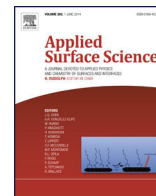




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Water molecules effect on pure Ti passive film structure in methanol solution

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ABSTRACT

To understand the role of water on titanium SCC properties in methanol solutions, composition and structure of the passive film were studied using X-ray photoelectron and electrochemical impedance spectroscopies. The passive film consists of the inner compact layer and a porous outer layer. The inner layer thickness is less than 4 nm and decreases with the increasing water content. Water improves the passive film properties, thus changes SCC susceptibility by altering the hydrogen bonding of methanol and reacting with titanium preferentially.

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1. Introduction

Titanium and its alloys have been extensively used in the past several decades as materials for orthopedic or dental implants, and medical devices [1–4]. Moreover, they have been proven to be technically superior and cost-effective construction materials for a wide variety of aerospace, industrial, marine and commercial applications [5,6]. Growth of titanium alloys' industrial, marine and commercial usage is expected, resulting in expansion of existing applications and the development of new ones. Titanium exhibits excellent corrosion resistance in a broad range of environments, including acids, alkali, natural water and industrial chemicals [7–10], mostly due to the protective surface film, which spontaneously forms in air. The oxidation of Ti: $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ is irreversible ($\Delta G_0 = -892.9 \text{ kJ mol}^{-1}$), yielding a native oxide film [11], even in aqueous solutions [12].

More attention should be paid to titanium alloys' passive film composition and structure, since they are closely related with the titanium excellent corrosion resistance. Titanium alloys' behavior under simulated physiological conditions has been extensively studied, especially for the implant applications [13–16]. Most of these studies used XPS and EIS to investigate the passive film behavior, which formed on the alloys surface when immersed in different

electrolytes. This film is typically composed of the inner and the outer layers. For traditional applications, titanium demonstrates excellent corrosion resistance, however, corrosion and stress corrosion will occur in certain solutions, such as methanol and other organic solvents [17–19]. Early studies have already found that water can play an inhibitive role during the corrosion and stress corrosion of titanium and its alloys [20–22]. The formation of the tenacious protective titanium oxide surface layer is responsible for the superior corrosion resistance of titanium. Normally the passive film is only a few nanometers thick, consisting predominantly of amorphous titanium dioxide. The surface film on titanium serves a dual role: (i) it can prevent direct contact between the environment and the bare metal; (ii) it can act as a barrier for hydrogen diffusion into the metal. The research shows that in anhydrous alcoholic solutions, the surface of most metals undergoes unstable passivation. The intermediate formation plays the role of a membrane inhibitor, rather than the passive oxide layer. It is removed at higher overpotentials, which has effects in uniform, or pitting corrosion [23,24]. Stability of the surface layer seems to grow with the alcohol molecular size. Oxide passivation in anhydrous alcoholic solutions is possibly due to the presence of undissociated acid molecules, which provide oxygen. Such molecules undergo decomposition on the metal surface and become the source of oxygen for the passivation process [25]. Intergranular or pitting attacks can occur under potentiostatic control at potentials more anodic than the breakdown potential of the oxide film. No attack is observed at potentials lower than the breakdown potential [26].

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In a previous study [27], pure titanium tended to crack along an intergranular path in the presence of applied stress in anhydrous methanol solutions. A large tensile stress, induced by the passive film, is a necessary condition for the α -Ti SCC in the methanol solution. At the same time, both film-induced stress and SCC susceptibility in the methanol solution are reduced by increasing water content [28]. The fracture morphology shows a discontinuous change from intergranular fracture to dimple fracture. Moreover, the film-induced and the film breaking stresses on pure titanium in methanol solution show discontinuous change with the water content. The film-induced tensile stress and fracture load decreased significantly when water content was more than 0.2% [29]. However, less attention has been paid to the passive film generated on the pure titanium immersed in methanol solutions with or without water. In particular, the thickness of the passive film is difficult to measure because it is very thin (usually in the range of several nanometers). Also, the passivation mechanism of Ti in methanol solution remains uncertain. Thus, it is necessary to clarify the real effect of water in methanol on the titanium passive film.

