Preparation and Characterization of Nano-Tetracalcium Phosphate Coating on Titanium Substrate

A.M.Fathi^{1,*}, H.K. Abd El-Hamid², M.M. Radwan²

¹ Physical Chemistry Department, National Research Centre, Dokki, Giza12622, Egypt ² Ceramics Department, National ResearchCentre,Dokki, Giza 12622, Egypt

^{*}E-mail: <u>amfathi70@yahoo.com</u>

Received: 7 December 2015 / Accepted: 28 January 2015 / Published: 1 March 2016

Nano-tetracalcium phosphate TTCP was prepared by solid-state reaction at high temperature and characterized by X-ray diffraction (XRD), Infrared spectroscopy (IR), and Transmission Electron Microscope (TEM). The results show the formation of fine particles size represent agglomerates of very small spherical well-ordered nanoparticles of TTCP with dimensions range from 10-17.8 nm. An inexpensive and relatively simple electrochemical method was used to promote the nucleation of TTCP on Titanium metal and assist the deposition of TTCP from slightly supersaturated solution. The microstructure of the deposited Ca-P-O was investigated by scanning electron microscope (SEM) and electron dispersive x-ray (EDX). A thin film of Ca-P-O deposit was observed after 30min of electrodeposition of TTCP at -1.7V and 3hrs immersion in the same solution at ambient temperature and neutral slightly supersaturated TTCP solution with Ca/P ratio of ≈ 2 . The growth of scarce crystals on this layer composed of primary agglomerated particles with large size after 3days immersion in a simulated body fluid containing phosphate (SBF2) with Ca/P ratio of 1.59. The results indicated that, the TTCP deposited first at Ti surface and it hydrolyzed to hydroxyapatite after few days of immersion in SBF2. Using this inexpensive coating protocol, the TTCP/Ti surface which deposited at different cathodic potentials shows a significant corrosion protection in the two synthesized body fluid solutions when compared with undeposited Ti. The corrosion current density decreases with the increase of immersion time.

Keywords: Titanium, Tetracalcium phosphate, Hydroxyapatite, Biocements, Electrodeposition, Corrosion.

1. INTRODUCTION

The ultimate goal of orthopedic and dental implants is to obtain a life-long secure anchoring of the implant in the native surrounding bone. The most commonly used of titanium (Ti) and its alloys is corrosion resistance, load bearing implant materials, as these metals possess excellent mechanical properties, corrosion resistance, good biocompatibility and osteoinegrability [1-3]. The spontaneous

formation of a stable passive film on the metallic surface protects it from further interaction with the environments [4, 5]. Although titanium is biocompatible, it does not possess the capacity to establish the formation of a tight and chemical bond with bone tissue unless chemically treated with alkali [6–8] or coated with calcium phosphate cement (CPC) [9, 10]. Calcium phosphate biocement makes better implant fixation by stimulating bone formation starting from the implant surface, because it is a truly bone-bonding material [11-14]. Consequently, the mechanical strength of metals is combined with the excellent biological properties of calcium phosphate cements (CPCs) by applying CPCs as coatings on mechanically strong implant materials [11-13], so that, different coating methods have therefore been improved [15–20]. Plasma-sprayed as a tool of coating showed excellent osseointegration. However, extremely high temperature is needed for the plasma spray method which affects the structure of titanium and the homogeneity of the hydroxyapatite coating [21]. Electrodeposition is an alternative tool used in coating various calcium phosphate biocements on metal that uses aqueous solutions at low temperatures without affecting the structure of the implant and can be applied to complex shapes. In addition, the electrodeposition process can be controlled the composition and the structure of the coating easily by varying the electrochemical potential and electrolyte concentration [3].

Different forms and phases of Calcium phosphates exist depending on pH, temperature, presence of impurities and the partial pressure of water [22, 23]. Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAp), monocalcium phosphate monohydrate (MCPM), β - tricalcium phosphate (Ca₃(PO₄)₂, β - TCP), α -tricalcium phosphate (α -TCP), biphasic calcium phosphate (BCP) and tetracalcium phosphate (Ca₄(PO₄)₂O, TTCP) are different forms of commercially available calcium phosphates currently used in biomedical application [24, 25]. Among these phases of calcium phosphate cement, particular attention has been given to tetracalcium phosphate (TTCP), which is a compound with a high Ca/P atomic ratio of 2.0 and it is the most basic calcium orthophosphate ceramic. The solubility of TTCP in water is higher than that of HAp; it slowly hydrolyzes to HAp and calcium hydroxide (CH) [26, 27].

