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Recent Development of Calcium Phosphate-Based Coatings on Titanium Alloy Implants[1]

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Abstract—Titanium alloy implants are widely employed in biomedical devices and components, especially as hard tissue replacements as well as orthopaedic applications, owing to their favourable properties such as high-strength to weight ratio, low density, low Young's modulus and biocompatibility. However, metallic implants cannot meet all of the clinical requirements. Therefore, in order to increase their clinical success and long term stability in the physiological environment, surface modification is often performed. This review focuses on the latest achievements in the field of surface modification techniques including sol-gel, thermal spray, magnetron sputtering, electrophoretic deposition and micro-arc oxidation of biocompatible calcium phosphates (CaP) based ceramics coatings for metallic implants with emphasis on the structure, morphological characterization, phase transformation and coating composition. A reflection on the results shows that CaP coatings can be grown with the each type of techniques and a stronger fixation can be enhanced with CaP fabrication on metallic implants. Advantages and limitations of the aforementioned techniques of CaP-based coatings from the point of view of the process simplicity as well as the most important challenges of each coating techniques are highlighted. Further, the most promising method for CaP deposition was identified and a specific area for improvement was discussed.

Keywords: titanium alloy implants, calcium phosphate, surface engineering, coating

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1. INTRODUCTION

Calcium phosphates (CaP) based ceramics is the most common family of bioceramics with inorganic components well known for the biological applications. Over the last three decades, CaP ceramics have attracted a lot of interest since it may be possible to use them as an artificial bone substitute because of their excellent biocompatibility, bioactivity and osteoconductability properties [1–3]. Several of CaP compounds such as dicalcium phosphate, tetracalcium phosphate, tricalcium phosphate, oxyapatite, and oxyhydroxyapatite and hydroxyapatite (HAp) do exist [4, 5], but among them, HA, $Ca_{10}(PO_4)_6(OH)_2$ has been widely used as the most bioactive material for orthopaedic and dental biometallic implants. HA is the most stable of CaP compounds and has intrinsic osseointegration potential which makes it a better candidate material of choice in orthopaedic and dental applications [6–8]. This is due to its chemical composition, biological and crystallographic similarity to natural human bones [9, 10]. Table 1 shows the physical properties of various chemical compounds of calcium phosphate bioceramics used in biomedical industry. Different chemical compounds have different applications depending upon whether a resorbable or bioactive material is desired [11]. A growing interest in CaP ceramics is mainly due to the rise in the number of patients that require bone replacement, especially those suffering from bone cancer, trauma and ageing. It is well known that a biomaterial must be biocompatible with suitable mechanical strength to support the weight of the human body. Bulk CaPs are inherently weak and brittle, making them unsuitable for load bearing purposes [12]. On the other hand, titanium (Ti) and its alloy are considered as bioinert and they do not show bone forming interaction with the surrounding tissues [13, 14]. The body responds to these materials usually by forming non-adhering layer of the connective tissue between a bone and an implant. A good integration of an implant with the bone is of paramount importance to ensure the safety and efficacy of the implant over its useful life. It is evi-

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Table 1. Physical properties of various compounds of CaP bioceramics [11, 27]

Chemical compounds	Abbreviation	Chemical formula	Ca/P ratio	Density, g/cm^3
Hydroxyapatite	HA	$Ca_{10}(PO_4)_6(OH)_2$	10/6	3.16
Amorphous CaP	ACP	$Ca_9(PO_4)_6$	9/6	NA
α-TriCaP	α-TCP	$Ca_3(PO_4)_2$	3/2	2.86
β-TriCaP	β-TCP	$Ca_3(PO_4)_2$	3/2	3.07
TetraCaP	TCP	$Ca_4O(PO_4)_2$	2/1	3.05
DiCaP	DCP	$CaHPO_4$	1/1	2.92
Oxyapatite	OA_P	$Ca_{10}(PO_4)_6O$	10/6	–
Calcium oxide	CaO	–	–	3.34
Octacalciumphosphate	OCA	$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	8/6	–

dent that under these conditions no solid and lasting mechanical connection between the bone and the implant can be achieved [15]. To proffer solution to this problem, it was suggested that implants could be improved by coating them with a thin layer of CaP ceramic using various types of surface engineering techniques available such as, sol-gel (SG) [16, 17], thermal spray (TS) [18, 19], magnetron sputtering (MS) [20, 21], electrophoretic deposition (EPD) [22, 23], and micro-arc oxidation (MAO) [24, 25]. These processes would combine the mechanical strength and toughness of metallic implants (titanium, stainless steel and cobalt chromium alloy) with the bioactive properties of CaP. Compared with uncoated devices, implants encapsulated with CaP ceramics have demonstrated longer lifetime for the underlying metallic implant material, toxic ion prevention as well as enhancing the bone bonding formation [26]. In addition, they have been found to be particularly beneficial for younger patients. The long term success rate of CaP coated metallic implants depends on coating properties such as thickness, porosity, phases, crystallinity and implant surface roughness.

The possibility of CaP to fast track the bone healing and bone bonding while reducing the risk of mechanical failure of metallic implant has given rise to the production of thin and thick film CaP coatings on metallic materials, which enables the combination of two materials to form a single functional component.

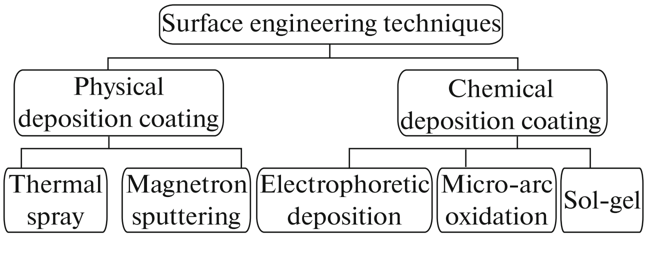

Fig. 1. Surface engineering techniques of fabrication of CaP thin film.

Due to the availability of previous comprehensive review articles covering different aspects of the theory and mechanisms of aforementioned surface engineering techniques [28–32], this review primarily focuses on the several of these new thin film technologies for the deposition of CaP coatings on medical and orthopaedic implants. This work attempts to describe the state of the art in the study of bioactive CaP coatings and it reviews the physiochemical properties of thin CaP coatings prepared by various thin film techniques. The outline of this paper is displayed in Fig. 1.

2. DEVELOPMENT OF CaPs COATINGS

The possibility of modifying the surface area of metallic implants by tailoring the composition and structure using various surface engineering techniques available has grown wider recently in the fields of biomedical industry. CaP coatings, especially, hydroxyapatite coating is commonly employed in orthopaedic applications. Many surface engineering methods have been developed for the deposition of CaP coatings on metallic implants [33]. Generally, coating fabrication methods can be broadly classified into two: chemical and physical deposition. Chemical deposition involves chemical treatment of metallic materials in an electrolyte solution. Three techniques are presented here: sol-gel, micro-arc oxidation and electrophoretic deposition. On the other hand, physical deposition includes those methods which involve atomization or vaporization of a material from a solid source and the deposition of these materials onto the substrate to form a dense coating. Physical deposition methods are classified into plasma spray, magnetron sputtering and physical vapour deposition, of which plasma spray is the most widely used for the deposition of CaP coatings because of its ability to produce a higher deposition rate and coating thickness of 30–20 μm [33], which improves the biological properties of the material. The reader can refer to the detailed review in [34] on various coating methods to modify orthopaedic implants.