Present work contributes to an understanding of the behavior of the passive film formed on Ti in methanol solutions by studying the role of water. In this paper, the electrochemical impedance behavior of commercially pure (CP) titanium immersed in methanol and the composition of the in situ formed passive film were investigated as functions of water content.

2. Experimental

All experiments were conducted using commercially pure titanium with the following composition: Ti 99.9 wt.%, Fe 0.1 wt.%, N 0.008 wt.%, H 0.006 wt.%. The specimens were obtained from the rod for the electrochemical tests and X-ray photoelectron spectroscopy measurements, respectively, as described below in detail. Before use, the specimens were heat treated at 720 °C for 1 h in a vacuum furnace (less than 5 Pa pressure) and cooled therein. Solutions of pure methanol, AR grade, without water, and with different water amounts of 0.1 vol.%, 0.2 vol.% and 1 vol.% were used.

2.1. Electrochemical experiments

Electrochemical experiments were conducted in a standard three-electrode cell with 3 cm² working electrode exposed area, having a platinum sheet as a counter electrode and a saturated silver–silver chloride (Ag–AgCl) electrode as the reference. Tests were carried out under automatic iR compensation (the solution resistance and the cell time constant were compensated for). Prior to any immersion, the working electrodes were abraded with 2000 grit silicon carbide paper. Open-circuit potential (E_{oc}), polarization curves and the electrochemical impedance spectroscopy (EIS) measurements for each condition were carried out on the freshly prepared samples. Potentiodynamic polarization scans were acquired at a scan rate of 20 mV min^{−1} in the −850 mV to 400 mV range vs. Ag–AgCl reference. Electrochemical impedance spectroscopy measurements were conducted at the open-circuit potential. The impedance spectra were acquired in the 0.01 Hz to 100 kHz frequency range with a perturbation signal of 10 mV. The experimental results were interpreted based on the equivalent circuits, using a suitable fitting procedure performed using the Z-view program.

2.2. XPS measurements

XPS samples were sectioned after the heat treatment, ground to the 2000 grit, and electropolished in a mixture of 60% H₂SO₄, 25% HF and 15% glycerin at approximately 30 V in reference with a titanium cathode to remove the surface oxide film, then immersed

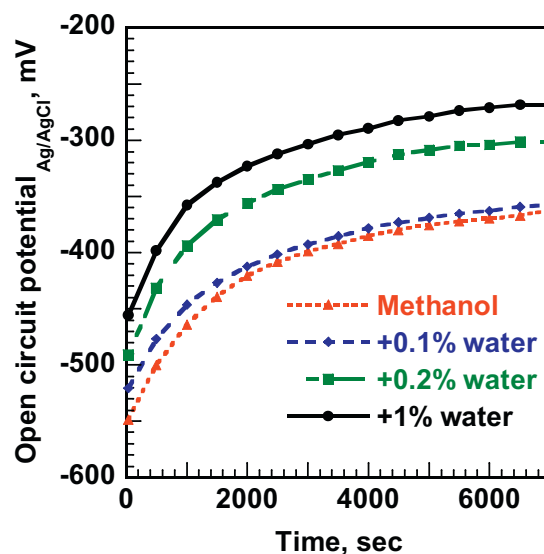


Fig. 1. Open-circuit potential vs. time profiles for pure Ti immersed in methanol.

in methanol solutions for 3 h. XPS measurements were performed in an AXIS ULTRA^{DLD} spectrometer (Kratos Instruments) using non-chromatized Al K α radiation (1686.6 eV) operating at 150 W.

3. Results and discussion

3.1. Electrochemical behavior of Ti in methanol solution

3.1.1. Open-circuit potential and polarization curves

The time profiles of the open-circuit potential obtained from the samples, shown in Fig. 1, are quite similar. E_{oc} changes quickly toward less negative potentials at the very beginning. After that, E_{oc} changes more slowly, until it plateaus at 100 min, not changing significantly after that. This fact indicates that titanium experiences spontaneous passivation as a result of the oxide film forming in the methanol solution. Cai et al. [30] reported a similar phenomenon, where an initial increase in the E_{oc} , followed by stabilization (−205 mV to −85 mV vs. SCE) was observed in all specimens (CP Ti, Ti-6Al4V, Ti-6Al-7Nb and Ti-13Nb13Zr), suggesting that a protective passive film formed rapidly on the metal surfaces in the artificial saliva. Similar behavior of the samples (CP Ti, Ti-6Mo, Ti-10Mo, Ti-15Mo, Ti-20Mo) in the Ringer physiological solution was observed by Oliveira et al. [31].

