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**Crystallization of Anatase from Amorphous Titania in Hot Water and In Vitro Biomineralization**

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Anatase of good crystallinity has been developed on titanium substrates by soaking in a 30 mass% hydrogen peroxide solution at 80°C for 8 h, soaking in distilled water at ambient temperature for 12 h, and subsequently aging in distilled water at 80°C for 3d. The anatase layers exhibit good bioactivity as inducing apatite deposition in Kokubo’s simulated body fluid within 2d.

[Received October 28, 2001; Accepted January 22, 2002]

Key-words: Hydrogen peroxide, Titanium, Anatase, Thin film, Hot water, Biomineralization

1. Introduction
Titanium and titanium alloys are widely used as orthopaedic and dental implant materials because of their low specific gravity, good wear and corrosion resistance, good biocompatibility, and long fatigue life. Bioactivity denotes ability for materials to spontaneously deposit apatite on their surfaces and to bond to living bone tissues when implanted in human body. In other words, bioactivity is ability of biomimeticization under body conditions. Since bone cement-less fixation of implants to tissues is advantageous in some cases, and bioactive materials are applicable as such implants, it is of practical importance to provide the biomaterial with bioactivity. Thus, several surface modification methods have been proposed for titanium, titanium alloys, and tantalum. Among them, Wang et al. reported that treatments of Ti substrates with H2O2 solutions containing tantalum chloride and subsequent heating at 400°C could yield bioactive hydrated titania layers on the surface. They suggested that anatase crystallized in the surface layer favored inducing biomimeticization. Wen et al. incubated Ti6Al4V in dilute NaOH solutions (0.001-0.4 M) at 140°C in a pressure canner (3 bar) to obtain a bioactive surface. They found apatite and octacalcium phosphate deposited on the alloy substrates but did not touch upon whether the surface layers consisted of anatase or rutile. Yang et al. studied the hydrothermal synthesis of titania particles and reported that their phases (rutile, anatase) depended on peptizing conditions. Yanagisawa and Osten reported crystallization of anatase from amorphous titania under hydrothermal conditions in which pH of the liquid was varied. However, they employed temperatures as high as 150 to 350°C. Li et al. proposed that the Ti-OH group in the hydrated titania layers is one of the key factors. Therefore, heating may decrease the amount of the Ti-OH groups and hence reduce bioactivity. This paper reports a much simpler and softer treatment to yield anatase on titanium substrates utilizing only H2O2 solution and hot water so that the substrates experience deposition of apatite or biomimeticization in Kokubo’s simulated body fluid.

2. Experimental procedure
A commercially available sheet of pure titanium, supplied by Kobe Steel Ltd., Osaka, Japan, was cut into pieces with a size of 10 mm × 10 mm × 1 mm. The samples were picked at 60°C for 2 min in a 1:1.5:6 (in volume) mixture of 55% HF, 60% HNO3 and distilled water, and ultrasonically rinsed three times in water for totally 15 min. Then each piece of samples was chemically treated at 80°C for 8 h in 10 ml of a H2O2 solution with a concentration of 30 mass% (Santoku Chemical Industries Co., Ltd., Tokyo) that was held in a polyethylene bottle (50 ml, 25 mm in diameter) with a tight screw cap (H2O2 treatment). These samples were soaked in water at room temperature for 12 h (RT-water soaking), and subsequently aged in water at 80°C for 3d (hot-water aging). After ultrasonically cleaned, thin-film X-ray diffraction (TF-XRD) patterns of the samples were taken to identify crystalline phases that might appear. The Rigaku RAD H2A X-ray diffractometer (Cu Kα) with a thin-film attachment was operated at 40 kV-25 mA and at a scanning rate of (1/3)°/min.

The chemically treated and ultrasonically cleaned samples were then autoclaved at 121°C for 20 min, and subsequently served in vitro biomineralization processes. Biomimeticization was conducted by soaking them for up to 3d at 36.5°C in a simulated body fluid of the Kokubo recipe (SBF) with pH adjusted to 7.4. SBF is an aqueous solution containing the same inorganic ions as the human blood plasma in similar concentrations, and is supersaturated for apatite. Thin-film X-ray diffractometry identified the crystalline phases depositing in SBF.