3. COATING FABRICATION TECHNIQUES

3.1. Thermal Spray

TS is an enabling group of coating technologies that provide a functional surface to protect or enhance the performance of biomedical metallic implants. The deposition of CaP thin films by TS was first described in [35–39]. There are many thermal spray processes, e.g. plasma spray, high velocity oxy-fuel, flame spray, liquid plasma spray, etc. which are used to fabricate CaP-based coatings. The basic difference among all these subsets of TS is the maximum temperature achieved. Recently, a newer cold spraying method for the deposition of bioactive HA has been proposed. However, powder plasma spraying also known as thermal printing is currently the most applied technique to produce protective biocompatible CaP coatings [40]. During TS, usually at the atmospheric pressure or in vacuum, the precursor material to be typically deposited as powder is introduced into the plasma jet and heated into the hot gaseous medium. The heated particles are accelerated and projected at a high velocity onto a prepared substrate to produce a dense coating. Figure 2 shows the schematic diagram of thermal spray HA coating fabrication. This technique offers unique advantages such as high deposition rates, less risk of coating degradation and low operating cost. At present, plasma gas composition, mostly (Ar, He, H_2, or N_2), plasma gun input power, spray stand-off distance, gas flow rate, powder feeding, rate etc are among the recognized deposition parameters that can influence the thermally sprayed HA coating properties [41].

3.1.1. Thermal spray for CaP coatings. Thermal spray allows production of HA onto metallic substrates with a thick layer ranging from 30 to 200 μm. Studies on the coatings of HA formed by TS show that the particle size is an important factor to obtain a good quality coating [43]. The interaction between the molten HA particles and the plasma beam have strong influences on the way the particles in the plasma beam melt and transform both physically and chemically. Generally, the HA particles should be of the similar shape and the uniformity of the size should be maintained. This is due to the fact that thermal sprayed HA particles of different sizes cause overheating and subsequent evaporation owing to a high thermal energy and kinetic effect of the plasma beam. The use of pure crystalline HA particle size is important but does not necessarily guarantee good quality of the desired mechanical and biocompatibility properties of thermal spray HA coatings. The researchers in [44] investigated the size and the crystalline effect of pure HA powder on the microstructure and mechanical properties of plasma spray. They found that at a larger particle size, there are numerous unmelted particle sizes, cavities and macropores with attendant poor mechanical properties due to poor interlamellar adhesion and cohesion of the coating. The use of weak agglomerated HA powder particles can further worsen coating inconsistency by allowing fragmentation of HA particles to take place during plasma particle interaction [45]. Figure 3 shows a typical scanning electron micrograph of an as-sprayed HAp coating formed.

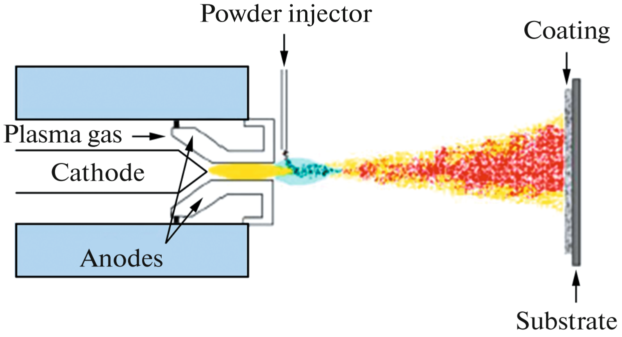

Fig. 2. Schematic diagram of thermal spray HA coating fabrication [42].

From the result, it is evident that the micrograph of that HAp coating is characterized by partially melted and unmelted particles with a mild crack running across the surface (Fig. 3a). The formation of pores and gaps across the coating thickness layer was attributed to poor mechanical interlocking between coating and substrate (Fig. 3b). Recent findings have revealed that thermal spray HA particles of various sizes can be produced under certain processing conditions and the problem that arises from variations of particle sizes can be avoided [42]. However, the technique requires a high sintering temperature, which produces cracks on the surface of the coating. In addition, the coating deposited by TS suffers from poor interfacial bonding strength and non-uniformity of the coating, which reduces the life span of metallic implant [33, 41].

3.2. Magnetron Sputtering

Magnetron sputtering is one of the physical vapour deposition methods used for depositing thin films and has been widely used in the electronic and automotive industries for many years. Generally, sputtering is a process where atoms or molecules are ejected from the target through the bombardment of a source or target by ions and accelerated neutrals, usually argon [32, 46, 47]. There are various sputtering processes, such as radio frequency (RF) magnetron sputtering, ion beam dynamic mixing sputtering, ion beam assited deposition sputtering, which have been used to form coatings on metallic implants [48–50]. Among these techniques, RF magnetron sputtering is currently the most frequently applied one to prepare bioactive coatings on metallic implants owing to its ability to produce dense and well adhered thin bioactive coatings on metallic substrates [51–53]. Between 1994 and 1996, pioneering experiments with RF magnetron sputtering to prepare biocompatible and bioactive HA films were car-

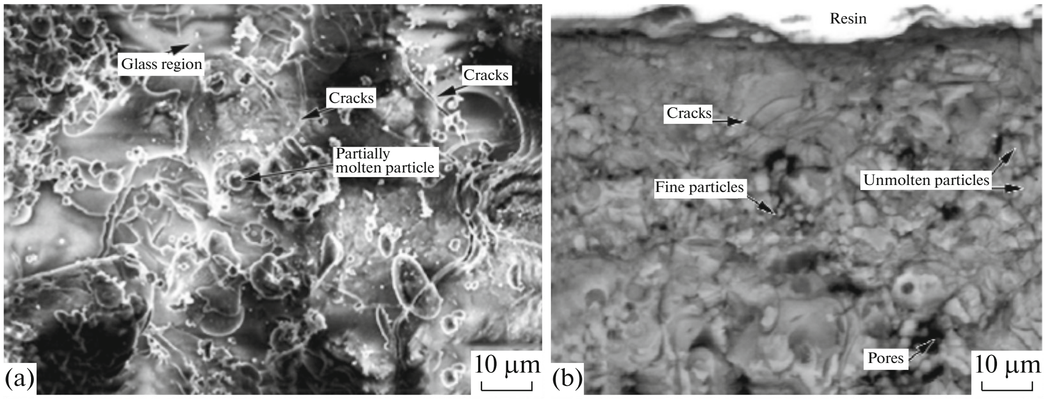

Fig. 3. Scanning electron micrograph of a typical as-sprayed HAp coating: (a) top surface; (b) cross-section [44].

ried out and thoroughly investigated [49, 54–56]. The development of high performance RF magnetron sputtering applied and studied by these research groups has offered many possibilities of a high degree of the process control with wide deposition areas making the sputtering process more effective. This technique allows the properties of the deposited thin film coatings to be tailored by varying the target composition or processing parameters. Figure 4 shows a typical setup for the the preparation of thin film layers.

