrate, and to achieve apatite structures inside the applied coating layers [51, 52]. However, the curing temperatures have been implemented below the melting point of the materials to prevent upsetting the surface integrity of the substrates. It has been indicating that the development of <1 μm thickness of HAp coating on 316L stainless steel was suited as the substrate also exposed to annealed temperatures of around 375–400°C [43]. The bonding strength of the as-produced coatings was about 44 MPa, which indicates good adhesion. For the presently investigated HAp/316L stainless steel system, the interlocking component of adhesion was maximised through surface roughening.

Lately, a modification of the sol-gel dip-coating has been proposed. TiO_2/HAp bi-layer coating and TiO_2/HAp composite coating were introduced into 316L stainless steel (316L SS) [53]. The two types of the coating were compared, and TiO_2/HAp exhibited better structural features and biocompatible properties due to the proper attachments of stem cells onto the surface, proliferated, and presented a polygonal morphology different from the fibroblastic-like morphology found on 316L SS.

The combination of sol-gel and dip-coating method have been classified as uncomplicated, inexpensive, and sustainable coating technique for coating the metal-based substrate that to be used as implants. In comparison to the natural precipitation approaches, this method can coats the complex shapes or design efficiently. Also, shortened the processing times and relatively low temperatures is applied by this method to cover with the HAp layers on metallic substrates.

3.3. Electrochemical deposition

Electrochemical deposition is one of the commercial coating methods for biomedical implants [54]. Anodic or cathodic systems frequently conducted by the electrodeposition process. In this process, anodic deposition alone is inadequate to produce small feature size materials on the substrates. Regarding this, cathodic deposition has unique advantages for modern and medical applications [55–57]. Through this method, two regular procedures are applied for the coating preparation: (1) the electrophoretic process (EPD) and (2) the electrolytic procedure (ELD). EPD is the process that provides the utilisation of suspensions of ceramic particles while the ELD is the process of formation of metal salts from solutions. The electrochemical deposition is extensively employed for coating on a titanium substrate. The subsequent filtrate is used as the electrolyte once the CaP proportion dissolved in distilled water [58, 59]. The procedure is performed from watery arrangements like those appropriated as a part of the wet substance deposition. Interestingly, graphite and also platinum has been engaged as the standard reference electrode for anodic material.

One of a kind favourable circumstances in HAp coating deposition process conducted through the electrochemical technique is the ability to form a uniform coating and the coating process quick [60]. The procedure can be performed at moderately low temperature [61]. 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 densify the close-packed of the fine particle and further leads to the formation of agglomerate-free structures [62]. The pre-sedimentation process can separate the aggregates [63]. Besides, defect areas could drive a 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.

The electrochemical deposition process can form a homogeneous coating layer which enhances the adhesion strength between the coating layer and implant surface [64]. The HAp coating on CoCrMo metal implant with the thickness of 200 nm can hold the coating quality of around 17.5 MPa which has been considered as the base prerequisite for the minimum adhesion quality of HAp deposition on metallic biomaterials [65, 66]. However, the HAp coated substrate was deposited at 10 mA/cm^2 and annealed for 1 h at 500°C showed the thickness of the coating is approximately 18.6 μm revealed stronger adhesion strength (106.3 MPa) of HAp coating [67]. The electrochemical deposition of HAp on metal substrates used common strategies to diminish their debasement; unfortunately, it contains abandon of it onto the coating surface [68]. Hydroxide (OH−) particles are created at the substrate (cathode) surface with the electric current crossed the electrodes as they immersed in an electrolyte during electrochemical deposition process [69]. The condition occurs due to the electrochemical response effect

that is typically significant as the system insignificantly response towards the water, in which leads to important in the arrangement of a lot of hydrogen gas [27, 70]. Development of the hydrogen gas air pockets on the surface of the substrate may rapidly occur and thus results in the decreasing of the nucleation and presence of calcium phosphate. In this manner, it may prompt the arrangement of non-uniform coating [71, 72]. To conquer the defects, the execution of HAp coating ought to tackled and enhanced higher current thickness.

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 replace the H_2O during the deposition process, thus brings down the current deposition method. Replacement of H_2O_2 will able to modify the entire part of the system of electrochemical response [73]. The impacts of H_2 development might be evacuated due to the expansion of peroxide. Therefore, the thick and uniform coating might be shaped [61]. The increased adhesion and crystallinity of the HAp coating were achieved by pulsed current electrodeposition method at lower current density with longer pulse off time. The results of pulsed electrodeposition show that the relaxation time of the pulse is beneficial for the growth of HAP because it allows the diffusion of ions from bulk solution to the surface of the electrode and thus lowers the concentration polarisation in the next pulse on time. Besides, by applying galvanostatic pulse electrodeposition to HAp coating on metal implants showed improvement in adhesion strength of HAp coating and metal implant due to pulsed current densities [74].

