Preparation of High Performance Titanium Oxide Films by Anodization Process

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Titanium oxide film, especially composed of anatase type phase, has been studied intensively, because of their activity in converting the light energy into chemical and electrical energy.[1,2]

Anatase type TiO_2 film was successfully formed by using the anodization process for nitrided titanium with DC power supply in the suitable electrolyte. In the ordinary anodization process, anatase type TiO_2 films were hardly formed on the surface of titanium metal. For obtaining the anodic oxide films with high activity, not only annealing under oxidizing atmosphere [3] but also removing the low valence oxide[4], such as TiO and Ti_2O_3, which created subsidiary in the anodization process, was necessary.

We examined the electrolyte and found that titanium nitride coating prior to the anodization process, was effective for getting anatase type TiO_2 film on the metallic titanium.

Titanium plate of the purity over 99.5% was annealed under nitrogen gas atmosphere at 750～950℃ for 6 hours. Titanium plate was anodized under applied voltage of 150～200V for 10min. The electrolyte was composed of sulfuric acid, phosphoric acid and hydrogen peroxide. The anatase type TiO_2 precipitation quantity was evaluated by using the peak area analysis of X-ray diffraction measurement.

Anatase type TiO_2 X-ray diffraction relative intensity of anodized oxide films after annealed at 750～950℃ under nitrogen atmosphere was shown in Fig. 1. Formation of TiO_2 composed of anatase phase, was dependent on the applied voltage and annealing temperature under nitrogen atmosphere. Especially at annealing temperature of 950℃, X-ray diffraction relative intensity was extremely high.

Anatase type TiO_2 X-ray diffraction relative intensity of anodized samples when changing the composition ratio of each chemical in the electrolytic solution was shown in Fig. 2. Anatase type TiO_2 production was dependent on not only the applied voltage but also concentration of sulfuric acid.

As a result of SEM image shown in Fig. 3, the titanium oxide layer seemed to grow mainly on the hole of about 1～3 μm in diameter by the electric discharge. Cross section SEM image of the films showed 5 μm in thickness about the oxidized layer of good contact with basement titanium layer.

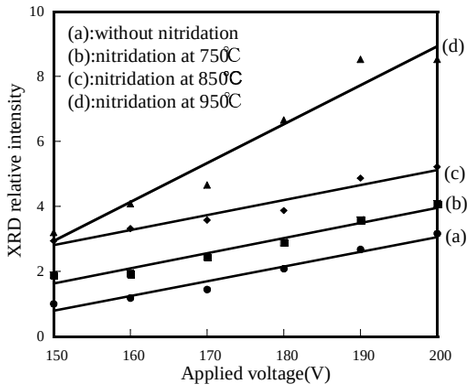

Fig. 1 Anatase type TiO_2(101) XRD relative intensity depending upon the applied voltage and nitridation.

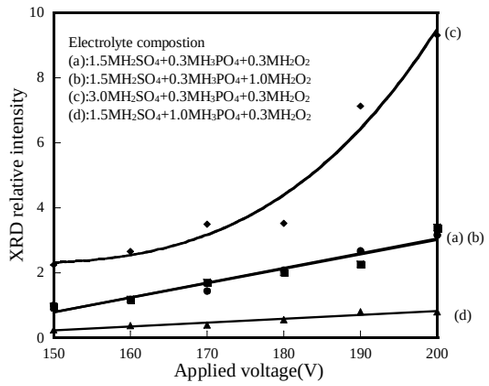

Fig. 2 Anatase type TiO_2(101) XRD relative intensity depending upon the applied voltage and composition of electrolyte.

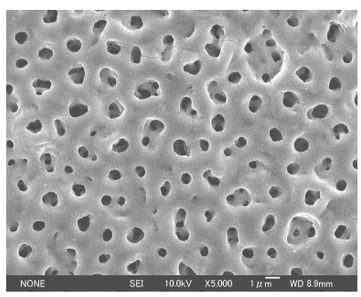

Fig. 3 SEM image of anodic oxide films at applied voltage of 200V without nitridation

Reference

1. K.Sunada, A.Fujishima et. al., *Environ. Sci. Technol.*, **32**,3831（1998）
2. T.Umebayashi, K.Asai et.al., *Chem.Lett.*,**32**,300(2003)
3. Japanese patent Publication Number 08-246192
4. J. Kuraki, S.Ito et.al., *Journal of Japan Institute of Light Metals*, **50**,603(2000)