 $3[Ca_4.P_2O_9] + 3H_2O \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 2Ca(OH)_2$

Consequently, in biomedical application TTCP has been used as a self-setting cement that develops desirable physical properties owing to the hydration reaction with H₂O. When TTCP dissolves in the body fluid, large amounts of Ca^{2+} and PO_4^{3-} ions can be released. The decomposition and the transformation of TTCP into apatite in neutrally buffered aqueous solutions supported early bone formation and led to optimal gap/interface healing [20]. As well as the release of CH as a byproduct in that hydration reaction will increase the pH of the reaction medium. This highly alkaline medium has an important role in destroying the bacterial colonies that may be present. The slow hydration reaction rate of TTCP is considered acceptable for dental and medical applications, so, the accretion of the hydrated compounds (HAp) will be found in the vicinities of the anhydrous particle surfaces depending upon the dissolution-precipitation reaction [28].

This study aims at the preparation of nano-tetracalcium phosphate (TTCP) by solid state reaction at high temperature to be used as a deposit on titanium via an electrically assisted deposition followed by immersion protocol. Characterization of the prepared TTCP powder and deposit will be studied. The corrosion behavior of metallic biomaterials in vitro is very important, so, the corrosion parameters of the deposited titanium are studied in two simulated body fluid (SBF) by polarization and

electrochemical impedance technique. The deposited layer is also studied by scanning electron microscope and FTIR spectroscopy.

2. EXPERIMENTAL

2.1. Preparation and Characterization of TTCP powder

The preparation of TTCP is fixed to solid-state reaction at high temperature [29-32] that is depended on mixing calcium carbonate (CaCO₃) and monocalcium phosphate monohydrate (Ca(H₂PO₄). H₂O) in a molar ratio of 3:1 in n-heptane for 16 hrs. The slurry was filtered, dried at room temperature and heated to 1450-1500 °C for 6-12 hrs and rapidly quenched to room temperature. The resulting powder was ground to a particle size of about 2.5 μ m in n-heptane for 8 hrs, dried at 100 °C, and kept under vacuum to avoid hydration [33, 34]. The reaction is given by the following equation:

 $3CaCO_3 + Ca(H_2PO_4)_2.H_2O \longrightarrow Ca_4(PO_4)_2O + 3CO_2 + 3H_2O$

The prepared powder component was investigated by X-ray diffraction (XRD) to verify the identity of the synthesized compound, using a copper target with radiation; wavelength = 0.154 nm, X-ray was generated at 40 kV with a current of 2-5 mA. The synthesized material was ground in an agate mill until the desired grain size. It was investigated by Transmission Electron Microscope (TEM) (JEM- 1230) at 100 kV to evaluate the particle size. Also IR spectra were recorded on TTCP powder with the aid of JASCO 4600 model FTIR spectrometer.

2.2. Electrically assisted deposition (ECAD) of TTCP

Pure Ti was used as the substrate material. Before the electrode immersion in the electrolyte, the electrodes were abraded using successive grades of emery paper down to 2,000 girt, then rubbed with a soft cloth until acquiring mirror bright surface and washed with double distilled water. The sample was used as cathode with an exposed surface area of 1.0 cm^2 and platinum counter electrode was used as anode. ECAD experiments were carried out in a three-electrode conventional glass cell containing a slightly supersaturated solution of TTCP at around neutral pH at constant potential (-0.8-1.7 V) and at room temperature. The potential of the working electrode was measured against Ag/AgCl reference electrode (E^o = 0.203 V vs. SHE) by using Autolab potentiostat/galvanostat PGSTAT302N. The pH was adjusted by using 0.2 g/l NaHCO₃.