3. Results and discussion

3.1 Crystalization of the films
Curve a) in Fig. 1 is the TF-XRD pattern of the titanium sample after the H2O2 treatment (soaking for 8 h in the H2O2 solution). The two peaks corresponding to anatase were very broad and low in intensity. Thus, the chemical oxidation due to H2O2 yielded amorphous titania or anatase with low crystallinity or small crystallite size. Curve b) is for the sample subject to the H2O2 treatment and immediate hot-water aging for 3d without RT-water soaking. The narrower peaks in curve b) indicate that soaking the H2O2...
Fig. 1. TF-XRD patterns of a cpTi substrate: a) treated with a 30 mass% H2O2 solution at 80°C for 8 h, b) treated with the H2O2 solution at 80°C for 8 h and soaked immediately in water at 80°C for 3d, and c) treated with the H2O2 solution at 80°C for 8 h and soaked in water at room temperature for 12 h and subsequently aged in water at 80°C for 3d. Note the growth of anatase film in good crystallinity.

treated samples immediately in hot water for 3d improved only a little crystallinity of the phase. However, the sample subject to the H2O2 treatment, RT-water soaking and hot-water aging for 3d gave anatase crystals mature enough to yield curve c) with very sharp XRD peaks. This concludes that the intermediate RT-water soaking is essential to obtain the anatase layer of good crystallinity. It was also found that the use of the same H2O2 solution at 80°C for up to 3d for the final treatment, instead of hot-water, would exhibit the same effects as to get well-crystallized anatase films giving XRD patterns similar to curve c) in Fig. 1 as far as RT-water soaking was applied. Note that the samples giving XRD patterns in Fig. 1 were not autoclaved. The result above thus not only confirms the effect of the intermediate soaking on the apatite deposition in SBF but also excludes the possibility for crystallization of the amorphous titania gel due to autoclaving.

3.2 Mechanism of amorphous to anatase transformation

Detail of the present transformation from amorphous to well-crystallized anatase is not clear at this moment. However, one may speculate the mechanism involves processes like:

(1) Dissolution of the previously deposited amorphous titania gel and reprecipitation of anatase;

(2) In situ atomic rearrangement of the amorphous titania gel involving Ti–O–Ti oxobonds cleavage and recombination into face-sharing polymerization of TiO6 units.

Combination of those two mechanisms could not be ruled out. Moreover, processes (1) and (2) could happen in the H2O2 solutions, too. Indeed, continuous soaking in the H2O2 solutions for 3d precipitated anatase. However, the diffractions were very weak and indicative of almost amorphous similar to curves a) and b) in Fig. 1. Thus, the treatment of the intermediate stage, i.e., RT-water soaking played a key role, helping the atomic rearrangement in the final treatment (hot-water aging). However, it is not clear why such intermediate treatment is essential. One of the possible roles is to eliminate peroxides (Ti–OOH), accompanying a structural relaxation and nucleation of anatase in the amorphous titania gel due to processes (1) and (2). Further work is underway to clarify the possible mechanisms.

The crystallization in the last stage (the hot-water aging) might be described according to the process involving the Ti–O–Ti bond cleavage and recombination or reconstruction of related atoms. Yanagisawa and Ovenstone11) proposed a reaction scheme where two H2O molecules should bridge the Ti–OH groups of (OH)2 Ti–O–O–Ti (–OH)2 while Yang et al.10) proposed H+- or OH--assisted rearrangement of TiO6 units. Garder et al.13) studied the effects of soaking alumina xerogels in water on their crystalization behavior at higher temperature. They pointed out the importance of water to lower the crystallization temperature (determined by DTA) from ~800 to 450°C. Seo et al.14) aged in boiling water for 24 h amorphous titanium hydroxide derived from the reaction between TiOCl2 and NH4OH solutions to obtain nanocrystalline powder of anatase. Unfortunately, they14) gave no explanations on the mechanism of amorphous to anatase transformation. However, all of those studies strongly suggest the involvement of H2O molecules in the atomic rearrangement leading to amorphous to crystalline transformation.

3.3 In vitro biomineralization on the anatase films in SBF

Figure 2 shows the TF-XRD patterns of the Ti substrates that were subject to the chemical treatments to yield well-crystallized anatase in the surface layers, to autoclaving, and subsequently to soaking in SBF for up to 5d at 36.5°C. The broad peaks near 31.8° and 25.9° for the 2d soaking sample corresponded to apatite in poor crystallinity. They grew with prolonged soaking in SBF. However, those samples giving curves a) and b) in Fig. 1, or having only poorly crystalline titania, deposited no apatite even after soaking in SBF for 7d after the autoclave treatment. The epitaxial effect for anatase to induce crystallization of apatite has already been reported.3) Moreover, the presence of large amounts of Ti–OH as confirmed by Fourier transform infrared reflection (FT–IR) spectra and X-ray photoelectron spectra (XPS) might also have certain contributions.
4. Conclusive remarks

The bioactive anatase films have been developed on titanium substrates through a simple soft solution approach. The present method possesses inborn advantages of chemical modifications, that is, simple, economy, and applicable to complicate-shaped implants. It is also a quite environment-friendly approach, as it does not employ high temperatures or toxic reagents.

Acknowledgements Financial supports by the QOL project of the Society of Non-Traditional Technology, NEDO 00Z45006x and Grant-in-Aid for Scientific Research, the Ministry of Education, Japan (No. 12558109) are gratefully acknowledged. Jin-Ming WU gratefully appreciates the financial support of the Venture Business Laboratories, the Graduate School of Natural Science and Technology, Okayama University. This work was performed when he was on leave from Zhejiang University, P. R. China.

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