Anodized titanium plates were produced as implant material, using powdered titanium oxide suspended in sulfuric acid aqueous solution electrolyte. Based on X-ray diffraction (XRD) and Auger electron spectrometry analyses, the formation of approximately 2800-nm-thick surface oxide film on titanium consisting of rutile and anatase phases was confirmed. This oxide film on titanium contained many submicron-size pores. The anodized titanium plate was immersed in simulated body fluid, and evaluated using scanning electron microscopy and XRD. Low-crystalline hydroxyapatite formed on the surface after seven days of immersion. In contrast, a 270-nm-thick oxide film was produced on titanium plate anodized in phosphoric acid aqueous solution. In this instance, no additional layer was observed on the surface even after seven days of immersion in simulated body fluid. The biocompatibility was presumed to have improved in the titanium plate anodized using titanium oxide suspended in sulfuric acid aqueous solution electrolyte, because of the formation of a thick oxide film that contained a large number of pores. This material was thus found to be promising for use in implants.

Key words: Titanium, Anodization, Hydroxyapatite
Anodized Titanium Production Using Titanium Oxide Suspended in Sulfuric Acid Electrolyte and Evaluation of Hydroxyapatite Formation in Simulated Body Fluid

An anode. The specimens used in the experiments are shown in Table I.

2.2 Auger analysis

Auger electron spectrometry (AES) measurements and analysis in the depth direction of the surface of the specimens were conducted using an AE spectrometer (JAMP-9500F, JEOL Ltd., Tokyo, Japan). The measurement conditions used were: primary beam: 10 keV, 2.0 × 10⁻⁸ A; beam diameter: φ30 μm; and sputter: Ar, 3 keV, 30 nm/min (in terms of SiO₂).

Table I List of Samples Used in the Experiment

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonprocessing</td>
<td>STD-Ti</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>P-Ti</td>
</tr>
<tr>
<td>Sulfate acid</td>
<td>S-Ti</td>
</tr>
<tr>
<td>Sulfate acid+TiO₂</td>
<td>Sp-Ti</td>
</tr>
</tbody>
</table>

2.3 SBF immersion

Each Ti plate was immersed in 1 L of SBF at 37 °C with similar inorganic ion concentrations to those of human body fluid. The inorganic ion concentrations of the SBF are shown in Table II. The Ti plates were immersed for three days and seven days, and then dried at 37 °C.

Table II Inorganic Ion Concentrations in SBF

<table>
<thead>
<tr>
<th>Ion</th>
<th>mM</th>
<th>Ion</th>
<th>mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142.0</td>
<td>Cl⁻</td>
<td>148.8</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.0</td>
<td>HCO₃⁻</td>
<td>4.2</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5</td>
<td>HPO₄⁻²</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
<td>SO₄²⁻</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.4 Evaluation of Ti plates after immersion

The surface of the Ti plates were observed using scanning electron microscopy (SEM) (JSM-1T100 from JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 10.0–15.0 kV.

For elemental analysis of the Ti plate surface, the SEM was equipped for energy-dispersive X-ray spectrometry (EDX).

The phase identification analysis of the Ti plates was conducted with powder X-ray diffractometry (XRD) (MiniFlex from Rigaku Corporation). A Cu X-ray tube was used, with an applied Kα filter. The scatter slit was set at 4.20°, and the receiving slit at 0.300 mm; sampling was conducted at 1.00 °/min with a sampling width of 0.01°, and the scanning range was set at 25°–30°.

3. RESULTS

3.1 Surface observation using SEM

Fig.1 shows SEM images of the anodic oxide film on the Ti plates. Slight undulations were observed on STD-Ti, but there were no pores. Slight undulations similar to STD-Ti were also observed on P-Ti. Significant development of pores was observed both on S-Ti and Sp-Ti. As shown in the enlarged SEM image of Sp-Ti in Fig.2, submicron-size pores are distributed over the entire surface. Moreover, unique protrusions on the periphery of the pores were also observed.

After finishing the anodic oxidation, no changes in turbidity or color could be visually confirmed in any of the electrolyte solutions. Moreover, no residual titanium oxide powder was observed on the Sp-Ti surface.

