J Mater Sci: Mater Med (2007) 18:565–575
DOI 10.1007/s10856-007-2303-7

Surface characteristics and bioactivity of oxide film on titanium metal formed by thermal oxidation

Yeong-Joon Park · Ho-Jun Song · In Kim · Hong-So Yang

Received: 22 March 2005 / Accepted: 1 March 2006

Abstract In this study, we characterized the surface of oxide film formed on titanium metal through the use of thermal treatment and investigated the effect of surface characteristics on the bioactivity of titanium. The as-received sample group was prepared by polishing and cleaning CP-Ti as a control group, and thermally oxidized sample groups were prepared by heat treating at 530, 600, 700, 800, 900, and 1000°C respectively. Micro-morphology, crystalline structure, chemical composition, and binding state were evaluated using FE-SEM, XRD, and XPS. The bioactivity of sample groups was investigated by observing the degree of calcium phosphate formation from immersion testing in MEM. The surface characterization tests showed that hydroxyl group content in titanium oxide film was increased, as the density of titanium atoms was high and the surface area was large. In MEM immersion test, initial calcium phosphate formation was dependent upon the thickness of titanium oxide, and resultant calcium phosphate formation depended on the content of the hydroxyl group of the titanium oxide film surface.

1 Introduction

Titanium implants are increasingly used in dentistry and orthopedics due to their excellent biocompatibility and mechanical properties, as well as their potential for osseointegration with bone tissue [1–4]. Titanium metal reacts with oxygen in the air and forms a dense and stable oxide film with a thickness of a few nanometers. The biocompatibility of titanium and its high corrosion resistance are attributed to its surface oxide film [5, 6].

However, titanium, a bioinert material, is not chemically connected to bone and the bone growth rate on the surface of titanium implants is low compared to that of implant materials coated with calcium phosphate [7–9]. Thus, a considerable number of studies have been made to improve the bioactivity of titanium using surface modification methods such as endowing roughness with TPS, SLA, laser ablation etc. [10–12], coating the titanium surface with Ca-P or BMP which have bioactivity superior to that of natural oxidation film [10–12], or changing the crystalline structure and morphology of the surface oxide film on the titanium surface by various preparation and oxidation techniques [5, 13–15].

Titanium metals could come in contact with the various thermal environments during various fabrication procedures, such as mechanical blasting with alumina (Al_2O_3) or RBM (resorbable blasting media), sintering for the coating of bioactive materials, or hydrothermal treatment of machined implants [16]. Titanium oxide films formed at various thermal environments have different surface characteristics, such as surface morphology, crystalline structure, crystallite size, and roughness. These different surface characteristics are important factors of bioactivity when titanium implants are used in clinical application.

While consulting the reports regarding the crystalline structure of titanium oxide, we found that anatase structure was observed in titanium oxide prepared by sol-gel or anodization method at low temperatures [17–20], while titanium oxide of rutile structure was usually formed by thermal treatment [14, 21, 22]. It has been reported that the crystalline structure of titanium oxide film is dependent on the oxide-

Y.-J. Park (✉) · H.-J. Song ·
Department of Dental Materials and Dental Materials Research Institute, School of Dentistry, Chonnam National University, Gwangju 500-757, Korea
e-mail: yjpark@chonnam.ac.kr

I. Kim · H.-S. Yang
Department of Prosthodontics, School of Dentistry, Chonnam National University, Gwangju 500-757, Korea

forming method, substrate type, and surface conditions [4]. Also, it has been reported that the contents of a hydroxyl group which existed on titanium surface oxide film played an important role in the improvement of bone growth because it acted as a nucleus for creating apatite [6].

However, although a large number of studies have reported the changes of crystalline structure and the contents of hydroxyl groups with surface treatments of titanium metal, more systematic studies are required to verify the effects of the changes of morphology, crystalline structure, chemical composition, and binding state induced by thermal treatments on bioactivity.

When titanium metal was treated at high temperatures over 700°C in air, it was difficult to be used as an implant because adhesion between oxide film and substrate metal abruptly decreased [23]. However, discussion regarding the effect of the surface characteristics of titanium oxide formed by thermal treatment at high temperature on bioactivity may furnish information regarding the satisfactory surface condition for titanium implant.

In this study, we have evaluated the morphology, crystalline structure, chemical composition, and binding state of titanium oxide film formed by thermal treatment at 530, 600, 700, 800, 900, and 1000°C in air, and investigated the correlation between its characteristics and the content of hydroxyl groups. We have also studied how changes to the surface characteristics of oxide film with various thermal treatments affect calcium phosphate formation upon immersing test in MEM solution.

2 Materials and methods

2.1 Materials

Commercially pure titanium (CP-Ti, ASTM Grade II) cut to a diameter of 10 mm, thickness of 1 mm, and degreased with acetone was used in the present study. The specimen surface was polished with #240 to #2000 SiC papers and cleaned by an ultrasonic cleaner in distilled water and ethanol. The as-received sample group (AS-R) was prepared by cleansing with distilled water and drying.

In order to investigate the characteristics of oxide film on titanium metal fabricated by thermal treatment, specimens were fabricated in following thermal treatment conditions. The Ti-530 group was fabricated by thermally treating AS-R specimens at 530 °C in air for 40 min and then slowly cooling to room temperature to relieve internal stress [24, 25]. The Ti-600 group was fabricated by thermally treating Ti-530 specimens at 600 °C in air for 40 min. The Ti-700 group was fabricated by fully annealing Ti-530 specimens for 90 min at 700 °C [24, 25]. The Ti-800, Ti-900, Ti-1000 groups were fabricated by thermally treating Ti-700 specimens at 800, 900, and 1000 °C, respectively, in air for 2 hours. Heating and cooling rates were 15 °C /min.

2.2 Surface characterization of titanium oxide film

The surface micro-morphologies of sample groups were observed using field emission scanning electron microscopy (FE-SEM; Hitachi S-4700, Japan)

Crystalline structure was identified using an X-ray diffractometer (XRD; Phillips, X‘Pert, Netherlands). Because the titanium oxide layer which formed on the titanium surface was so thin that X-rays could penetrate into the titanium substrate, the sample tilting X-ray diffraction method (ST-XRD) was carried out in order to decrease the diffraction intensity of the titanium substrate and increase the diffraction area of the oxide film layer.