It can be observed that Ti in methanol with 1% water had the least negative E_{oc} values, as seen in Fig. 1. At the same time, Ti in methanol with 0.2% water had the most negative values, while Ti in methanol with 0.1% water and in methanol without water had similar negative values. These results indicate that the addition of water into methanol, up to 0.2%, seems to improve the protection characteristics of titanium spontaneous oxides. This conclusion agrees with the idea that the oxide film stability on titanium alloys in methanol and ethanol solutions is strongly influenced by the water content [21].

Fig. 2 shows the anodic behavior of titanium in the pH neutral methanol solution, containing various amounts of water. It can be seen from the polarization curves that the passive current density of all alloys was similar. The nature of polarization curves indicates that the surface film had more stable passive behavior with the water content greater than 0.2%. Such behavior is similar to the one observed with titanium in aqueous solutions [21]. Fig. 2 shows the inhibiting effect of water in methanol solutions. As expected, water does not affect the ionic conductivity of the surface film, and only increases the breakdown potential.

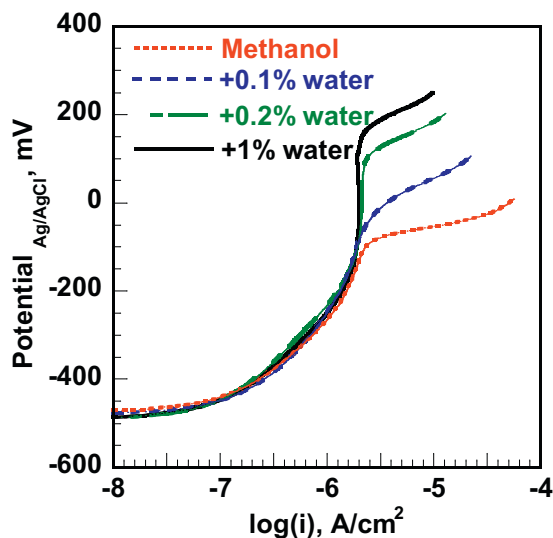


Fig. 2. Polarization curves for pure Ti immersed in methanol.

There is not much fluctuation in the current density near zero potential, observed in the polarization curves. This kind of oscillation has also been reported in the literature for Fe in phosphoric acid, attributed to the competition between film formation and dissolution [32]. It indicated that film formation is the dominant process when CP Ti is immersed in methanol with or without water at potentials lower than the breakdown potential. Both open-circuit and breakdown potentials are increased by the water content, as seen in Figs. 1 and 2, and there is a significant increase between 0.1% and 0.2% water, indicating different properties of the passive film with different water content. Water changes the methanol molecules spatial orientation when six and/or eight methanol molecules form hydrogen-bonded chains and rings [33]. Thus the entropy of the system increases much less than expected when methanol is mixed with water. The discontinuous entropy change affects the electrochemical performance.

3.1.2. Electrochemical impedance spectroscopy

Impedance spectra are presented as the Bode phase and the Bode magnitude plots in Figs. 3 and 4 and for the CP Ti immersed in methanol with various water content, respectively. For all

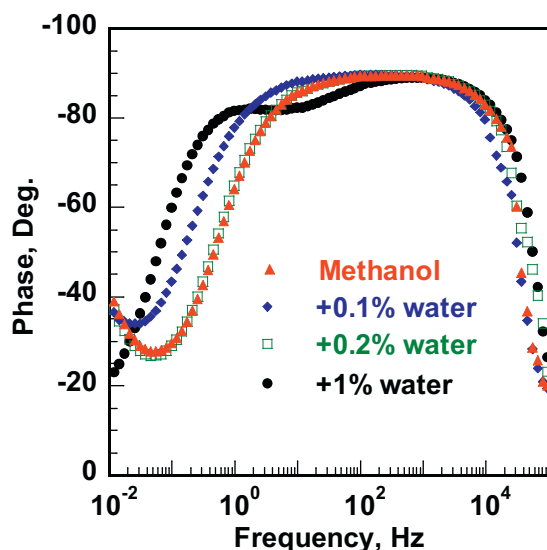


Fig. 3. Bode phase plots for pure Ti immersed in methanol.