Fig.3 and 4 show SEM images of anodic oxide film on Ti plate immersed in SBF for three days and seven days, respectively. In the specimens immersed in SBF for three days, no new film formation was observed. As shown in Fig.4, no new film formed on the surfaces of STD-Ti and P-Ti, even after immersion for seven days. In contrast, for S-Ti and Sp-Ti, new spherical film was generated covering the anodic oxide film after immersion in SBF for seven days. Additionally, cracks were observed in certain locations on the newly generated film.

Fig.1 SEM images of anodic oxide film
3.2 Depth direction analysis using AES

Fig. 5 shows the distance (in terms of SiO2) in the depth direction of the surface oxide film of each Ti specimen measured using AES, and the results of the elemental analysis. Although the thickness of the surface oxide film on STD-Ti was only approximately 10 nm, on P-Ti it was approximately 270 nm. Phosphate at 5–6% concentration was confirmed uniformly in the film. Although on S-Ti, the surface oxide film thickness increased to approximately 2000 nm, in anodic oxidation using titanium oxide suspended in sulfuric acid solution electrolyte, the thickness of the film on Sp-Ti increased to approximately 2800 nm.

Therefore, even thicker oxide film could be developed on Ti plates by adding powdered titanium oxide to sulfuric acid solution electrolyte.

3.3 Elemental analysis using EDX

Fig. 6 shows the EDX elemental analysis results of the anodized film on Ti plate, and Fig.7 and 8 show those after immersion in SBF for three and seven days, respectively.

Although P was detected only in P-Ti, as shown in Fig.6, no element other than Ti was detected in the other Ti plates. As shown in Fig.8, Ca was detected in S-Ti and Sp-Ti. In contrast, Ca was not detected in STD-Ti and P-Ti. Based on these results, the calculated Ca/P molar ratios for S-Ti and Sp-Ti were 1.32 and 1.34, respectively.
Fig. 6 EDX on the surface of the anodized film result

Fig. 7 EDX results on the surface of anodized film immersed in SBF for three days

Fig. 8 EDX results on the surface of anodized film immersed in SBF for seven days

3.4 Phase identification analysis using XRD

Fig. 9 shows the XRD patterns of an anodic oxide film on Ti plate. In STD-Ti and P-Ti, no peaks due to titanium oxide crystalline phases were observed. However, in S-Ti and Sp-Ti, anatase and rutile phases were confirmed.

Fig. 10 and 11 show the XRD patterns of anodic oxide film after immersion in SBF for three and seven days, respectively. As shown in Fig. 10, no new film formation was observed after immersion. In the phase identification analysis of specimens after seven days of immersion, as shown in Fig. 11, a broad diffraction peak at around 26°, likely attributable to HAp, was observed in S-Ti and Sp-Ti. This peak is shown as HAp (002).

Fig. 10 XRD patterns of anodic oxide film

Fig. 11 XRD patterns of anodic oxide film immersed in SBF for seven days

4. DISCUSSION
4.1 Oxide film generated by anodic oxidation

As shown in Fig. 1, in S-Ti and Sp-Ti, a large number of pores were present on the anodic oxide film. These pores showed unique protrusions formations around the periphery. Pores with submicron diameters were found to be widely distributed.

These changes in the surface film can likely be attributed to a breakdown of the insulating oxide films as the voltage increases. It has been reported that when the supply voltage was increased in anodic oxidation, the dissolution of titanium due to spark discharge also increased, increasing the size of spark discharge marks, resulting in the formation of such pores [6]. Accordingly, the surface pores in this study were also likely formed as a result of spark discharges occurring during anodic oxidation [10–11].

It is presumed that the increase in film thickness with the addition of powdered titanium oxide was due to the suppression of sudden increases in voltage by the presence of suspended powder in the electrolyte solution, which in turn allowed for smooth progress in oxidation. Therefore, it may be likely that similar results can be obtained by using other forms of suspended powder, such as ceramics, instead of titanium oxide.