The chemical composition and binding state of titanium oxide film were analyzed using X-ray photoelectron spectroscopy (XPS; VG Scientific LTD, ESCALAB 200R, UK). XPS spectra were recorded using monochromatic Al Kα radiation and the take-off angle was 90°. Wide energy survey scan was carried out for quantitative and qualitative elemental analysis and high-resolution narrow scanning was performed to analyze the chemical binding state of each of the elements for Ti 2p, O 1s, and C 1s peaks which were dominant in survey spectra.

2.3 Immersion test in MEM solution

We examined the effect of thermal treatment of titanium specimens on calcium phosphate formation which is related to bioactivity using the immersing test in Eagle’s Minimum Essential Medium (MEM) [26]. MEM was refreshed every two days. The samples were taken out in 3 days or 7 days, respectively, and were then washed with distilled water and dried in a desiccator for 5 hours. The micro-morphology of calcium phosphate formed on the titanium oxide surface was observed using FE-SEM. Quantitative and qualitative analysis of elements was carried out using EDS (energy dispersive spectrometer, Kevex, Sigma, USA).

3 Results

3.1 Micro-morphology of titanium oxide films

Figure 1 shows photographs of sample groups observed using FE-SEM. Only scratched lines created by polishing were observed on the AS-R specimen. From high resolution SEM images, 10–20 nm sized crystallites were observed on the surface of Ti-530 and Ti-600 samples, and those of the Ti-600 group were distributed more densely than those of the Ti-500 group. The size of crystallites in the Ti-700 samples was

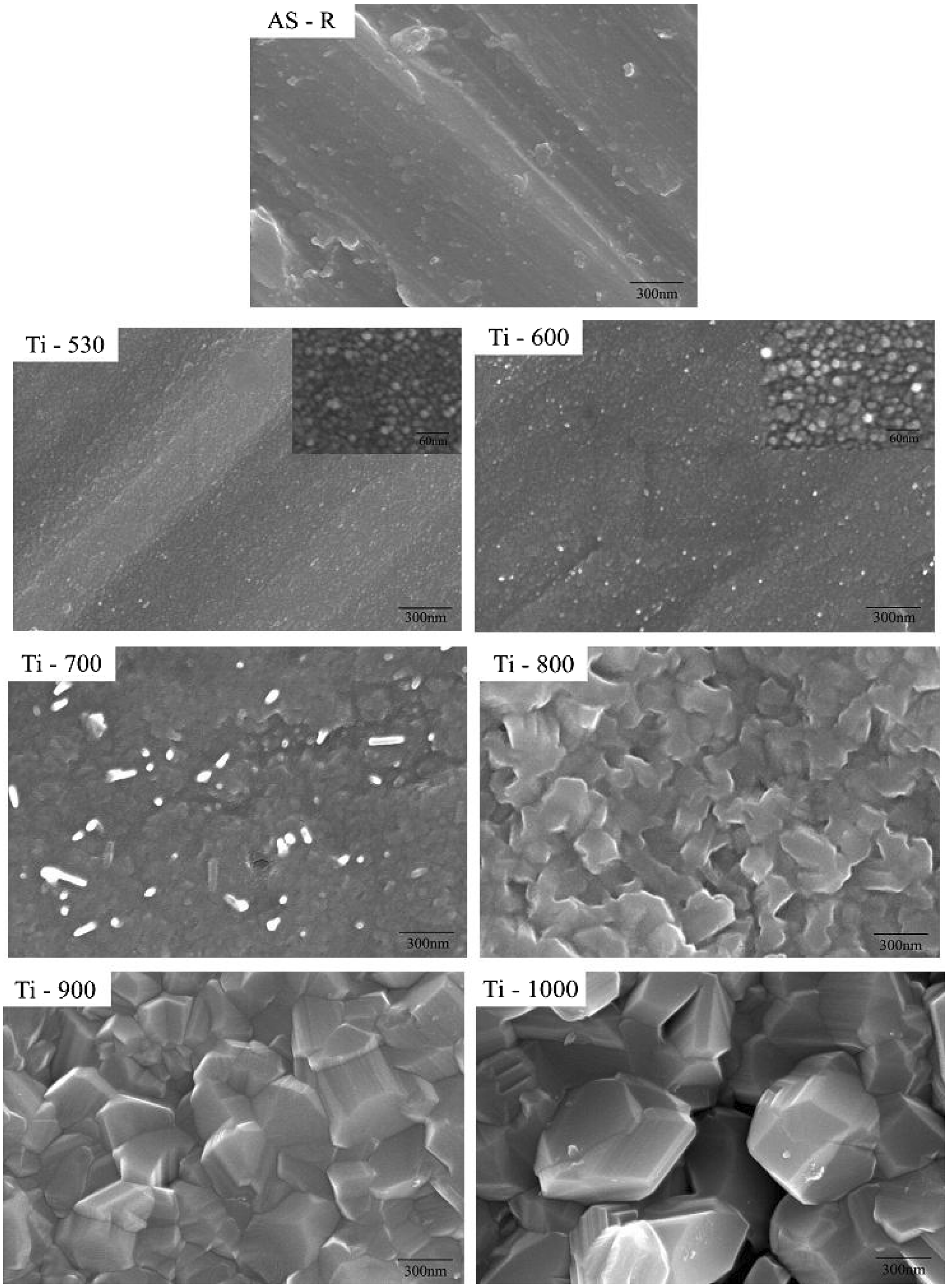


Fig. 1 SEM photographs of sample groups

50–70 nm and the crystals were needle-like in appearance. Crystallite size was increased dramatically as the thermal treatment temperature increased, to 0.1–0.3μm for Ti-800, 0.3–0.5μm for Ti-900, and 0.7–0.9μm for Ti-1000.

3.2 Crystalline structure of titanium oxide film

Figure 2 shows the X-ray diffraction patterns of sample groups. XRD peaks assigned to titanium metal only were observed in the AS-R group. It is difficult to analyze the crystal structure of naturally oxidized films on titanium metal using ordinary XRD because the film thickness is very thin, about a few nanometers, and has an amorphous structure [27].