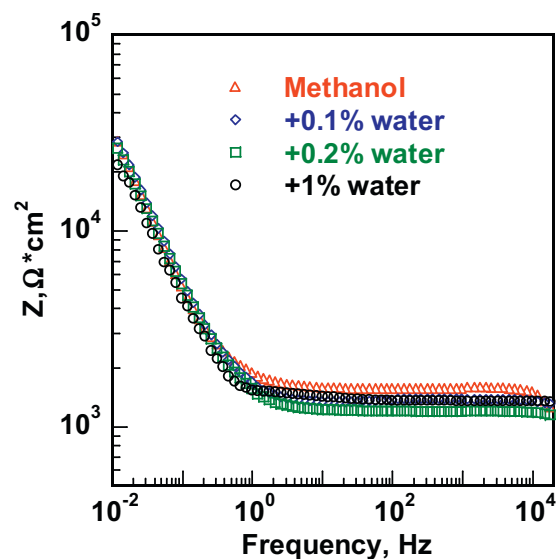


Fig. 4. Bode magnitude plots for pure Ti immersed in methanol.

solutions, the phase angle (Fig. 3) drops toward zero degrees at very high frequencies, indicating that the impedance is dominated by the solution area specific resistance in this frequency range (no phase shift between the current and the potential due to the presence of a resistor in the AC circuit). It may also be noted that the phase angle decreases significantly toward lower values in the low frequency region, demonstrating that the impedance acts as a pure resistance of the surface film. However, the phase remains close to -90° over a wide range of frequencies, indicating a near capacitive Ti response in all solutions. This behavior is indicative of a typical thin passive oxide film present on the surface [34]. Bode magnitude plots, presented in Fig. 4, are also similar in nature in all cases. Bode magnitude plots are characterized by the two distinct regions. In the higher frequency region (1–10 kHz), the Bode magnitude plots exhibit constant $\log|Z|$ values vs. $\log(f)$. This is due to the response of the electrolyte area specific resistance, R_e (resistive region). In the broad low and middle frequency ranges, the spectra display a linear slope of about -1 . This is a characteristic response of the surface film capacitive behavior [34–36].

The chosen equivalent circuit, shown in Fig. 5a, consists of a parallel combination of resistance and capacitance elements (RC) that are in series with R_s , which represents the electrolyte area specific resistance. The circuit is just one of the possible equivalent circuits to fit the impedance spectra [37,38]. The model proposed by Pan et al. [39], describing a bi-layer structure of the oxide film on titanium in a saline environment comprises a dense inner layer of TiO_2 and a porous outer layer. This equivalent circuit can be used successfully to describe the EIS behavior in this paper as well (Fig. 5b). The values of the fitted parameters of the equivalent circuit with various water content are presented in Table 1. A schematic representation of this system is shown in Fig. 5b.

The high frequency parameters R_{pr} and Q_{pr} represent the properties of the reactions at the outer porous passive film/solution interface. The symbol Q signifies the possibility of a non-ideal capacitance (CPE, constant phase element). The impedance of the CPE is given by [40]:

$$Q = Z_{CPE}(\omega) = [C(j\omega)^n]^{-1} \quad (1)$$

where for $n=1$, the Q element reduces to a capacitor with the capacitance C and for $n=0$, to a simple resistor. The parameter R_b coupled with Q_b describes the processes at the inner barrier layer at the electrolyte/dense passive film interface. The parameter R_s varies from $1555 \Omega \text{ cm}^2$ to $1675 \Omega \text{ cm}^2$ and is ascribed to solution

Table 1
Values of fitted parameters of the equivalent circuit of pure Ti in methanol solutions.