2.3. Corrosion Studies

Electrochemical experiments were carried out in a three-electrode conventional glass cell. The potential of the working electrode was measured against Ag/AgCl reference electrode ($E^{\circ} = 0.203 V$ vs. SHE) and pure Pt-foil used as counter electrode. Potentiodynamic polarizations of the as received and deposited sample were carried out after immersion for 5 min in two different simulated body fluid solutions one for animal SBF1 and the other for human SBF2 at 37°C with scan rate of 1 mV/sec. The effect of immersion time was also conducted in the same manner after 180 min. SBF solution

compositions are given in Table 1. The electrochemical impedance spectroscopy (EIS) of the as received and deposited sample in SBF solutions at 37° C has been carried out with Ac voltage amplitude of 10 mV using an electrochemical impedance system at open circuit potential. The frequency range used in the study was $0.02-10^{5}$ Hz.

Simulated	Constituents of the	Concentration		
body fluid	buffer	(g/L)		
SBF1	NaCl	8.6		
	KCl	0.3		
	CaCl ₂	0.33		
SBF2	NaCl	8.77		
	Na ₂ HPO ₄	1.42		
	KH_2PO_4	2.72		
	CaCl ₂	0.29		

Table 1. The composition of the simulated body fluids used.

2.4. Characterization of the Ca-O deposit

Scanning electron micrographs (SEM) and energy dispersive x-ray spectra (EDX) were performed for untreated Ti and two treated Ti samples, deposited at -1.7 V and left in supper saturated solution of TTCP for 3 hrs with continuous stirring and the other sample deposited at -1.7 V and left in supper saturated solution of TTCP for 3 hrs with continuous stirring, then immersed in freshly prepared SBF2 at room temperature for 3 days. The second sample was characterized also by FTIR spectrometer

3. RESULTS AND DISCUSSION

3.1. Characterization of the prepared TTCP



Figure 1. XRD spectral analysis (2-Theta-scale) of the synthesized TTCP powder.



Figure 2. Transmission electron Microscope (TEM) of TTCP powder.

The prepared tetracalcium phosphate biocement has been emphasized by XRD analysis (JCPDS 25-1137). The characteristic XRD pattern for prepared pure TTCP material is given in Fig. 1. The detailed TEM analysis of TTCP powder in Fig. 2 showed ultra-fine nanoparticles of size range from 10-17.8 nm present in very small spherical well-ordered agglomerates.

3.2 Electrically assisted deposition (ECAD) of TTCP



Figure 3. The current transient recorded during potentiostatic deposition at -0.8 V and -1.5 V versus Ag/AgCl.

TTCP potentiostatically deposited on Ti electrodes by applying different potentials (-0.8 to - 1.7 V) for 30 min in neutral slightly supper saturated solution of TTCP (0.2 g/l NaHCO₃ was added for adjusting pH). Fig. 3 shows the current transient recorded during potentiostatic deposition at -0.8 V and -1.5 V versus Ag/AgCl (as an example). The current increases with time due to the growth of nuclei on the surface. In air saturated solution following reactions take place at the Ti surface due to cathodic potential applied [35, 36]:

$$2H_2O + 2e' \rightarrow H_2 + 2OH^-$$

$$O_2 + 2H_2O + 4e' \rightarrow 4OH^-$$

These reactions result in the formation of OH ions at the surface of Ti causing a local increase in pH, which leads to an increase in the relative super saturation of the electrolyte resulting in the nucleation of Ca-P-O deposit.

3.3 Stability of TTCP-Ti deposit in SBF



Figure 4. Potentiodynamic polarization curves of TTCP/Ti coated at different deposition potential immersed in naturally aerated stagnant (a) SBF1 solution (b) SBF2 solution at 37°C and scan rate 1 mV/s.

Type of	Immersion	SBF1			SBF2				
electrode	time, min	b _a	b _c	E _{corr} ,	I _{corr} ,	b _a	b _c	E _{corr} ,	I _{corr} ,
		mV/dec	mV/dec	mV	A/cm ²	mV/dec	mV/dec	mV	A/cm ²
Ti	5	123	299	-420	0.75x10 ⁻⁶	99	154	-500	7.75 x10 ⁻⁶
TTCP/Ti at		139	180	-415	0.63 x10 ⁻⁶	174	295	-425	6.50 x10 ⁻⁶
-0.8 V									
TTCP/Ti at		69	160	-360	0.62 x10 ⁻⁶	76	96	-427	4.00 x10 ⁻⁶
-1.2 V									
TTCP/Ti at		101	137	-190	0.56 x10 ⁻⁶	100	74	-360	1.30 x10 ⁻⁶
-1.5 V									
TTCP/Ti at		100	151	-260	0.32 x10 ⁻⁶	125	754	-301	1.08 x10 ⁻⁶
-1.7 V									
TTCP/Ti at	180	185	127	-210	14 x10 ⁻⁹	63	206	-213	199 x10 ⁻⁹
-0.8 V									

Table 2. The Corrosion parameters for Ti and TTCP/Ti after immersion in simulated body fluids (SBF1) and (SBF2) at 37°C, pH = 7.4.

