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Formation of Titania Submicron-Scale Rod Arrays on Titanium Substrate and *In Vitro* Biocompatibility

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ABSTRACT

Titania submicron-scale rod arrays were fabricated on metallic titanium (α -Ti) surfaces by coating a layer of sodium tetraborate on titanium substrates and subsequent thermal treatment. Thin-film X-ray diffraction analysis indicated that the sodium tetraborate gave rutile (TiO_2 : PDF# 21-1276) submicron-scale rod arrays. The rods in the arrays are parallel to each other in the grain of metallic titanium surface. The titania submicron-scale rod arrays deposited apatite within 7 days after being soaked in a simulated body fluid, indicating that the rod arrays exhibit *in vitro* bioactivity.

INTRODUCTION

Commercially available pure titanium (c.p. Ti) and its alloys are widely used for dental and orthopedic implants because of their high fracture toughness and good biocompatibility, although they cannot directly bond to bone. Many physical and chemical methods for surface modification of titanium implants have been already developed or proposed to provide them with the ability of direct bonding to bone tissues. Note that essential for such tissue-implant bonding is the *in vivo* apatite-forming ability of implant materials [1-4]. Chemical treatments of titanium substrates proposed so far [1-11] primarily aimed at controlling the formation of titania [2-10] or titanates [1,11] on the titanium substrate surfaces that induced apatite formation when those substrates were soaked in a simulated body fluid (SBF of the Kokubo's recipe[12]). SBF was similar in inorganic ion composition to human blood plasma.

In this study, we prepared titania submicron-scale rods array on metallic titanium (α -Ti) surfaces by coating a layer of sodium tetraborate on titanium substrates and subsequent thermal treatment. Thin-film X-ray diffraction analysis indicated that the sodium tetraborate gave rutile (TiO_2 : PDF# 21-1276) submicron-scale rod arrays. The *in vitro* biocompatibility of the titania

submicron-scale rod arrays was examined by the immersion experiment in a simulated body fluid in terms of the apatite-forming ability.

EXPERIMENTAL DETAILS

Reagent grade sodium carbonates and boron oxides (Nacalai Tesque Inc., Kyoto, Japan) were used to prepare the batches of $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ composition. They were melted in a platinum crucible with a cover and subsequently placed in an electric furnace at 1200°C for 1 h. The melts were then poured on a sheet of steel plate. The quenched glasses were grounded into powders that were less than $45\text{ }\mu\text{m}$ in diameter by a planetary micro-mill pulverizer, pulverisette-7 (Fritsch, Germany) at speed of 600 rpm for 10 min. A sheet of commercial pure titanium (Nilaco, Osaka, Japan) was cut to give pieces of Ti substrate with of $10 \times 10 \times 0.1\text{ mm}$ in size. The micro-scale glass powders obtained above were put directly onto Ti substrates in the thickness of about 0.5 mm. Then, the samples were heated up to 700°C at the rate of $10^\circ\text{C}/\text{min}$ in an electric furnace, and maintained for 5 h. After cooling down to room temperature, the glass-coated samples were subsequently immersed in 80°C water and kept for 5h to remove the coating. Microstructures of the samples were observed after coating 30nm gold by a scanning electron microscopy (JSM-6300, JEOL, Japan) which was operated under 20kV acceleration voltage and 300 mA emission current. Crystal phases present in the samples were identified by thin-film X-ray diffraction (TF-XRD: $\text{CuK}\alpha$) patterns taken by an X-ray diffractometer (RINT2500, Rigaku, Tokyo, Japan) operated at 40kV-200mA and at a scanning step of $0.1^\circ/\text{s}$. The apatite-forming ability of the titania submicron-rod arrays was examined *in vitro* by soaking them for 7 days in 20 ml of SBF [12] at 36.5°C and pH 7.4. The surface structure of the titania submicron-rod arrays after being soaked in the SBF was investigated by TF-XRD.