Moreover, it was found by visual observation that, compared to S-Ti that was anodized using sulfuric acid only, the surface color was darker for Sp-Ti that was anodized by adding powdered titanium oxide to sulfuric acid solution. Because Ti tends to exhibit a darker color as the thickness of the oxide film increases, the increase in film thickness could be confirmed from simple visual observation.

As shown in Fig. 6, although the EDX of S-Ti and Sp-Ti detected S in the oxide film, this may be due to the presence of residual S on the surface coming from the sulfuric acid solution electrolyte.

4.2 Evaluation of biocompatibility using SBF immersion

In the XRD patterns of anodic oxide film on S-Ti and Sp-Ti after seven days of immersion in SBF, a broad peak attributed to HAp was observed, suggesting the presence of low-crystallinity HAp on the Ti surface. It has been reported that presence of microscale surface irregularities affected the biological response of human tissues [9]. Based on such findings, in the S-Ti and Sp-Ti specimens with numerous pores on the surface, as shown in Fig. 1, it may be likely that they were more prone to HAp deposition on the surface compared to the other specimens.

Based on EDX results for specimens after immersion in SBF for seven days, the Ca/P molar ratio for the hydroxyapatite film was approximately 1.3, being lower than the ideal HAp molar ratio of 1.67. Previous studies have assumed that HAp was formed through phases with smaller molar ratios than HAp, such as octacalcium phosphate (OCP: Ca8H2(PO4)6·5H2O), dicalcium phosphate dihydrate (DCPD: CaH(PO4) · 2H2O), and β-tricalcium phosphate (βTCP: Ca3(PO4)2). Moreover, it is assumed that amorphous calcium phosphate (ACP: Ca3(PO4) · 2H2O) may also be present.

Additionally, it may be likely that ion exchange occurs between Ca2+ in HAp crystals and Na+ or Mg2+ in SBF. These may be considered as likely factors of a lower HAp molar ratio.

Moreover, as shown in Fig. 4, numerous cracks were observed in the HAp layer on S-Ti and Sp-Ti. These cracks likely formed due to density changes occurring at the time of conversion to HAp from ACP or OCP generated as precursors.

It can thus be inferred that HAp and ACP with low crystallinity were formed on the S-Ti and Sp-Ti surfaces immersed in SBF, through intermediate phases of ACP or OCP formation.

Furthermore, because the anodic oxide film was thick on the anodized titanium plate with HAp formation, this may have contributed to the deposition of HAp [9].

Based on the aforementioned results, because S-Ti and Sp-Ti have better bone conductivity than STD-Ti or P-Ti, these can likely be considered as suitable materials for use in artificial tooth implants with higher biocompatibility.

5. CONCLUSION

In this study, the following points were elucidated using experiments in which Ti plates were anodized in solutions of phosphoric acid, sulfuric acid, and sulfuric acid with powdered titanium oxide, and then immersed in SBF.

1. Using surface analysis, it was confirmed that titanium oxide phases occurred in the oxide surface on the anodized specimens. On specimens anodized using sulfuric acid solution electrolyte, submicron-size fine pores were observed, and a mix of rutile and anatase phases of titanium oxide was confirmed.

2. The approximate thicknesses of surface oxide film were 300 nm for phosphoric acid solution electrolyte, 1800–2000 nm for sulfuric acid
solution electrolyte, and 2800 nm for the sulfuric acid solution electrolyte with titanium oxide powder. The increase in film thickness by adding powdered titanium oxide to the electrolyte was most likely due to smooth progress in oxidation as a result of the suppression of sudden changes in voltage by the presence of powdered particles in the electrolyte.

3. In the specimens S-Ti and Sp-Ti after seven days of immersion in SBF, low-crystalline HAp deposition was confirmed. This suggests that S-Ti and Sp-Ti have a higher bone conductivity compared to STD-Ti or P-Ti.

As discussed above, in the anodization using sulfuric acid electrolyte solution, especially with the addition of powdered titanium oxide, a mixture of anatase and rutile phases could be obtained, resulting in increases in the film thickness and pore formation. Because superior bone conductivity was also confirmed, this process can likely be used in developing artificial tooth implants with even higher biocompatibility.

REFERENCES