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Hydrothermal nucleation of hydroxyapatite on titanium surface

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Abstract

Titanium plates were submitted to nucleation and growth of hydroxyapatite (HAp) under hydrothermal conditions. A group of these plates were submitted to nucleation without any previous treatment and another group was treated with NaOH 1 M at 130°C inside an autoclave followed by heat-treatment at 600°C. The nucleation were performed by soaking all these titanium pieces, in a simulated body fluid (SBF) solution, containing calcium, phosphate and other ions, in order to promote the nucleation and growth of hydroxyapatite under hydrothermal conditions on the titanium surface. The results show that hydrothermal nucleation and growth of HAp occurs even on the non-treated titanium surface at 150°C. However, a better uniformity of the hydroxyapatite layer was observed on the pre-treated titanium surface, at 80°C, with the renewal of the SBF solution.

Keywords: Apatite; Coating; Hydrothermal nucleation; Hydroxyapatite; Titanium implant

1. Introduction

The objective of coating titanium implants with hydroxyapatite is to improve the bioactivity already present in this metal. There are several methods for coating titanium with hydroxyapatite.[1–8] The phase composition of the coating is an important requirement. In some cases the apatite coating results in a partially amorphous calcium phosphate and its conversion to the desired hydroxyapatite requires a suitable subsequent treatment such as the hydrothermal treatment as investigated by Yamashita et al.[9–11]

Another important requirement of hydroxyapatite coating is its adhesion to the titanium substrate. It is known that, as the surface roughness is increased, through mechanical and chemical action, the better is the implant osseointegration. Consequently, a good chemical adhesion of the hydroxyapatite to the titanium substrate will provide a new bone more firmly grown onto the implant. Biomimetic methods[4–8,12–28] of titanium coating with hydroxyapatite are based on the nucleation and growth of this calcium phosphate, in simulated body fluid (SBF), at 37°C. Association of these methods with chemical pre-treatment of the titanium substrate significantly increases the chemical adhesion, of the nucleated and grown hydroxyapatite on the titanium surface.

The present work is concerned with accelerating the biomimetic process, which can provide an adequate coating on the titanium surface, in about 4 weeks. Therefore, the experimental conditions used in the biomimetic process to achieve the nucleation and growth of hydroxyapatite were changed into hydrothermal conditions in order to obtain a faster coating formation on the titanium substrate, with and without its chemical pre-treatment in hot NaOH aqueous solution.

2. Experimental procedures

Pure titanium plates of 10×10×1 mm were polished with fine grained (400 and 600#) silicon carbide grinding paper, washed with dilute nitric acid, in order to degrease and to remove eventual iron contaminant. The majority of the titanium pieces were submitted to a previous attack of NaOH 1 M, for 1 h inside an autoclave at 130°C. After the titanium pieces were gently

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washed with distilled water and then heat-treated at 600°C for 1 h. After cooling, all the titanium pieces (pre- and non-treated) were submitted to hydrothermal nucleation and growth of the hydroxyapatite in the SBF solution at two different temperatures: (a) 80°C in glass tubes in a thermal bath, with a residence time of 1, 8 and 32 h; and; (b) 150°C in tetrafluoroethylene (TFE) tubes, inside an autoclave, with a residence time of 1 and 6 h.

After the residence time, each plate was washed with bi-distilled water and dried at room temperature, and characterised by scanning electron microscopy (SEM), energy dispersive spectroscopy analyser (EDS) and Fourier-transform infrared spectroscopy (FTIR). For the SEM characterisation, the samples were coated with carbon. For the FTIR spectroscopy, the spectra were collected using the diffuse reflectance technique, since it allows the detection of contents in the ppb range, it does not require any sample preparation and it is a non-destructive test, capable of analysing up to 0.5 μm depth.[29]

3. Results and discussion

Unless otherwise stated, the following results will refer to the nucleation and growth of hydroxyapatite on titanium pre-treated with NaOH 1 M, followed by its heat-treatment at 600°C for 1 h.

