Corrosion Resistance of Titanium Alloy on the Overpack for High-level Radioactive Waste Disposal*

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Abstract
Crevice corrosion of titanium and its alloys were investigated in 10% sodium chloride at 100 °C simulating the environment of the overpack near the seaside. The pH and Chloride ion concentration inside the crevice were monitored by using W/WO₃ and Ag/AgCl microelectrode, respectively. The pH and Cl⁻ concentration within the crevice were calculated from the standard potential-pH and potential-log [Cl⁻] calibration curves. The effect of Mo on the crevice corrosion of titanium was mainly studied. The passivation behavior of the titanium and Ti-15%Mo alloy were also studied using electrochemical impedance studies. A marginal decrease in pH and increase in Cl⁻ ion concentration were observed for pure titanium at 100 °C, where there was large increase of the crevice current. On other hand, there was no apparent change in pH and Cl⁻ ion activity inside the crevice for Ti-15%Mo alloy, where there was no increase of the crevice current. Based on the results, it has been documented that the Ti-15%Mo alloy was not susceptible to crevice corrosion in 10% NaCl solutions at 100 °C. The corrosion reaction resistance (Rₑ) was found to increase with addition of Mo as an alloying element and also increase with applied anodic potential. Hence, Mo is able to be an effective alloying element, which enhanced the crevice corrosion resistance of titanium under the environment simulating the overpack near the seaside.

Key words: Overpack, Titanium, Crevice Corrosion, Impedance, Microelectrode, Monitoring, pH, Chloride

1. Introduction
It is required that the overpack should be guaranteed the geological disposal of high-level radioactive waste for more than several hundred years. However, candidate materials of the overpacks are suffered from the corrosion by the attack of surrounding groundwater. The corrosion of metals depend mainly on the chemical composition of groundwater, and in Japan, there is a high possibility to contain high chloride solution from the sea. Moreover, the temperature on the surface of overpack is up to 100 °C by the radioactive waste. In these corrosive condition Ti alloy is able to be a candidate material. While extensive studies have been carried out on the corrosion behavior of Ti, very little information is available on the crevice corrosion in the simulating environment of the overpack under the ground near the seaside. In general, excellent corrosion resistance offered by Ti is directly related to formation of stable surface oxide film of TiO₂. However, Ti is susceptible to crevice corrosion when exposed to environments containing high concentration of chloride at elevated temperatures 1-6). Much attention is paid to improve the stability of the surface film of Ti by suitable alloying. Although Pd bearing Ti alloy was...
developed and it could have high resistance against crevice corrosion at 100 °C, Pd is very rare and expensive. Instead of Pd-Ti alloy, we have been interested in Mo bearing Ti-alloy, however, its investigations of the crevice corrosion are scarce. On the other hand, it is important to understand the mechanism of crevice corrosion of Ti alloys. Hence, in the present work, the changes in chloride ion concentration, pH and potential within the crevice were monitored for long periods of exposure by using microelectrodes. These results and the results obtained from polarization and EIS techniques were correlated to understand the crevice corrosion resistance of 15%Mo bearing Ti-alloy.

2. Experimental Method

The pH microelectrode was fabricated from 0.3 mm diameter tungsten (W) wire, which was partially sealed in a capillary tube. The W wire was then oxidized in 10% nitric acid solutions for 18 hours, formed the W/WOx microelectrode. The chloride ion selective microelectrodes of Ag/AgCl were made from 0.3 mm silver wire partially sealed in a capillary tube. And they were electrolyzed in 0.1M HCl solutions under the potential of 500 mV for 12 hours.

As shown in Figure 1, the working electrodes of Ti and alloy were covered in a Teflon shim of 0.1mm thickness and tightly screwed on an acrylic board to make the crevice cell. The counter electrode was large and the same metal as working one. Three capillary holes of 1 mm diameter were made over the acrylic board to insert the microelectrodes such as Ag/AgCl, W/WOx and micro-SSE. The current in the crevice was measured using zero resistance ammeter. Moreover, the potential inside the crevice was measured by using the micro-SSE. The chloride ion concentration and pH were determined from their corresponding potential - log [Cl⁻] and potential – pH calibration curves.

