

Critical Temperature for Fabrication of Ti Metal Electrode Produced by Alkali, Acid and Heat Treatment in N₂ Gas

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Abstract—It is important for the fuel cell electrodes to show high total surface area, electrical conductivity and ability for catalyst fixation on the surface. On the other hand titanium oxide is useful as an electrode for fuel cell, solar cell, or electrolysis of water, since it can fix catalyst, dye and enzyme on its surface. In the present study, titanium (Ti) metal was chemically and thermally treated to form nano structure with high specific surface area, conductivity, scratch resistance and ability for catalyst fixation on its surface. Ti metal electrode with nano-network structure composed of titanium nitrides, titanium oxynitride and titanium oxide on its surface was prepared by NaOH and HCl solution treatments and subsequent heat treatments in N₂ gas. The effect of the temperature of heat treatment in N₂ gas on the structure, total surface area and conductivity of the Ti metal surface were studied. The fine network structure with high total surface area was formed on the surfaces of the Ti metal heated at 600°C to 1000°C. However, it was partially densified over 900°C. The electrical conductivity became higher with increasing temperature of the heat treatment because of the formation of the highly conductive titanium nitrides and oxygen deficient titanium oxide. Consequently, the highly conductive Ti metal electrode without reducing its total surface area could be prepared, when it was heated at 850°C. A redox catalyst could be fixed on the treated titanium metal surface.

Index Terms—Titanium, electrode, surface treatment, nano-structure, catalyst, fuel cell.

I. INTRODUCTION

It is quite important that electrode for electro chemical reactions such as fuel cell and water electrolysis system has large reaction area. Therefore, nano-size titanium oxides are gaining more attention, since they can fix the large amount of catalyst on its surface due to their high surface area. On the other hand, our research groups found that nano-network layer composed mainly of titanium oxide can be produced on the surface of the titanium metal by NaOH solution treatment and heat treatments in air environment [1]-[3]. This technique was established not for electrode but for biomaterials use. The nano-structure formed on its surface has a graded structure and show high scratch resistance, but does not show high conductivity because of the formation of fully crystalized anatase (TiO₂) during the heat treatment

process. Therefore the atmosphere of the heat treatment was changed from air to N₂ gas to provide high conductivity. In the present study, the effects of temperature of the heat treatment in N₂ gas on the structure, total surface area and electrical conductivity of the nano-network structure prepared on the surface of the treated Ti metal were studied.

II. MATERIALS AND METHOD

Commercial pure titanium (Ti>99.5%, Nilaco Co., Japan) was cut into the size of 10 × 10 × 1 mm³, abraded with #400 diamond plates, and washed ultrasonically in acetone, 2-propanol, and ultrapure water for 30 min each. These specimens were soaked in 5 ml of 5M-NaOH aqueous solution at 60°C for 1 h, gently rinsed with ultrapure water, subsequently soaked in 10 ml of 0.5 mM HCl solution at 40°C for 3 h, washed with ultrapure water and rapidly dried under N₂ gas flow. Thus treated specimens were subsequently heated up to 1000°C at a rate of 2.5°C/min, kept for 1 h and then followed by cooling at a rate of 2.5°C/min to ambient temperature under 99.999% N₂ gas flow with 1.5 L/min in an atmosphere furnace (Motoyama, Japan). During the heat treatment process in N₂ gas, the specimens were set in a tailored alumina vessel with a hole of 1 mm in diameter covered by a porous Ti filter to reduce oxygen contamination in the N₂ gas.

Surfaces of the specimens were examined by a field emission scanning electron microscope (FE-SEM: S-4300, Hitachi Co., Japan) and thin-film X-ray diffractometer (TF-XRD: RINT-2500, Rigaku Co., Japan). Scratch resistance against abrasion of the surfaces was examined by a scratch-tester machine (CSR-2000, RHESCA Co., Ltd., Japan).

III. RESULTS AND DISCUSSION

A. Morphology

The FE-SEM images of the surface morphologies of the given specimens by various treatments are shown in Fig. 1. The fine nano-network structure was formed by the first NaOH treatment. It did not change essentially by the following HCl and heat treatments irrespective of the atmosphere at the heat treatment. The formed nano-network structure became denser with the increasing depth from the top surface and its thickness was about 600 nm. This means that the graded structure was formed by these treatments. The total surface of the treated specimen after the heat treatment in N₂ became about 100 times more than that of untreated

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titanium metal by these surface treatments.

As shown in the Fig. 1, the fine structure did not change basically even after the subsequent heat treatment below 850°C, while it was slightly densified after heat treatment at 900°C. This indicates that the formed fine network structure was gradually disappeared and the total surface was gradually decreasing with increasing temperature of the heat treatment in N₂ gas.

