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Effect of ultrasonication on anodic oxidation of titanium

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Porous titania (TiO_2) was synthesized under ultrasonic vibration via an anodic oxidation of titanium metal in various kinds of electrolyte such as HNO_3, H_2SO_4, and their mixture. HNO_3 resulted in amorphous or poorly-crystalline particles with mesopores while H_2SO_4 resulted in dense and crystalline film with macropores. Ultrasound in general decreased the maximum voltage, film thickness, and a rutile phase, while it increased the region for the formation of mesoporous structure. Role of ultrasound on the anodic oxidation is discussed.

Key-words : Anodization, Mesoporous titania, Sonochemistry, Ultrasound

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1. Introduction

Titania (TiO_2) has been intensively studied in both academe and industry. Routes to synthesize or prepare titania materials are quite various; hydrolysis of alkoxide[1),2)] or inorganic salt,[3)–6)] and so forth. Aqueous system is rather preferred for both cheaper and environmentally-benign production. In this paper, we employed anodic oxidation method where metallic titanium is electrochemically oxidized in an aqueous electrolyte. The influential factors in the anodization process[7)–12)] are species and concentration of electrolyte, temperature, voltage, and so forth.

Sonochemistry, i.e., chemical application of a power ultrasound, has been widely accepted as a common science recently. Nucleation, growth, and collapse of cavitation bubbles in acoustic vibration induce extraordinary high temperature depending on the vapor and the dissolved gas in the system. Also, microjet and microstreaming around cavitation bubbles greatly enhances mass transportation in solution. Another specific term, sonoelectrochemistry is known in several organic films,[13)] but ultrasonic effects on anodic oxidation is rarely known.

The present study is to clarify the sonoelectrochemical effects on the formation, microstructure, and property of anodized titania in various electrolytes.

2. Experimental procedure

High purity Ti sheet (99.5%, 0.3 mm thickness) was cut into a rectangle of 15 × 50 mm, cleaned with a diluted mixture of HF and HNO_3. Then, an insulating tape was masked on the working electrode of Ti so that the constant area of 10 × 10 mm away from the edges can be exposed to anodic oxidation in electrolyte. Acid concentration of 1 N (e.g., 1 M HNO_3 or 0.5 M H_2SO_4 etc.) was mainly studied. Counter electrode of 40 × 60 mm was the same Ti metal and no referential electrode was used. Anodic oxidation was conducted at a constant current of 100 mA in a thermostated bath of 5–40°C.

Ultrasonic (US) treatment was made by using a commercial homogenizer (Branson Model 450), whose horn was dipped into the electrolyte perpendicular to the working electrode and irradiated at 5 mm away from the electrode surface throughout the synthesis. Ultrasonication usually resulted in a temperature raise of several degrees, which were found to be insignificant considering the results of the other runs at different temperatures. In order to better understand the ultrasonic effect, referential syntheses were run by a mechanical stirring (MS) with a magnetic stirrer. In addition, the effect of sonochemical atmosphere was examined by bubbling Ar, N_2, or O_2 before and during anodization.

After a fixed time of oxidation, 120 min for HNO_3 and 30 min for H_2SO_4, the products were carefully washed with distilled water several times, and then dried at 100°C in air. In addition, a portion of the product was occasionally subjected to a heat treatment at 400°C for 2 h in air. Evaluation of the products was mainly done by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The concentration of titanium ion in the supernatant or the filtrate electrolyte was determined by colorimetry at λ = 408.9 nm after forming a complex with H_2O_2.[14)]

3. Results and discussion

3.1 Anodization in HNO_3

The oxidation product in HNO_3 electrolyte was a powder or a very brittle plate which could be softly removed from the metal substrate. As the latter product can be easily broken or dispersed by cavitation, the product under ultrasonic irradiation was always powder.

Figure 1 shows the yield (mass) of the collected product as a function of the HNO_3 concentration. The yield decreased with increasing concentration and also with the sonication. It is interpreted that both a high concentration of the acid and a sonication enhanced the dissolution of titanium and thus decreased the yield.