XRD peaks corresponding to titanium metal (002) had shoulders in the Ti-530, Ti-600, and Ti-700 groups. These peaks were resolved to Gaussian peaks, as shown in Fig. 3, and the (004) plane of anatase structure in TiO_2could be clearly distinguished from the (200) peak of titanium metal. Full-width, half-maximum height (FWMH) of these peaks was wider than that of other peaks. It was known that the FWMH of the XRD peak was related to the size of crystalline particles [18]. The size of crystalline particles is small when FWMH is wide. The large FWMH values of anatase (004)

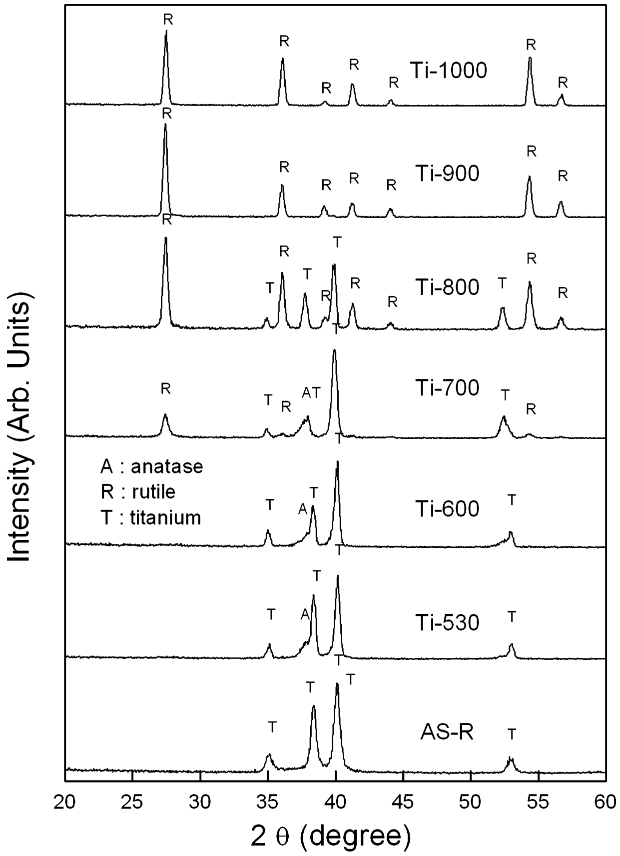


Fig. 2 X-ray diffraction patterns of sample groups

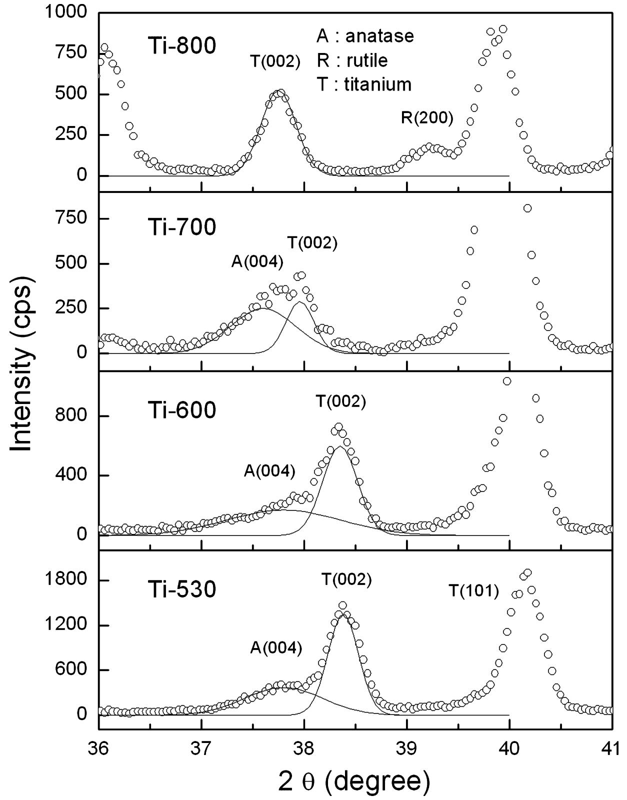


Fig. 3 XRD peak resolved to anatase (004) and titanium (002), using Gaussian peaks

peaks observed in the Ti-530 and Ti-600 groups resulted from nano-sized titanium oxide crystallites as shown in FE-SEM photographs of Fig. 1.

The rutile structure of titanium oxide, which is more stable than anatase structure in thermal atmosphere, was observed in the Ti-700 sample group as the temperature of thermal treatment increased. Complete rutile structure was observed in the Ti-800, Ti-900, and Ti-1000 groups, and the main XRD peak of that was (110) plane peak.

The XRD peak analysis showed that nano-sized TiO_2 crystallites that have anatase structures were observed in the Ti-530 and Ti-600 groups, anatase and rutile structures co-existed in the Ti-700 group, and rutile structures were observed in the Ti-800, Ti-900, and Ti-1000 groups.

3.3 Chemical composition and binding state of titanium oxide

Table 1 shows the quantitative analysis of elements calculated from XPS survey spectra for all sample groups. Ti and O which originated from TiO_2, C and N which originated from organic contamination, and Si that had been doped during thermal treatment were detected. The ratios of oxygen to titanium of thermally-treated sample groups were high compared to that of AS-R samples. This result indicated that thermal treatment of titanium induced an increase in the oxygen concentration of titanium oxide surfaces [13].

Figure 4 shows the high resolution XPS spectra of Ti 2p. Titanium has four oxide states, Ti^0(Ti metal), Ti^{2+}(TiO), Ti^{3+}(Ti_2O_3), and Ti^{4+}(TiO_2). As can be seen in Fig. 4, the Ti^{4+} peak was dominant in Ti 2p high-resolution spectra for all sample groups. The titanium metal peak with a very low intensity was observed in the AS-R group which has a thin oxide film.

Figure 5(a) shows the high-resolution XPS spectra of O 1s for sample groups. O 1s spectra could be divided into O^{2-}(oxide of TiO_2) and hydroxyl (OH^-) groups. Also, the oxide layer of TiO_2 is known to have two types of hydroxyl groups, basic and acidic OH, according to the methods of attachment to metal by chemisorptions. Fig. 5(b) shows the O 1s high-resolution XPS spectrum of the AS-R group resolved to three deconvolution peaks, such as O^{2-} due to TiO_2, OH_a(acidic hydroxyl group), and OH_b(basic hydroxyl group) [6, 28]. Using the above method to calculate the area of each resolved peak for all of the sampling groups, the contents of oxygen species depending on chemical binding states are shown in Fig. 6.