3.1. Nucleation of hydroxyapatite on titanium at 150°C

The nucleation at 150°C occurred even when the time of exposure in SBF, of the pretreated titanium pieces, was only of 1 h, as it can be seen by the photomicrography on Fig. 1(a). Fig. 1(b) shows the surface of the pretreated titanium piece exposed to SBF at 150°C for 6 h, with the calcium phosphate layer formed. Using the EDS technique, just a very thin layer of the calcium phosphate coating can be detected, since the calcium and phosphorous peaks are weak, as can be seen in Fig. 2.

The presence of calcium phosphate on both titanium piece surfaces, was detected by FTIR spectroscopy, presented on the spectrum in Fig. 3(a) which also shows a wide band, from 500 to 700 cm^{-1}, indicating the presence of the TiO_3^{2-} group. The peak corresponding to this group can be detected because the low thickness of the phosphate layer formed; which is characterised by the presence of the peaks at 1049 cm^{-1}. The well-defined peaks at 1449 and 1533 cm^{-1} are related to the CO_3^{2-} group and 1599 cm^{-1} to the OH^- group in the water molecule.

It is important to observe that the untreated titanium could also nucleate hydroxyapatite on its surface, when soaked in the SBF solution for 6 h, at 150°C inside the autoclave, as can be seen by the photomicrography in Fig. 4. This fact is confirmed on the FTIR spectrum by the peak at 1052 cm^{-1} corresponding to the phosphate functional group [see Fig. 3(c)]. This result was also

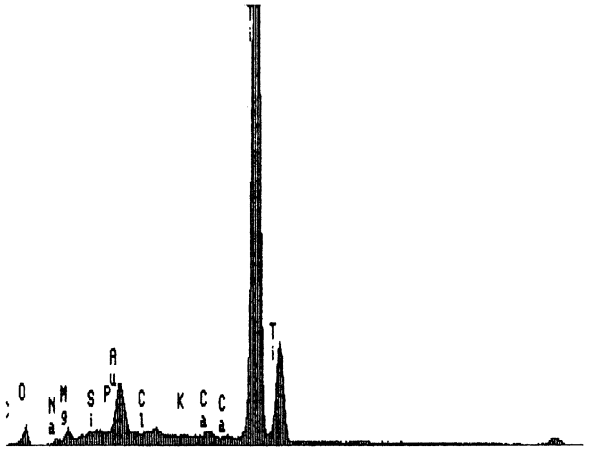

Fig. 2. Energy dispersive X-ray spectrum (EDS) of the hydroxyapatite coated titanium surface of Fig. 1(a).

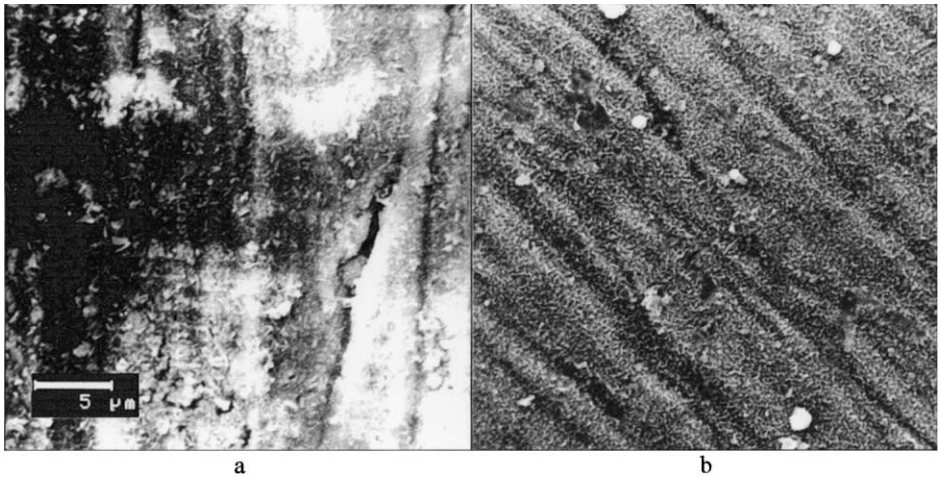

Fig. 1. Photomicrographs of the titanium pieces coated with hydroxyapatite at 150°C in SBF solution for: (a) 1 h; (b) 6 h. The titanium was pre-treated with NaOH 1 M at 130°C and heat-treated at 600°C for 1 h.