The growth of crystalline structures, composition and performance of RF magnetron sputtering of thin film coatings depend strongly on the process parameters including the RF power, substrate temperature, gas composition and pressure, pressure bias and substrate distance, initial target material, deposition parameters and post heat treatment [57, 58]. It can be used to produce coatings of uniform thickness, dense porosity and, more importantly, the coating structure can be easily controlled.

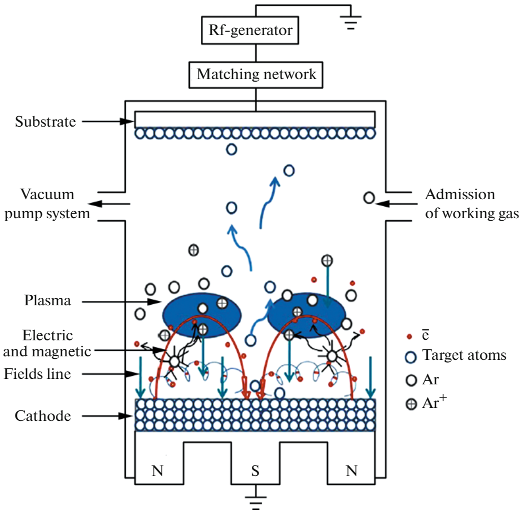

Fig. 4. Schematic setup of the typical RF magnetron sputtering [40].

3.2.1. Magnetron sputtering for CaP coating. The deposition of CaP thin film coatings by RF magnetron sputtering is usually in the form of the amorphous phase and post heat treatment is usually carried out which is typically in the range of 400–700°C [20, 57, 59, 60], thus ensuring highly crystalline and better stability on metallic implant materials. However, the CaP thin films produced under a lower post heat treatment temperature ≤400°C [61, 62] displayed poor crystallinity and greater phosphates as compared to as sputtered at higher temperatures. RF magnetron sputtering allows preparation of CaP thin films with a composition close to that of the initial target by keeping the substrate temperature at 100°C [63] or 250°C [64]. Currently, several types of biocompatible CaP-coatings have been prepared by RF-magnetron sputtering, such as pure HA [65–67], silicon-containing HA (Si-HA) [68–70], Ag-HA [71, 72], HA-Ti [48], FA-HA [73], HA-TiO_2 [60]. The coating thickness deposited from RF magnetron sputtering is typically in a range of 0.5–4 μm while the surface roughness varies from 0.05–0.28 μm. It is a well-known fact that the surface morphology plays a vital role in the overall success of metallic implant materials [74]. RF magnetron sputtering allows to prepare homogeneous continuous coatings that are highly dense, uniform, of lower porosity and without any microcracks. The typical pattern of the surface morphology of CaP thin film coating prepared by RF magnetron sputtering is presented in Fig. 5. The figure shows the surface morphology of the etched titanium surface (Fig. 5a) and the SEM cross-sectional view of the CaP grown on Ti etched surface (Figs. 5b–5d).

Various thickness of the surface of CaP (170 ± 20; 250 ± 40 and 440 ± 50 nm) grown via magnetron sputtering revealed a thin, fine layer of CaP (~ 30–50 nm thick) with a regular grain-like morphology. An increase in the average grain size is noticed as well as an increase of the thickness. Despite the remarkable

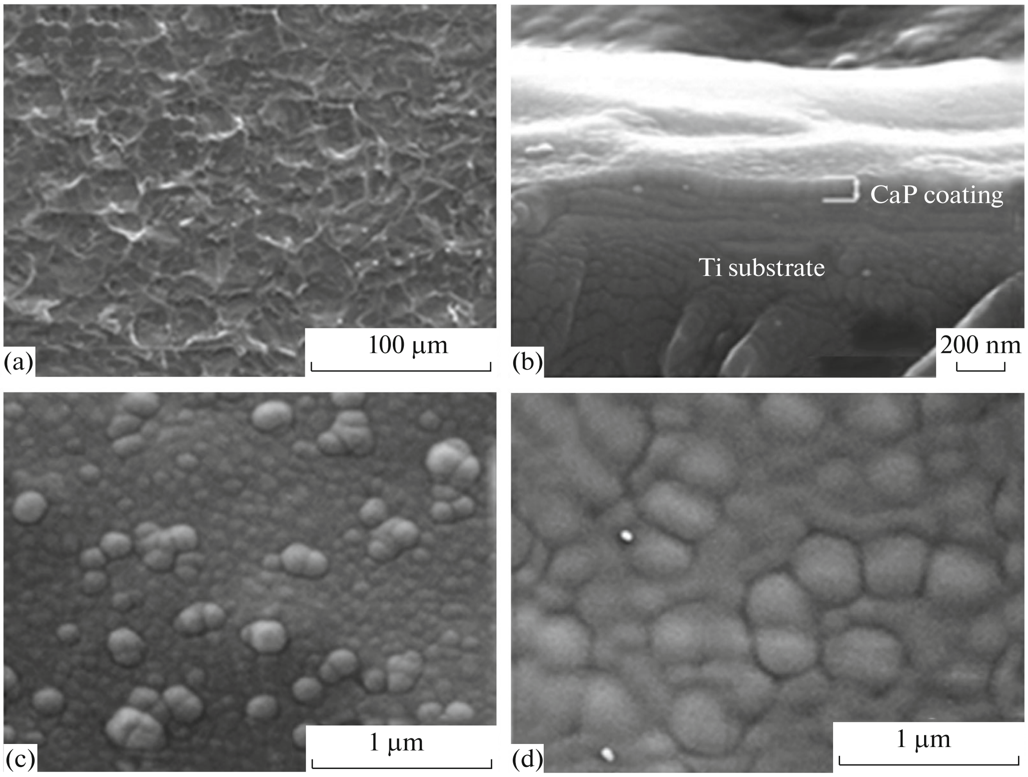

Fig. 5. SEM image of: acid-etched uncoated titanium surface (a), cross-section of the deposited CaP coating (b) and the surface morphology (c, d) of the CaP coating deposited on acid-etched titanium surfaces over different amounts of time. Thickness: (b, c) 170, (d) 440 nm [53].

success, RF magnetron sputtering for deposition of CaP coatings, requires postheat treatment in order to obtain highly crystalline and dense coatings. Moreover, magnetron sputtering is expensive and time consuming [63]. To guide against the post-heat treatment, the geometry of magnetron sputtering can be altered using right-angled radio frequency magnetron sputtering to produce thin, highly stoichiometry crystalline films at room temperature [73, 75, 76].

3.3. Electrophoretic Deposition

EPD is one of the chemical conversion techniques to deposit thin films of materials of technological interest [77, 78]. The deposition of bioactive CaP thin film coatings onto the surface of metallic implants by EPD was first described in [79–81]. EPD is a well-known electrochemical colloidal processing method which is gaining increasing interest in recent years as a simple and versatile deposition technique for the production of CaP thin film coatings on metallic implant materials. EPD is typically achieved through the motion of suspended, charged particles dispersed in a suitable liquid between two electrodes under an applied electric field and a deposit is formed via particle coagulation [82–84]. The positively charged particles are deposited on the surface of the cathode (cataphoresis) while negatively charged particles are deposited on the anode (anophoresis). The increasing significance of this electrochemical conversion technique arises from its low cost, simplicity, versatility, high reproducibility, simple set-up of equipment and ability to scaled-up to large product volumes. Figure 6 shows the schematic setup for EPD.

