Corrosion Resistant Evaluation of Oxygen Solid-Solution Strengthened Pure Titanium

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ABSTRACT

Titanium and its alloy have passive state film, which were formed on the surface by oxidation and water in atmosphere. Titanium shows superior corrosion resistance due to the protection of passive state film. Recently, oxygen solid-solution strengthened pure titanium that made by powder metallurgy process is developed to achieve high strength, high ductility and low cost. However, evaluation of corrosion resistant property has not been carried out. For the purpose of evaluating the corrosion resistance of the material quantitatively, we employed electrochemical methods. Four kinds of oxygen solid-solution strengthened pure titanium with different TiO₂ contents (0, 0.6, 1.0 and 1.5 mass%) and pure titanium were prepared. Potentio-dynamic polarization curve measurement and electrochemical impedance spectroscopy were used for these materials. According to the results of polarization curve, corrosion rate of oxygen solid-solution strengthened pure titanium increased with oxygen level. However, it shows approximately equivalent corrosion resistant to pure titanium. The results of electrochemical impedance spectroscopy suggest that the corrosion mechanism of solid-solution strengthened pure titanium is consistent with pure titanium.

Keywords: solid-solution strengthened titanium, TiO₂, corrosion mechanism, polarization curve, electrochemical impedance spectroscopy

1. INTRODUCTION

Titanium and its alloys are widely used as industrial materials because of their excellent characteristics such as lightness, corrosion-resistance and high-strength. However, they are expensive in general. Especially, the Ti-6Al-4V alloy that is lightweight and having the highest strength is too expensive to be used for usual products as it is hard to work and contains an expensive rare metal, vanadium. This limits its application to specific industries like aircraft or competition machine that can accept its higher price. In recent years, the
study on solid solution strengthening by interstitial impurities for pure titanium has progressed [1]. Consequently the new alloy has been developed, that is fabricated using powder metallurgy with TiO₂ powder for controlling oxygen concentration in solid solution and has a finer crystalline structure [2]. This strengthened titanium alloy (0.80 mass%) by oxygen solid solution shows higher strength and ductility than those of the Ti-6Al-4V alloy (oxygen content is 0.20 mass%) and expected as a new light weight, corrosion-resistant and high strength material replacing the Ti-6Al-4V alloy.

A superior corrosion-resistance of titanium arises from passive film formation on the surface by the reaction of oxygen and moisture in the air. The film protects the bulk titanium effectively. As the oxygen solid solution strengthened titanium contains none of metallic elements such as Al or V unlike existing alloys, it is not likely to undergo galvanic corrosion which is caused by the difference in potential at the interface between the titanium matrix and compounds composed of those elements. However, higher content of oxygen solute may lead to deterioration of the corrosion-resistance, which is still unknown.

This study aims to evaluate corrosion-resistance of titanium after solid solution strengthening by oxygen quantitatively and to investigate an influence of sintering on the corrosion-resistance in comparison with that of existing pure titanium for industrial use. It is also intended to investigate an influence of the oxygen content on the corrosion-resistance of titanium after solid solution strengthening by oxygen.

2. Specimens and Experimental Procedure

2.1 Specimens

Four oxygen solid solution strengthened titanium with different TiO₂ content were prepared; Ti-0% mass TiO₂, Ti-0.6 mass% TiO₂, Ti-1.0 mass% TiO₂ and Ti-1.5 mass% TiO₂.

Commercially available pure titanium, TP-270 was also prepared as a standard specimen for the corrosion-resistant material and the effect of sintering on the corrosion-resistance was also evaluated as it is an ingot material.

Starting materials for the fabrication of the oxygen solid solution strengthened titanium were pure titanium powder (provided by TOHO Tech Corp., a purity of 99.5%, median diameter: 21.9 um) and titanium oxide (TiO₂) powder (provided by KISHIDA Chemical Corp., a purity of 99.5%, mean particle radius: 1.7um). After blending of these materials with pre-fixed ratios (0, 0.6, 1.0, 1.5 mass% TiO₂), they were encapsulated in a plastic bottle (air atmosphere in a bottle) and mixed using a table ball mill (AV-2 made by ASAHI RIKAI Corp.) at a rotation rate of 90 rpm during 7.2 ks. For titanium specimens having more than 1.0 mass% TiO₂ powder, zirconia (ZrO₂) media balls of 10 mm in diameter were added into TiO₂ powder by 10 to 1 in weight (powder : media) to avoid agglomeration of TiO₂ particles with an additional 21.6 ks mixing period. Mixed powder was consolidated by using a spark plasma sintering machine (SPS-1030S made by SPS SINTEX Corp.) at 1073K and 6 Pa with a loading pressure of 30 MPa during 1.8 ks to obtain sintered billets of 42 mm Φ. The oxygen solid solution strengthened titanium densified completely was fabricated by hot extrusion process applied to the sintered billet immediately after preheating at 1273K during 180 s in an Ar atmosphere.

