Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Materials Letters 60 (2006) 2573–2577
materials letters
www.elsevier.com/locate/matlet

Bioactivity of calcium phosphate coatings prepared by electrodeposition in a modified simulated body fluid

Ji-Ho Park, Doug-Youn Lee, Keun-Taek Oh, Yong-Keun Lee, Kwang-Mahn Kim, Kyoung-Nam Kim *

Brain Korea 21 Project for Medical Science, Research Institute and Department of Dental Biomaterials and Bioengineering, Yonsei University College of Dentistry, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-752, South Korea

Received 6 January 2004; accepted 11 July 2005
Available online 13 February 2006

Abstract

The purpose of this study was to investigate bioactivity of calcium phosphate coatings prepared by electrodeposition in a modified simulated body fluid (SBF). Calcium phosphates were electrodeposited on commercially pure titanium substrates in the modified SBF at 60 °C for 1 h maintaining the cathodic potentials of −1.5 V, −2 V, and −2.5 V (vs. SCE). Subsequently, the calcium phosphate coatings were transformed into apatites during immersion in the SBF at 36.5 °C for 5 days. The apatites consisted of needle-shaped crystallites distributed irregularly with different grain sizes. As the coatings were electrodeposited at higher cathodic potential, the crystallite of the apatites got denser and the grain sizes of the apatites became bigger during subsequent immersion in the SBF. However, as the coatings were electrodeposited at higher cathodic potential, the coatings were transformed into apatites with lower crystallinity and the Ca/P atomic ratio of the apatites got higher than 1.67, that of stoichiometric hydroxyapatite, after subsequent immersion in the SBF. In addition, CO_3^{2-} ions contained in the modified SBF were incorporated in the calcium phosphate coating during electrodeposition and had an influence on transforming the calcium phosphate into bonelike apatite during subsequent immersion in the SBF showing that CO_3^{2-} incorporated in the apatites disturbed crystallization of the apatites. These results revealed that the coating electrodeposited at −2.0 V (vs. SCE) in the modified SBF containing CO_3^{2-} ions was the most bioactive showing transformation into carbonate apatite similar to bone apatite.

Keywords: Bioactivity; Calcium phosphate; Coating; Electrodeposition; Hydroxyapatite (HA); Simulated body fluid (SBF)

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) coating onto metallic substrates has been widely used in the medical and dental fields in order to combine excellent mechanical properties of metal alloys and bioactivity of HA [1]. A currently prevailing method for the HA coating is the use of plasma spraying. However, the plasma spraying method does not allow accurate control of the chemical composition, crystallographic structure and crystallinity of the coating [2]. In addition, it cannot produce a uniform coating of devices with complicated shapes. In order to improve on these disadvantages of plasma spraying, an electrodeposition method was introduced with good properties, such as quick and uniform coating of the substrates with complex forms at low temperatures and the control of the film thickness and chemical composition of the coating [3–10].

Several solutions have been used as electrolytes in order to coat calcium phosphates using the electrodeposition method. Ban and Maruno used a simulated body fluid (SBF) similar to human blood plasma as an electrolyte for electrodeposition [4]. Shirkhanzadeh used a mixed solution prepared by 0.167 M $CaCl_2$ and 0.1 M $NH_4H_2PO_4$ [5], and Yen and Lin used a mixed solution of 0.042 M $Ca(NO_3)_2{\cdot}4H_2O$ and 0.025 M $NH_4H_2PO_4$ [10]. Recently, Ban and Maruno used a modified SBF containing 137.8 mM NaCl, 1.67 mM K_2HPO_4, and 2.5 mM $CaCl_2{\cdot}2H_2O$, which has the composition of SBF without $MgCl_2{\cdot}6H_2O$, KCl, and $NaHCO_3$, in order to prevent the formation of $Mg(OH)_2$ and $CaCO_3$ in electrodeposited calcium phosphates [6]. And it was reported that the presence of Mg^{2+}

* Corresponding author. Tel.: +82 2 2228 3081; fax: +82 2 364 9961.
E-mail address: kimkn@yumc.yonsei.ac.kr (K.-N. Kim).

