J Mater Sci: Mater Med (2008) 19:137–142
DOI 10.1007/s10856-007-3127-1

Apatite formation on titanium substrates by electrochemical deposition in metastable calcium phosphate solution

Masakazu Kawashita · Satomi Itoh · Kazunori Miyamoto · Gikan H. Takaoka

Received: 19 June 2006 / Accepted: 25 July 2006 / Published online: 21 June 2007

Abstract An apatite layer was successfully formed on titanium substrates by electrochemical deposition in a metastable calcium phosphate solution, which had 1.5 times the ion concentrations of a normal simulated body fluid, but did not contain $MgCl_2 \cdot 6H_2O$, at 41 °C for 40 or 60 min at 13 mA. The current did not produce large effects on the crystalline size of the apatite, but the thickness of the apatite layer could be controlled by deposition conditions such as electrolyte temperature, current and deposition time. It is expected that the present electrochemical deposition will be useful to rapidly coat apatite on metallic materials.

Introduction

It is well known that some metallic materials such as stainless steel, Co–Cr–Mo alloys, titanium and its alloys have been widely used for dental and orthopedic implants under load-bearing conditions. However, these metals themselves cannot directly bond to living bone. So far, various surface modifications based on physical coating with ceramic materials with bone-bonding ability have been attempted to provide these metals with bone-bonding ability [1–6]. Currently, the most common coating for actual clinical application is hydroxyapatite coating plasma sprayed onto titanium alloys at high temperatures near 10,000 °C [7–9], but problems often occur in controlling the composition, crystallinity and structure of hydroxyapatite [10–15]. Recently, metals such as titanium, its alloys [16] and tantalum [17], have been found to bond to living bone after being exposed to a sodium hydroxide solution and heat treatment. Thus surface-modified titanium and its alloys gave good results in clinical assessment as artificial hip joints, and approval for sales is now expected from the Ministry of Health Labor and Welfare of Japan [18]. However, a few days are required for a dense and uniform apatite formation on the NaOH-treated titanium [16], which was soaked in simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma [19–21]. From the viewpoint of an apatite coating process, the soaking time should be decreased.

Electrochemical deposition is a useful method for coating calcium phosphate on metal substrates with complicated shapes, such as dental and orthopedic implants [22–33], and the deposition time in this method is usually within few hours. Ban et al. extensively investigated the morphology and microstructure of calcium phosphate deposited on titanium substrates [25, 26, 28–33], and found that needle-like apatite crystals were deposited on titanium in a modified simulated body fluid having the composition of SBF [19–21] without $MgCl_2 \cdot 6H_2O$, KCl and $NaHCO_3$, at an electrolyte temperature higher than 52 °C, and at a current density higher than 12.9 mA/cm^2 [30]. However, as far as we know, they did not investigate the apatite deposition on titanium in the electrolyte of a metastable calcium phosphate solution (1.5SBF) [34] that had 1.5 times the ion concentrations of a normal simulated body fluid [19–21]. It is expected that apatite might be formed rapidly on titanium by electrochemical deposition in 1.5SBF at a lower temperature and lower current density, because the degree

---

M. Kawashita (✉) · S. Itoh · K. Miyamoto · G. H. Takaoka
Photonics and Electronics Science and Engineering Center, Graduate School of Engineering, Kyoto University, Nisikyo-ku, Kyoto 615-8510, Japan
e-mail: kawashita@kuee.kyoto-u.ac.jp

of supersaturation of 1.5SBF with respect to apatite is much higher than that of normal SBF. In the present study, apatite coating on titanium was attempted by electrochemical deposition in 1.5SBF, and the surface structure of the titanium after the deposition and the adhesive between apatite and titanium were investigated.