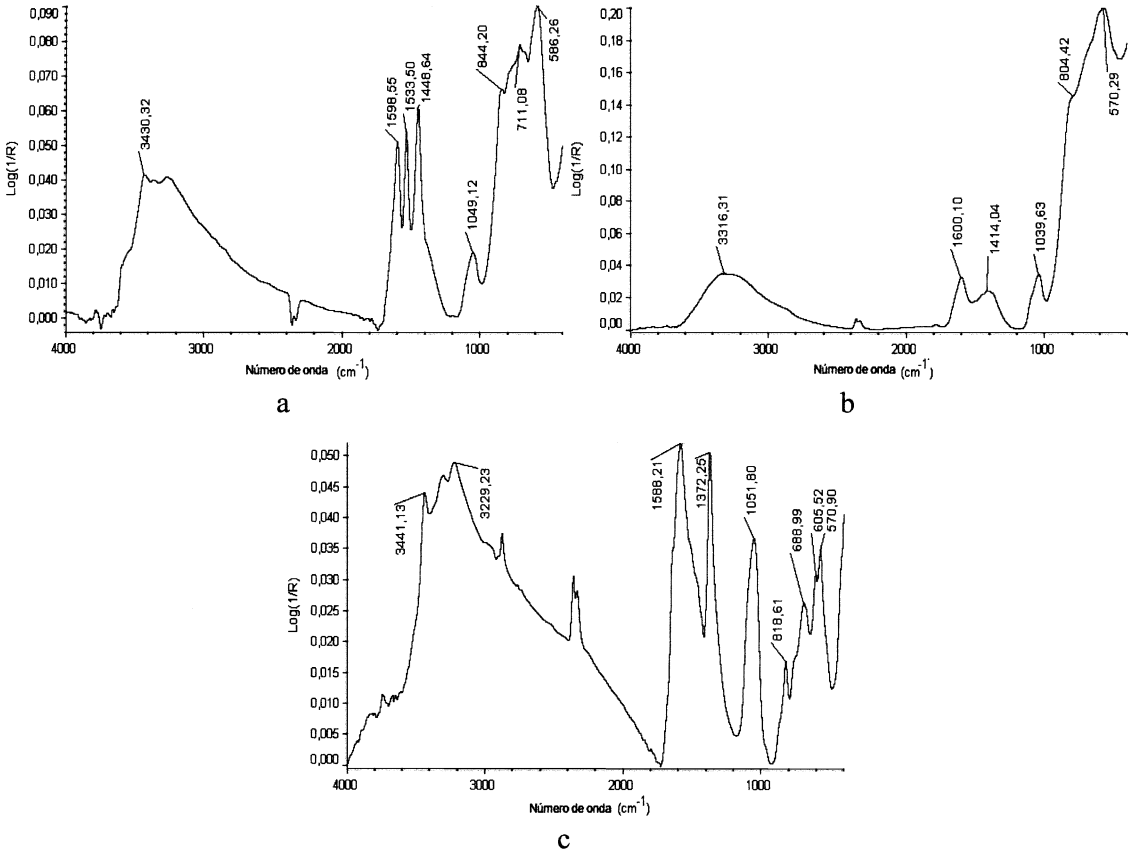

Fig. 3. FTIR spectra of the pretreated titanium pieces coated with hydroxyapatite at 150°C in SBF solution for: (a) 1 h, (b) 6 h, and (c) untreated titanium with hydroxyapatite nucleated in SBF at 150°C for 6 h.

thermodynamically predicted: calcium ions should interact with the titanate anions at the titanium surface, producing calcium titanate, which should later evolve to the titanate-apatite. On this apatite nucleus, hydroxyapatite nucleation would be easier to occur than directly onto the titanium surface. Another advantage of this process is that the chemical bonding of the hydroxyapatite to the titanium surface will provide a better adhesion of the hydroxyapatite coating to the titanium substrate.[28]