In EPD coating formation, many parameters play very important roles in the final properties of CaP films, the parameters that directly affect the quality and mechanical stability of CaP thin film coatings are: the applied electric field, deposition time, electrical nature of the electrodes, powder preparation, post sintering temperature, deposition voltage, dispersant medium and dispersant in suspension [85, 86].

3.3.1. Electrophoretic deposition for CaP coatings. Basically, EPD of CaP coatings is mostly carried out at the cathode as high anodic potentials may adversely affect the metallic material surface [87]. Several standard anodic electrode materials have been used during the deposition of CaP coatings on metallic materials including graphite, platinum, lead, carbon rod and stainless steel [88, 89]. Higher deposition and uniformity of the coatings on implant materials can be obtained during EPD by keeping the separating distance between the electrodes within a range of 6–20 mm [90–92]. Deposition time used by investigators varies

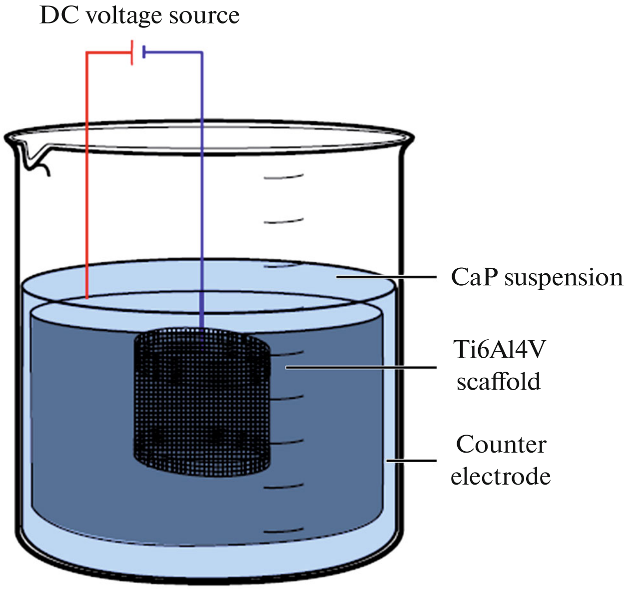

Fig. 6. Schematic representation of EPD process [14].

depending on the electrolyte ingredients, current, voltage and dispersant in suspension. The deposition time from 1 min to 2 h has been reported to have successfully produced a highly dense, adherent thin layer (~ 0.1–2 mm) and a homogeneous coating on prosthetic devices [41, 93–95]. The coatings obtained by EPD have been described as rough and porous and densification at higher temperature has been suggested to create a more uniform, dense and well adhered coatings on metallic implants [96]. However, a higher sintering process improves densification and the bonding of coatings formed via EPD, but also promotes HA decomposition as well as a high degree of shrinkage and appearance of micro-cracks within the coating layer (Fig. 7) while lower densification leads to inadequate adhesion strength [89].

To solve the problem of HA decomposition and cracking of CaP coatings obtained using EPD, the authors in [14] investigated the effect of alginate incorporation in HA on Ti6Al4V scaffolds. Figure 8 shows the optical microscopic images of bare and HA-alginate coated Ti6Al4V scaffolds. In general, it was shown that the presence of alginate improves the homogeneity of the coating and eliminates the microstructural defects. However, then the coating is not smooth, which was attributed to the roughness of the bare Ti6Al4V.

Recent findings have also shown that the addition of certain concentrations of TiO_2 [97, 98], CNT [99], Y_2O_3 [100], Zn [101], CNT/TiO_2 [102] and Si [103] to an ultra high surface area of HA particles is necessary to produce a densely packed deposit and a crack-free coating surface.

3.4. Micro-Arc Oxidation

MAO [112], also named anodic spark deposition (ASD) [113], electrolytic plasma processing (EPP) [114], micro-plasma oxidation (MPO) [115] or plasma electrolytic oxidation (PEO) [116] in recent literature sources, is a hybrid of conventional electrolysis and an atmospheric plasma process to produce porous, relatively tough and firmly adherent ceramic like coatings structure on lightweight metallic materials such as Ti, Al, Nb, Mg, Zr, Ta and their alloys. The available reports in literature from 2001 to 2006 are mostly concerned with producing highly adherent oxide ceramic coatings with different chemical compositions on Al and Mg for anti-corrosion and anti friction applications [117]. The advantages of MAO over its counterpart techniques is that it can produce coatings of high microporous oxide layers (<100 μm) on implant surfaces [108, 109], which is important for anchoring of bones; moreover the coating is uniformly deposited on a large implant area with complex geometry. In a typical PEO process, the working electrode (anode) together with the counter electrode (cathode) (usually of stainless steel) of a larger surface area is immersed in a suitable electrolyte of interest. An external power supply is connected to the two electrodes providing

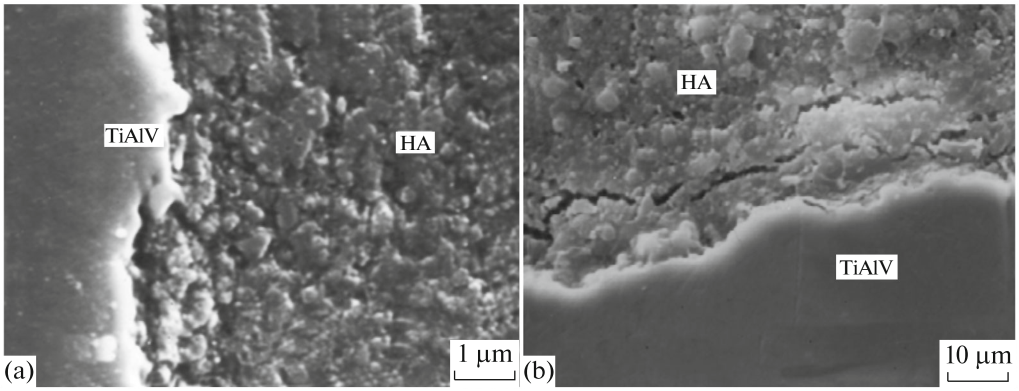

Fig. 7. SEM images of sintered HA coatings on TiAlV substrates [85].