The electrochemical behavior of TTCP/Ti deposited at different potentials was evaluated by the interaction between the material and two simulated body fluid solutions (SBF1 and SBF2).

In this series of experiments, TTCP was deposited from neutral supper saturated solution of TTCP on Ti surface by applying different potentials (-0.8 to -1.7 V) for 30 min. After deposition, the samples were washed with double distilled water, and then immersed in the electrochemical cell. Potentiodynamic polarization curves of the as received and the deposited substrate were carried out after immersion in SBF1 or SBF2 for 5 min as shown in Fig. 4 (a, b). As shown from the figures, there is a passive area on the anodic branch appears at low current density for the deposited substrate due to the anodic and cathodic parts of Tafel plot shifted to more passive values. The polarization parameters with these substrates obtained according to the following Tafel equation [37] are presented in Table 2:

$E = a + b \log i$

It was observed that, the corrosion potential (E_{corr}) shifted to more positive potential and there is a slight decrease in the corrosion current (I_{corr}) values towards more passive values for samples immersed in SBF1 while a greater decrease in I_{corr} values of the samples immersed in SBF2. This is due to the presence of phosphate and calcium ions in SBF2 which adsorbed on the active sites of the electrode surface leading to a decrease in the corrosion of Ti substrate [38], while SBF1 contains more chloride ions which attack the deposited layer. The change in cathodic and anodic Tafel slopes (b_c , b_a) values indicating that the oxidizing dissolution as well as the reduction process is suppressed by the adsorption of CaP. To show the effect of time of immersion on the corrosion behavior of TTCP/Ti, potentiodynamic polarization curves of the samples coated at -0.8 V were carried out after immersion in SBF1 or SBF2 for 5 min and 180 min. Fig. 5 (a, b) shows a decrease in the I_{corr} value with 180 min of immersion whereas, D. Gopi, et al., have reported the I_{corr} of HAP coating on the electrically treated Ti alloy substrate as 0.38 μ A [3] and a shift of E_{corr} to more passive value indicating more passivation with long immersion.



Figure 5. Potentiodynamic polarization curves of Ti bare and TTCP/Ti(deposited at -0.8 V) at different times of immersion in naturally aerated stagnant (a) SBF1 solution and (b) SBF2 solution at 37 °C and scan rate 1 mV/s.

To confirm the potentiostatic polarization results, EIS investigations of the samples coated at - 0.8 V were carried out. The impedance spectra were recorded after 5 min and 180 min of immersion in SBF1 and SBF2 solutions under open circuit conditions and presented as Bode plots in Fig. 6 (a, b). The plots for samples after 5 min of immersion show a resistive region at high frequencies, a capacitive region at intermediate frequencies and no plateau at low frequencies beside a broad phase maximum which is a characteristic property of passive surface [39]. The splitting in the phase diagram into two maxima with long immersion means the presence of two layers, which are innercompact layer and outer layer which is an evidence of deposit growth kinetics [40, 41]. The increase in the resistance of the film with time as shown from impedance plots are in good agreement with those calculated from polarization measurements.



Figure 6. Bode plots of TTCP/Ti deposited at -0.8 V after 5min and 180 min of immersion in naturally aerated stagnant (a) SBF1 solution and (b) SBF2 solution at 37 °C.

3.4 Morphology and Characteristic of the Ca-P layer



Figure 7. (a) Scanning electron micrograph of mechanically polished Ti. (b) Micrographs of potentiostatically TTCP/Ti deposited at -1.7 V for 30 min after 3 hrs of immersion in SBF2 (c) Micrographs of potentiostatically TTCP deposited Ti at -1.7 V for 30 min after 3 days of immersion in SBF2.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) measurements were carried out. Fig. 7a presents the SEM of the mechanically polished Ti-surface,

which represents the typical morphology of the mechanically polished polycrystalline metallic surface [42]. Fig. 7b shows the SEM of the potentiostatically deposited Ca-P-O at -1.7 V after 3 hrs of immersion in stirred slightly neutral supersaturated solution of TTCP, the formation of very thin film of deposited Ca-P-O compound can be observed.