Materials and methods

Electrochemical deposition of calcium phosphates on titanium plate

The working electrode was a pure titanium substrate (TI-453511, The Nilaco Corporation, Tokyo, Japan) 15 mm × 10 mm × 1.0 mm in size, and the counter electrode was a platinum plate 20 mm × 10 mm × 0.2 mm in size. The distance between the working electrode and the counter electrode was set at 3 cm. The surface of titanium substrate was polished using a #400 diamond pad to remove the passive oxidized layer. We used two kinds of electrolytes in this study. One electrolyte was a metastable calcium phosphate solution (1.5SBF) [34] that had 1.5 times the ion concentrations of a normal simulated body fluid [19–21]. The 1.5SBF was prepared by dissolving NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 (Nacalai Tesque, Kyoto, Japan) in ultrapure water, buffered at pH 7.40 at 36.5 °C with tris(hydroxymethyl)aminomethane ($(CH_2OH)_3CNH_2$) and 1.0 M HCl (Nacalai Tesque). Another electrolyte was a modified 1.5SBF (m-1.5SBF) with the composition of 1.5SBF, but without $MgCl_2 \cdot 6H_2O$. The ion concentrations in these solutions are listed in Table 1. The electrolyte was heated to 36.5–60 °C using a magnetic stirrer with an electric heater. The current was maintained at 1–40 mA. The deposition time was varied from 1 min to 60 min. The electrolyte was agitated using a magnetic stirrer during the electrochemical deposition. After the deposition, the titanium substrates were rinsed with distilled water and dried at 37 °C in air.

Table 1 Ion concentrations of SBF, 1.5SBF, m-1.5SBF and human plasma

Ion	Ion concentration/mM			
	Human plasma	SBF	1.5SBF	m-1.5SBF
Na^+	142.0	142.0	213.0	213.0
K^+	5.0	5.0	7.5	7.5
Mg^{2+}	1.5	1.5	2.3	0
Ca^{2+}	2.5	2.5	3.8	3.8
Cl^-	103.0	147.8	221.7	217.2
HCO_3^-	27.0	4.2	6.3	6.3
HPO_4^{2-}	1.0	1.0	1.5	1.5
SO_4^{2-}	0.5	0.5	0.8	0.8

Surface characterization

The morphology of the titanium substrates before and after the electrochemical deposition was observed by field emission scanning electron microscopy (FE-SEM; S-4500, Hitachi, Tokyo, Japan). The thickness of the surface deposited layer was measured using a scanning electron microscope (SEM; VE9800, Keyence, Osaka, Japan). The surface structure of the substrate was investigated by thin-film X-ray diffraction (TF-XRD; RINT2500, Rigaku, Tokyo, Japan) and Fourier transform infrared reflection spectroscopy (FT-IR; Nicolet Magna 860, Thermo Electron K.K., Kanagawa, Japan). The crystallite size of apatite was calculated by Scherrer's equation [35] using a full width at half-maximum diffraction peak of apatite (002).

Results and discussion

Figure 1 shows TF-XRD patterns of titanium substrates after electrochemical deposition in 1.5SBF and m-1.5SBF at 41 °C for 60 min at a constant current of 13 mA. Peaks attributed to apatite (002), (102) and (211) planes were observed at 26°, 28° and 32° in 2θ for substrates deposited in m-1.5SBF, whereas they were not observed for substrates deposited in 1.5SBF. Figure 2 shows FE-SEM photographs of titanium substrate after electrochemical deposition in m-1.5SBF at 41 °C for 60 min under 13 mA. Tiny apatite crystals were formed on substrate after the electrochemical deposition in m-1.5SBF. These results indicate that magnesium ions may play an important role in the apatite formation in this method. Ban et al. previously reported that calcium phosphates including apatite and octacalcium phosphate ($Ca_8H_2(PO_4) \cdot 5H_2O$) were formed on titanium substrates in a modified simulated body fluid without $MgCl_2 \cdot 6H_2O$, KCl and $NaHCO_3$ [30]. However, in this study, apatite was formed on titanium substrates in m-1.5SBF that did not contain $MgCl_2 \cdot 6H_2O$, but that did contain both KCl and $NaHCO_3$. We speculated from this result that the apatite formed is more similar to bone apatite in its composition and structure than the apatite that was reported by Ban et al., although the composition and structure of the present apatite should be further investigated.