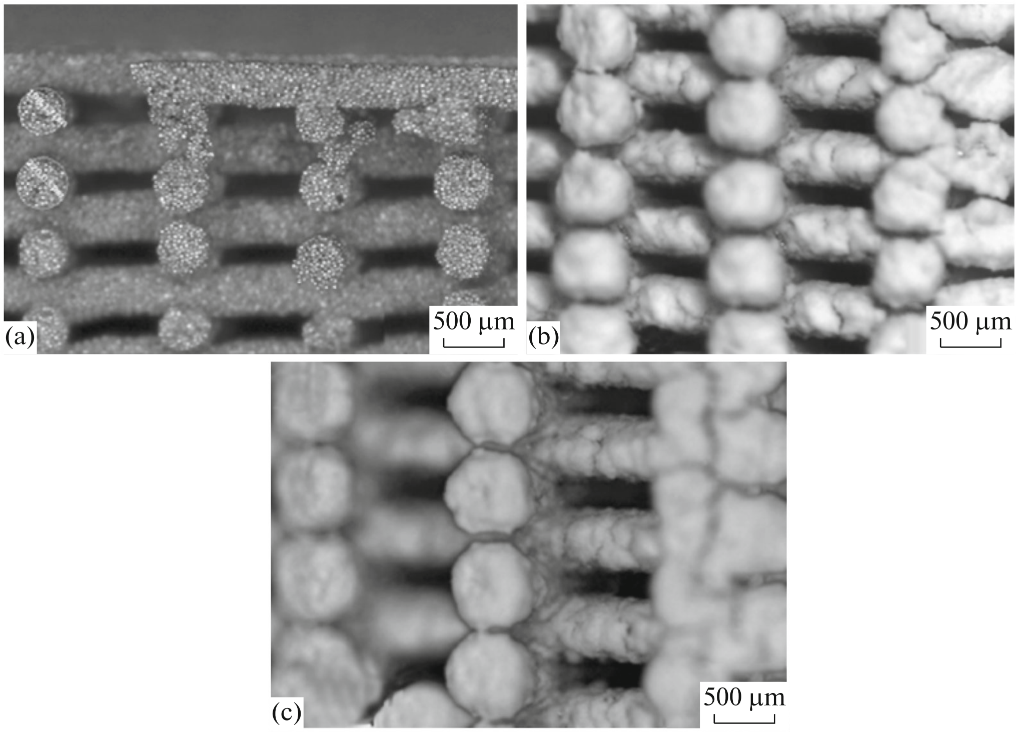

Fig. 8. Optical micrographs of (a) uncoated and HA–Alg-coated sample (0.4 mm; 1,1) before (b) and after (c) sintering.

energy necessary for the coating process. Figure 9 shows the schematic view of the MAO process.

In general, the MAO process is considered to be a multifactor controlled process which is influenced by many factors such as composition of substrate materials, electrolyte composition/concentration, electrical parameters, electrolyte temperature, oxidation time, additives, etc. [118, 119].

3.4.1. Micro-arc oxidation derived CaP coatings. In recent years, researchers have made attempts to see the possibility of enhancing the bioactivity and biocompatibility of metallic materials through incorporation of Ca and P ions into the surface layers by controlling the composition and concentration of electrolytes. The authors in [120, 121] were the pioneers to make use of MAO to prepare HA layers on Ti; however, unfortunately, they were not successful using only MAO technique to produce HA layers. The incorporation of Ca and P into coatings and the preparation of CaP coating via MAO on the surface of metallic materials have been considered to be difficult and complex and infrequently reported so far. The preparation of CaP thin film coatings by MAO can be categorized into two types of processes. The processes are summarized below.

3.4.1.1 One step process. This is a process where HA is directly produced using MAO technique without the need for further treatment. Before 2007, there had not been any successful result in the production of highly crystalline HA coatings by a single step of the MAO process using electrolytes containing Ca and P. Recently, crystalline TiO_2/HA coatings on Ti substrates using calcium acetate and sodium phosphate concentrations have been prepared [122]. By changing the Ca/P ratio of the concentrations, different phase structures were obtained as shown by the XRD diffraction pattern and SEM morphologies in Fig. 10. A significant amount of Ca/P (1.07) was incorporated into the microporous oxide film layer.

Some researchers have also shown the possibility of incorporating CaP into the Ti surface using the single-step MAO process under a higher voltage and prolonged time [123, 124]. With the increase in the MAO voltage, the Ca and P in the MAO coating increased as a result of incorporation of Ca and P ions in the elec-

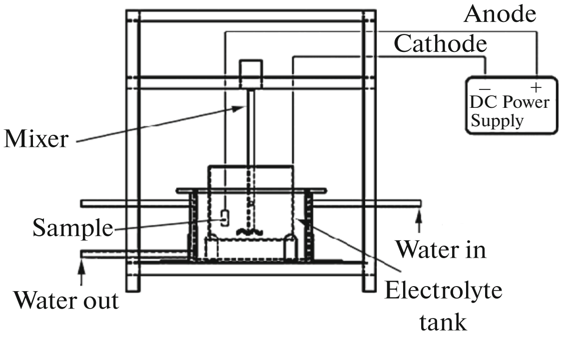

Fig. 9. Schematic representation of MAO setup.

Table 2. Techniques for deposition of HA coatings

Technique	Thickness	Advantages	Disadvantages	References
TS	~30–300 μm	High deposition rates; less risk of coating degradation; high micro-rough surface; low operating cost	Poor interfacial bonding strength; lack of uniformity of coating	[33, 104, 105]
MS	~ 0.5–4 μm	Uniform coating thickness; dense porous coating; ability to control coating structure	Expensive and time consuming; low crystallinity	[63, 106]
EPD	~ 0.1–2 mm	Low operating cost; simple setup; can be scaled up to large product volumes	HA decomposition during sintering; difficult to produce crack-free coating	[41, 107]
MAO	<100 μm	Non-line of sight process; can be easily scaled up to large product; ease of application; high adhesion strength; coatings have high micro-porous surface to enhance anchoring of bones, high corrosion resistant	Difficult to obtain crystalline HA films; sometimes require post treatment process; crack appearance at higher deposition time and voltage	[108–110]
SG	~ 0.1–2 μm	Non-line-of sight process; ease of application; low processing temperature; high purity; relatively cheap	Porosity control is difficult; expensive raw materials; not suitable for industrial scale	[41, 111]

trolyte. Deposition at a high voltage and time improved the surface roughness, porous structure and HA crystallinity of MAO coating. However, the incorporation of CaP which was accomplished using a high voltage has some limitations, because when increasing the incorporation of CaP by increasing the voltage, cracks were generated and failure within the coating followed [109].