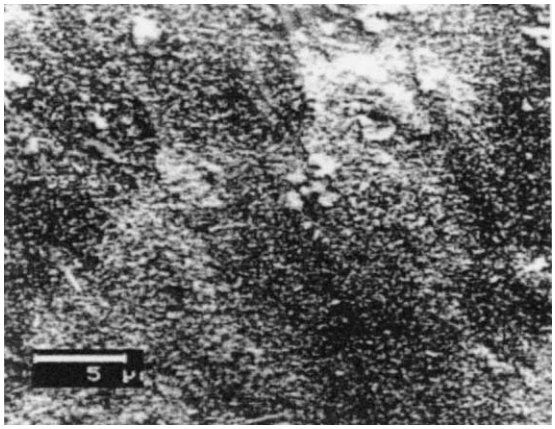

Fig. 4. Photomicrograph of the non-treated titanium with hydroxyapatite nucleated hydrothermally at 150°C in a SBF solution for 6 h.

The spectrum of Fig. 3(b) presents a difference in intensity, for the peaks at 1449 and 1533 cm^{-1} corresponding to the CO_3^{2-} group, in comparison to Fig. 3(a). A lower intensity for the peaks corresponding to the CO_3^{2-} group can be related to the formation of a more crystalline phosphate. The phosphate peak at 1040 cm^{-1} is still present in both spectra. These data show that a difference of 5 h for the hydrothermal precipitation time did not provide a significant growth of the calcium phosphate layer on the titanium surface, but only an increase of crystallinity.

The peak at 1372 cm^{-1} is related to the CO_3^{2-} group from carbonate-apatite, [Fig. 3(c)]. The 1052 cm^{-1} peak corresponds to the stretching of the P=O bond on the hydroxyapatite and the peak at 3441 cm^{-1} defines clearly the presence of the O–H group of the hydroxyapatite.

Therefore, it is clear that performing the nucleation of the hydroxyapatite on titanium substrate under hydrothermal conditions, at 150°C, the chemical pre-treatment of the titanium surface in NaOH solution, followed by heat-treatment at 600°C, can be dismissed.

3.2. Nucleation of the hydroxyapatite on titanium at 80°C

Nucleation of the hydroxyapatite on chemically pretreated titanium also occurred at 80°C with soaking

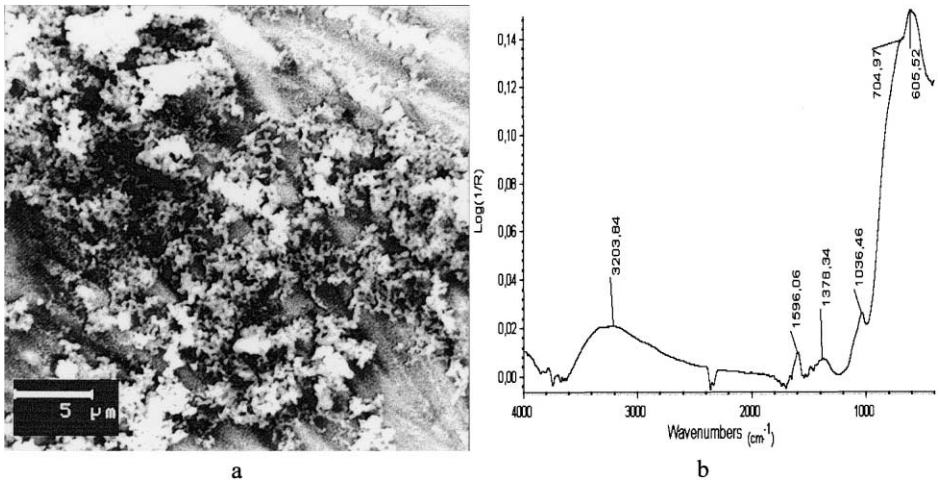

Fig. 5. Pretreated titanium coated with hydroxyapatite nucleated at 80°C in a SBF solution for 1 h: (a) photomicrography and (b) FTIR spectrum.