Table 1 Chemical compositions of sample groups calculated from XPS survey spectra

	AS-R	Ti-530	Ti-600	Ti-700	Ti-800	Ti-900	Ti-1000
O	52.2	59.7	57.6	57.5	50.7	59.1	62.7
Ti	19.4	19.3	17.9	18.2	14.8	16.8	21.3
N	1.8	1.0	1.3	1.1	1.3	1.5	0.6
C	26.6	16.4	18.8	20.4	29.1	19.4	11.0
Si	–	3.6	4.4	2.8	4.1	3.2	4.4
O/Ti	2.69	3.09	3.21	3.16	3.43	3.52	2.94

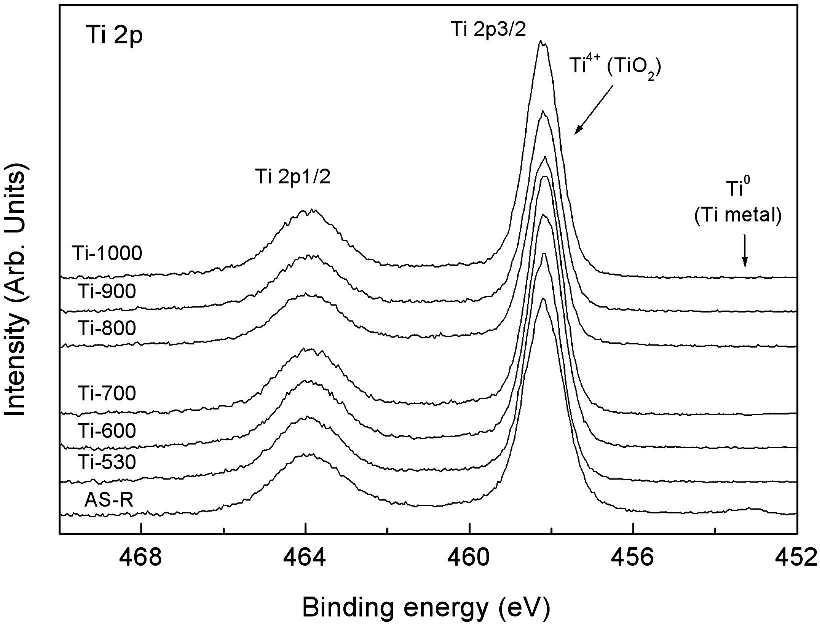


Fig. 4 XPS high-resolution spectra of Ti 2p of sample groups

However, the contents of the hydroxyl groups shown in Fig. 6 should be corrected because the binding energy of organic carbon contamination includes oxygen-containing functional groups, e.g., C-O and O-C=O species, and would affect that of the OH group in O 1s high-resolution XPS spectra. Fig. 7(a) shows the high-resolution spectra of C 1s for each sample group. The C 1s peak can be resolved to hydrocarbon(C-C, C-H), alcohol, alkoxide, ether (C-OH, C-O-Ti, C-O-C), and carboxylate or ester(COOH, COO-R, COO-Ti) species. Fig. 7(b) shows the deconvolution peaks of C 1s for the AS-R group. Then, the contents of the hydroxyl group were corrected using the correction method presented by McCafferty et al. [29] on the basis of the area of deconvoluted peaks of O 1s and C 1s high-resolution spectra shown in Fig. 5 and Fig. 7, respectively. In order to eliminate the errors dependent on the experimental environment of each sample group, the relative contents of hydroxyl group to oxide (O^{2-}) group ($I(OH)/I(O^{2-})$) are shown in Fig. 8. The results indicated that the contents of hydroxyl groups for the Ti-530, Ti-600, Ti-800, and Ti-900 groups were high compared to those of the other sample groups.