After immersing the deposited sample in SBF2 solution for 3 days, it was found that scarce crystals were formed on this thin layer, which is composed of primary agglomerated particles with large size as shown in Fig 8c. The growth of Ca-P-O layer and precipitation of more nuclei on the Ti surface makes it hydrophilic and rough enough to enhance cell attachment [43], as well as the ability of Ti to induce apatite nucleation in SBF [44].



Figure 8. (a) EDX photograph of potentiostatically TTCP deposited on Ti at -1.7 V for 30 min after 3hrs of immersion in SBF2 (b) EDX photograph of potentiostatically TTCP deposited Ti at -1.7 V for 30 min after 3 days of immersion in SBF2.

The energy dispersive spectra of the two deposited Ca-P-O is presented in Fig.8 (a, b). Ti, O, Ca and P were the major elements identified in the coatings as shown in Table 3. The oxygen content

3175

in the samples was nearly the same. The atomic% of Ti is used to represent the degree of coverage resulting from the deposit. Ca content in the coat was increased consequently with immersion; the content of Ca was more than the content of P in both samples. The ratio of Ca/P was recorded ≈ 2 in the first sample indicating the formation of TTCP deposit and ≈ 1.6 which are relatively close to the value of stoichiometric HA, which had been recorded before refs.[45, 46]. The previous studies showed that the CaP/Ti is reactive in SBF, after immersion in SBF for a period as short as 3 hrs, apatite layer appears on the surface of the coating. With longer immersion periods, the layer becomes dense and the granular apatite grows gradually, which is considered to be the symbol of the activity for biomaterials [44, 47, 48].

Time of immersion	Composition							
	Ca	Κ	РК		Ti K		O K	
	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %
3 hrs	31.40	18.24	10.48	7.87	11.01	5.35	47.11	68.54
3 days	30.88	16.83	15.07	10.63	1.36	0.62	52.69	71.92

Table 3. The composition of the deposited layer on Ti after 3 hrs and 3 days of immersion in SBF2.

3.5. IR analysis of the prepared nano-TTCP powder and TTCP/Ti

The IR spectra of the anhydrous TTCP powder and the coated titanium after immersion for 3 days in SBF2 solution are given in Fig. 9 and illustrated in Table. 4. The IR spectra shows the apatite bands at 490, 560, 960 and 1030 cm⁻¹, OH stretching-very broad band at 490 which is overlapped with apatite band and also OH stretching band at 3648, 2500 to 3700 cm⁻¹. The IR bands characteristic for carbonated apatite (Aragonite v_2 , $\dot{v}_3 CO_3^{2-}$ antisymmetric stretching) at 974, 1490 and 1460 cm⁻¹ are formed due to the possible carbonation with the atmospheric CO₂. The IR spectra reveals the clear disappearance of almost phosphate bands characteristic for the anhydrous synthesized calcium phosphate and those characteristics for HAp could be detected as given in Table. 3. As TTCP is the mineral constituent of hard tissues, it is highly bioactive and after its electrodeposition on Ti and soaking in SBF2 for 3days, the deposition of the bone like apatite will take place on the surface of the coated area due to the formation of HAp as a result of the hydrolysis of the TTCP, in addition to that precipitated from SBF [20]. This deposition of hydroxyapatite on the surface of the coated titanium as was found in SEM and EDX analyses, which was in accordance with the work of X. Zheng, et al. [43].



Figure 9. IR spectra of: (a) TTCP powder (b) TTCP/Ti deposited at -1.7V and immersed for 3days in SBF2.

Table 4. Results of FTIR analysis.