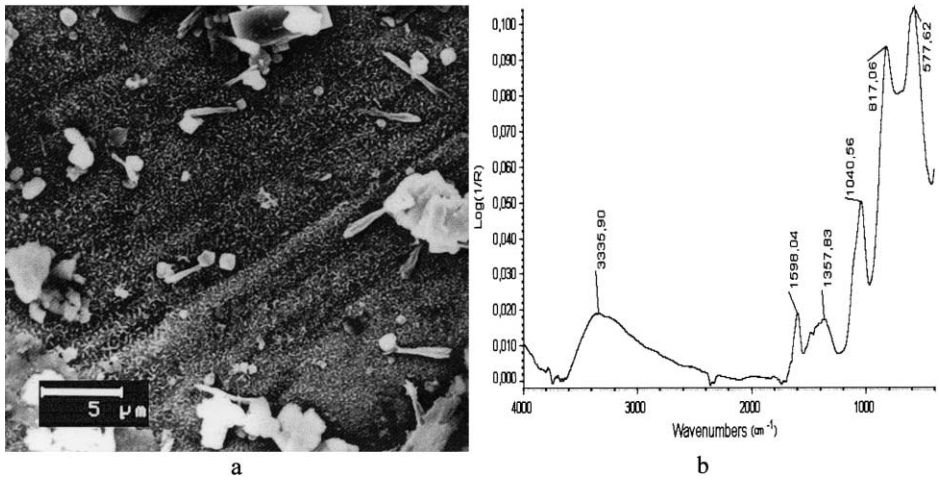

Fig. 6. Pretreated titanium coated with hydroxyapatite nucleated at 80°C in a SBF solution for 8 h: (a) photomicrography and (b) FTIR spectrum.

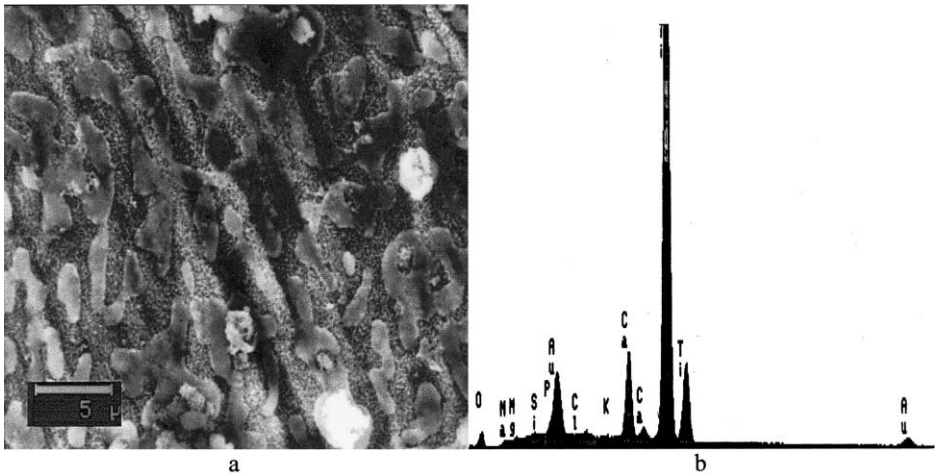

Fig. 7. (a) Photomicrograph and (b) energy dispersive X-ray spectrum (EDS) of the pretreated titanium surface coated with hydroxyapatite by nucleation and growth in SBF at 80°C for 32 h.

time in SBF as short as 1 h, as can be seen in the SEM photomicrography of Fig. 5(a), and by Fig. 5(b) presenting the FTIR spectrum using diffuse reflectance technique.

Fig. 5(b) presents the spectrum with the peak 1036 cm^{-1} from the phosphate functional group. This peak is displaced and not well defined compared to the spectrum corresponding to that of hydroxyapatite obtained by a biomimetic process (37°C).[28] Also, the presence of two peaks at 705 and 605 cm^{-1} can be detected, related to the phosphate as well as titanate groups, which has a wide peak in the same region. This may indicate that the short reaction time did not allow the formation of a homogeneous phosphate.

The surface of the pretreated titanium piece soaked in SBF at 80ºC for 8 h can be seen in Fig. 6(a), while Fig. 6(b) presents the FTIR spectrum taken from this surface. The spectrum in Fig. 6(b) shows a more intense peak at 1036 cm^{-1}, related to the phosphate functional group, than that observed in Fig. 5(b). Furthermore, the spectrum in Fig. 6(b) presents all peaks better defined and less displaced, indicating the formation of a crystalline HAp.