In order to investigate the reason why apatite was not formed on the substrate in 1.5SBF, surface structure of titanium substrate after the electrochemical deposition in 1.5SBF was measured by XPS. Figure 3 shows an XPS survey spectrum of titanium substrate after electrochemical

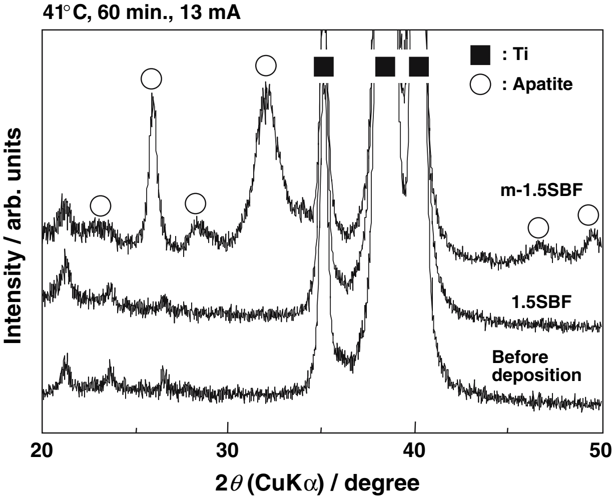


Fig. 1 TF-XRD patterns of titanium substrates after electrochemical deposition in 1.5SBF and m-1.5SBF at 41 °C for 60 min at 13 mA

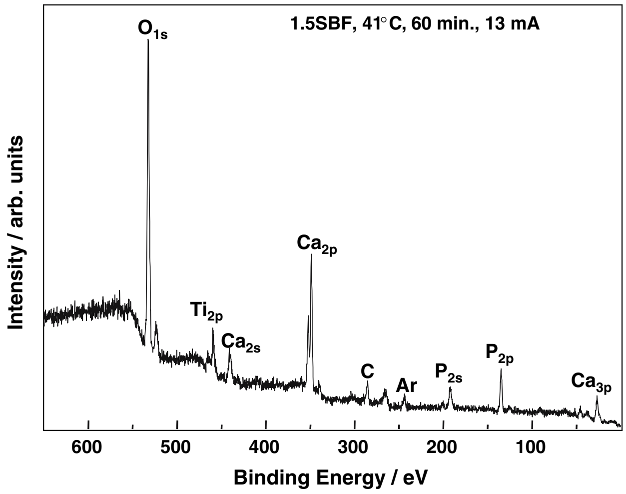


Fig. 3 XPS survey spectrum of titanium substrates after electrochemical deposition in 1.5SBF at 41 °C for 60 min at 13 mA

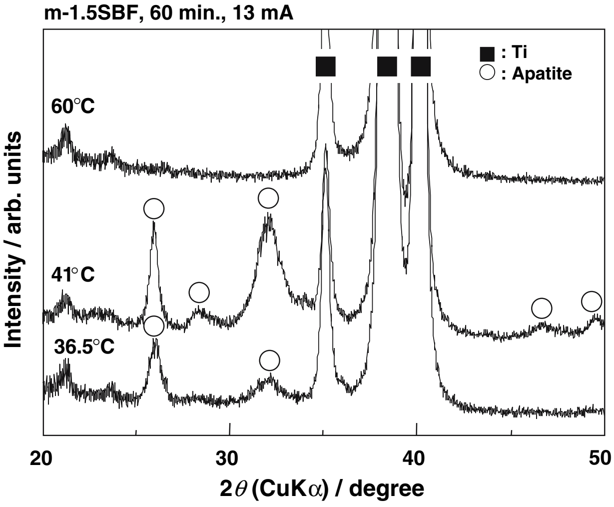


Fig. 4 TF-XRD patterns of titanium substrates titanium substrates after electrochemical deposition in 1.5SBF at different temperatures for 60 min at 13 mA

deposition in 1.5SBF at 41 °C for 60 min at 13 mA. Besides titanium (Ti_{2p} at 460 eV), peaks of calcium (Ca_{3p} at 30 eV, Ca_{2p} at 350 eV, Ca_{2s} at 450 eV), phosphorus (P_{2p} at 140 eV, P_{2s} at 200 eV) and oxygen (O_{1s} at 540 eV) were observed. This means that calcium and phosphorus ions were adsorbed onto the surface of titanium substrate. We speculate from these results that magnesium ions did not inhibit the adsorption of calcium and phosphate ions, but did inhibit the transformation of amorphous calcium phosphate into crystalline hydroxyapatite [36, 37]. We therefore used m-1.5SBF as an electrolyte in the following experiments.