Wave number (cm ⁻¹)	Vibrational mode	Crystal phase
490	$v_2 OH^-$	OH stretching in Ca(OH) ₂ or HAP
3648 2500 to 3700	vOH ⁻ OH ⁻	A very broad OH absorption bands
1490-1460	$\dot{\upsilon}_3 \text{CO}_3^{2-}$ antisymmetric	Aragonite and/or vaterite, B-type
	stretching	carbonated apatite
1030	$\dot{\upsilon}_3 PO_4^{3-}$	Antisymmetric stretching
600 – 560	$\dot{\upsilon}_4 \operatorname{PO}_4^{-3}$	Amorphous calcium phosphate

4. CONCLUSION

The nano-TTCP was prepared by solid-state reaction at high temperature, then deposited by electrically assisted deposition at different cathodic potentials on Ti substrate. The cathodic potential results in the formation of OH ions at the Ti surface and enable the formation of Ca-P-O compounds. The Ca-P-O layer formed on Ti leads to:

- 1) Enhancing the corrosion resistance of Ti in both SBF1 and SBF2 by long time immersion in simulated body fluids, especially in SBF2 due to the presence of phosphate and calcium salts on it.
- 2) The ratio of Ca/P obtained by EDX was ~1.6 indicating the growth of bone like apatite deposit with long immersion of TTCP/Ti in simulated body fluids (SBF2).

The ability to form apatite like precipitation layer has been regarded as the evidence of bioactivity of the TTCP/Ti.

References

- 1. M. Batazic, J. Kopac, J.M. Jackson, and W. Ahmed, Int. J. Nano. Biomater., 1 (2007) 3.
- 2. S. Kumar, T.S.N. Sankara Narayanan, S.G.S. Raman, S.K. Seshadri, *Mater. Chem. Phys.* 119 (2010) 337-346.
- 3. D. Gopi, E.M. Sherif, D. Rajeswari, L. Kavitha, R. Pramod, J. Dwivedi, S.R. Polaki, *Journal of Alloys and Compounds*, 616 (2014) 498-504.
- 4. L.J. Knob, D.L. Olson, Metals Handbook Corrosion, 9th ed., 13 (1987) 669.
- 5. B.D. Ratner, J. Biomed. Res., 27 (1993) 837.
- 6. H. Takadama, H.M. Kim, T. Kokubo and T. Nakamura, *Sci. Tech. Adv. Mater.*, 2 (2001) 389.
- 7. T. Kokubo, H.M. Kim and M. Kawashita, *Biomaterials*, 24 (2003) 2161.
- 8. M. Takemoto, S. Fujibayashi, M. Neo, J. Suzuki, T. Matsushita, T. Kokuboand T. Nakamura, *Biomaterials*, 27 (2006) 2682.
- 9. P. Habibovic, J. Li, C.M. Van DerValk, G. Meijer, P. Layrolle, C.A. Van Blitterswijk and K. De Groot, *Biomaterials*, 26 (2005) 23.
- 10. E. Goyenvalle, E. Aguado, J.M. Nguyen, N. Passuti, L. LeGuehennec, P. Layrolle, and G. Daculsi, *Biomaterials*, 27 (2006) 1119.
- 11. F. Barrere, C.M. Van Der Valk, G. Meijer, R.A. Dalmeijer, K. De Groot and P. Layrolle, *J Biomed Mater Res B Appl. Biomater.*, 67 (2003) 655.
- 12. L.T. De Jonge, S.C.G. Leeuwenburgh, J.J.J.P.Van Den Beucken. J.T. Riet, W.F. Daamen, J.G.C. Wolke, D. Scharnweber, J.A. Janse, *Biomaterials*, 31 (2010) 2461-2469.
- 13. S.C. Leeuwenburgh, J.G. Wolke, M.C. Siebers, J. Schoonman, and J.A. Jansen, *Biomaterials*, 27 (2006)3368.
- 14. O. Albayrak and S. Altintas, J. Mater. Sci. Technol., 26 (2010) 1006-1110
- 15. C.X. Wang, Z.Q. Chen, L.M. Guan, M. Wang, Z.Y. Liu and P.L. Wang, *Nucl. Instr. Meth. Phy. Res. Sect. B: Beam Inter. Mater. Atoms*, 179 (2001) 364.
- 16. I.S. Lee, D.H. Kim, H.E. Kim, Y.C. Jung and C.H. Han, *Biomaterials*, 23 (2002) 609.
- 17. B. Feng, J.Y. Chen, S.K. Qi, L. He, J.Z. Zhao and X.D. Zhang, *Biomaterials*, 23 (2002) 173.
- 18. S.W.K. Kweh, K. A. Khor and P. Cheang, *Biomaterials*, 23 (2002) 775.
- 19. L. Yan, Y. Leng and L.T. Weng, *Biomaterials*, 24 (2003) 2585.
- 20. C.L. Ko, Y.Y. Chang, C.H. Liou , W.C. Chen, *Materials Science and Engineering* C 49 (2015) 7–13.
- 21. H.C. Gledhill, I.G. Turner and C. Doyle, *Biomaterials*, 22 (2001) 1233.
- 22. K. De Groot, C.P.A.T. Klein, J.G.C. Wolke and J.M.A. Blieck-Hogervorst, *Chemistry of calcium phosphate bioceramics, CRC Handbook of bioactive Ceramics, Calcium phosphate and Hydroxylapatite Ceramics, vol. II, CRC press, Boca Raton, FL*, (1990).
- 23. L.C. Chow, Mater. Res. Symp. Proc., 599 (2000) 27-37.
- 24. L.H. Wong and B. Tip, X. Miao, *Mater. Sci. Eng.*, *C*, 20 (2002) 111.
- 25. W.G. Billotte, J.B. Park and J.D. Bronzino (Eds.), *Ceramic Materials in Biomaterials: Principles and Applications, CRC Press, Boca Raton, FL*, (2002).
- 26. P. W. Brown, Cem. Concr. Res., 29 (1999) 1167.
- 27. C. Jeon, S. Chun, S. Lim and S. Kim, *Biomaterials Research*, 15 (2011) 1-6.
- 28. S. J. Kalita, A. Bhardwaj and H.A. Bhatt, *Mater. Sci. Eng.*, C 27 (2007) 441.
- 29. S. Jalota, A.C. Tas and S.B. Bhaduri, J. Am. Ceram. Soc., 88 (2005) 3353.
- 30. W.F. Brown and L.C. Chow, Dental restorative cement pastes. US patent No. 4518, 430 (1985).
- 31. L.C. Chow and S. Takagi, Self-setting calcium phosphate cements and methods for preparing and using them. *US patent No.* 5525, 1996; 148.
- 32. Y. Matsuya, S. Matsuya, J.M. Antonacci, S. Taagi, L.C. Chow and A. Akamine, *Biomaterials*, 20 (1999) 691.
- 33. C. Moseke and U. Gbureck, *Acta Biomaterialla*, 6 (2010) 3815-3823.