A better uniformity of the calcium phosphate layer on the pretreated titanium surface was observed when a test of hydrothermal nucleation and growth was carried out, inside a thermal bath, by replacing the SBF solution, each 6 h of soaking, up to a total of 32 h soaking time. This layer can be observed on the photomicrography shown in Fig. 7(a) and by the EDS spectrum in Fig. 7(b).

4. Conclusions

From the results obtained in this work it is clear that the pre-treatment with NaOH would not be required in order to obtain a HAp coating on the titanium surface, under hydrothermal conditions (at 150°C). Also the temperature is a factor that accelerate the nucleation and growth of HAp on the titanium surface: (a) at 80°C with a periodic renewal of the SBF solution; and (b) at 150°C that presents an even faster crystallisation kinetics that direct the research to develop an efficient method to renew the SBF solution at short intervals of time or even to a continuous replacing schedule for the SBF solution.

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References

1. Soballe, K., Hansen, E. S., Rasmussen, H. B., *et al*. Enhancement of osteopenic and normal bony ingrowth into porous coated implants by hydroxyapatite coatings. In *Proceedings of the 2nd International Symposium on Ceramics in Medicine*. Heidelberg, Germany, 1989, pp. 264–265.
2. Soballe, K., Hansen, E. S., Rasmussen, H. B., *et al*. Early fixation of allogenic bone graft in titanium and hydroxyapatite coated implants. In *Proceedings of the 2nd International Symposium on Ceramics in Medicine, Heidelberg, Germany*, 1989, pp. 262–263.
3. Anderson, D., Hastings, G. W., Morrey, S., *et al*. Hydroxyapatite ceramic coatings. In *Proceedings of the 2nd International Symposium on Ceramics in Medicine*. Heidelberg, Germany, 1989, pp. 251–261.
4. Nishiguchi, S., Nakamura, T., Kobayashi, M., *et al*. The effect of heat treatment on bone bonding ability of alkali-treated titanium. In *Proceedings of the 10th International Symposium on Ceramics in Medicine*. Paris, France, 1997, pp. 561–564.
5. Kim, H.-M., Miyaji, F., Kokubo, T., *et al*. Preparation of Bioactive Ti and its alloys via simple chemical surface treatment. *J. Biomed. Mater. Res.,* 1996, **32**, 409–417.
6. Kim, H. M., Miyaji, F., Kokubo, T., *et al*. Surface structure of bioactive titanium prepared by chemical treatment. In *Proceedings of the 10th International Symposium on Ceramics in Medicine*. Paris, France, 1997, pp. 215–218.
7. Kim, K. M., Miyaji, F., Kokubo, T., *et al*. Effect of heat treatment on apatite-forming ability of Ti metal induced by alkali treatment titanium. *J. Mater. Sci.: Mater. Med.*, 1999, 341–347.
8. Kokubo, T., Miyaji, F., Kim, H.-M., *et al*. Spontaneous formation of bonelike apatite layer on chemically treated titanium metals. *J. Am. Ceram. Soc.,* 1996, **79/4**, 1127–1129.
9. Hamagami, J., Nakamura, K., Sekine, Y., *et al*., Low temperature crystallization of hydroxyapatite sputtered films in an autoclave. In *Proceeedings of the 10th International Symposium on Ceramics in Medicine*. Paris, France, 1997, pp. 207–210.
10. Yamashita, K., Yagi, T. and Umegaki, T., Bonelike coatings onto ceramics byreactive magnetron sputtering. *J. Am. Ceram. Soc.,* 1996, **79**, 3313–3316.
11. Ohgaki, M., Komiya, T., Hamagami, J., *et al*. Biocompatibility and crystal growth of poled hydroxyapatite ceramics and coatings. In *Proceeedings of the 11th International Symposium on Ceramics in Medicine*. New York, USA, 1998, pp. 493–496.
12. Kokubo, T., Biomimetics applied to bioceramics. In *Proceedings of the 11th International Symposium on Ceramics in Medicine*. New York, USA, 1998, pp. 51–56.
13. Kokubo, T., Kushitani, H., Abe, Y., *et al*. Apatite coating on various substrates in simulated body fluid. In *AW Glass–Ceramic*, ed. T. Yamamuro. Kyoto. Japan, 1994, pp. 235–242.
14. Kokubo, T., Hata, K., Nakamura, T., *et al*. Apatite formation on ceramics, metals and polymers induced by a $CaO–SiO_2$ based glass in a simulated body fluid. In *Proceeedings of the 4th International Symposium on Ceramics in Medicine*. London, UK, 1991, pp. 615–622.
15. Tanahashi, M., Hata, K., Kokubo, T., *et al*. Effect of substrate on apatite formation by a biomimetic process. In *AW Glass–Ceramic*, ed. T. Yamamuro Kyoto, Japan, 1994, pp. 623–630.
16. Kokubo, T., Tanahashi, M., Yao, T., *et al*. Apatite-polymer composites prepared by process: improvement of adhesion of apatite to polymer by glow-discharge treatment. In *Proceeedings of the 6th International Symposium on Ceramics in Medicine*. Philadelphia, USA, 1993, pp. 652–657.
17. Rhee, S.-H. and Tanaka, J., Hydroxyapatite coating on a collagen membrane by a biomimetic method. *J. Am. Ceram. Soc.,* 1998, **81**, 3029–3031.
18. Miyaji, F., Handa, S., Kokubo, T., *et al*. Apatite formation on polymers by biomimetic process using sodium silicate solution. In *Proceedings of the 10th International Symposium on Ceramics in Medicine*. Paris, France, 1997, pp. 7–10.
19. Kotani, S., Yamamura, T., Nakamura, T., *et al*. The bone-bonding behaviour of two glass-ceramics (KGS and A-W GC). In