The specimens of pure Ti and 15%Mo Ti-alloy were cut in to 1 x 1 x 0.2 cm for the polarization and EIS (Electrochemical Impedance Spectroscopy) studies. These studies were conducted in simulated crevice solution that was 20% NaCl solution adjusted to different pH values at 100º C. The polarization behavior measurements were performed with a scan rate of 1 mV/sec. A frequency response analyzer (FRA) was used for EIS measurements and experiments were conducted with an amplitude of 10 mV and the frequency range from 10 KHz to 3 MHz. Impedance spectra were obtained with specimens in open circuit (OCP) condition and in passive region of 500 mV. The brake down behavior of passive film was observed by EIS using the specimens kept at OCP up to 24 hours after setting at 500 mV (passive region) for 1 hour.

![Schematic diagram of crevice cell using micro electrodes for monitoring.](image-url)
3. Results and Discussion

3.1 Crevice corrosion monitoring

Figure 2(a) shows the results of changes in crevice current, potential inside and outside the crevice of pure Ti and 15%Mo bearing Ti-alloy in neutral 10% NaCl at 100°C. Absence of significant change in crevice current was noted for both Ti and 15%Mo Ti-alloy up to 96 hours of monitoring, and then the crevice current of Ti increased suddenly to higher values. At the same time simultaneous change of potential outside and inside the crevice of Ti from -130 mV to -196 mV and -165 mV to -306 mV respectively were observed in Figure 2(b) and (c). These changes in potentials to more active region reflected the decrease in stability of passive film over the Ti surface and the lead to active dissolution reaction \(^1,3-4\) within the crevice. The potential inside the crevice was more sharply detected by micro SSE than that outside of the crevice. The absence of changes in the above parameters for 15%Mo Ti-alloy suggested the passive film of alloy was kept stably in this test.

Figure 3 depicted the changes in pH and chloride ion concentration inside the crevice of pure Ti and alloy in 10% NaCl at 100°C. An increase in chloride ion concentration was shown from 10% to 17% at 96 hours within the crevice. This was expected that in order to maintain electro neutrality within in the crevice, migration of chloride ions from the bulk to crevice was occurred. The pH within the crevice slowly shifted towards lower values and reached a value of pH 2.3 after 96 hours for Ti, which was indicating the predominant dissolution reaction was operating within the crevice. This process resulted in producing Ti ions, and subsequently undergoing hydrolysis reaction to produce hydrogen ions and contributing to further change in pH to lower values. \(^4\)

The change in solution chemistry observed in the crevice by the combination of increased acidity and higher chloride concentration might result in the continuous propagation of crevice corrosion on pure Ti after 96 hours. These phenomena were corresponding to the shift of crevice potentials from passive to active region and the increase in crevice current. However, only marginal changes were observed in the above parameters for the Mo bearing Ti-alloy. This behavior of alloy suggested that the addition of Mo was effective to keep the passive film stably even in the high chloride and high temperature condition. In this way, Mo bearing Ti-alloy had no susceptibility to crevice corrosion at high temperature of 100°C.

![Fig. 2 Changes of (a) Crevice Current, (b) Potential outside and (c) inside crevice.](image1)

![Fig. 3 Changes of (a) pH and (b) NaCl concentration in the crevice.](image2)
3.2 Open circuit potential (OCP) monitoring and potentiodynamic polarization measurements

To understand the effect of Mo alloying on the crevice corrosion of Ti alloy in higher chloride environment, open circuit potential (OCP) monitoring was carried out in Figure 4. The sample had no crevice assembly and the solution was simulating the crevice condition that was 20 % NaCl at different pH values at 100 °C. At pH 4.0 solution Ti exhibited a passive OCP value of – 420 mV which was shifted to less noble values with a decrease in pH. Thus, Ti was thought to have easily the crevice corrosion under pH 4.0 of 20% NaCl solution. These results were corresponding to those of Figure 1. It was understood that the increase of Cl ions and decrease of pH were proceeding in the crevice, and the pH was attained below 4.0, then, active corrosion was occurred. On the other hand, a quite different behavior was observed with alloy that showed an OCP value of – 210 mV in pH 0.5 solution, which was the passive condition. In this way, it was found that under the solution of 20 % NaCl at very low pH of 0.5, 15%Mo bearing Ti-alloy could keep the passive condition. Thus, it was expected that 15%Mo bearing Ti-alloy had no corrosion in the crevice of 0.5 pH and 20%NaCl.