- 34. L. Medvecky, M. Giretova and T. Sopcak, *Materials Letters*, 100 (2013) 137-140.
- 35. S.K. Yen and C. Mlin, *Chem. Phys.*, 77 (2002)70.
- 36. N. Eliaz, M. Eliyahu, J. Biomed. Mater. Res., 80A (2007) 621.
- 37. J. Tafel, Z. phys. Chem., 50 (1905) 641
- 38. I.M. Zin, S.B. lyon, V.I. Pokhmurshii, *Corros. Sci.*, 45(2003)777.
- 39. W.A. Badawy, K.M. Ismail, A.M. Fathi, *Electrochim. Acta.*, 50(2005)3603
- 40. Y. Mao, T.-J. Park, F. Zhang, H. Zhou and S.S. Wong, *Small*, 3 (2007)1122.
- 41. A.P. Li, F. Muller, A. Birner, K. Nielsch and U. Gosele, J. Appl. Phys., 84 (1998)6023.
- 42. W.A. Badawy, A.M. Fathi, R.M. El-Sherief and S.A. Fadl-Allah, *J. of Alloys and Compounds*, 475 (2009) 911
- 43. M. Svehla, P. Morberg, W. Bruce, B. Zicat and W.R. Walsh, J. Arthoplastry, 17 (2002)304.
- 44. X. Zheng, M. Huang and C. Ding, *Biomaterials*, 21(2000) 841-849.
- 45. T.N. Kim, Q.L. Feng, J.O. Kim, J. Wu, H. Wang, G.C. Chen and F.Z. Curi, *J.Mater.Med.*, 9 (1998)129.
- 46. M. Tlotteng, E. Akinlabi, M. Shukla and S. Pityana, *Materials Science and Engineering C*, 43 (2014) 189-198.
- 47. Li. Panjian, I. Kangasniemi and K. De Groot, J. Am. Ceram. Soc., 77 (1994) 1307.
- 48. R.Z. LeGeros and J.P. LeGeros, Dense hydroxyapatite. In: L.L. Hench, J. Wilson, editors. *An introduction to bioceramics. USA: World Scientific*, (1993) 162-5.

© 2016 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).