Figure 2 shows the changes in voltage during anodization. Ultrasonication was found to lower the voltage slightly from ca. 26 V to 24 V. It is inferred that thin barrier layer is formed at the initial stage of anodization prior to the formation of porous structure which will be shown later. Although we cannot directly observe the thin barrier layer by SEM at present, we consider that ultrasonication decreased the thickness of insulating barrier layer and thus lowered the voltage of galvanostatic electrolysis at 100 mA. The ultrasonic effect on the layer thickness will also

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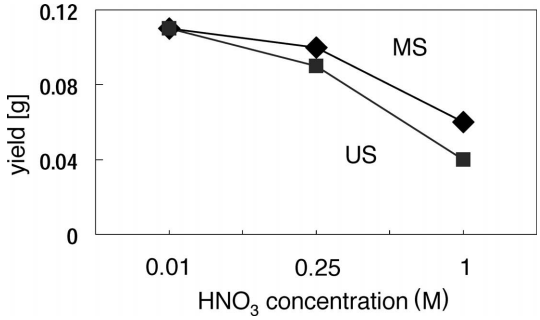

Fig. 1. Yield of the anodized product at 5°C as a function of the HNO_3 concentration (MS; mechanical stirring, US: ultrasonic).

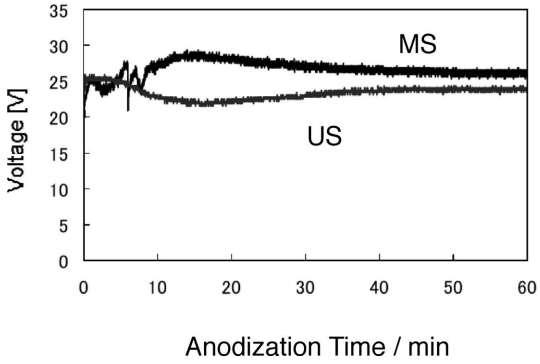

Fig. 2. Voltage change during anodization in 1 M HNO_3 at 5°C (MS; mechanical stirring, US: ultrasonic).

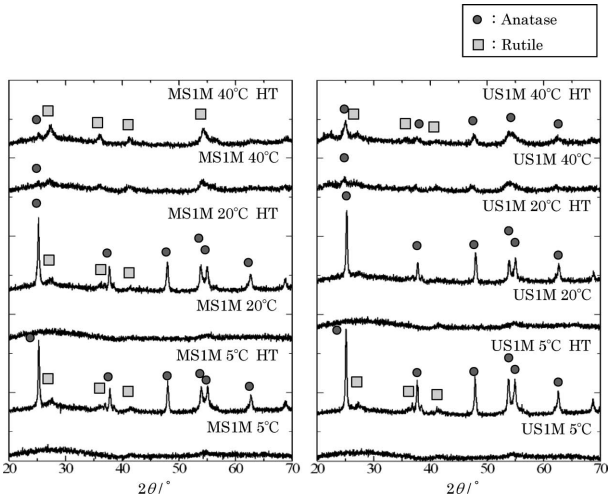

Fig. 3. XRD patterns of titania specimens prepared in 1 M HNO_3 at different temperatures (5–40°C) and subsequently subjected to a heat treatment (HT) of 400°C for 2 h. (MS; mechanical stirring, US: ultrasonic).

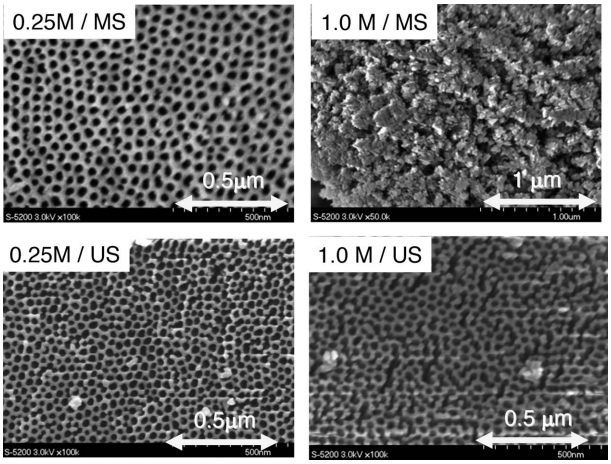

Fig. 4. Scanning electron micrographs of titania prepared in different concentrations of HNO_3 at 5°C (MS; mechanical stirring, US: ultrasonic).

appear clearly in the case of sulfuric acid.

Figure 3 summarizes the X-ray diffraction patterns of the MS and the US samples prepared at different temperatures, also before and after a heat treatment at 400°C in air. The as-precipitated products at lower temperatures were amorphous, while those at higher temperature of 40°C showed (poor) crystallinity. Careful observation of the latter XRD patterns (MS/US 1 M 40°C) indicates that anatase is formed in the US sample, while rutile is formed in the MS sample before the heat treatment.