The previous research has confirmed that by deposition of HAp coating onto metallic biomaterial showed the improvement of corrosion performance [75]. Moreover, the coatings have significantly changed by forming new apatite crystal after 7 days immersion in SBF solution [76]. These indicate that HAp has bioactivity and biocompatibility properties which can provide improvement between tissues and metal implants.

An anodization process has been introduced as pre-treatment for electrochemical deposition [77]. The purpose of anodization is to support developing mechanical interlocks flanked by the metal substrate and HAp coating [78, 79]. Without post-treatment, homogenous and pure HAp coating can be accomplished through the anodising process. It was stated by He et al. [80] that the Al coating on Ti substrate with anodization and hydrothermal treatment. The results from the holes of anodised aluminium oxide (Al_2O_3) within the coating deposition, there is a growth of CaP. Besides, Yang et al. [81] have conducted anodic oxidation treatment for bioactive Ti metal. Even though the electrochemical and pre-treatment process has become vital, the studies on HAp coating deposited by an electrochemical method on the porous anodised Ti substrate still in progress stage [82].

Nowadays, a few methods have been presented to enhance mechanical properties of the implants. One of those methods is through reinforcing materials such as zirconia oxide (ZrO_2), carbon nanotubes (CNTs), and titanium oxide (TiO_2) [11, 83–87]. On the other hand, several reported regarding the HAp-based coating showed the enhancement in adhesion strength approaching 70% greater compared to pure HAp coating [88]. HAp coating with the addition of single-walled nanotubes (SWNT) managed to get homogenous, high crystallinity and crack-free coatings formation. Additionally, the adhesion strength of the coating and substrate after introducing SWNT is approaching from 15.3 to 25.7 MPa [88].

In correlation to a single layer coating of HAp, the result of a double layer of HAp coating showed uniformity with good adhesion strength [89]. Furthermore, the formation of the oxide layer as an intermediate layer between the substrate and coating helps to maintain the diffusion of harmful impurities from the substrate towards the coating surface to avoid decomposition of HAp [90]. By applying high-temperature annealing or sintering in the formation of a uniform and denser CaP coating post-electrodeposition [91], a superior adhesion behaviour of coated layer can be formed. Albayrak et al. [92] have reported the same technique used by Yuan and Golden [89]. Titanium oxide (TiO_2) was introduced as an oxide layer on the Ti6Al4V substrate prior 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 as 10, 20, and 50 V. With decreasing the voltage value, the result showed an increment of adhesion strength. Comparison of the adhesion strength between electrodeposition methods was listed in **Table 1**.

In conclusion, HAp coatings conducted via electrochemical deposition technique are formed progressively by nucleation and growth processes and lead to form a uniform structure. The electrochemical deposition technique can form a broad range of coating thickness. Also, the electrochemical deposition process decreases the corrosion behaviour of the substrate through the coating. Consistently, sintering procedure enhances densification, bonding and adhesion behaviours of the coating. An interlayer between the substrate and the coating has been introduced to overwhelm the issue of HAp decomposition. Therefore, the electrochemical deposition technique can be one of great guarantee of the future edition for metallic biomaterials.

Composition	Thickness (μm)	Adhesion strength (MPa)	Reference
CoCrMo + HAp	0.2	17.5	[66]
1. Ti6Al4V + HAp (flake-shaped)	10	6.8	[83]
2. Ti6Al4V + HAp (spherical)	10	10.7	
3. Ti6Al4V + sHAp/CNT-Ti	10	10.6	
4. Ti6Al4V + HAp (needle-shaped)	10	8.5	
1. Ti + HAp (without oxidation)	3	5.0	[82]
2. Ti + HAp (with oxidation)	3	7.3	
1. Ti + HAp	10	15.3	[88]
2. Ti + SWNTs/HAp	10	25.7	
1. Ti6Al4V + HAp	30	13.8	[92]
2. Ti6Al4V + TiO_2 (10 V)/HAp	30	21.0	
3. Ti6Al4V + TiO_2 (20 V)/HAp	30	13.1	
4. Ti6Al4V + TiO_2 (50 V)/HAp	30	11.9	

Table 1. Values of adhesion strength of HAp coatings deposited by electrodeposition process [33].

3.4. High-velocity suspension plasma-spraying

Currently, High-Velocity Oxygen-Fuel (HVOF) flame spraying method has been advanced. The method gives promising results regarding allowing the formation of suspension spraying layer [93–95]. By introducing the axial powder injection, the new high-velocity suspension flame spraying (HVSFS) process typically would be able to resolve the injection complications [96–98]. Regarding this, the highest velocity of the particle would be able to produce better coating protection with low porosity. This innovative suspension thermal spray technique is ideally becoming the most in-demand technique in depositing a thin layer of coating on the substrate [99, 100]. In comparison to the other method such as electrophoretic coating for pure HAp, the coating does not require any heat treatment or post-deposition for consolidation. Furthermore, the method features relatively lower processing cost with high and efficient productivity [101, 102]. As compared to conventional dry powders, the suspension based feedstock could ignite more flexibility in creating new composite materials by altering the material compositions in which controlling the primary particle morphology [103, 104]. Furthermore, a fine powder particle either in micro- or nano-sized particles could be fabricated by thermal spray community. The method enables direct delivery of the particles into the gas or plasma jet. Direct processing of fine particles dispersed in liquid solvent significantly yield smaller lamella size of the coating layer that depends on the standard parameters of spray powder processing [105].