As a sample preparation for electrochemical evaluation, wet-polishing using fine abrasive papers of 80 to 2000 grades was operated. Surfaces of these
specimens were cleaned with ethyl alcohol promptly. Then, they were immersed in acetone and cleaned by ultrasonic vibration during 0.3 ks. The specimen after these treatments was fixed to the electrode and the surface was coated with silicone rubber for insulation except a reaction area of 1.0\times10^{-4} \text{m}^2 for electrochemical measurements to be mentioned below.

2.2 Polarization Curve Measurements by The Potentio-dynamic Method

Measurement of polarization curve by the potentio-dynamic method was carried out to investigate polarization behavior and corrosion rate \( I_{\text{corr}} \) in a natural immersion for each specimen. Experimental apparatus used in this study is shown in Figure 1. There are a H shaped electrolysis vessel with 5.0\times10^{-4} \text{m}^3 capacity containing both a specimen cell and a platinum cell, an intermediate cell and an Ag/AgCl (3.33 kmol⋅m^{-3}KCl) referential electrode cell in an isothermal bath. The specimen cell is connected to the referential cell in a bridge or a salt bridge configuration via an intermediate cell. Specimen electrode, platinum electrode and referential electrode are connected to a potentiostat respectively, which can be controlled by a personal computer and potentials and log values of current density are recorded automatically. All the potential values in this study were referred to Ag/AgCl (3.33 kmol⋅m^{-3}KCl) electrode. Testing liquid used was 2.5M \( \text{H}_2\text{SO}_4 + 0.2 \text{M NaCl (pH}= -0.51) \) solution which provided an environmental condition easily generating stress corrosion cracking of a stainless steel. The electrode vessel was kept on an isothermal bath controlled to 298K to maintain the temperature of the solution at 298K. The solution was deoxidized completely by using pure nitrogen gas. The test electrode was immersed into the deoxidized test solution and kept for 1.8ks. Then, the potential was varied from -1.2V to +0.8V in a scanning range of the potential with a sweeping rate of +5.0\times10^{-4} \text{Vs}^{-1}. Corresponding current density was measured and the value was shown in a logarithmic scale. The corrosion rate of each specimen was evaluated from the obtained polarization curve using the Tafel extrapolation method [3].

Figure 1. Experimental apparatus for electrochemical measurement.
2.3 Electrochemical Impedance Measurements

Potential-controlled electrochemical impedance measurements were carried out to clarify the results of the polarization curves by the potential measurements using the potentio-dynamic method and to investigate the corrosion resistance $R_{ct}$ of each specimen and the mechanism of the corrosion in detail. As is the case in the polarization curve measurements using the potentio-dynamic method, a H shaped electrolysis vessel with $5.0 \times 10^{-4}$ m$^3$ capacity containing both a specimen cell and a platinum cell, an intermediate cell and an Ag/AgCl (3.33 kmol-m$^{-3}$ KCl) referential electrode cell were placed in an isothermal bath and the specimen cell was connected to the intermediate cell via a glass tube bridge, then, the intermediate cell was connected to the referential electrode cell via a salt bridge. Specimen electrode, platinum electrode and referential electrode were connected to the potentiostat respectively. A HZ-3000 potentiostat made by HOKUTODENKO was combined with a potentiostatic polarization circuit and a 5080 Frequency Response Analyzer (hereafter quoted as FRA) made by NF Corporation. A sine wave of amplitude $\pm 10$ mV generated from the latter was superimposed to the polarized sample electrode via the potentiostat. This enabled to evaluate the amplitude and the phase of the alternative current that flowed and the impedance could be evaluated by comparing to the applied voltage. The impedance was measured automatically by the computer supplied with the FRA [3].