3.4.1.2. Two-step process. This is a process where MAO deposition in Ca and P containing electrolyte is subsequently treated using hydrothermal treatment (HT) or by immersion in simulated body fluid (SBF) to increase crystalli-nity of the films. The purpose of hydrothermal treatment is to make Ca and P inside the MAO coating recrystallize after the MAO process. Generally, HA produced by MAO is of low crystallinity and the amorphous coating is not as stable and bioactive as crystalline HA. This is why further hydrothermal treatment is usually carried out to transform amorphous calcium phosphate to the crystalline HA [3, 108]. When HT is applied after MAO, the Ca^{2+} and PO_4^{3-} ions from internal layers of the amorphous coating can successfully diffuse to the coating surface and dissolve into the solution during HT and finally precipitate on the outer layer with a higher degree of crystallinity. The hydrothermal treatment is performed by placing the MAO coated samples in the bottom of an autoclave or in the pressure of controlled reactors con-

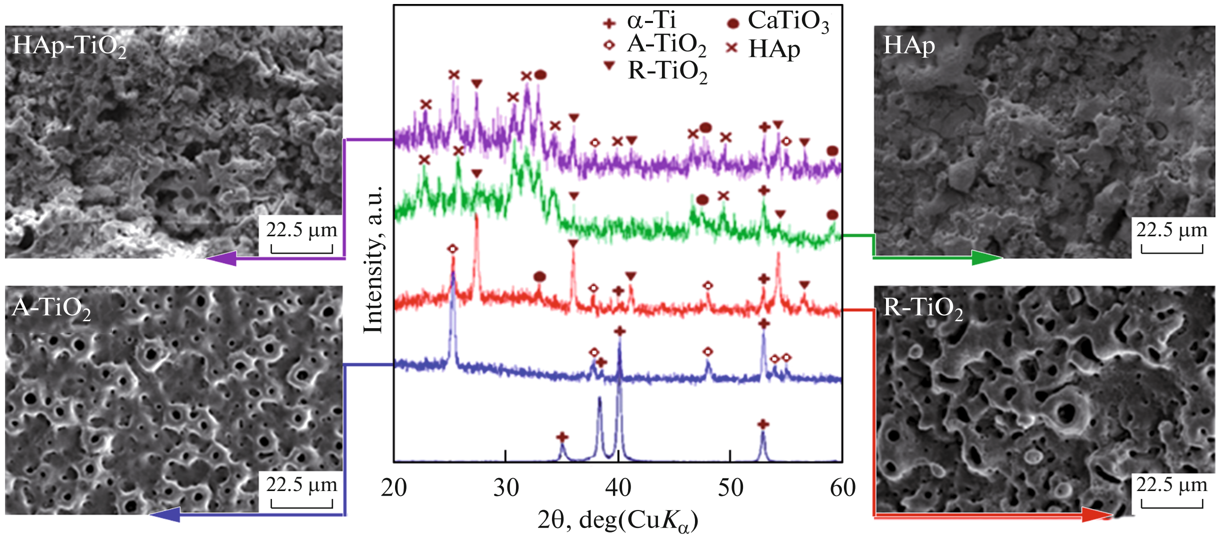

Fig. 10. XRD pattern and SEM-determined morphology of MAO coatings [122].

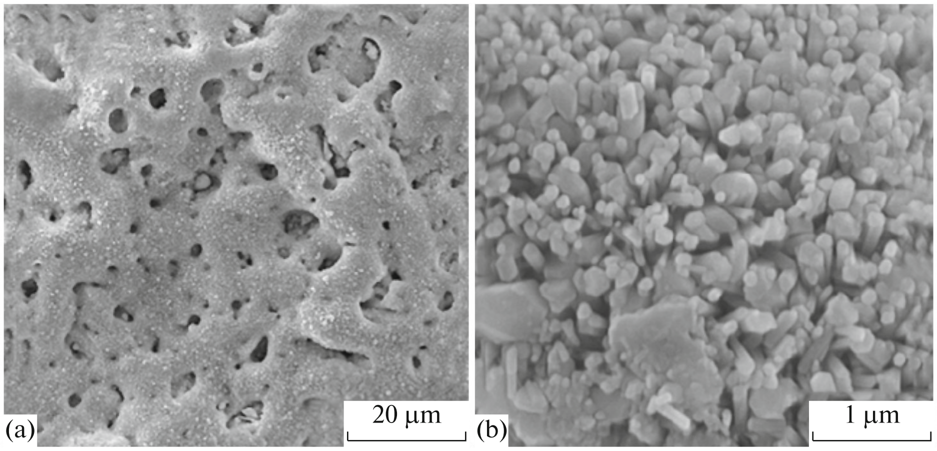

Fig. 11. Microstructure of hydrothermally treated MAO coating at 190°C for 15 h (a) 2000× and (b) 40000× [108].

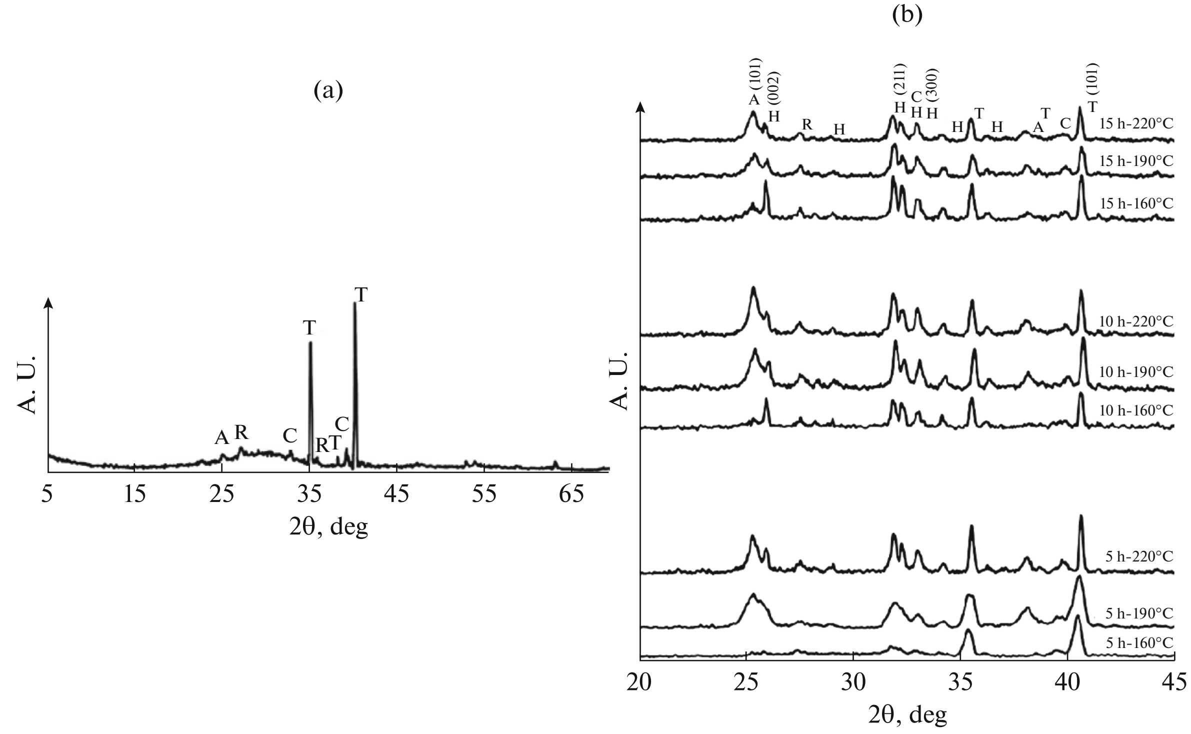

Fig. 12. X-ray diffraction patterns of coated samples: (a) before and (b) after hydrothermal treatment under various conditions. (Abbreviations: T: Ti, H: hydroxyapatite, A: anatase, R: rutile and C: calcium titanate) [108].

taining neutral or alkaline aqueous solutions and treated hydrothermally within a temperature range of 100–250°C for 2–24 hours at pH 7–11 [125, 126]. It has also been reported that HA amorphous phase of MAO coating can be grown in SBF during HT at relatively low temperatures (230°C) and pressure (2–3 MPa) [127]. The existence of calcium and phosphorous containing phases on MAO surfaces exposed to SBF assisted the induction of HA layer [128]. The morphology of HA-Ti6Al4V layer (15 μm) hydrothermally treated is very uniform, with a surface roughness of 1.5 μm (Fig. 11).