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.07.091

Table 1
Compositions of the modified SBF as an electrolyte for electrodeposition coating

Order	Reagent	Amount
1	Double-distilled water	1 l
2	NaCl	7.996 g
3	$NaHCO_3$	0.350 g
4	$K_2HPO_4{\cdot}3H_2O$	0.228 g
5	$CaCl_2$	0.278 g

ions in the solution during electrodeposition resulted in the incorporation of these ions in the coating and suppressed to transform octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_6{\cdot}5H_2O$) into apatite [11]. However, CO_3^{2-} ions in the solution are necessary to form a carbonate calcium phosphate coating similar to bone apatite using the electrodeposition method. The carbonate calcium phosphate coating is expected to show more bioactivity in the human body than other calcium phosphates. Therefore, we used the modified SBF containing CO_3^{2-} ions as an electrolyte for electrodeposition different from the modified SBF used previously by Ban and Maruno.

Bioactivity is defined as the property of the material to develop a direct, adherent, and strong bonding with the bone tissue [12]. To evaluate this bioactivity of the materials, it has been proposed that materials that form an apatite on their surfaces in the SBF also can form the apatite in a living body and can bond to bone through the apatite layer. In other words, the apatite-forming ability in the SBF is a measure of in vivo bioactivity [13]. However, few reports have been produced on the evaluation of bioactivity of electrodeposited calcium phosphate coatings by forming the bonelike apatite during subsequent immersion in the SBF. In this study, we investigate bioactivity of calcium phosphate coatings electrodeposited at −1.5 V, −2 V, and −2.5 V (vs. SCE) in the modified SBF containing CO_3^{2-} by forming the bonelike apatite during subsequent immersion in the SBF for 5 days.

2. Experimental

A commercially pure titanium plate ($10\times10\times0.8$ mm^3) was used as a substrate. Its surface was ground with #100 and #600 SiC paper. In order to avoid an edge effect during electrodeposition, the edges of the titanium substrates were rounded. The electrodeposition of calcium phosphates was performed at 60 °C for 1 h in a conventional cell fitted with a saturated calomel electrode (SCE) maintaining the cathodic potentials of −1.5 V, −2 V, and −2.5 V (vs. SCE). A modified SBF was used as an electrolyte for electrodeposition. The modified SBF was prepared by dissolving reagent-grade NaCl, $NaHCO_3$, $K_2HPO_4{\cdot}3H_2O$, and $CaCl_2$ into double-distilled water and buffering at pH 7.4 at 60 °C with tris-hydroxymethylaminomethane [$(CH_2OH)_3CNH_2$] and 1 M hydrochloric acid (HCl). The composition of this modified SBF is shown in Table 1. Titanium substrates were used as cathodes for electrodeposition. A potentiostat/galvanostat (Model 263A, EG and G Instruments, USA) operating in potentiostatic mode was used to maintain the cathodic potentials of −1.5 V, −2 V, and −2.5 V (vs. SCE). The solution was stirred during electrodeposition.

In order to evaluate bioactivity of the coatings, the coatings were immersed in 20 ml of an acellular SBF with ion concentrations close to that of human blood plasma at 36.5 °C for 5 days, respectively. The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, and Na_2SO_4 into double-distilled water and buffering at pH 7.4 at 36.5 °C with tris-hydroxymethylaminomethane [$(CH_2OH)_3CNH_2$] and 1 M hydrochloric acid (HCl) [14]. The SBF was renewed each day.

The crystallinity and structure of the coatings were examined using X-ray diffraction (XRD, D-Max Rint 240 Model, Rigaku, Japan). The morphology of the coatings was examined using scanning electron microscopy (SEM, S-2700 model, Hitachi, Japan). The chemical composition of the coatings was analyzed by energy dispersive spectroscopy (EDS, Kevex Superdry model, Kevex Instruments, USA) and Fourier transform infrared spectroscopy (FTIR, Avatar 360, Thermo Nicolet, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the titanium substrate before electrodeposition, the coating formed on the titanium substrate after electrodeposition at −1.5 V (vs. SCE), and the coating transformed on the titanium substrate after electrodeposition at −1.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days. The main structures of the coating that formed on the titanium substrate by electrodeposition at −1.5 V (vs. SCE) were amorphous calcium phosphate (ACP) and dicalcium phosphate dehydrate (DCPD, $CaHPO_4{\cdot}2H_2O$). After this coating was immersed in the SBF at 36.5 °C for 5 days, the structure of the coating transformed ACP and DCPD into HA, DCPD, and OCP. It indicates that the process transforming DCPD into HA was not finished