Testing liquid in this study was 2.5M H$_2$SO$_4$+0.2M NaCl (pH=-0.51) solution which provide an environmental condition easily generating stress corrosion cracking of a stainless steel. The electrode vessel was kept on an isothermal bath controlled to 298K to maintain the temperature of the solution at 298K. The solution was deoxidized completely by using pure nitrogen gas. The test electrode was immersed into the deoxidized test solution and kept for 1.8 ks. Then, the potentials of anode and cathode were regulated to $E_{corr} \pm 0.0$V, $E_{corr} \pm 0.02$V, $E_{corr} \pm 0.04$V, $E_{corr} \pm 0.06$V, $E_{corr} \pm 0.10$V, $E_{corr} \pm 0.15$, and $E_{corr} \pm 0.20$V respectively referred to a natural immersion potential $E_{corr}$ and an alternative current of amplitude 10mV was superimposed in the frequency range of 100 kHz to 1 mHz. Impedance was measured at 5 different frequencies during a frequency change of an order of magnitude for a superimposed AC component.

A real part ($\text{Re} \ Z$) and an imaginary part ($\text{Im} \ Z$) of measured impedance were plotted in a complex plane and an electrode impedance locus was obtained. This graph is known as the Nyquist diagram. In this case, a half plane above a real axis -Im (the 1st and 2nd quadrants) represents a capacitive reactance and a lower half plane (the 3rd and 4th quadrants) represents an inductive reactance on the other hand. The peak frequency $f_0$ of a capacitive semi-circle is also indicated in the impedance locus [4].

An important parameter of corrosion characteristic, namely a corrosion resistance (charge transfer resistance) $R_{ct}$ can be obtained from a diameter of the capacitive semi-circle. The corrosion resistance is proportional to the reciprocal of the corrosion rate. An electric double-layer capacitance $C_{dl}$ and a time constant $\tau_0$ can be calculated from the corrosion rate and $f_0$, the peak frequency of the capacitive semi-circle on the Nyquist diagram by using equation (1).

\[ (2\pi f_0)^{-1} = R_{ct} \times C_{dl} = \tau_0 \] (1)
3. Results and Discussion

3.1 Influence of Sintering on Corrosion-resistance

Experimental result of the oxygen solid solution strengthened titanium of sintered Ti-0 mass% TiO₂ was compared to that of the pure titanium for industrial use, TP-270 that is an ingot material containing almost no oxygen to examine an influence of sintering on corrosion-resistance.

3.1.1 Results of polarization curve measurements

Polarization curves were obtained using the potentio-dynamic method for both specimens to compare the polarization behavior and the corrosion-rate $I_{corr}$. Results are shown in Figure 2. The vertical axis shows a potential referred to Ag/AgCl (3.33 kmol·m⁻³ KCl) electrode, while the horizontal axis shows a current density corresponding to each potential in a logarithmic scale.

![Figure 2. Polarization curve for the specimens of Ti in 2.5M H₂SO₄ + 0.2M NaCl solution at 298 K.](image)

A comparison of polarization behaviors of these specimens reveals that a polarization curve of a sintered material Ti-0 mass% TiO₂ and that of an ingot material TP-270 are approximately overlapped or almost identical polarization curves. A natural immersion potential $E_{corr}$ was -0.56V both in a sintered material Ti0 mass% TiO₂ and in an ingot material TP-270.

Corrosion current density (hereafter quoted as $I_{corr}$) which represents the corrosion rate under a natural immersion was obtained using the Tafel extrapolation method in order to compare corrosion rates of both specimens. $I_{corr}$ of an ingot material TP-270 was 0.15 Am⁻² at a potential level of $E_{corr} = -0.56V$, while $I_{corr}$ of a sintered material Ti-0 mass% TiO₂ was 0.16 Am⁻² at a potential level of $E_{corr} = -0.56V$. Therefore, it can be said that a corrosion rate of a sintered material Ti-0 mass% TiO₂ is almost same as that of an ingot material TP-270. These indicate that the polarization behavior and corrosion rate of a sintered material Ti-0 mass% TiO₂ are comparable to those of an ingot material TP-270. It can be concluded that sintering scarcely affects a corrosion rate on the basis of these measurements of polarization curves.