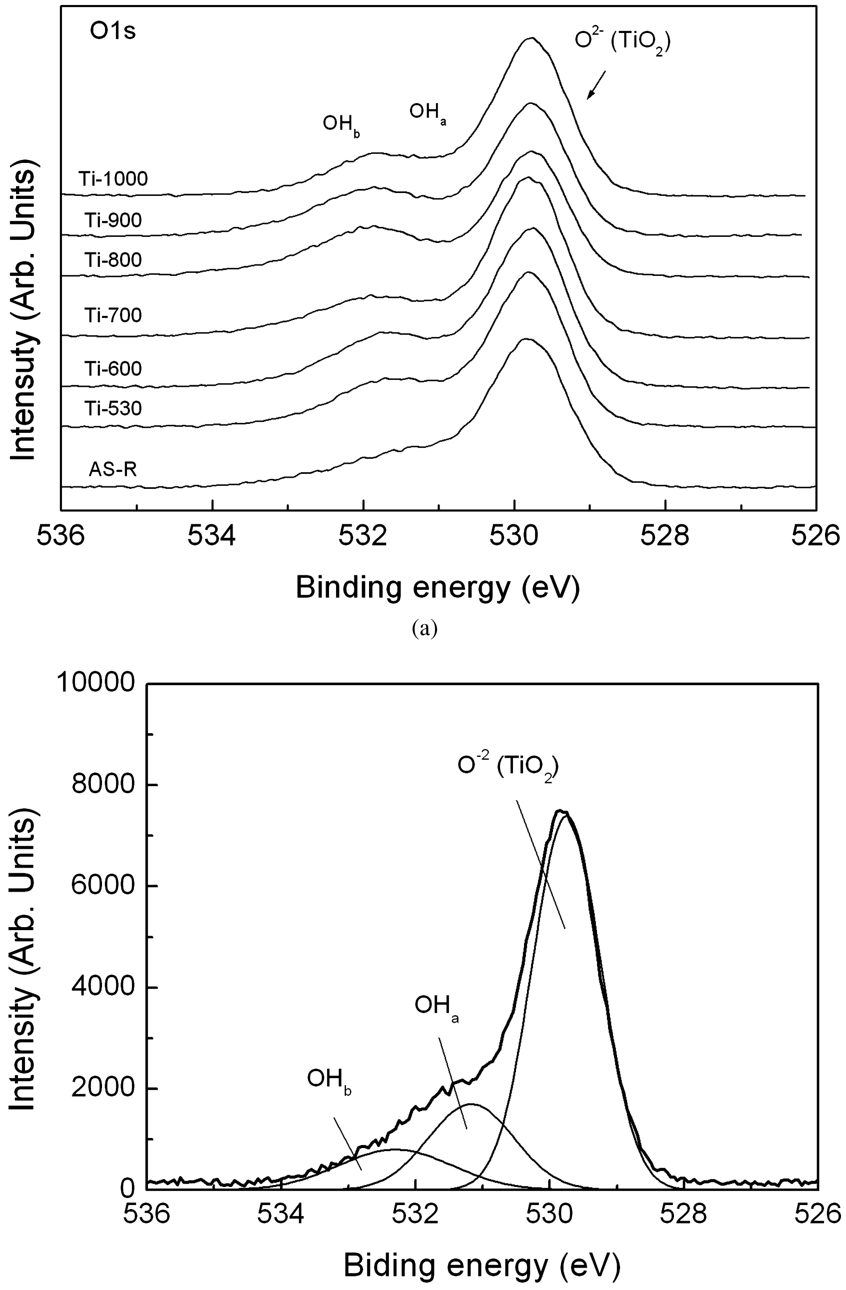
3.4 Immersion test in MEM solution

Figure 9 shows FE-SEM photographs of the titanium surface after immersion in MEM solution for 3 days. The initial degree of calcium phosphate formation was different by sample groups. There were no distinguishable deposit materials on the surfaces of AS-R, Ti-530, and Ti-600. Calcium phosphate has started to form in the Ti-700 group, and it covered the entire surfaces in the Ti-800 and Ti-900 groups. However, calcium phosphate was not observed in the Ti-1000 group.

Figure 10 shows FE-SEM images of titanium surface after immersion in MEM solution for 7 days. Calcium phosphate did not form on the AS-R sample group, but formed well on thermally-treated sample groups. The micro-morphology of calcium phosphate was different depending on sample groups.

4 Discussion

The above results showed that the surface morphology, crystalline structure, chemical composition, and binding state of oxide film were different as thermal treatment temper-



(a)

(b)

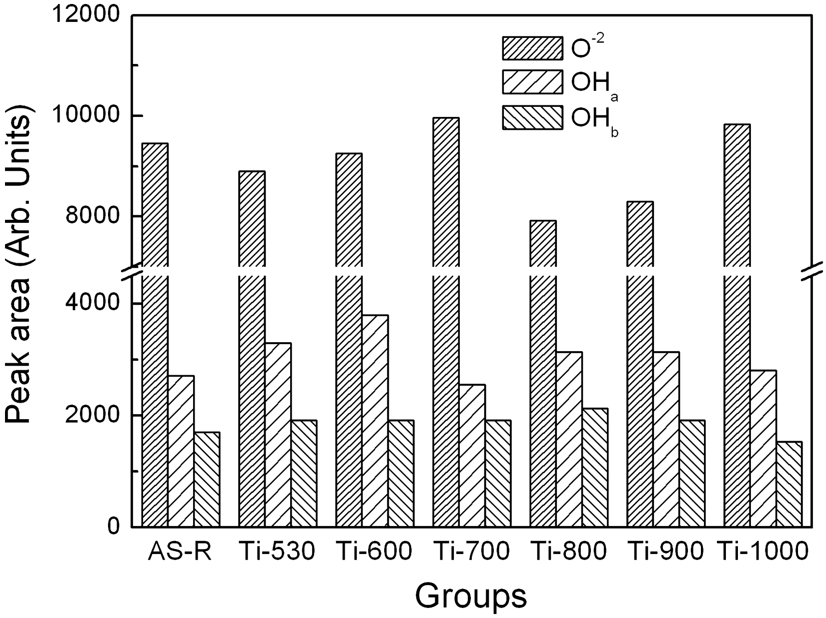
Fig. 5 (a) XPS high-resolution spectra of O 1s of sample groups;(b) Deconvolution of O 1s high-resolution XPS spectrum of AS-R group

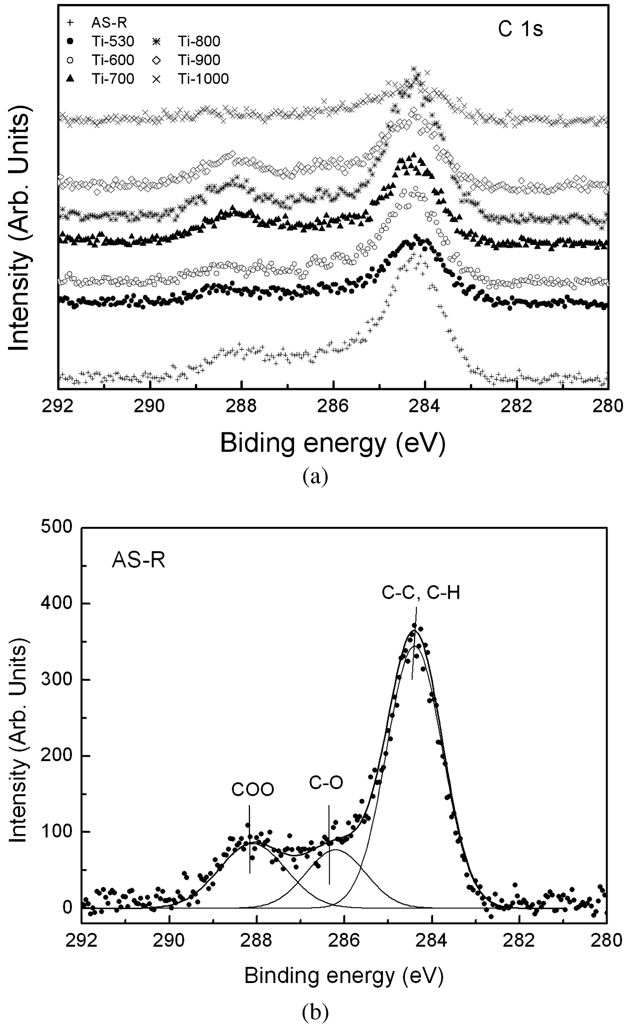
ature changed. The content of the hydroxyl groups, which have negative charge, was an important factor for surface modification of implants because it positively affected bone growth when titanium was used for dental implants. The various parameters were related to the content of the hydroxyl groups. In this study, the effects of the hydroxyl group on the bioactivity of titanium implants were systematically discussed.

There are two types of hydroxyl groups, the acidic hydroxyl group (OH_a) and the basic hydroxyl group (OH_b), as OH is connected with one or two titanium atoms. The acidic hydroxyl groups tend to act as cation exchange sites, while the basic hydroxyl groups may act as anion exchange sites. It has been suggested that the hydroxyl groups contribute to bone growth as calcium ions bind with the acidic groups and phosphate molecules bind with the basic groups [6, 13, 28].