In a thermodynamic sense, anatase is less stable than rutile. Similar type of *sonochemical switching* can be sometimes observed in the other systems;[15),16)] that is, ultrasonication tends to yield a phase of less-stable structure. Such phenomenon may or may not be explained by high temperature of cavitation or subsequent quenching effect. In the present case, however, we presume that the switching is not due to temperature or quenching, judging from the following fact. When we changed the sonochemical atmosphere (air, N_2, O_2, Ar) during the anodization in nitric acid, which is a convenient way is to alter the bubble temperature in cavitation, no significant change occurred. The independence of dissolved gas also indicates that dissolved oxygen does not play an important role in the oxidation. Ultrasound in electrochemical process would work rather physically (microjet, mass transfer, … etc.) than chemically as the other sonochemists reported.[13)] After annealed at 400°C, the amorphous products anodized at 5 and 20°C transformed to well crystallized anatase, also as shown in Fig. 3. The 40°C specimens which were poorly crystallized during anodization grew their initial phase or nucleus on heating.

Figure 4 shows SE micrographs of the MS and the US specimens anodized in 0.25 and 1.0 M nitric acid at 5°C. An obvious feature at 1.0 M is that straight and aligned mesopores were formed in US but not formed in MS. At lower concentration of 0.25 M, however, the aligned mesopores were obtained both in the presence and in the absence of ultrasound. Colorimetrically determined Ti^{4+} ion concentrations in the filtrate were ~40 ppm for 0.25 M, and ~60 ppm for 1.0 M, and there were no significant difference between MS and US. At higher concentration of 1.0 M, it is inferred that the dissolution of electrochemically formed titania is likely to occur and the concentration of dissolved species nearby the electrode surface is high. In the absence of ultrasonic mixing, thus high concentrated species would agglomerate free from forming aligned structure. Ultrasonication could homogenize the distribution of such species near the electrode. At lower concentration, the difference is that the number density of mesopores were higher, also the wall widths were thinner in US than in MS. This may be attributed to the number of etch-pits formed at very initial stage of anodization, which were increased by ultrasonication.

Specific surface area (SSA) was measured by N_2 adsorption, expecting that the mesoporous structure significantly enhanced SSA. By contraries, SSA's of the sample MS and US (1.0 M) before annealing were 120 and 71 m^2/g, respectively. It is inferred that the agglomeration in the sample MS, as shown in Fig. 4, was loose enough to enhance the surface area. These pores were found to be stable after annealed at 400°C. The SSA of the sample MS decreased to 73 m^2/g by annealing, but that of the sample US did not change much.

It should be mentioned here that the product in HNO_3 appeared in yellowish color. This color remained after annealed for crystallization. Nakahira et al.[8] reported that the anodic oxidation of titanium metal in nitric acid results in nitrogen doping in other words photocatalytic responsiveness to a visible light. **Figure 5** shows the photocatalytic property of the titania samples (MS, HNO_3 1 M, 5°C) under visible light (< 420 nm). Details on the measurement procedure are described elsewhere.[17] Although the absolute value is not very large, it is obvious that the annealed specimen shows a higher photocatalytic response than a typical and commercial titania (P–25, Degussa). The ultrasonic effects on N_2 doping nor photocatalytic property were scarcely observed.

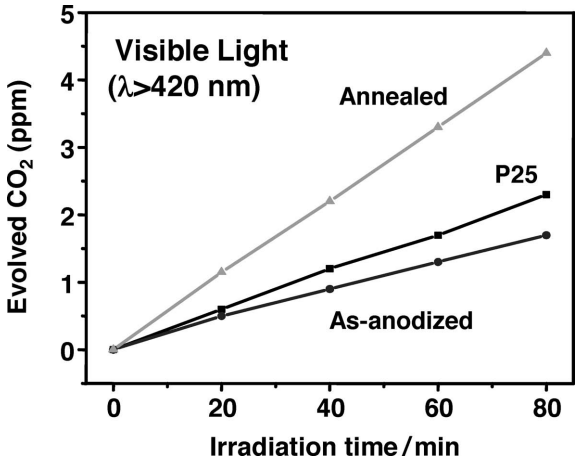

Fig. 5. Photocatalytic activity of prepared titanias (as-anodized and annealed at 400°C) and commercial P–25 (Degussa) under visible light; Model compound = 2-Propanol in gas phase, Catalyst = 6 mg of each sample was coated on the Pyrex substrate, Substrate area = 15 × 15 mm, Light Source = 300 W Xe lamp + water filter + UV cut-off filter.

