Synthesis of self-ordered titanium oxide nanotubes by anodization of titanium

A.Yaadhav Krishnan, S.Sivabalan, S.Subhachandhar, Balakrishnan, Dr.R.Narayanan*

Department of metallurgical engineering, PSG college of technology

Abstract

Self-ordered arrays of titanium oxide nanotubes were prepared by anodization of Ti in sodium sulphate solution containing sodium fluoride. The dimensions of the nanotubes (diameter: 20-100 nm and length: 1000-1500 nm) could be tuned by changing the synthesis parameters. The as-anodized nanotubes showed amorphous structure which upon annealing at 500°C in oxygen atmosphere turned crystalline, according to XRD analysis. The pit morphologies show that pit initiation occurs due to NaF content in the electrolyte and nanotube formation starts after pit growth terminates.

Keywords: anodization; Titanium oxide; crystalline

1. Introduction

Since the appearance of the first report on formation of nanoporous anodic oxide film of Ti in 1999 by Zwilling et al [1], a significant number of reports are available on the anodization of Ti in different fluoride solutions [2-4]. Synthesis of homogeneously ordered arrays of TiO$_2$ nanotubes by anodization of pure Ti is considered straightforward because of a single phase microstructure. Nanodimensional titanium oxide is of interest because of its application as gas sensors, photovoltaic cell and electrode for solar hydrogen generation [5]. Among various methods of processing nanometer scale titania, anodization of Ti substrate to form nano-tubular surface has been reported recently and found to be suitable for high sensitive gas sensor applications [6]. Understanding the formation of nano-tubular structure of the anodized Ti surface is important in order to have controlled dimensions for specific applications. Pitting has been considered to initiate pore formation in the anodic oxide film. However, pitting considered from corrosion point of view would be different, as it involves break down of barrier layer leading to localized dissolution of bare substrate; whereas, pitting from anodization point of view leads to pore formation only in the outer oxide layer keeping the barrier layer intact. Therefore, the mechanism of pit initiation during localized corrosion cannot be extended to pore formation during anodization even though fluoride ions are found to
be necessary for formation of porous anodic film of titanium.

2. Experimental
Microstructure of the as-received material was evaluated by polishing using standard metallographic procedure and etching with a solution containing 85 mL water + 5 mL HF +10 mL HNO₃. A stainless steel (304) electrode served as a cathode. The anodization was carried out at 20V using a rectifier. The anodization current was monitored continuously from the rectifier itself. The electrolyte used, being 2M NaSO₄ + 0.138M NaF in a beaker containing 200mL distilled water. The anodized samples were properly washed with distilled water to remove the occluded ions from the anodized solutions, dried in an air oven, and processed for characterization. The anodized nanotubular oxide arrays were annealed in a oxygen atmosphere at 500°C for 3 h in a muffle furnace.

3. Results and discussion

3.1. Anodization in 2M NaSO₄ + 0.138M NaF solution
If fluoride ions are necessary for porous anodic film formation then addition of fluoride as NaF could be less hazardous than HF addition from personal-safety point of view. The current recorded during anodization of Ti decreased drastically from an initial value of about 100mA to about 2mA within a few milliseconds and the trend continued for about 200s. Then the current started to increase and reached a steady state value, as shown below.

![Current density vs Time graph](image)

3.2. Mechanism of self-ordered nano-tubular oxide formation
The sequence of nano-tubular oxide layer formation during anodization of Ti could be described as:

1. formation of a passive inner barrier-type film during first few seconds of application of anodization potential;
2. thickening of barrier layer and subsequent micro-fissuring, normally referred as formation of ‘easy paths’ [7,8];
3. secondary oxide nucleation through these ‘easy paths’ and pore nucleation;
4. coverage of the secondary oxide on the entire surface and growth of pores;
5. pore separation to form individual, self-ordered nanotubes.

The samples were observed under a field emission scanning electron microscopy to record the surface morphology. X-Ray Diffraction (Co target (λ=1.7889)) study is carried out on a selected group of samples before and after annealing.
SEM photograph of self-ordered TiO$_2$ nanotubes at constant anodization voltage of 20V for 1 hour. Different tube diameters has been found to exist as reported.

SEM photograph of TiO$_2$ nanotubes by anodization for 2 hours at 20V. Increase in tube diameter is due to increased anodization period.

4. Conclusions

- Room temperature anodization of Ti at 20V in 2M NaSO$_4$ solution with addition of 0.138M NaF resulted in self-ordered nanotubular oxide structure.
- NaF addition proved better results than HF addition.

- Separation of individual nanotubes of TiO$_2$ layer from the interconnected nano-pores could be attributed to the possible repulsion forces of the cation vacancies.
- Increasing the coating time increases the size of nanotubes formed on Ti substrate.

References