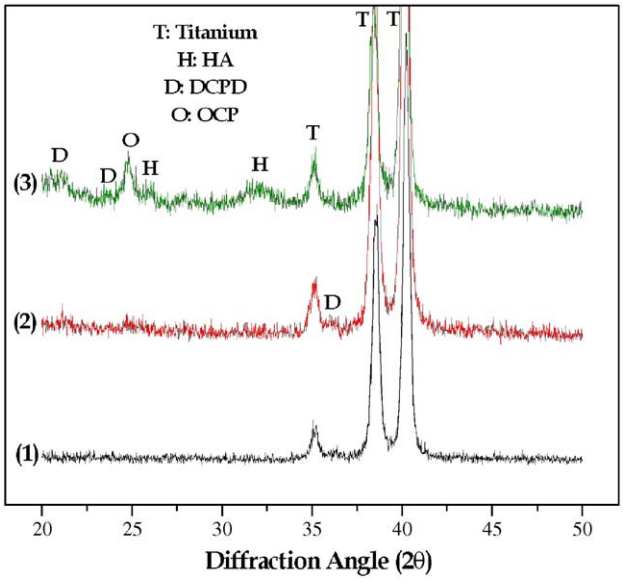

Fig. 1. XRD patterns of (1) the titanium substrate before electrodeposition, (2) the coating formed on the titanium substrate after electrodeposition at −1.5 V (vs. SCE), and (3) the coating transformed on the titanium substrate after electrodeposition at −1.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days.

completely and OCP, an intermediate structure of transformation DCPD into HA for the bone formation, appeared with strong peak.

Fig. 2 shows the XRD patterns of the titanium substrate before electrodeposition, the coating formed on the titanium substrate after electrodeposition at −2.0 V (vs. SCE), and the coating transformed on the titanium substrate after electrodeposition at −2.0 V (vs. SCE) and subsequent immersion in the SBF for 5 days. The main structures of the coating that formed on the titanium substrate by electrodeposition at −2.0 V (vs. SCE) were ACP and DCPD similar to that of the coating by electrodeposition at −1.5 V (vs. SCE). However, after this coating was immersed in the SBF at 36.5 °C for 5 days, the structure of the coating transformed ACP and DCPD into mainly HA with minor OCP and DCPD. It indicates that the process transforming DCPD into HA was almost finished.

Fig. 3 shows the XRD patterns of the titanium substrate before electrodeposition, the coating formed on the titanium substrate after electrodeposition at −2.5 V (vs. SCE), and the coating transformed on the titanium substrate after electrodeposition at −2.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days. The main structures of the coating that formed on the titanium substrate by electrodeposition at −2.5 V (vs. SCE) were ACP and DCPD with very weak HA. After this coating was immersed in the SBF at 36.5 °C for 5 days, the structure of the coating transformed ACP and DCPD into mainly HA. It indicates that the process transforming DCPD into HA was finished. And it is observed that titanium peaks shifted to a smaller diffraction angle after electrodeposition. It indicates that the coating formed on a titanium substrate by electrodeposition at −2.5 V (vs. SCE) was thick enough to interfere with X-ray diffraction compared to the coatings formed by electrodeposition at −1.5 V and −2.0 V (vs. SCE).

In order to compare bioactivity of the coatings electrodeposited at various cathodic potentials, Fig. 4 shows XRD patterns of the coatings transformed on the titanium substrate after electrodeposition at −1.5 V, −2.0 V, and −2.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days. As the coatings were electrodeposited at higher cathodic potential, the main structures of the coatings transformed during immersion in the SBF changed OCP to HA. The coating transformed