Figure 4 shows the TF-XRD patterns of titanium substrates after electrochemical deposition in m-1.5SBF for 60 min at 13 mA at different temperatures. Peaks of apatite were observed for the electrolyte temperatures of 36.5 and 41 °C, whereas they were not observed for an electrolyte temperature of 60 °C. When the electrolyte temperature was increased to 60 °C, a homogeneous nucleation of apatite occurred in the electrolyte, and the color of the electrolyte became slightly opaque. As a result, apatite was not deposited on the titanium substrate at 60 °C. The intensity of the apatite peak increased with increasing electrolyte temperature from 36.5 °C to 41 °C. This indicates that apatite deposition is promoted when the electrolyte temperature is increased. We can see from these

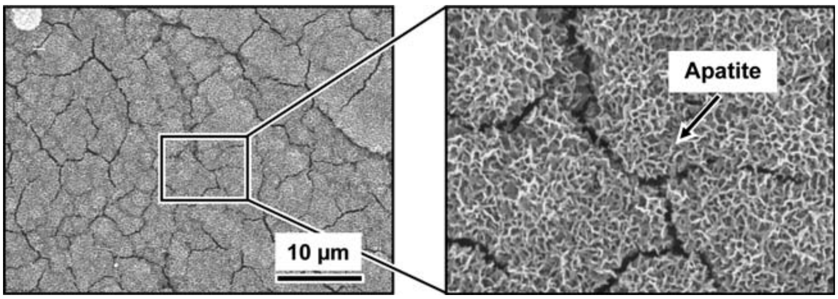


Fig. 2 FE-SEM photographs of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for 60 min at 13 mA

Fig. 5 TF-XRD patterns (**a**) and FT-IR spectra (**b**) of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for 60 min at different currents

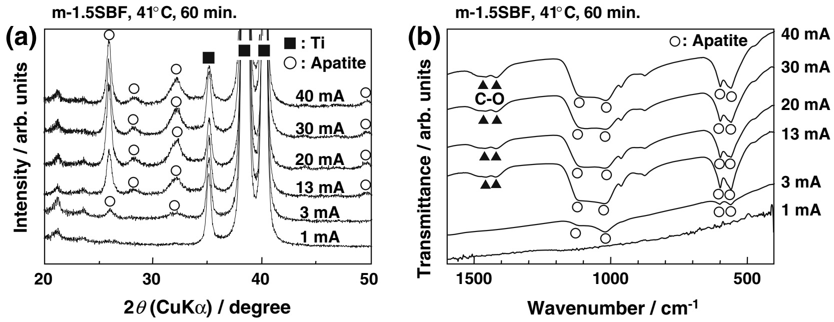
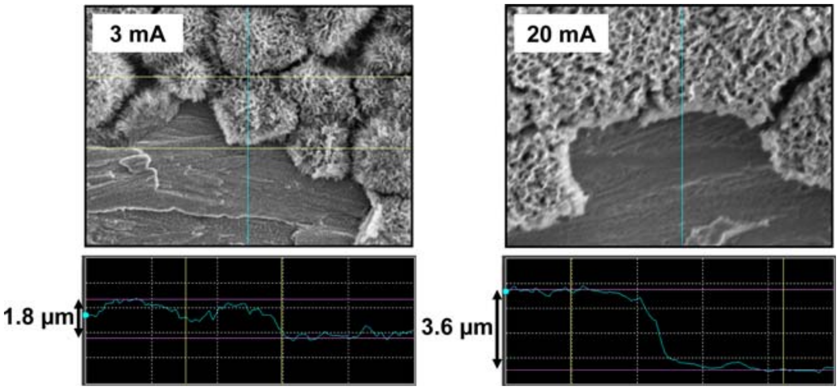


Fig. 6 SEM photographs and surface profiles of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for 60 min at 3 and 20 mA



results that uniform apatite coating on titanium substrate was achieved even at the lower temperature of 40 °C compared with the previous study (52 °C) [30], when m-1.5SBF was used as an electrolyte.