It could be assumed that the content of the hydroxyl group was related to the number of titanium atoms exposed on the titanium oxide surface because the hydroxyl group binds with titanium atoms. Total number of titanium atoms exposed on the titanium oxide surface depends on the density of titanium atoms determined by the preferred orientation of TiO_2 crys-

Fig. 6 Content of three oxygen species calculated by the area of deconvolution peaks





(a)

(b)

Fig. 7 (a) XPS high-resolution spectra of C 1s of sample groups; (b) Deconvolution of C1s high-resolution XPS spectrum for AS-R

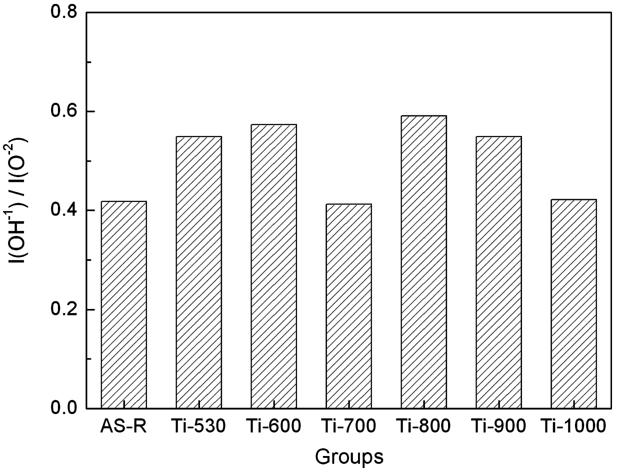


Fig. 8 Relative contents of hydroxyl group to oxide group ($I(OH)/I(O^{2-})$)

talline plane and surface area. The content of the hydroxyl group in the AS-R group was low compared to those of the other sample groups, because titanium oxide film on the AS-R group was very thin and has amorphous structure.

Examining the number of titanium atoms per unit area in TiO_2 crystalline structure, the (110) plane of rutile structure has the most densely-packed titanium atoms, which shows higher density than in the case of (004) plane of anatase structure. The possibility that hydroxyl groups were able to attach to the titanium oxide surface was highest at the (110) plane of rutile structure. It could be inferred that the contents of the hydroxyl group were high on the Ti-800, Ti-900, and Ti-100 sample groups, which have completely rutile structure.

Although Ti-530 and Ti-600 groups have anatase crystalline structures whose titanium atom density was lower

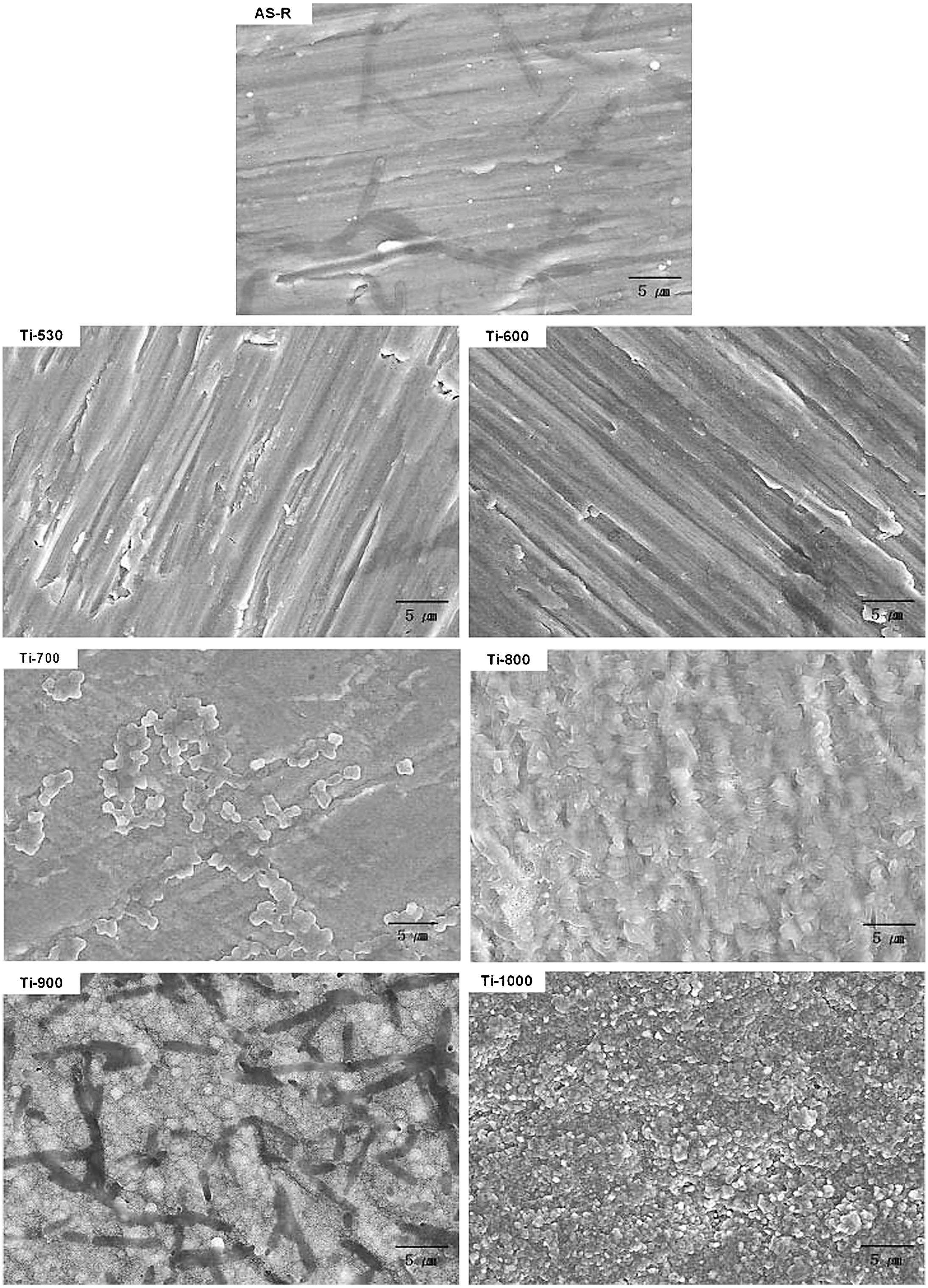


Fig. 9 Fig. 9. FE-SEM photographs of sample groups after immersion test in MEM solution for three days

than that of the rutile (110) plane, the content of the hydroxyl group was comparatively high. This result could be analyzed through careful consideration of the surface area. Two sample groups have nanometer-sized granular crystalline particles, as shown in the SEM-images in Fig. 1. Surface area per unit volume increases as the shape of the grains becomes rounder and their sizes decrease. Therefore, because the surface area of Ti-530 and Ti-600 was higher than that of other sample