H ₂ O (%)	Re (Ω cm ²)	Q ₁ (μΩ ⁻¹ s ⁿ cm ⁻²)	n1	R ₁ (Ω cm ²)	Q ₂ (μΩ ⁻¹ s ⁿ cm ⁻²)	n2	R ₂ (Ω cm ²)
0	1675	1.20×10^{-9}	0.80	2625	2.72×10^{-5}	0.80	2.23×10^5
0.1	1665	1.94×10^{-9}	0.91	8268	2.88×10^{-5}	0.84	2.21×10^5
0.2	1565	4.26×10^{-10}	0.80	8331	2.90×10^{-5}	0.86	6.41×10^5
1.0	1555	2.13×10^{-10}	0.80	14,240	3.01×10^{-5}	0.85	9.17×10^5

resistance. The R_{pr} values are smaller than the R_b values, indicating that the outer porous layer exhibits a smaller resistance than the inner barrier layer. High R_b values are observed in all solutions, confirming the formation of a barrier layer with high corrosion protection ability.

The reciprocal passive oxide capacitance ($1/C_p$) is proportional to the oxide layer thickness. To calculate the thickness, the reciprocal capacitance value can be taken either from the Bode plot at $\log \omega = 0$, where the impedance data give a straight line with a slope of about 1, or from the results of the equivalent circuit parameters fit [41]. One can estimate the layer thickness based on the following equation [42]:

$$d = \frac{\varepsilon \varepsilon_0 r}{C_p} \quad (2)$$

Here, d is the oxide layer thickness, ε is the relative dielectric constant of the oxide, ε_0 the permittivity of the free space (8.85×10^{-14} F cm⁻¹), r is the oxide layer surface and C_p the oxide layer capacitance. Unfortunately, only Q_b can correspond to the capacitance of the inner barrier layer, while Q_{pr} , corresponding to the capacitance of the outer porous layer is unreliable, since the calculation error of the Q_{pr} value of is greater than 20%. The surface roughness and the film thickness differ by orders of magnitude. This is also the reason why the surface film cannot be observed. Thus, the barrier layer thickness slightly decreased, accompanied by improved corrosion protection, as seen in Fig. 6. In other words, the film, which has a better protective role, is not necessarily thicker. This demonstration showed that the thinner layer is better. This result is consistent with the previous study [29]: passive film-induced stress and film mechanical properties of α -Ti in a methanol solution are reduced by water. Thinner passive film means that the volume of the metal oxide generated during corrosion is smaller, so

is the Pilling–Bedworth ratio. That is why the film-induced stress of pure titanium in methanol solution decreased significantly when water content was more than 0.2%. The reduction of the passive film strength can be discussed in the same way. In general, the film strength with similar composition is determined by its thickness. Thinner film is more likely to break under externally applied stress.

3.1.3. XPS surface analysis

XPS O 1s and Ti 2p spectra recorded from the pure Ti samples after immersion in methanol solutions with various water content are shown in Fig. 7. The oxide film formed on the Ti surface in methanol solutions consists mainly of TiO₂, since Fig. 7 shows the Ti 2p_{3/2}, 2p_{1/2} doublet. Fig. 8 shows the Ti 2p signal deconvolution and presents a small amount of trivalent titanium, forming in pure methanol without water. However, the oxide film, formed by adding water to methanol, consists solely of tetravalent titanium TiO₂ with no evidence of the Ti₂O₃ suboxide presence. Tetravalence is the maximum valence of this element, which cannot be further oxidized, so TiO₂ is more stable than other suboxides. Compared with the electrochemical test, water improved corrosion protection ability, ascribed to the stability of the oxide film, improved by water. The presence of Ti₂O₃ suboxide in the passive film makes the passive film not as stable as the passive film with pure tetravalent titanium, TiO₂, although the amount of Ti(III) in the film is actually very small. It acts as a defect, making the passive film more susceptible to breaking [29] and the metal more susceptible to SCC [28].