Figure 5 shows TF-XRD patterns (a) and FT-IR spectra (b) of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for 60 min at different currents. As shown in Fig. 5(a), apatite diffraction peaks were observed for currents from 3 mA to 40 mA, whereas they were not observed for a current of 1 mA. This means that the current in the present deposition method has a threshold. The intensity of diffraction peak of apatite increased with increasing current from 3 mA to 20 mA, but saturated at currents of 20 mA and over. The saturation of peak intensity might be attributed to the decrease in ion concentration of calcium and phosphorus in SBF by the growth of apatite layer. The apatite is assumed to be a carbonate-containing bone-like one, since FT-IR peaks at about 1,420 and 1,450 cm^{-1} ascribed to C–O bonding due to CO_3^{2-} ion

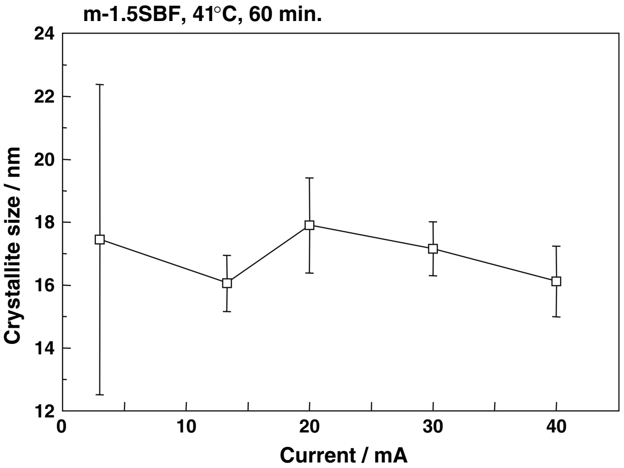


Fig. 7 Change in crystallite size of apatite as a function of current

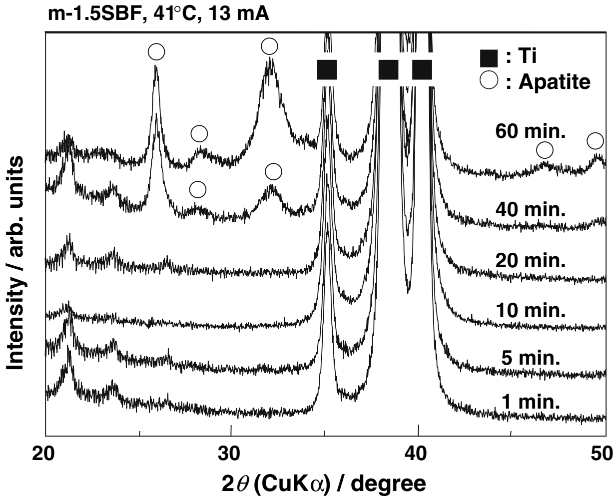


Fig. 8 TF-XRD patterns of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for different deposition times at 13 mA

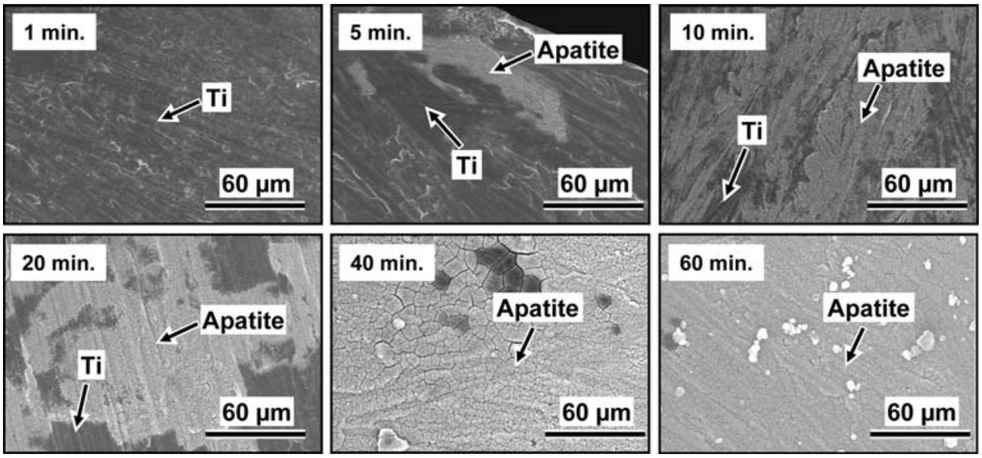


Fig. 9 FE-SEM photographs of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for different deposition times at 13 mA