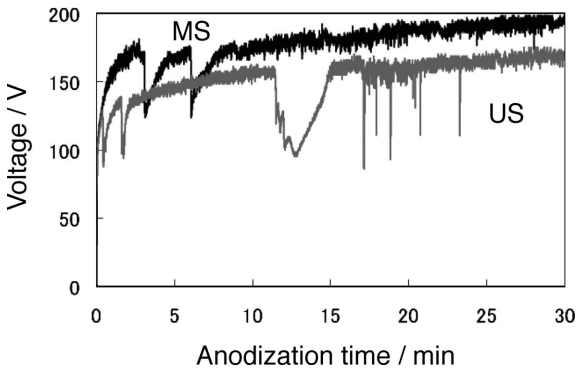

Fig. 6. Voltage change during anodization in 0.5 M H_2SO_4 5°C (MS; mechanical stirring, US: ultrasonic).

3.2 Anodization in H_2SO_4 and H_2SO_4–HNO_3 mixture

In case of sulfuric acid, formed were dense and crystalline films without annealing. **Figure 6** compares typical voltage diagrams for MS and US. Frequency and depth of the occasional drops in the diagram were not very reproducible, but their influences on the morphology of the product were found to be negligible. Compared with the case of nitric acid in Fig. 2, it is found at a glance on Fig. 6 that the order of MS/US is similar and that the absolute value of the voltage is much higher, which suggests the product here is dense and insulating. Lower equilibrium voltage (~160 V) for US than that for MS (~200 V) implies smaller film thickness (0.8 ± 0.2 μm) of US than that (1.0 ± 0.2 μm) of MS, which were confirmed by a SEM observation on the cross-section of the film. **Figure 7** shows XRD patterns of the MS/US products. It is found that ultrasonication preferred the anatase formation rather than rutile. This tendency is similar to the case of nitric acid, as were shown in Fig. 3.

The upper limit of voltage for the power supply employed in this study was usually set at 200 V, to which the MS anodization in sulfuric acid reached as shown in Fig. 6. In order to examine the effect of voltage, the limit was reset at 160 V, and then anodization was executed with mechanical stirring. Thus simple procedure allowed the similar voltage profile as the US case. Results are also shown as "MS (max 160 V)" in Fig. 7. It is suggested that the preference to anatase under ultrasonication could be caused by lower voltage. Such tendency as high voltage prefers the rutile phase agrees to a previous report.[7] Also, the sample US and the sample MS (max 160 V) resemble each other in the sur-

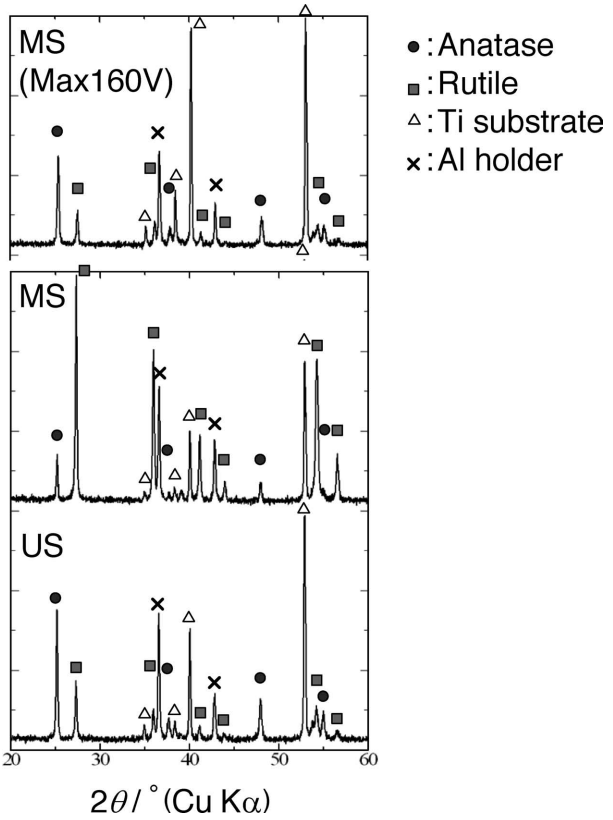

Fig. 7. XRD patterns of titania specimens prepared in 0.5 M H_2SO_4 at 5°C. (MS; mechanical stirring, US: ultrasonic) Upper limit of the voltage was usually set at 200 V. In the upper figure, the limit was occasionally set at 160 V.