Proceedings of the 2nd International Symposium on Ceramics in Medicine. Heidelberg, Germany, 1989, pp. 105–112.
20. Kokubo, T., Ohtsuki, C., Kotani, S., *et al*. Surface structure of bioactive glass-ceramic A-W implanted into sheep and human vertebra. In *Proceedings of the 2nd International Symposium on Ceramics in Medicine*. Heidelberg, Germany, 1989, pp. 113–120.
21. Layrolle, P., Van Blitterswijk, C. A. and de Groot, K., Biomimetic hydroxyapatite coating on Ti6Al4V induced by a pre-calcification. In *Proceedings of the 11th International Symposium on Ceramics in Medicine*. New York, USA, 1998, pp. 465–468.
22. Miyazaki, T., Kim, H.-M, Miyaji, F., *et al*. Apatite-forming ability of sodium tantalate gels. In *Proceedings of the 11th International Symposium on Ceramics in Medicine*. New York, USA, 1998, pp. 481–484.
23. Miyaji, F., Iwai, M., Kokubo, T., *et al*. Chemical surface treatment of silicone for inducing its bioactivity. *J. Mater. Sci.: Mater. Med.,* 1998, **9**, 61–65.
24. Wen, H. B., de Wijn, J. R., Liu, Q., *et al*. A simple method to prepare calcium phosphate coatings on Ti6Al4V. *J. Mater. Sci.: Mater. Med.,* 1997, **8**, 765–770.
25. Wen, H. B., Liu, Q., de Wijn, J. R., *et al*. Preparation of bioactive microporous titanium surface by a new two-step chemical treatment. *J. Mater. Sci.: Mater. Med.,* 1998, **9**, 121–128.
26. Hanawa, T., Kon, M., Doi, H., *et al*. Amount of hydroxyal radical on calcium-ion implanted titanium and point of zero charge of constituent oxide of the surface-modified layer. *J. Mater. Sci.: Mater. Med.,* 1998, **9**, 89–92.
27. Wen, H. B., Wolke, J. G. C., de Wijn, J. R., *et al*. Fast precipitation of calcium phosphate layers on titanium induced by simple chemical treatments. *Biomaterials,* 1997, **18**, 1471–1478.
28. Andrade, M. C., Filgueiras, M. R. T. and Ogasawara, T., Nucleation and growth of hydroxyapatite on titanium pretreted in NaOH solution: experiments and thermodynamic explanation. *Journal of Biomedical Materials Research,* 1999, **46**(4), 441–446.
29. Hench, L. L. and Ethridge, E. C., Characterization of ceramic surfaces. In *Biomaterials, an Interfacial Approach*. 1982 Academic, pp. 76–83.