[38] were observed for the substrates after deposition at currents of 11 mA and more. Figure 6 shows SEM photographs and surface profiles of titanium substrates after electrochemical deposition at 41 °C for 60 min at 3 and 20 mA. The apatite formed on the titanium substrate under 3 mA had an island-like shape, and its thickness was approximately 1.8 µm. On the other hand, the apatite deposited on titanium substrates at 20 mA forms a dense and uniform layer, and its thickness was 3.6 µm. These data indicate that current affects the thickness of apatite layer, and that the thickness of apatite layer can be controlled by the current. Figure 7 shows the change in the crystallite size of apatite as a function of current. The crystallite size of apatite took on almost constant values between 16 nm and 18 nm irrespective of the current. This suggests that the current does not cause large effects on the crystallite size of apatite.

Figure 8 shows TF-XRD patterns of titanium substrates after electrochemical deposition in m-1.5SBF at 41 °C for different deposition times at 13 mA. Peaks of apatite were not observed for deposition times from 1 min to 20 min, but they were observed for deposition times of 40 and 60 min. The intensity of the peak ascribed to apatite increased with increasing deposition time from 40 min to 60 min. These results suggest that deposition time has a large effect on apatite formation. Figure 9 shows FE-SEM photographs of titanium substrates after electrochemical deposition at 41 °C for different times at 13 mA. Apatite was not observed after 1 min deposition, but it started to precipitate after 5 min deposition. The area of apatite increased after 10 min deposition, and a dense apatite layer was partially formed after 20 min deposition. After 40 and 60 min deposition, a dense and uniform apatite layer covered whole surface of the titanium substrates. These results are consistent with the TF-XRD results shown in Fig. 7.

Conclusion

Apatite layer was successfully formed on titanium substrates by electrochemical deposition in a metastable calcium phosphate solution, which had 1.5 times the ion concentrations of a normal simulated body fluid, but did not contain $MgCl_2 \cdot 6H_2O$, at 41 °C for 40 or 60 min at 13 mA. It was found that magnesium did not inhibit the adsorption of calcium ions and phosphate ions, but did inhibit the transformation of amorphous calcium phosphate into crystalline hydroxyapatite. The current did not have a large effect on the crystallite size of the apatite, but the thickness of the apatite layer could be controlled by deposition conditions such as electrolyte temperature, current and deposition time. It is expected that electrochemical deposition will be useful as a rapid apatite coating process for metallic materials.

Acknowledgments This work was supported in part by a Grant-in-Aid for Scientific Research, the Ministry of Education, Culture, Sports, Science and Technology, Japan and Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1. S. D. COOK, K. A. THOMAS, J. F. KAY and M. JARCHO, *Clin. Orthop.* **230** (1988) 303
2. P. DUCHEYNE, S. RADIN, M. HEUGHEBAERT and J. C. HEUGHEBAERT, *Biomaterials* **11** (1990) 244
3. L. C. LUCAS, W. R. LACEFIELD, J. L. ONG and R. Y. WHITEHEAD, *Colloids Surf. A: Physicochem. Eng. Asp.* **77** (1993) 141
4. L. L. HENCH and Ö. H. ANDERSSON, in ‘‘*An Introduction to Bioceramics*’’, Edited by: L. L. HENCH and J. WILSON (World Scientific, Singapore, 1993) p. 239
5. K. TAKATSUKA, T. YAMAMURO, T. KITSUGI, T. NAKAMURA, T. SHIBUYA and T. GOTO, *J. Appl. Biomat.* **4** (1993) 317