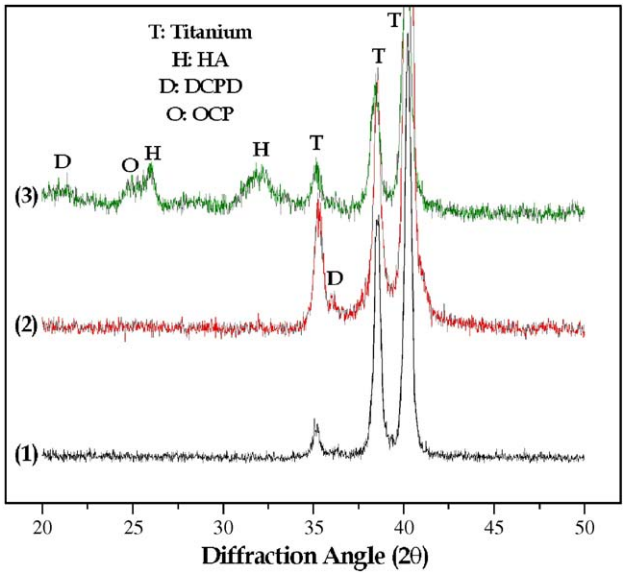

Fig. 2. XRD patterns of (1) the titanium substrate before electrodeposition, (2) the coating formed on the titanium substrate after electrodeposition at −2.0 V (vs. SCE), and (3) the coating transformed on the titanium substrate after electrodeposition at −2.0 V (vs. SCE) and subsequent immersion in the SBF for 5 days.

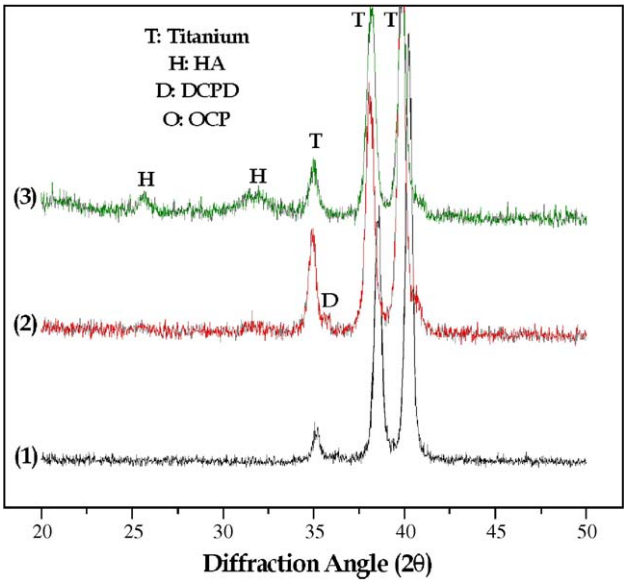

Fig. 3. XRD patterns of (1) the titanium substrate before electrodeposition, (2) the coating formed on the titanium substrate after electrodeposition at −2.5 V (vs. SCE), and (3) the coating transformed on the titanium substrate after electrodeposition at −2.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days.

after electrodeposition at −2.5 V (vs. SCE) and subsequent immersion in the SBF showed the very weak and broad peaks of HA meaning very low crystallinity. It indicates that this coating is unstable in the human body and may dissolve easily. However, the coating transformed after electrodeposition at −2.0 V (vs. SCE) and subsequent immersion in the SBF showed the broad and high peaks of the HA with the weak peak of the OCP and DCPD. It indicates that this coating can be transformed into the HA with a bonelike crystallinity and density in the human body and induce stable bonding to bone [15]. The immersion test in the SBF in order to evaluate bioactivity of the coatings was performed for 5 days in this study. If the immersion test in the SBF is performed over 1 week,

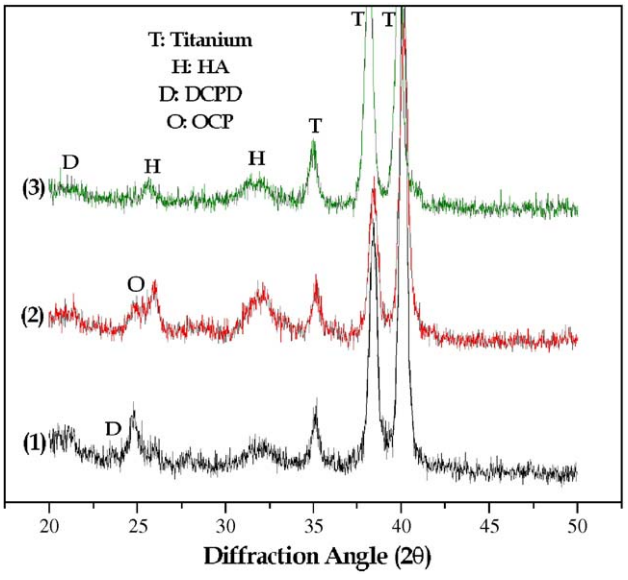

Fig. 4. XRD patterns of the coatings transformed on the titanium substrate after electrodeposition ((1) at −1.5 V, (2) at −2.0 V, and (3) at −2.5 V (vs. SCE)) and subsequent immersion in the SBF for 5 days.