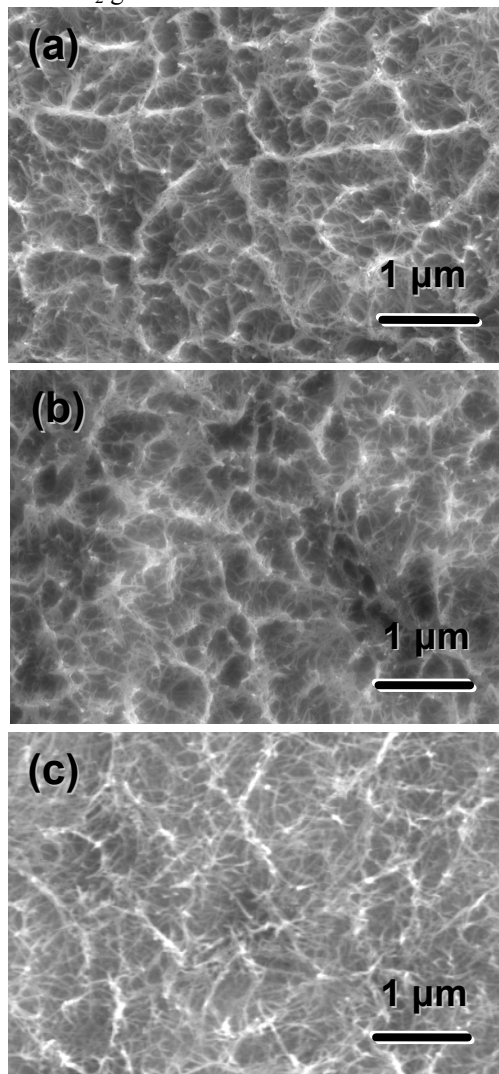


Fig. 1. FE-SEM images of the surface of the Ti metals subjected to the NaOH, HCl and heat treatments in N₂ gas for 1h at (a) 800, (b) 850 and (c) 900°C, respectively.

B. Phase Structure

It is revealed by thin film X-ray diffraction analyses that the fine network prepared by the NaOH, HCl and heat treatments was composed of titanium nitrides (TiN and Ti₂N), Ti oxynitride (TiO_xN_y) and titanium oxide with oxygen deficiency. It is also revealed by the depth profile analyses of X-ray photoelectron spectroscopy (XPS) and Glow discharge-optical emission spectroscopy (GD-OES) that titanium oxide was mainly formed near the surface and titanium nitrides in deeper area on the surface of the Ti metal.

The TF-XRD patterns of the given specimens by various treatments are shown in Fig. 2. The sodium hydrogen titanate (Na_xH_{2-x}Ti₃O₇) was formed by NaOH treatment. It was changed into hydrogen titanate (H₂Ti₃O₇) by HCl treatment as a result of the exchange of the sodium and hydronium ions.

The hydrogen titanate was transformed into anatase (TiO₂) and rutile (TiO₂) by the heat treatment in Air [3]-[5]. However, new phase did not appear by the heat treatment in Ar. Two kinds of titanium nitride such as TiN, oxynitride and Ti₂N and oxide such as anatase with small amount of Ti₄O₇ were formed on the surface of the titanium metal by the heat treatment in N₂.

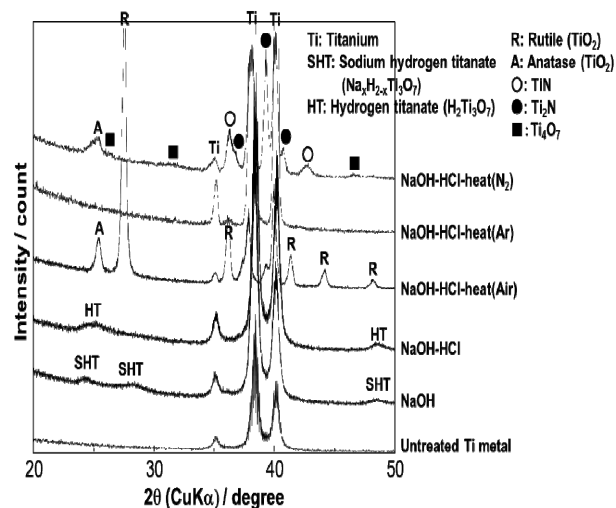


Fig. 2. TF-XRD patterns of the surface of titanium metal treated with NaOH and HCl solutions, subsequently subjected to heat treatment in various atmosphere.

The scratch resistance of the titanium metal after NaOH and NaOH-HCl treatments were both around 6 mN and very weak. It dramatically increased to about 100 and 70 mN by the heat treatment in Air and N₂ atmosphere, respectively, while it decreased to about 3 mN by the heat treatment in Ar. The scratch resistance obtained for Ar condition was too low for the practical application. The increase in scratch resistance for Air and N₂ conditions were attributed to the formation of hard materials of titanium oxide and/or titanium nitride, while the decrease for Ar condition was attributed to the lack in the formation of any crystalline phase.