The micrograph of micro-arc oxidized films revealed that HA can be precipitated and the rough and porous structure of MAO coating can still be retained after hydrothermal treatment.

As it can be seen from Fig. 12, hydrothermally MAO coating treated at different temperatures shows a higher crystallinity of HA compared to the micro-arc oxidized surface (Fig. 12a). Hydrothermal treatment crystallizes MAO coatings containing Ca and P (Fig. 12)

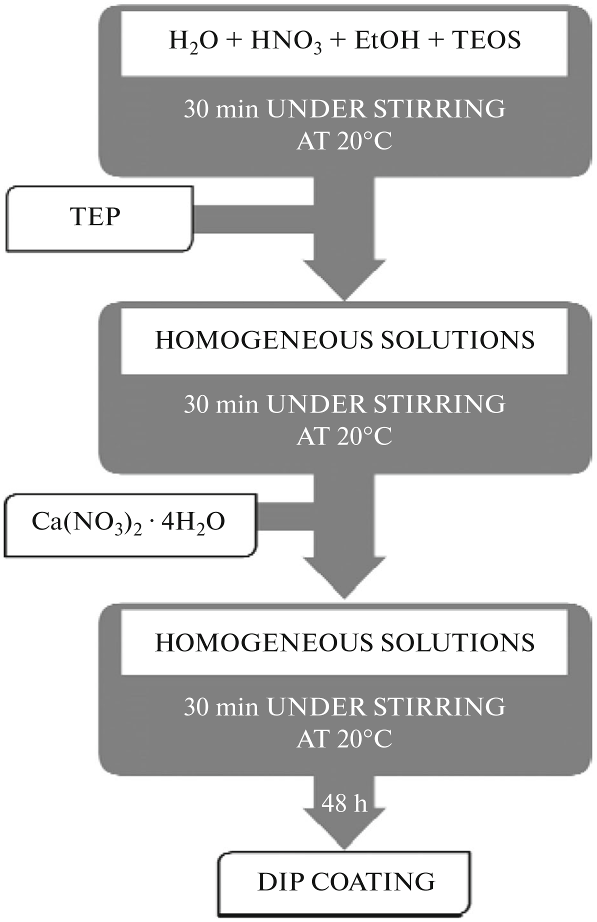

Fig. 13. Flow chart of SG process [129].

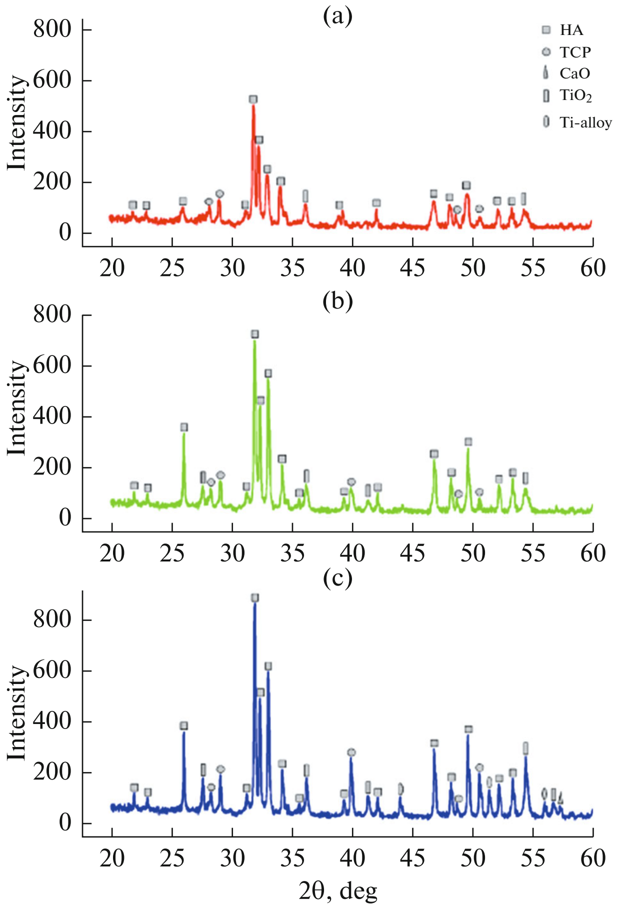

Fig. 14. XRD coatings sintered at different temperatures: (a) 500, (b) 600, and (c) 700°C for 30 min [130].

reduces the interfacial bonding strength between the implant and coating because of introduction of an additional interface [121].

Deposition of CaPs on metallic implants is possible by MAO technique, but in many cases, satisfactory results were not achieved due to a poor control of calcium and phosphorus containing electrolytes or an insufficient amount of Ca and P incorporated in TiO_2 layer. At the current stage of our knowledge, it is difficult to draw a conclusion on the applicability of MAO to produce a hydroxyapatite coating without the introduction of subsequent treatment.

3.5. Sol-Gel Coating Fabrication

SG is a surface engineering technology developed to produce a thin layer of (~ 0.1–2 μm) CaP coatings on metallic implants at a relatively low temperature for biomedical and engineering applications. The SG process involves five main stages: (1) hydrolysis and polycondensation; (2) gelation; (3) aging; (4) drying; (5) densification and crystallization. It is considered to be a non-line-of sight process. Compared to traditional thin film techniques, this process offers a better control of the chemical composition and structure, uniform coating over complex geometries, relative ease of production and high degree of homogeneity, purity of thin films coating, and relative cheapness [129]. When SG is used to prepare biocompatible CaP thin films, Ca and P containing compounds are commonly used. The Ca precursor, most often calcium nitrate ($Ca(NO_3)_2$) and the P precursor, commonly phosphorus pentoxide or triethy phosphite, are separately dissolved in ethanol. In some instances a little amount of water is added to achieve hydrolysis of the sol. The calcium nitrate solution is added to hydrolysed phosphorus sol in a dropwise approach. Figure 13 shows the flow chart of the SG synthesis of the coating procedure.