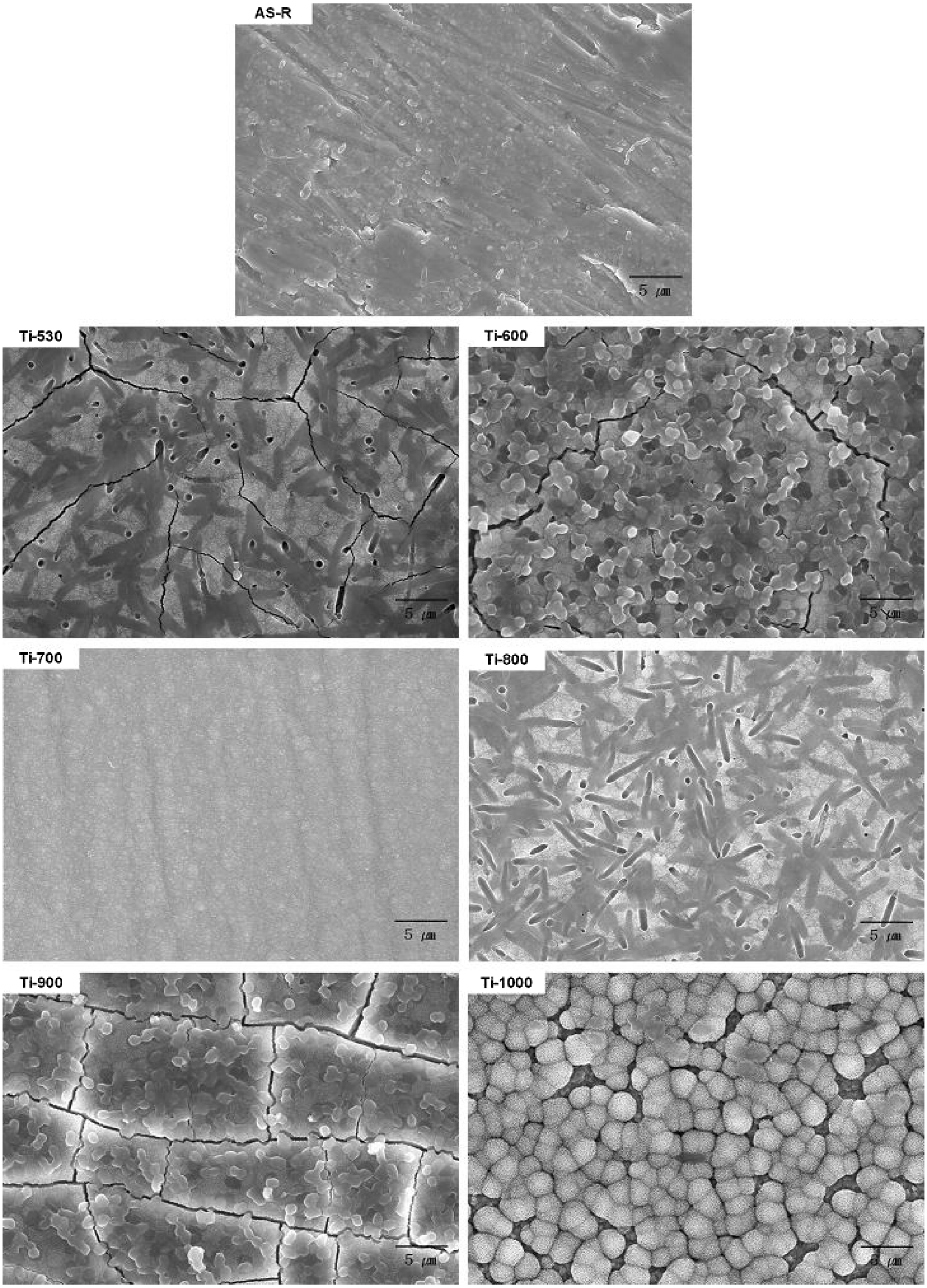


Fig. 10 Fig. 10. FE-SEM photographs of sample groups after immersion test in MEM solution for seven days

groups, the Ti-530 and Ti-600 groups both have comparatively high hydroxyl group contents. The hydroxyl group content of Ti-600 was higher than that of Ti-530 due to its denser surface.

The hydroxyl group content decreased as the temperature of thermal treatment increased to over 800°C. This result could be attributed to the decreasing of total surface area as grain size rapidly increased. More specifically as shown in Fig. 8, the hydroxyl group content was low in the Ti-1000 group, whose titanium oxide crystallite size was large and large-sized pores existed on the less dense surface, as shown in the SEM image in Fig. 1. However, the reason for the decreasing amount of hydroxyl group content in Ti-700 remained unclear. We inferred it to be due to changes of the morphology and crystalline structure from anatase to rutile.

It was concluded that the amount of hydroxyl group of the titanium oxide film depended on the density of titanium atoms exposed on the surface, which is determined by the crystalline structure and surface area of the titanium oxide film. These results are in agreement with the findings of FENG et al. [13].

By inspecting the specimens immersed in MEM solution for 3 days, calcium phosphate formation was observable from the thermal treatment temperature above 700°C, while Ti-1000 group did not show appreciable calcium phosphate formation. Even though the hydroxyl group amounts in the Ti-530 and Ti-600 groups, as calculated by XPS spectra, was comparatively high, the calcium phosphate formation was not observable. Therefore, it is believed that the initial formation of calcium phosphate in MEM was not determined by the hydroxyl group content on titanium oxide film.

Bangcheng et al. [31] reported that a limited content of titanium oxide was needed for bioactivity of titanium metal from the immersion test of the anodic oxidized titanium metal in SBF solution. The result of this study also showed that calcium phosphate formation did not occur in short immersion period until the thickness of titanium oxide formed by thermal oxidation treatment was over the limit value. Although thick oxide film was formed on Ti-1000, the degree of early calcium phosphate formation was low. This result could be due to the facts that large-sized and weakly attached crystallites were easily separated from the surface and the film surface was not dense.

After an immersion test in MEM for 7 days, calcium phosphate formed well on the surface of all sample groups, with the exception of the AS-R group. However, the Ti-700 and Ti-1000 sample groups, which have low hydroxyl group content compared to that of other thermally-treated sample groups, showed different micro-morphologies. In the Ti-700 sample group, calcium phosphate layer which has a homogeneous micro-morphology cracked easily and detached from the surface very easily. This could be attributed to the specific characteristics of the Ti-700 group, in which rutile and anatase structures co-existed. The shape of calcium phosphate formed on the Ti-1000 sample group was spherical and the thickness of the calcium phosphate layer was low. This indicated that calcium phosphate formation was in its initial stage when the Ti-1000 group was immersed in MEM for 7 days.