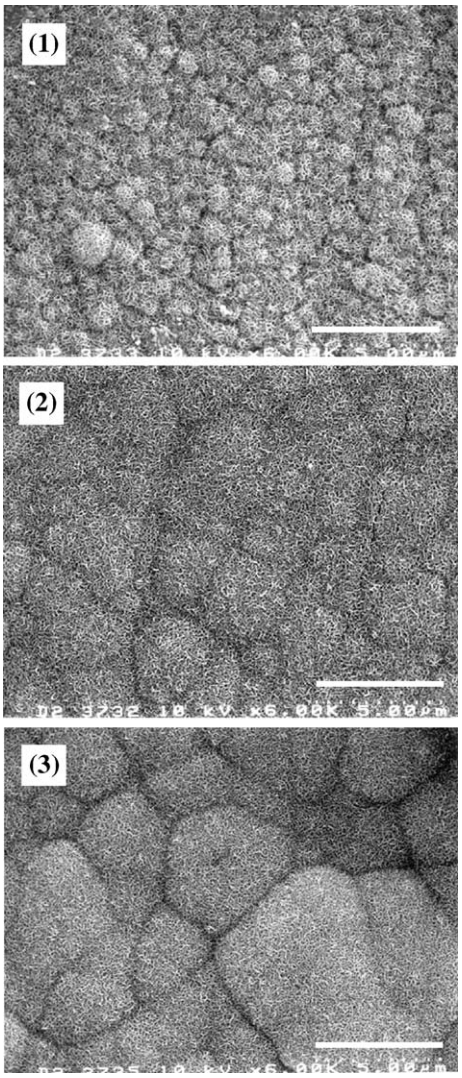

Fig. 5. SEM images showing the morphology of the coatings transformed on the titanium substrate after electrodeposition ((1) at −1.5 V, (2) at −2.0 V, and (3) at −2.5 V (vs. SCE)) and subsequent immersion in the SBF for 5 days. Scale bar: 5 μm.

it is expected that the minor OCP in the coating transformed after electrodeposition at −2.0 V (vs. SCE) and subsequent immersion in the SBF for 5 days would be transformed into HA completely. Therefore, it is believed that the coating electrodeposited at −2.0 V (vs. SCE) has the most appropriate bioactivity.

Fig. 5 shows SEM images of the coating transformed on the titanium substrate after electrodeposition at −1.5 V, −2.0 V, and −2.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days. All calcium phosphate coatings formed after electrodeposition at various cathodic potentials were transformed into apatites after immersion in the SBF for 5 days. The apatites consisted of needle-shaped crystallites distributed irregularly with different grain sizes according to loaded cathodic potentials. The average grain sizes of the apatites transformed after electrodeposition at −1.5 V, −2.0 V and −2.5 V (vs. SCE) and subsequent immersion in the SBF were approximately 1 μm, 3 μm, and 5 μm, respectively. As the cathodic potential loaded during electrodeposition got higher, the average grain sizes of the apatites also got bigger. It is considered that this difference of the grain sizes is due to the difference of the structure and crystallinity of the apatite, which can be confirmed in abovementioned XRD results. In addition, as the cathodic potential loaded during electrodeposition got higher, the crystallite of the apatites got denser. Although the crystallite of the apatite transformed after electrodeposition at −2.5 V (vs. SCE) and subsequent immersion in the SBF was interconnected the most densely, the apatite showed the lowest crystallinity in abovementioned XRD results. The bone apatite contains 2 to 6 wt.% CO_3^{2-} that generally substitutes for PO_4^{3-} and has relatively low crystallinity since CO_3^{2-} disturbs crystallization [16]. It is considered that the coating formed during electrodeposition at −2.5 V (vs. SCE) in the modified SBF have already incorporated an amount of CO_3^{2-} during electrodeposition and shows the lowest crystallinity after subsequent immersion in the SBF. Therefore, it is believed that the coating formed during electrodeposition at −2.0 V (vs. SCE) in the modified SBF have incorporated the most appropriate amount of CO_3^{2-} during electrodeposition and is transformed into carbonate apatite similar to bone apatite after subsequent immersion in the SBF.