HVSFS technique could produce high-quality and low-thickness coatings especially when the layer thickness is below 50 μm [96, 106]. 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 minimising risks of delamination [107, 108]. The coated properties especially the one involves bonding strength between the substrate and coated layer produced from HVSFS techniques tends to be affected severely 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., [106], bioceramic coatings could be based on dry spray HAp powder used for HVOF and APS nanoscale and HAp suspension (water-based) for HVSFS.

By introducing different suspension solution medium such as diethylene glycol (DEG) as a substitute of water suspension, the result of the adhesion strength of the HAp coatings is enhanced and supposed to be superior [106]. The DEG-based solution increases the adhesion strength compared to the water-based suspension. In fact, DEG-based suspension offers many advances properties such as low interlayer porosity with denser coatings. The resulting condition is due to the higher adhesion strength. The maximum adhesion strength is around 25 N/mm^2 as reported for HVSFS-HAp coating [106]. Additional of TiO_2 layer acts as a thermal insulating layer onto commercially pure Ti slows down heat extraction from the deposited material to the substrate [109, 110]. The HVSFS deposited HAp coatings are typically dense with 27–37 μm in thickness and some transverse micro-cracks. Even the crystallinity characteristic is of between 10 and 70%, depending on the deposition parameters and the amount of a TiO_2 concentration. The adhesion strength between the metal substrate and HAp coating enhanced due to the presence of TiO_2 layer as shown in **Figure 1**.

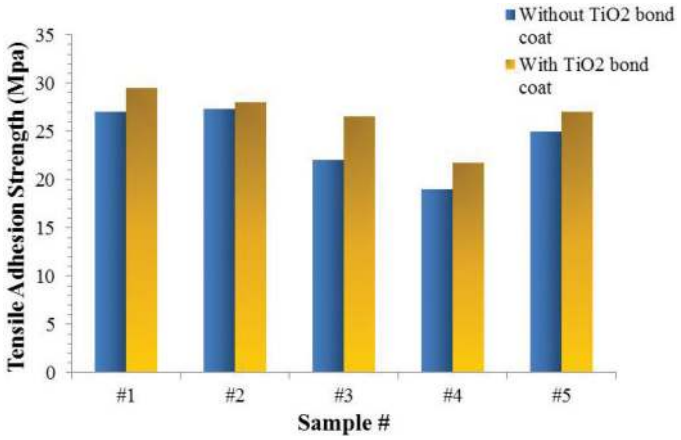

Figure 1. Adhesion strength of the HVSFS-deposited HAp coatings [110].

The APS, HVOF and HVSFS methods are extensively practised for HAp coating processes especially the one involves Ti metal as substrates [111, 112]. The processing parameters such as gas flow, air-fuel ratio, electric arc current and spray distance are the primary factor in determining the coating properties performance concerning the adhesion strength between substrate and coating of these thermal spraying techniques [113, 114]. The increment of the flow rate of oxygen enhances the behaviour of the coating composite. Besides that, fuel flow rate also plays a significant role in influencing the coating performance. Increasing oxygen flow rate along with fuel flow rate leads to higher adhesion strength. Other than that, reducing the spray distance also brings to stronger adhesion strength [98, 104, 115].

4. Summary

The choice of metallic biomaterials such as 316L stainless steel, cobalt-based alloy, titanium and its alloys will continue to be used extensively in the medical field as medical implants due to their excellent mechanical properties and adaptability within the physiological environment. Currently, a major issue of metallic implants is the failure to perfect pair to the local tissue environment in the human body. This inharmonious is due to the different chemical compositions between metallic implants and human bone. The surface modification of the metal-based materials via four common coating techniques namely plasma-spray, sol-gel, dip-coating, electrochemical deposition and high-velocity suspension plasma-spraying (HVSPS) was introduced to enhance bioactivity, to prevent wear and corrosion and to control harmful metal ions released into the body. It is proven that the surface modification via coating can succeed the limitation of the metallic biomaterials.

Acknowledgements

Authors would like to acknowledge the kind assistantship from the Green Research for Advanced Materials Laboratory (GRAMsLab) and Human Engineering Group (HEG), Universiti Malaysia Pahang (UMP). This work was supported by the Qatar National Research Fund NPRP88762375 (UIC161504), internal grant of Universiti Malaysia Pahang RDU140354, RDU160337, and the support of Research Acculturation Grant Scheme provided by the Ministry of Higher Education, Malaysia RDU151404.

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