RESULTS

Fig.1 and 2 show the scanning electron microscope image and the TF-XRD patterns for the microstructure on titanium substrates obtained by the coating of sodium tetraborate glass and subsequent removal with hot water treatment, respectively. After the glass coating was dissolved away in the hot water, the rod array structure appeared in discrete regions within the range of dozens of micrometers in length and width on the titanium surface. Note that the discrete regions are in agreement with the grain of metallic titanium (not shown here). These rods in the grain showed an array structure in which each rod has a tilt against the line perpendicular to the substrate

surface, as seen in Fig.1. These rods had a rectangular bottom shape with dozens of nanometers in width and, while the length was estimated to be a few micrometers.

TF-XRD patterns in Fig.2 gave sharp and strong diffraction peaks at 27.48° which was assigned to (110) plane of rutile (PDF#21-1276). The peaks at 38° and 40° were assigned to metallic α -Ti. The EDX analysis (not presented here) detected only Ti and oxygen elements with the rough ratio of 1:2. This indicated that the sodium tetraborate glass coating yielded submicron-scale rods of rutile (TiO_2) on the titanium substrate.



Fig. 1. A SEM image of the submicron-scale rod arrays on titanium substrate.

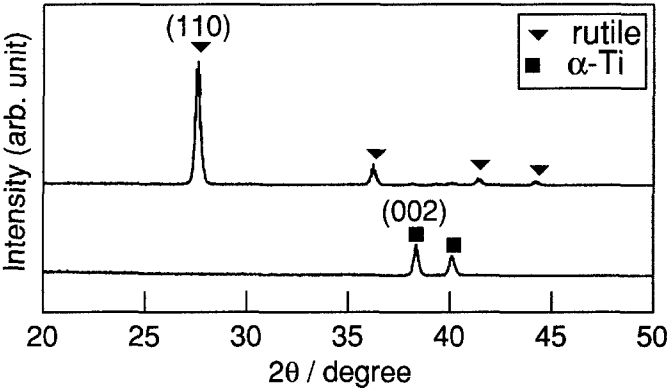


Fig. 2. TF-XRD patterns of the submicron-scale rod arrays on titanium substrate and as-received titanium substrate.

Fig. 3 shows the TF-XRD pattern of the titania submicron-scale rod arrays after being soaked in the SBF for 7 days. This indicated the diffractions at 26° and 32° in 2θ due to apatite.

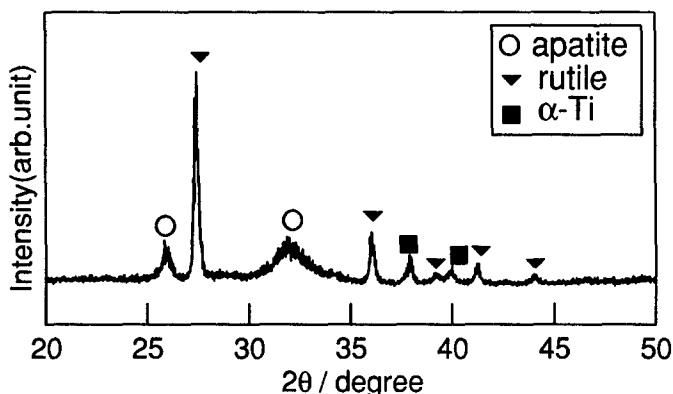


Fig. 3. TF-XRD pattern of the titania submicron-scale rod arrays after being soaked in the SBF for 7 days.

DISCUSSION

The submicron-scale rod arrays of rutile can be obtained on titanium surfaces after the heat treatment when the alkali-borate glass coatings were applied to the Ti substrates. Noted that the diffraction of rutile (110) plane and the diffraction of α -Ti (002) plane are predominant in Fig. 2. We can consider the topotaxy between the α -Ti (002) plane and rutile (110) plane, as shown in Fig. 4. We can notice a good correlation between the Ti-Ti atomic distances in α -Ti (002) plane: $2.9506\text{\AA}$ and rutile (110) plane: $2.9587\text{\AA}$ along c-axis.