Based on the previous research [28,29], the mechanism of pure Ti SCC in methanol solution can be inhibited by water, explained by the passive film breakdown theory. Four main mechanisms of passive film rupture exist: penetration mechanism [43]; film breaking mechanism [44]; adsorption mechanism [45], and point defect mechanism [46]. For titanium in methanol, film breaking and point defect mechanisms can be used. For the film breaking mechanism,

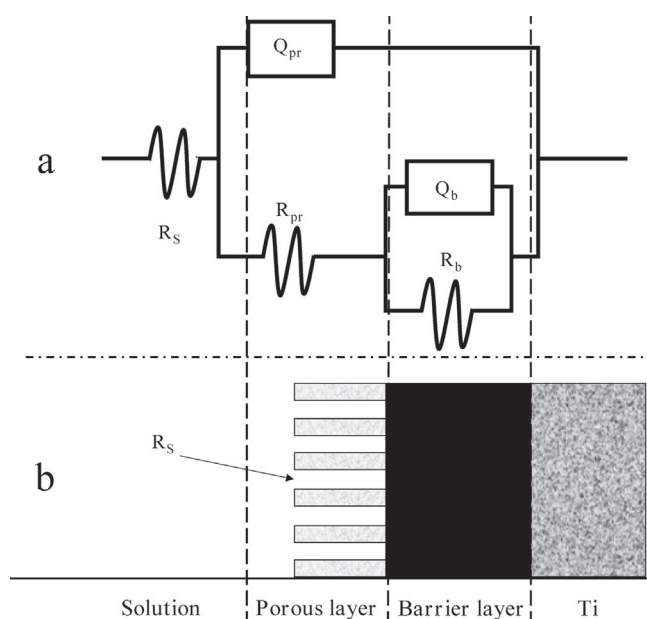


Fig. 5. (a) Equivalent circuit used for fitting the experimental data. (b) Schematic representation of the outer and inner layers for the surface film.

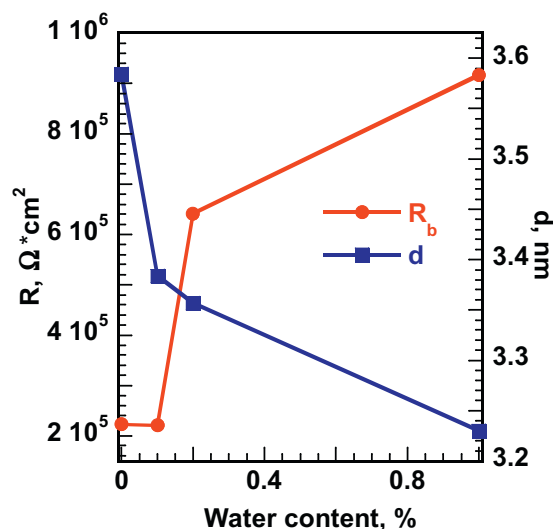


Fig. 6. Resistance and thickness as functions of water contents for the inner barrier layer.

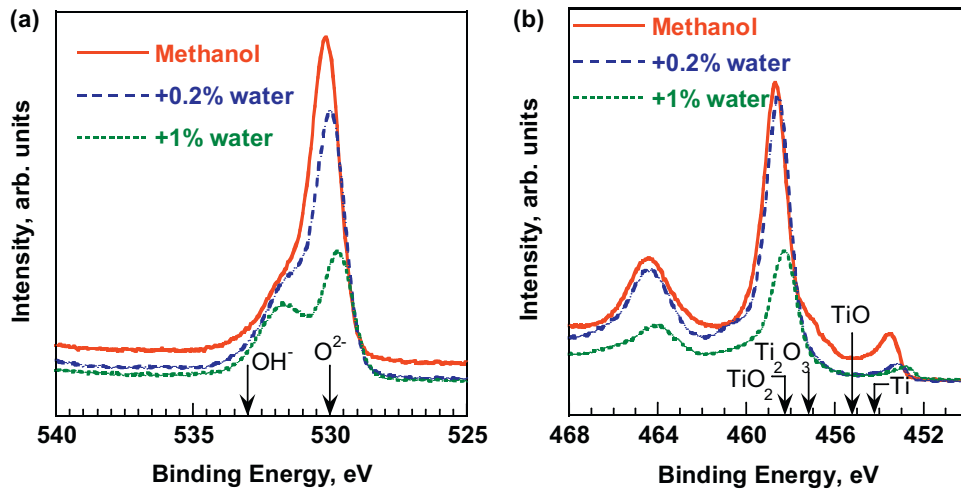


Fig. 7. Normalized (a) O 1s and (b) Ti 2p XPS spectra recorded for pure Ti after immersion in methanol.