The polarization behavior measurements of Ti and 15%Mo Ti-alloy were performed in simulated crevice environment of 20 % NaCl at pH 1.0 in Figure 5. High cathodic current was observed for 15% Mo Ti-alloy than that of Ti. Against the active peak current of 9.8 X 10⁻⁴ mA.cm⁻² obtained by Ti, there was no apparent peak with the alloy in pH 1.0 environment. The higher cathodic current and lower active peak were contributed to ennoble the corrosion potential (Ecorr) around -200mV which was within the passive region. In this way, 15% Mo Ti-alloy kept the passive condition even in low (1.0) pH solution. Therefore, alloy could keep the passive film even in the acidic crevice environment. However, the passive current density of alloy was slightly higher than that of Ti. This might be due to the transpassive dissolution of Mo through the passive film. It was found that the ennobling of corrosion potential and keeping the passive condition resulted in the high resistance of 15% Mo-Ti alloy in the simulating crevice solution.

3.3 Electrochemical Impedance Spectroscopy (EIS) Observations

To confirm the influence of Mo alloying on the resistance of the passive film against crevice attack, the EIS measurements were carried out. Figure 6 showed the impedance spectra for Ti and 15%Mo Ti-alloy with no crevice assembly at OCP condition in different pH values of 20% NaCl at 100° C. The impedance spectra observed for Ti in pH 0.5 and 1.0 solutions suggested the presence of two capacitances. The low resistance value at low frequency region suggested an active dissolution of pure Ti in low pH value.
However, Ti was thought to have the unstable film on the surface and show the capacitance in the impedance spectra. Thus, the capacitance at low frequency was corresponding to the double layer capacitance, and that at high frequency was caused by the unstable film.

On the other hand, the 15% Mo Ti-alloy exhibited very high resistance values of 4400 and 4600 Ohm.cm² even in highly acidic conditions of pH 0.5 and pH 1.0 respectively. The impedance spectra observed in alloy showed the presence of only one capacitance. This enumerated that the EIS spectra for the alloy were completely dominated by the passive film properties and revealed the superior stability of the passive films in low pH condition. These results were corresponding to the polarization curves.

In this way, the impedance spectra obtained for Ti and 15% Mo-Ti alloy were depicted by the equivalent circuit as shown in Figure 7. As for pure Ti, the impedance spectra from Figure 6 showed the presence of only one capacitance at pH 2.0, which was corresponding to the passive condition of Fig 7(a). And at pH 0.5 and 1.0 the impedance spectra were shown active condition of Fig 7(b). The 15% Mo Ti-alloy exhibited the impedance spectra of passive condition of Fig 7(a) even in the acidic solution of pH 0.5.

![Impedance spectra](image)

**Fig.6 Impedance behavior of Ti and 15%Mo Ti-alloy at OCP in the various pH of 20% NaCl at 100ºC.**

![Equivalent circuits](image)

**Fig.7 Equivalent circuits for Ti and 15Mo Ti-alloy in acidic solutions of 20% NaCl at 100ºC.**

(a) passivated, (b) active condition
From the impedance spectra in Figure 6, the plot of resistance ($R_t$) values at 3 mHz were given in Figure 8. Here the resistance value of 3mHz was corresponding to (a) the film resistance ($R_f$) at passivated condition, and (b) corrosion reaction resistance ($R_{ct}$) at active one, respectively. Actually, $R_t$ was changed from $R_{ct}$ to $R_f$ by the making of the passive film. Moreover, the unstable film was shown for the impedance spectra for Ti. In this paper, the corrosion resistance was estimated by using $R_t$ values at 3mHz including both the passive ($R_f$) and active ($R_{ct}$) condition. Pure Ti exhibited a very low $R_f$ value of 85 and 163 at pH 0.5, 1.0, and higher value of 4500 Ohm.cm$^2$ at pH 2.0. Thus, critical pH for the breaking down the passive film of pure Ti was existing around 2.0. In the case of 15% Mo-Ti alloy, $R_t$ kept higher values even in the low pH (0.5 and 1.0), which showed the passive condition. Thus, the estimation of $R_t$ was corresponding to the results of OCP in Fig.3 and could evaluated the corrosion resistance of Ti and alloys in the simulating crevice conditions.

In order to examine the passive behavior, the specimens were passivated at 500mV for one hour and impedance spectra were obtained at the same potential. The impedance spectra of Ti and 15%Mo-Ti alloy were shown in Figure 9. The passive film capacitances were observed for Ti and alloy, and the impedance values were very high. Moreover, the 15%Mo-Ti alloy showed high $R_t$ value of 15000 Ohm.cm$^2$ than that at OCP condition in Figure 6. Thus, $R_t$ was increased by ennobling the potential in the passive region. At low frequency region, the capacitances were slightly shown for Mo bearing Ti alloy in the impedance spectra. These capacitances were thought to be corresponding to the transpassive behavior by Mo, which were under the examination.