6. H. HERǾ, H. WIE, R. B. JǾRGENSEN and I. E. RUYTER, *J. Biomed. Mater. Res.* **28** (1994) 343
7. K. DE GROOT, R. GEESINK, C. P. A. T. KLEIN and P. SEREKIAN, *J. Biomed. Mater. Res.* **21** (1987) 1375
8. R. G. T. GEESINK, K. DE GROOT and C. P. A. T. KLEIN, *Clin. Orthop.* **225** (1987) 147
9. C. P. A. T. KLEIN, P. PATKA, H. B. M. VAN DER LUBBE, J. G. C. WOLKE and K. DE GROOT, *J. Biomed. Mater. Res.* **25** (1991) 53
10. P. DUCHEYNE, W. VAN RAEMDONCK, J. C. HEUGHEBAERT and M. HEUGHEBAERT, *Biomaterials* **7** (1986) 97
11. K. A. THOMAS, J. F. KAY, S. D. COOK and M. JARCHO, *J. Biomed. Mater. Res.* **21** (1987) 1395
12. S. R. RADIN and P. DUCHEYNE, *J. Mater. Sci.: Mater. Med.* **3** (1992) 33
13. C. P. A. T. KLEIN, J. G. C. WOLKE, J. M. A. DE BLIECK-HOGERVORST and K. DE GROOT, *J. Biomed. Mater. Res.* **28** (1994) 961
14. K. A. GROSS and C. C. BERNDT, *J. Mater. Sci.: Mater. Med.* **5** (1994) 219
15. K. A. MANN, A. A. EDIDIN, R. K. KINOSHITA and M. T. MANLEY, *J. Appl. Biomat.* **5** (1994) 285
16. H.-M. KIM, F. MIYAJI, T. KOKUBO and T. NAKAMURA, *J. Biomed. Mater. Res.* **32** (1996) 409
17. T. MIYAZAKI, H.-M. KIM, F. MIYAJI, T. KOKUBO and T. NAKAMURA, *J. Biomed. Mater. Res.* **50** (2000) 35
18. T. KOKUBO, H.-M. KIM and M. KAWASHITA, *Biomaterials* **24** (2003) 2161
19. T. KOKUBO, H. KUSHITANI, S. SAKKA, T. KITSUGI and T. YAMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 721
20. S. B. CHO, K. NAKANISHI, T. KOKUBO, N. SOGA, C. OHTSUKI, T. NAKAMURA, T. KITSUGI and T. YAMAMURO, *J. Am. Ceram. Soc.* **78** (1995) 1769
21. T. KOKUBO and H. TAKADAMA, *Biomaterials* **27** (2006) 2907
22. J. REDEPENNING and J. P. MCISAAC, *Chem. Mater.* **2** (1990) 625
23. M. SHIRKHANZADEH, *J. Mater. Sci. Lett.* **10** (1991) 1415
24. H. MONMA, *J. Ceram. Soc. Jpn.* **101** (1993) 737
25. S. BAN and S. MARUNO, *Jpn. J. Appl. Phys.* **32** (1993) L1577
26. S. BAN and S. MARUNO, *Jpn. J. Appl. Phys. Lett.* **33** (1994) L1545
27. H. MONMA, *J. Mater. Sci.* **29** (1994) 949
28. S. BAN and S. MARUNO, *Biomaterials* **16** (1995) 977
29. S. BAN, S. MARUNO, N. ARIMOTO, A. HARADA and J. HASEGAWA, *J. Biomed. Mater. Res.* **36** (1997) 9
30. S. BAN and S. MARUNO, *Biomaterials* **19** (1998) 1245
31. S. BAN and S. MARUNO, *J. Biomed. Mater. Res.* **42** (1998) 387
32. S. BAN and J. HASEGAWA, *Biomaterials* **23** (2002) 2965
33. S. BAN, A. KAMIYA and T. SONODA, *Dent. Mater. J.* **21** (2002) 306
34. M. TANAHASHI, T. YAO, T. KOKUBO, M. MINODA, T. MIYAMOTO, T. NAKAMURA and T. YAMAMURO, *J. Am. Ceram. Soc.* **77** (1994) 2805
35. H. P. KLUG and L. E. ALEXANDER, in ‘‘X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials’’ 2nd edn. (John Wiley & Sons, Inc., New York, 1974)
36. A. L. BOSKEY and A. S. POSNER, *Mater. Res. Bull.* **9** (1974) 907
37. R. Z. LEGEROS, D. MIJARES, J. PARK, X. F. CHANG, I. KHAIROUN, R. KIJKOWSKA, R. DIAS and J. P. LEGEROS, *Key Eng. Mater.* **284–286** (2005) 7
38. J. C. ELLIOT, in ‘‘Structure and Chemistry of the Apatites and Other Calcium Orthophosphates’’ (Elsevier, Amsterdam, 1994) p 267