The topotaxy will dominate the crystal nucleation and subsequent growth of TiO_2 layers (rutile), irrespective of sodium tetraborate glass coatings.

The chemical reaction and rutile crystal rods nucleation and growth processes may involve five key points: 1) Nano-crystalline TiO_2 (rutile) nucleated by thermal oxidation of α -Ti (002) plane in the oxygen environment, on the basis of topotaxy described in Fig. 4. 2) Nano-crystalline TiO_2 (rutile) were attacked and eroded by alkali metal oxide component of alkali borates, and the erosion may be dependent on the basicity. 3) The as-formed TiO^x species transported and then combined with alkali metal oxide such as Na_2O forming titanates, all of which were thermodynamically stable under these given conditions. 4) The existence of B_2O_3 in the glass

may play the role of slowing down not only the chemical reaction process but also the crystal growth by the diluting effect on alkali metal oxides. 5) Very small amounts of titanates $\text{Na}_2\text{Ti}_6\text{O}_{13}$ crystallized on the titanium surface and nano-crystalline TiO_2 (rutile) grew up competitively over the titanium substrate surface as the complex process of erosion, transportation, combination and crystal growth proceeds. Since the solubility of the sodium tetraborate in hot water is high and titanates is easily removed by the ultrasonic treatment, TiO_2 rutile rods can be seen on titanium substrate. The titania submicron-scale rod arrays deposited apatite within 7 days after being soaked in a simulated body fluid, indicating that the rod arrays exhibit *in vitro* bioactivity.

One-dimensional nanostructures of polymers, metals and semiconductors in forms of rods and

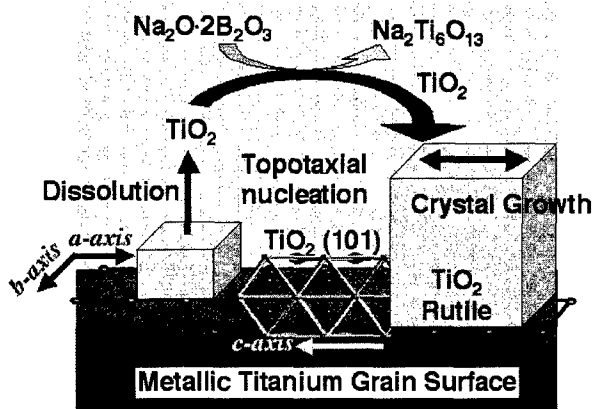


Fig. 4. Relation between the α -Ti (002) plane and rutile (110) plane.

tubes have attracted much attention for a broad range of potential applications, including catalysts, electronics, sensors, photonics, micromechanical devices and biomedical devices, etc. However, to obtain scale-up functional devices with highly ordered nanorod or nanotube arrays are essential. This novel technique promises us one simple method to prepare highly ordered nano-scale arrays of various functional materials on various substrates. Webster *et al.* [13] reported the evidence of the enhancement of osteoblast proliferation, alkaline phosphatase synthesis, and the concentration of extracellular matrix calcium on several nanophase ceramics of decreased grain size. Therefore, the control of the titania crystal size and the orientation of titania rods will be crucial for protein adsorption and configuration that play important roles in the host response processes including the osteoblastic cell adhesion, etc.

CONCLUSIONS

TiO₂ (rutile) in the form of submicron scale-rod arrays was fabricated on titanium substrates by a simple interface reaction between glassy coatings and metallic titanium. The as-achieved titania submicron-scale rod showed well-ordered array structures in the grain of metallic titanium surface. The titania submicron-scale rod arrays deposited apatite within 7 days after being soaked in a simulated body fluid, indicating that the rod arrays exhibit *in vitro* bioactivity.

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