The chemical composition of the coatings transformed on the titanium substrate after electrodeposition at −1.5 V, −2.0 V, and −2.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days was analyzed by EDS and FTIR. The Ca/P atomic ratios of the apatites transformed after electrodeposition at −1.5 V, −2.0 V, and −2.5 V (vs. SCE) and subsequent immersion in the SBF for 5 days were 1.39, 1.55, and 1.72, respectively. The Ca/P atomic ratio of the apatite transformed after electrodeposition at −2.0 V (vs. SCE) and subsequent immersion in the SBF was similar to that of bone apatite slightly less than 1.67, that of stoichiometric hydroxyapatite although the Ca/P atomic ratio became lower due to minor DCPD and OCP in the apatite. However, the Ca/P atomic ratio of the apatite transformed after electrodeposition at −2.5 V (vs. SCE) and subsequent immersion in the SBF was higher than 1.67. It is considered that the apatite have more CO_3^{2-}, that generally substitutes for PO_4^{3-}, than bone apatite and the Ca/P atomic ratio of the apatite became higher than 1.67. Finally, it was confirmed by FTIR that the coatings electrodeposited at −1.5 V, −2.0 V and −2.5 V (vs. SCE) and the apatites transformed after electrodeposition and subsequent immersion in the SBF had small CO_3^{2-} content.

4. Conclusions

Calcium phosphates were electrodeposited on commercially pure titanium substrates at −1.5 V, −2.0 V, and −2.5 V (vs. SCE) in the modified SBF and subsequently, transformed into apatites during immersion in the SBF for 5 days. First, CO_3^{2-} ions contained in the modified SBF were incorporated in the calcium phosphate coating during electrodeposition and had an influence on transforming the calcium phosphate into bonelike apatite during subsequent immersion in the SBF showing that CO_3^{2-} incorporated in the apatites disturbed crystallization of the apatites. In addition, among the coatings electrodeposited at various cathodic potentials, the coating electrodeposited at −2.0 V (vs. SCE) in the modified SBF is the most bioactive showing transformation into carbonate apatite similar to bone apatite.

Acknowledgements

This work was supported by grant No. R01-2001-000-00157 from the Basic Research Program of the Korea Science and Engineering Foundation.

References

[1] J.E. Lemons, Clin. Orthop. 235 (1988) 220–223.
[2] C.Y. Yang, R.M. Lin, B.C. Wang, T.M. Lee, E. Chang, Y.S. Hang, P.Q. Chen, J. Biomed. Mater. Res. 37 (1997) 335–345.
[3] M. Shirkhanzadeh, J. Mater. Sci. Lett. 10 (1991) 1415–1417.
[4] S. Ban, S. Maruno, Jpn. J. Appl. Phys. 32 (1993) L1577–L1580.
[5] M. Shirkhanzadeh, J. Mater. Sci. Lett. 12 (1993) 16–19.
[6] S. Ban, S. Maruno, Biomaterials 19 (1998) 1245–1253.
[7] M. Kumar, H. Dasarathy, C. Riley, J. Biomed. Mater. Res. 45 (1999) 302–310.
[8] M.C. Kuo, S.K. Yen, Mater. Sci. Eng., C, Biomim. Mater., Sens. Syst. 20 (2002) 153–160.
[9] H. Benhayoune, P. Laquerriere, E. Jallot, A. Perchet, L. Kilian, J.L. Bubendorff, G.D. Sockalingum, J. Mater. Sci., Mater. Med. 13 (2002) 1057–1063.
[10] S.K. Yen, C.M. Lin, Mater. Chem. Phys. 77 (2002) 70–76.
[11] R.Z. LeGeros, Calcium Phosphates in Oral Biology and Medicine, Karger, New York, 1991, p. 73.
[12] L.L. Hench, J. Am. Ceram. Soc. 74 (1994) 1487–1510.
[13] T. Kokubo, J. Non-Cryst. Solids 120 (1990) 138–151.
[14] P. Li, I. Kangasniemi, K. de Groot, T. Kokubo, J. Am. Ceram. Soc. 77 (1994) 1307–1312.
[15] A.S. Posner, Clin. Orthop. Relat. Res. 200 (1985) 87–99.
[16] R.Z. LeGeros, Prog. Cryst. Growth Charact. 4 (1981) 1–45.