The obtained solution is thereafter refluxed at different temperatures until a more viscous solution is achieved. The particular solvent employed can have a strong influence on the particle morphology and characterization. Many parameters can affect the composition, structural properties, chemical and mechanical properties of the deposited coatings in SG. The most important processing parameters in the SG process

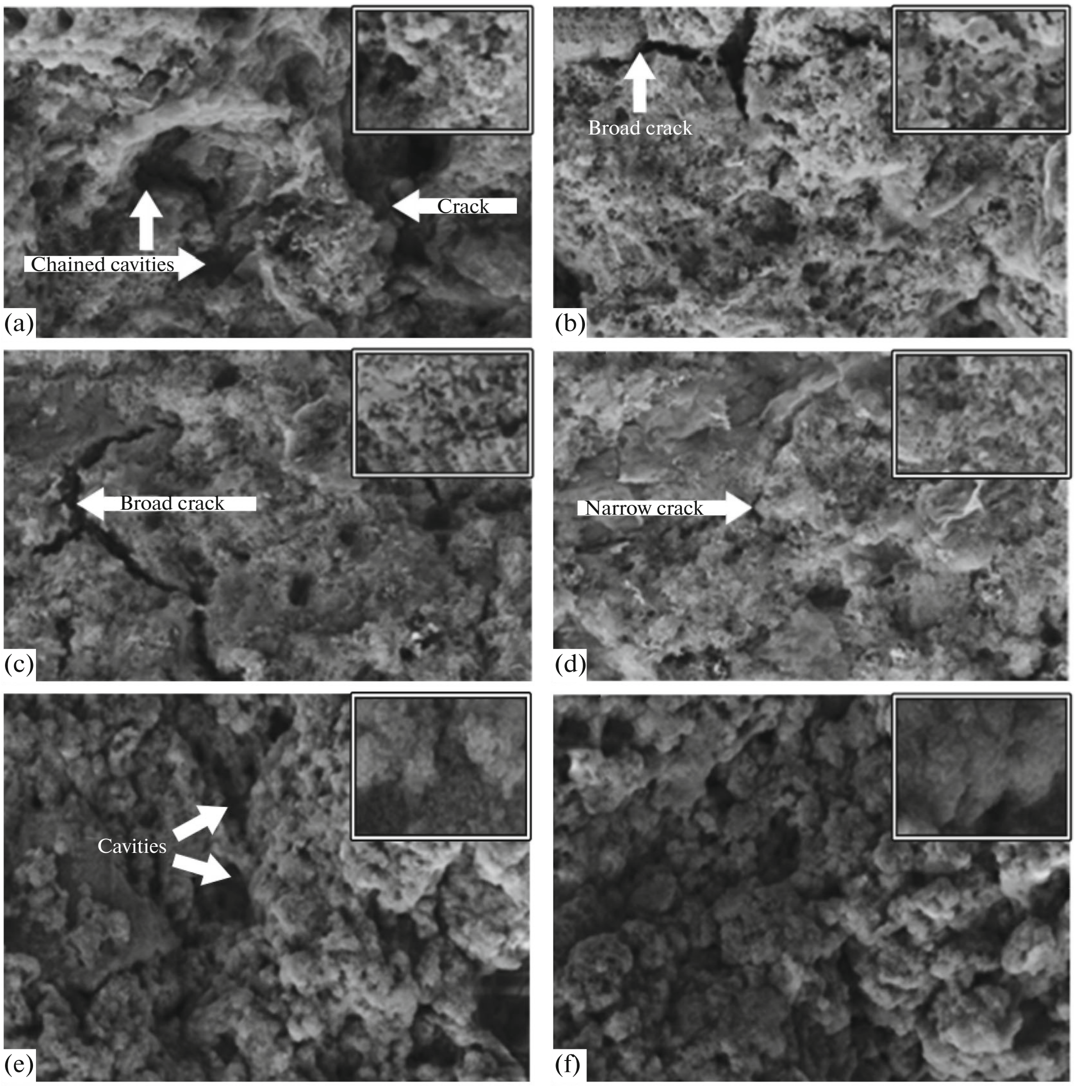

Fig. 15. FESEM images of nano-HA coatings after sintering at: (a) 500°C for 10 min; (b) 500°C for 30 min; (c) 600°C for 10 min; (d) 600°C for 30 min; (e) 700°C for 10 min, and (f) 700°C for 30 min [130].

are: annealing temperature, heating rate, aging time and cooling rate [129].

3.5.1. Sol-gel derived CaP coatings. The SG method is a relatively simple way to prepare hydroxyapatite coatings on metallic implants because of the easy formation of the compound coatings at a relatively low temperature. The authors in [130] investigated the production of SG-deposited HA coating on a Ti-14Zr-13Nb alloy substrate using calcium chloride ($CaCl_2H_2O$) and Na_3PO_4-$12H_2O$. X-ray diffraction of the coatings heated to different temperature and within different time span, as illustrated in Fig. 14, indicated that raising the sintering temperature from 500 to 700°C increased the crystallinity of nano HA. However, sintering at high temperatures introduces Ti ions into the thermally insulated HA coating layer leading to the formation of the oxide layer. The reaction of Ti ion with HA led to the formation of TiO_2 on Ti alloy surface, which eventually led to decomposition of HA into TCP, $CaTiO_3$ and CaO. Thus, for the SG technique, it is suggested that the processing temperature should be below 700°C to prevent phase transformation and ion migration from the Ti alloy substrate into the coating layer.

SG allows preparation of nano-grained HA coatings. Figure 15 shows a field emission scanning electron microscope (FESEM) of the coating obtained at three different sintering temperatures for the span time of 10 and 30 min. The sintered coating obtained at 500°C for 30 min appeared more compacted than that sintered for 10 min. At the sintering temperature from 500 to 600°C and the sintering time span from 10 min to 30 min, broad crack was conspicuously seen at a shorter time period; the crack become narrower at a higher sintering time. At above 600°C, the sintering time span shows no significant impact on the coating morphology.

The absence of a crack at a higher sintering temperature was attributed to a higher diffusion rate (HDR) of Ti ions into the HA coating. With a HDR, more TiO_2 is formed as evidenced by high sharp peaks in Fig. 14c. The formation of an oxide layer enhances the coating grain interface and subse-quently suppresses coating crack propagation.

Production of SG derived HA on metallic implants requires very stringent process parameters, especially for the thermal processing phase such as sintering time and temperature, chemical composition of the precursor and substrate type. The major issue includes the crystalline nature of the phase, porosity control, bonding strength and biocompatibility of the obtained coatings [41]. In addition, it uses an expensive raw material so this technique is not suitable for industrial use [111].

4. CONCLUSIONS

Surface modification is an important and predominant technique to improve the clinical performance of metallic implants for biomedical use. Several surface modification techniques used to fabricate CaP based coatings on metallic implants have been reviewed. The properties of metallic implants can be upgraded upon surface modification with CaP using suitable surface modification techniques. Reflection on these several processes of coating formation portends that MAO is of a very great advantage over other techniques owing to its ability to form a highly adherent microporous layer, which is of prime importance for clinical purposes as its simplicity and cost effectiveness are definitely established. In the next few years, it would be of both theoretical and practical interest to follow an important contribution of this technique into biomedical engineering. Specific areas where MAO of CaP coatings is expected to improve are: fabrication of coatings containing significant amount of CaPs using short deposition time and production of high quality HA coating with high surface roughness and superior cohesive strength. Though MAO process has been noted as an indispensable technique for generating functional nanostructures, it is still of desire to investigate the correlation between hydrothermally treated MAO and the processing parameters. It is also recognized that most of the experimental work in the deposition of CaP by MAO were executed in an unstructured fashion, therefore further research efforts in the field of predictive analytical and numerical modelling of the MAO process of CaP coatings are necessary in order to give strong evidence of statistical data and reproducibility of the experimental outcomes.

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