3.1.2 Results of electrochemical impedance measurements

Potential-controlled electrochemical impedance measurement was applied to compare the corrosion mechanism and the corrosion resistance $R_p$ for both specimens. Obtained results were plotted on the Nyquist diagram: Results of controlled potential application to an anode-side in incremental steps are shown in Figures 3 and 4, while these to a cathode-side are shown in Figures 5, 6 and 7. The left-hand side shows the results of an ingot material TP-270, and the right-hand side shows results of a sintered material Ti-0 mass% TiO₂. Favorable capacitive semi-circles can be seen for both specimens in the results of potential application on anode-side. Meanwhile, this capacitive semi-circle is equivalent to a
parallel circuit consists of a corrosion resistance $R_c$ and a capacitance of an electrical double layer $C_{dl}$. Comparison of capacitive semi-circles of both specimens reveals that both an ingot material (TP-270) and a sintered material (Ti-0 mass% TiO$_2$) have two capacitive semi-circles and their sizes are almost identical. Further, the peak frequencies of the first semi-circles of both specimens are identical or only one adjacent measuring frequency apart. In addition, a negative loop was observed in the Nyquist diagram both in an ingot material TP-270 and in a sintered material (Ti-0 mass% TiO$_2$) when the controlled potential $E_{corr} = +0.20\text{V}$ was applied in the former and $E_{corr} = +0.15\text{V}$ was applied in the latter. This suggests that forming of a passive film on a surface of the specimen had almost completed [4]. By comparing the results of potential application on cathode-side, both an ingot material (TP-270) and a sintered material (Ti-0 mass% TiO$_2$) show single capacitive semi-circles and their sizes are almost identical. Further, the peak frequencies of capacitive semi-circles of both specimens are placed at the same frequency or displaced only one adjacent frequency apart.

![Figure 3](image-url). Electrode impedance excursion of Ti in 2.5M H$_2$SO$_4$ + 0.2M NaCl solution at 298 K on $E_{corr}$, $E_{corr} + 0.02\text{V}$, $E_{corr} + 0.04\text{V}$ and $E_{corr} + 0.06\text{V}$. 
Figure 4. Electrode impedance excursion of Ti in 2.5M H$_2$SO$_4$ + 0.2M NaCl solution at 298 K on $E_{\text{corr}} + 0.10$ V, $E_{\text{corr}} + 0.15$ V and $E_{\text{corr}} + 0.20$ V.

Figure 5. Electrode impedance excursion of Ti in 2.5M H$_2$SO$_4$ + 0.2M NaCl solution at 298 K on $E_{\text{corr}}$, $E_{\text{corr}} - 0.02$ V and $E_{\text{corr}} - 0.04$ V.
Figure 6. Electrode impedance excursion of Ti in 2.5M H₂SO₄ + 0.2M NaCl solution at 298 K on $E_{corr}$ 0.06 V and $E_{corr}$ 0.10 V.

Figure 7. Electrode impedance excursion of Ti in 2.5M H₂SO₄ + 0.2M NaCl solution at 298 K on $E_{corr}$ 0.15 V and $E_{corr}$ 0.20 V.
An important parameter of corrosion characteristic, the charge transfer resistance (hereafter quoted as $R_{ct}$) that represents corrosion resistance was evaluated from a diameter of a capacitive semi-circle in the Nyquist diagram for each controlled potential. The influence of potential on a corrosion resistance $R_{ct}$ can be seen in Figure 8 for both specimens.

It can be found that $R_{ct}$ of an ingot material (TP-270) is almost identical to that of a sintered material (Ti-0% mass TiO$_2$) on both an anode-side and a cathode-side by comparison. The maximum $R_{ct}$ was reached at a natural immersion potential for both specimens.

These mean that dissolution of sintered material is caused by the same corrosion mechanism as that of an ingot material and values of corrosion resistance are similar. Therefore, it becomes clear that significant effect cannot be found on corrosion-resistance by sintering based on the results of electrochemical impedance measurements.

### 3.2 Influence of Oxygen Content on Corrosion-resistance

Experimental results on oxygen solid solution strengthened titanium with various TiO$_2$ content were compared to examine an influence of oxygen content on corrosion-resistance; Ti-0 mass% TiO$_2$, Ti-0.6 mass% TiO$_2$, Ti-1.0 mass% TiO$_2$, and Ti-1.5 mass% TiO$_2$.

#### 3.2.1 Results of polarization curve measurements

Polarization curves were obtained using the potentio-dynamic method for each specimen to compare the polarization behavior and the corrosion-rate $I_{corr}$. Results are shown in Figure 9. The vertical axis shows a potential referred to Ag/AgCl ($3.33$ kmol⋅m$^{-3}$ KCl) electrode, while the horizontal axis shows a current density corresponding to each potential in a logarithmic scale.