These results lead to the conclusion that the thickness of titanium oxide film affected the initial formation stage of calcium phosphate in MEM solution, and the resultant calcium phosphate formation was affected by the hydroxyl group content.

5 Conclusions

In conclusion, micro-morphology, crystalline structure, content of hydroxyl group, and bioactivity of titanium oxide film were affected by the difference of thermal treatment. Nano-sized granular oxide was observed in the Ti-530 and Ti-600 sample groups and its crystalline structure was anatase. In the Ti-700 group, needle-like crystals became noticeable, and rutile structure co-existed with anatase structure. Larger-sized crystallites, which have complete rutile structure, were observed in the Ti-800, Ti-900, and Ti-1000 groups. The crystallite sizes of those groups were increased as treatment temperature increased. The results of XPS analysis showed that the hydroxyl group content in titanium oxide film was increased as the density of titanium atoms was high and the surface area was large. The result of immersion test in MEM showed that initial calcium phosphate formation is dependent upon the thickness of titanium oxide and resultant calcium phosphate formation depends on the content of the hydroxyl group of the titanium oxide surface.

Acknowledgements This work was supported by Korea Research Foundation Grant (KRF-2003-041-E20218)

References

1. J. L. BERNIER and C.P. CANBY, *J. Am. Dent. Assoc.* **30** (1943) 188.
2. S. HOBO, E. ICHIDA and L.T. GARCIA, “Osseointegration and occlusal rehabilitation” (Quintessence Int., Tokyo, 1989).
3. L. R. RUBIN, “Biomaterials in reconstructive surgery”, (C.V. Mosby Company, St. Louis, 1983).
4. T. ALBREKTSSON, *CRC Critical Reviews in Biocompatibility* **1** (1984) 54.
5. M. JOBIN, M. TABORELLI and P. DESCOUTS, *J. Appl. Phys.* **77(10)** 5149.
6. T.M. LEE, E. CHANG and C.Y. YANG, *J. Mater. Sci.: Mater. Med.* **9** (1998) 439.
7. P. DUCHEYNE P and K. E. HEALY, *J. Biomed. Mater. Res.* **22(12)** (1988) 1137.
8. J. CHEN, W. TONG, Y. CAO, J. FENG and X. ZHANG, *J. Biomed. Mater. Res.* **34** (1997) 15.
9. K. V. DIJK, H. G. SCHAEKEN, J. C. G. WOLKE, C. H. M. MARÉE, F. H. P. M. HABRAKEN, J. VERHOEVEN J. and J. A. JANSEN, *J. Biomed. Mater. Res.* **29** (1995) 269.
10. C. A. BABBUSH, J. N. KENT and D. J. MISIEK, *J. Oral. Maxillofac. Surg.* **44** (1986) 274.

11. A. WENNERBERG, T. ALBREKTSSON, C. JOHANSSON and B. ANDERSSON, *Biomaterials* **17** (1996) 15.
12. A. GAGGL, G. SCHULTES, W. D. MÜLLER, and H. KÄRCHER, *Biomaterials* **21** (2000) 1067.
13. B. FENG, J. Y. CHEN, S. K. QI, L. HE, J. Z. ZHAO and X. D. ZHANG, *J. Mater. Sci. Mater. Med.* **13** (2002) 457.
14. J. R. BIRCH, T. D. BURLEIGH, *Corros. Sci.* **56(12)** (2000) 1233.
15. E. HRISTOVA, L. ARSOV, B. N. POPAV and R. E. WHITE, *J. Electrochem. Soc.* **144(7)** (1997) 2318.
16. G. N. RAIKAR, J. C. GREGORY, J. L. ONG, L. C. LUCAS, J. E. LEMONS, D. KAWAHARA and M. NAKAMURA, *J. Vac. Sci. Technol.* **13(5)** (1995) 2633.
17. P. LI, I. KANGASNIEMI, K. DE GROOT and T. KOKUBO, *J. Am. Ceram. Soc.* **77** (1994) 1307.
18. N. N. DINH, N. TH. T. OANH, P. D. LONG, M. C. BERNARD and A. HUGOT-LE GOFF, *Thin Solid Films* **423** (2003) 70.
19. Y. T. SUL, C. B. JOHANSSON, S. PETRONIS, A. KROZER, Y. S. JEONG, A. WENNERBERG and T. ALBREKSSON, *Biomaterials* **23** (2002) 491.
20. J. P. SCHRECKENBACH, G. MARX, F. SCHLOTTIG, M. TEXTOR and N. D. SPENCER, *J. Mater. Sci. Mater. Med.* **10** (1999) 453.
21. L. S. HSU, R. RUJIKORAKARN, J. R. SITES, and C. Y. SHE, J. Appl. Phys. **59**(10) (1986) 3475.
22. E. HRISTOVA, L. ARSOV, B. N. POPAV and R. E. WHITE, *J. Electrochem. Soc.* **144(7)** (1997) 2318.
23. L. J. ALEMANY, M. A. BAÑARES, E. PARDO, F. MARTÍN-JIMÉNEZ, and J. M. BLASCO, *Mater. Charact.* **44** (2000) 271.
24. P. DUCHEYNE and G. W. HASTINGS, “Metal and ceramic biomaterials”, (CRC Press Inc., Boca Raton, 1984).
25. BROOKS C. R., “Titanium-Base Alloys. in: Heat Treatment, Structure and Properties of Nonferrous Alloys” (American Society for Metals, p. 329, 1982).
26. H. EAGLE, *Science* **130** (1959) 432.
27. D. M. BRUNETTE, P. TENGVALL, M. TEXTOR and P. THOMSEN, “Titanium in Medicine”, Springer, (2001).
28. M. BROWNE, P. J. GREGSON and R. H. WEST, *J. Mater. Sci. Mater. Med.* **7** (1996) 323-329.
29. E. MCCAFFERTY and J. P. WIGHTMAN, T. FRANK CROMER, *J. Electrochem. Soc.* **146(8)** (1999) 2849.
30. B. YANG, M. UCHIDA, H.-M. KIM, X. ZHANG and T. KOKUBO, *Biomaterials* **25** (2004) 1003.