It was important to investigate the breakdown behavior of the passive film on Ti and 15%Mo bearing Ti-alloy for longer duration in simulating crevice condition. Thus, samples were passivated at 500 mV for one hour, then, kept at open circuit condition (OCP) for 24 hours. The potential decays of the samples were monitored in Figure 10. The OCP of Ti in pH 0.5 and pH1.0 environments reached the low value of around -700 mV within 1 hour. This was almost the same OCP value observed for Ti in these pH values in Figure 6. The breakdown of passive film on Ti was occurred in a very short time. However, potential decay of 15%Mo Ti-alloy in those pH revealed high value around -270mV even after 24 hours, which indicated that the passive film of alloy was kept after 24 hours.

In the same way, the stability of the passive film on Ti and 15%Mo Ti-alloy for longer duration was evaluated by using EIS method. Passivated at 500mV, then, kept at OCP for 24 hours, the impedance spectra were taken in Figure11.
In pH 0.5 and pH 1.0 solutions, R_t of pure Ti showed very low values of 130 and 160 Ohm.cm², which was almost similar behavior as observed in OCP condition. Thus, in the case of Ti, the passive film was broken down completely and active corrosion occurred at pH 0.5 and 1.0. In the case of 15%Mo Ti-alloy, the impedance spectra showed only one capacitance and high R_t value of 9100 Ohm.cm² at pH 0.5 for 24 hours. The passive film of alloy was kept at pH 0.5 and showed high impedance values after long duration. It was revealed that 15%Mo bearing Ti-alloy could keep the passive film even in the solution of high chloride concentration and high temperature.

3.4 Crevice corrosion behavior of Ti and Mo bearing Ti-alloy

In this paper, crevice corrosion of Ti and Mo bearing Ti-alloy were monitored by microelectrodes under the simulating condition for the overpacks. In the case of pure Ti, the concentration of chloride ions was increased and pH was reducing in the crevice, also, the crevice current was increased. This behavior was explained by the hydrolysis reaction in the crevice, and pure Ti showed the susceptibility to crevice corrosion at a temperature of 100°C. On the other hand, in the case of Mo bearing Ti-alloy, there were little changes in the concentration of chloride ions and pH in the crevice, also, little increase in crevice current.

From the OCP and polarization measurements, it was explained that pure Ti could not keep the passive film in the solution of low pH and high chloride concentration. Thus, according to the hydrolysis reaction in the crevice, the concentration of chloride ions was increased and pH was reducing, then, the passive film of pure Ti was easily to be broken down. At 100°C, the depassivation pH was estimated almost 4.0 for the pure Ti in high chloride solution. However, the corrosion potential of Ti-alloy was kept in the passive region by the high cathodic current and low anodic peak current caused by the Mo addition. In the case of Mo bearing Ti-alloy, the passive film was kept even in the solution of low pH of 0.5 and high chloride concentration.

EIS measurement confirmed the above statement by showing the corrosion resistance R_t. R_t of pure Ti showed very little value in the low pH solution, and even in the case that sample was kept at passive region, R_t was immediately changed to low value because of the break down of the films. However, R_t of alloy was kept at high value even in the solution of...
low pH and high chloride concentration, which showed that the passive film was kept. In this way, it was found that Mo bearing Ti-alloy could keep the passive film in the simulating crevice solution and show the high resistance against the crevice corrosion under the environment simulating the overpack near the seaside.

4. Summary

It was elucidated from the microelectrode monitoring that the pH within the crevice environment was reduced and reached very low values with a simultaneous increase in chloride ion concentration. Moreover, higher crevice corrosion resistance was observed for 15%Mo Ti-alloy in more acidic and higher chloride environments. Polarization measurements showed that the cathodic current for 15%Mo Ti-alloy was increased and the corrosion potential was existing within the passive region even in the acidic solution. EIS revealed that 15%Mo bearing Ti-alloy could keep the passive film in the acidic solution and show the high impedance resistance against the crevice corrosion even in the high chloride concentration at 100 °C, which explained that this alloy could use under the environment simulating the overpack near the seaside.

References