C. Catalyst Fixation and Electrochemical Study

A redox catalyst such as ferrocene with phosphate end group could be fixed on the surface of the Ti metal prepared by NaOH, HCl and heat treatments in N₂. By the FT-IR analysis, the peaks around 1050 and 1080 cm⁻¹ attribute to P-O-Ti bond was detected. This indicates that the hydrogen titanate formed on the treated titanium surface and phosphate group in ferrocene catalyst chemically combines to form P-O-Ti bond. However, the Ti metal prepared by chemical and heat treatments in Air did not show any peaks attribute to P-O-Ti bond. This indicates that the Ti metal treated chemically and heated in Air could not fix the catalyst on its surface. The Ti metal prepared by NaOH, HCl and heat treatments in N₂ showed the redox wave by cyclic voltammetry measurement. However, this wave was not observed on the titanium metal treated chemically and heated in Air.

D. Total Surface Area

It was previously revealed by our group that the total

surface of the Ti metal increased more than 100 times by the NaOH and HCl solution treatments because of the formation of nano-structure on its surface as shown in Fig. 1. In the present study, the total surface areas of the Ti metals prepared by heat treatments in N_2 gas for 1 h at different temperatures after NaOH and HCl treatments were examined. As shown in Fig. 3, the total surface areas of the Ti metals did not decrease even after the heat treatment below 850°C, while decreased above 900°C.

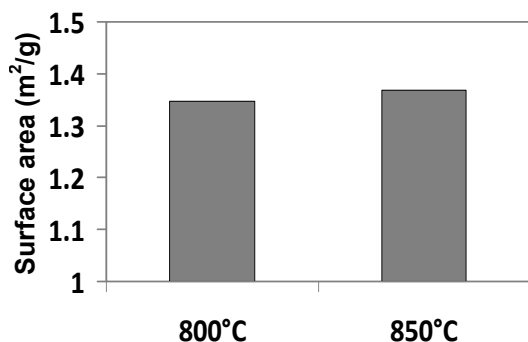


Fig. 3. The bar graph of the total surface areas of the Ti metals subjected to the NaOH, and HCl solution treatments and the heat treatment in N_2 gas for 1 h at 800 or 850°C.

E. Electrical conductivity

The electrical resistances of the Ti metals treated with NaOH and HCl solutions and followed by the heat treatment in N_2 gas for 1 h at 700, 800 and 850°C, respectively, were shown in Fig. 4. The resistances became lower, in other words its conductivity increased with increasing temperature of the heat treatment. This is due to the formation of highly conductive titanium nitride such as TiN and Ti_2N and oxygen deficient titanium oxide.

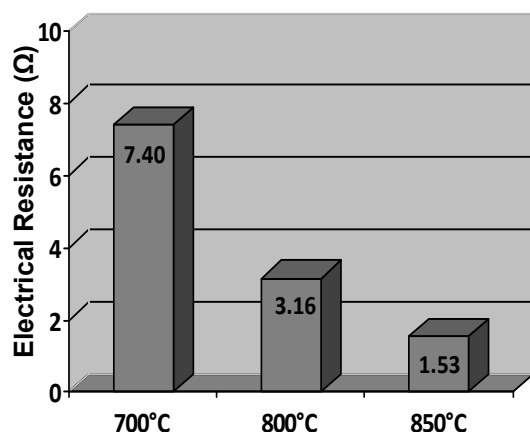


Fig. 4. The bar graph for electrical resistances of Ti metal subjected to the NaOH, and HCl solution treatments and the heat treatment in N_2 gas for 1 h at 700, 800 or 850°C.

Based on the data which was shown in this study the chemically treated sample in NaOH aqueous solution for 1 h and HCl aqueous solution for 3 h and subjected to N_2 gas at 850°C for nitridation shows more electrical conductivity and

no change in total surface area compare to the samples which were treated at 800 and 900°C. Therefore the 850°C temperature is critical temperature to prepare a nano structure with highest electrical conductivity and total surface area.

IV. CONCLUSION

Nano-network structure was prepared on Ti metal surface by the chemical and heat treatments. The phase structure of the chemically treated surface was composed of titanium nitrides (TiN and Ti_2N), Ti oxynitride (TiO_xN_y) and titanium oxide with oxygen deficiency. The total surface decreased due to the densification and the conductivity increased due to the formation of the highly conductive titanium nitride titanium oxide with oxygen deficiency with increasing temperature of the heat treatment. The Ti metal prepared by NaOH, HCl and heat treatments in N_2 showed the redox wave by cyclic voltammetry measurement. The Ti metal subjected to heat treatment at 850°C showed the highest total surface area and the electrical conductivity. Conclusively, the Ti electrode with high specific surface area, conductivity and ability for catalyst fixation on its surface can be prepared by the present method, and additionally 850°C is the critical temperature among all possible temperatures for nitridation of Ti metal surface covered by using this method.

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