In comparison with polarization behavior of each specimen, a slight increase in current density of the anode-side was found with an increase in oxygen content from Ti-0 mass% TiO$_2$ that scarcely include oxygen, Ti-0.6 mass% TiO$_2$, Ti-1.0 mass% TiO$_2$, to Ti-1.5 mass% TiO$_2$. An increase in a natural immersion potential was also found along with it. This indicates that cathode reaction is
promoted by an increase in oxygen content.

A slight increase in current density with increase in oxygen content was also found in an anode-side. However, an increase in a natural immersion potential is thought to be caused by more active cathode reaction rather than anode reaction.

$I_{\text{corr}}$ in a natural immersion was evaluated and compared by use of the Tafel extrapolation method for each specimen to examine promotion effect of the cathode reaction due to increase in oxygen content in detail. Figure 10 shows an influence of the oxygen content on corrosion rate $I_{\text{corr}}$. Based on this, it can be concluded that the influence given to a corrosion rate is small because a difference of $I_{\text{corr}}$ by the oxygen content is suppressed within two times even though $I_{\text{corr}}$ increases linearly with the oxygen content.

$I_{\text{pass}}$ was evaluated which is a corrosion rate in the passive state and considered as the most important factor in titanium material. In this study, 0.5V was defined as the representative potential and the current density under that condition was measured for each specimen and considered as $I_{\text{pass}}$. Figure 12 shows an influence of oxygen content on the corrosion rate $I_{\text{pass}}$ in a passivation region. It can be seen that $I_{\text{pass}}$ increases linearly with increase in oxygen content. However, an inclination of the line becomes much smaller than that of corrosion rate in a natural immersion $I_{\text{corr}}$ shown in Fig.10. An influence of oxygen content on a corrosion rate is smaller in a passivation state ($I_{\text{pass}}$) than in a natural immersion ($I_{\text{corr}}$).

Based on this, it was found that an influence given to a corrosion rate is small in the oxygen solid solution strengthened titanium even though promotion of the cathode reaction and the increase in corrosion rate in a passivation state were observed.
Therefore, it can be concluded that an influence of oxygen content on corrosion resistance is small in the oxygen solid solution strengthened titanium, which have a corrosion resistance almost equivalent to that of the industrial pure titanium.

3.2.2 Electrochemical impedance measurements

Potential-controlled electrochemical impedance measurements were carried out to compare the corrosion-resistance of each specimen. Obtained results were plotted in the Nyquist diagram and the important parameter of corrosion characteristic $R_{ct}$ was extracted from a diameter of a capacitive semi-circle in the Nyquist diagram for each controlled potential. Figure 13 shows an influence of the potential on a corrosion-resistance for each specimen.

By comparing $R_{ct}$ of each specimen, it was found that all the specimens showed their maximum values at a natural immersion potential. Further, a slight decrease in $R_{ct}$ at a cathode-side was found with an increase in oxygen content from Ti-0mass%TiO$_2$ that scarcely include oxygen, Ti-0.6 mass% TiO$_2$, Ti-1.0 mass% TiO$_2$ to Ti-1.5 mass% TiO$_2$, accompanied with an increase in a natural immersion potential. Promotion of the cathode reaction with increase in oxygen content was found from the results of electrochemical impedance measurements. In addition, a slight decrease in the value of $R_{ct}$ of an anode-side with increase in oxygen content was also found.

![Figure 12. Influence of passivity current density at 0.5V on the mass% of TiO$_2$.](image1)

![Figure 13. Influence of potential on charge transfer resistance.](image2)
From these results, it can be said that corrosion resistances of both an anode and a cathode-side decrease slightly with increase in oxygen content in the oxygen solid solution strengthened titanium. However, their changes in magnitude are small from the perspective of influence on the corrosion resistance. Accordingly, it was confirmed that an influence of oxygen content on the corrosion resistance is small in the oxygen solid solution strengthened titanium. It was also confirmed that the corrosion-resistance of it is almost equivalent to that of the industrial pure titanium by electrochemical impedance measurements.

4. CONCLUSIONS

Major results in this experimental study are summarized as follows:

1) The corrosion-resistance of the oxygen solid solution strengthened titanium is almost equivalent to that of the industrial pure titanium in spite of the fact that the measurements of polarization curves of the former showed a slight increase in the corrosion rate according to increase in oxygen content.

2) Electrochemical impedance measurements showed that the corrosion-resistance of the oxygen solid solution strengthened titanium decreases with increase in the oxygen content. However, the change is small enough to show equivalent corrosion-resistance to that of the pure titanium and the same corrosion mechanism causes dissolution in both materials.

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