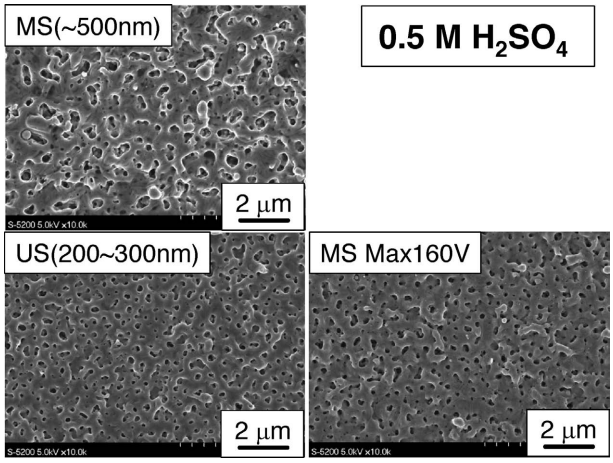

Fig. 8. Scanning electron micrographs of titania prepared in 0.5 M H_2SO_4 at 5°C (MS; mechanical stirring, US: ultrasonic) Upper limit of the voltage was usually set at 200 V. In the right figure, the limit was occasionally set at 160 V.

face microstructure, as shown in **Fig. 8**.

However, the ultrasonic effect here is not that simple. If the voltage is simply determined by the film thickness, that of the MS (max 160 V) should be almost the same as that of the US. SEM observation of the MS (max 160 V) sample was not successful because the film/substrate boundaries were not as clear as the cases of US and MS (200 V). It can be seen from Fig. 7 that the peak intensity of titanium substrate is much higher in MS 160 V than in US, which implies that the film thickness of the sonicated sample is higher. In summary, the order of the film thickness could be MS(200 V) > US(160 V) > MS(160 V), and the crystalline phase was rutile for 200 V and anatase for 160 V. Ultrasonication resulted in thicker film of anatase.

In the sulfuric acid alone, always formed were dense films with macroscopic pore of several hundred nm, whether with or without ultrasonication. **Figure 9** shows the microstructure formed in a mixture of 0.4 M HNO_3 and 0.3 M H_2SO_4 at 5°C. In the case of MS, the microstructure is similar to that for sulfuric acid alone, as shown in Fig. 8. The "wall" section appeared solid and dense when observed at higher magnification. In the presence of ultrasonication, very large pores or craters of 10 μm were observed. Inside the crater, on the other hand, clearly observed was the mesoscopic roughness, whose size resembles to mesopores formed in nitric acid alone. It is inferred that ultrasonication enhanced the activity of nitric acid to form mesopores by etching accompanied with cavitation.

4. Conclusions

Effect of ultrasonication during galvanostatic anodization of titanium at constant current in nitric acid, sulfuric acid, and their mixture was investigated. In nitric acid, the products were peeled off from the Ti substrate. Ultrasonication decreased the maximum voltage, preferred anatase, reduced the mesopore size, and expanded the region of mesopore formation. The nitric-acid-derived titania showed yellow color which implies the nitrogen doping, but there was no US effect on the doping. In sulfuric acid, the products were macroporous film tightly attached to the Ti substrate. Ultrasonication decreased the maximum voltage, preferred anatase, and reduced the pore size. In the mixture of

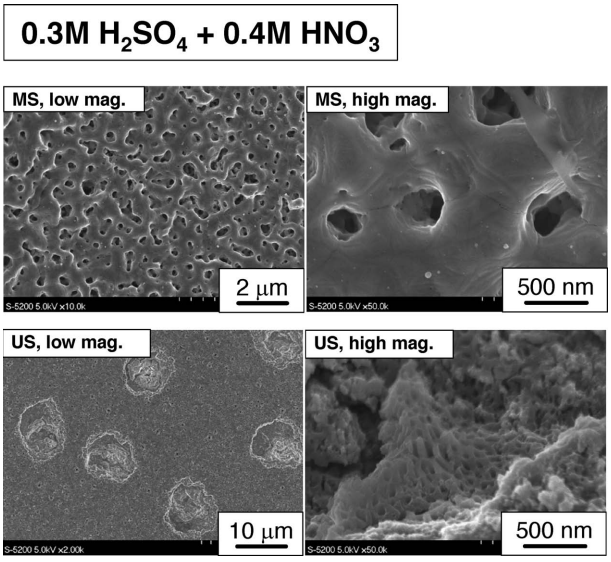

Fig. 9. Scanning electron micrographs of titania prepared in an acid mixture of 0.4 M HNO_3 plus 0.3 M H_2SO_4 at 5°C (MS; mechanical stirring, US: ultrasonic).

nitric and sulfuric acids, ultrasonication may have activated nitric acid to encourage the mesopores formation.

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