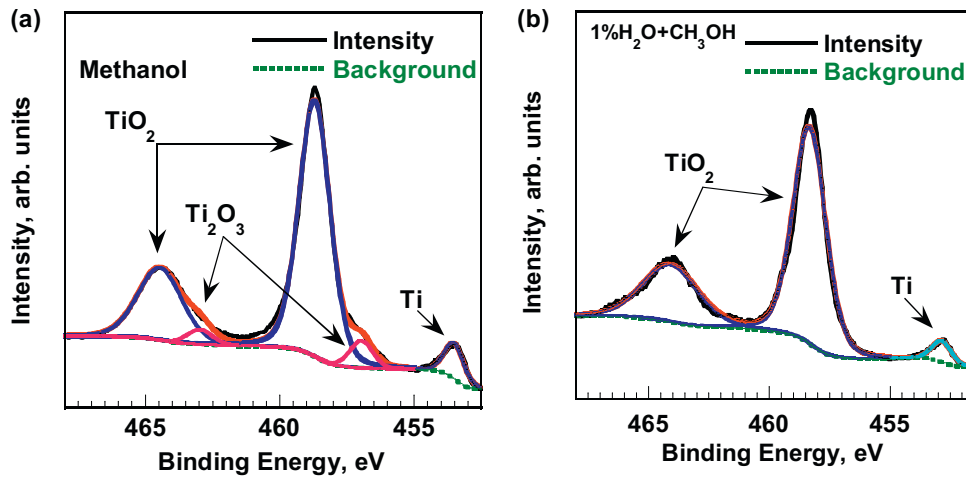


Fig. 8. Deconvoluted Ti 2p XPS spectra for pure Ti after immersion in methanol: (a) no water and (b) 1% water.

the stress generated in the passive film during corrosion would break the film. An additional tensile stress can be generated at the metal/passive film interface during a-Ti corrosion in the methanol solution, while water makes the passive film stronger [29]. For the point defect mechanism, the defects can cause the oxidation to continue. The presence of Ti_2O_3 suboxide in the passive film of Ti in

pure methanol allows for ionic migration, leading to further oxidation. For the synergistic effect of the two mechanisms (as shown in Fig. 9), the passive film formed on titanium in methanol without water can be easily broken, while after adding enough water, the passive film would be strong enough not to be broken. The easier passive film can be broken, the more Ti is susceptible to SCC

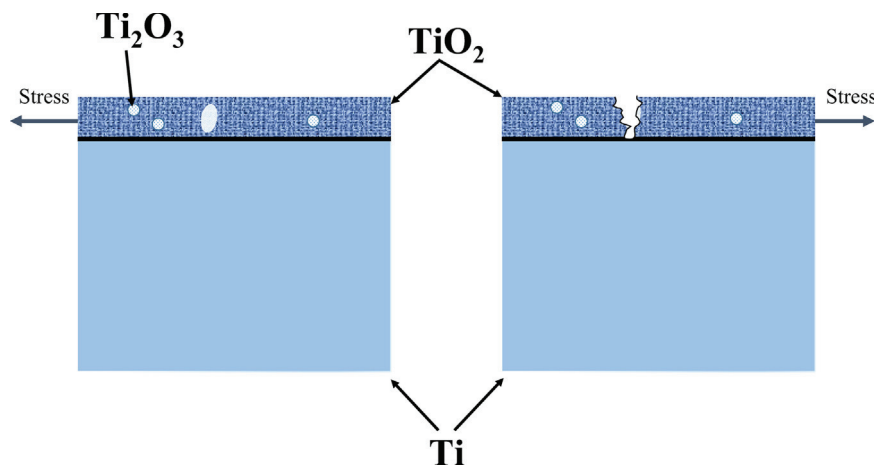


Fig. 9. Schematic representation of the passive film of titanium in methanol breaking due to the synergistic effect of the two mechanisms.

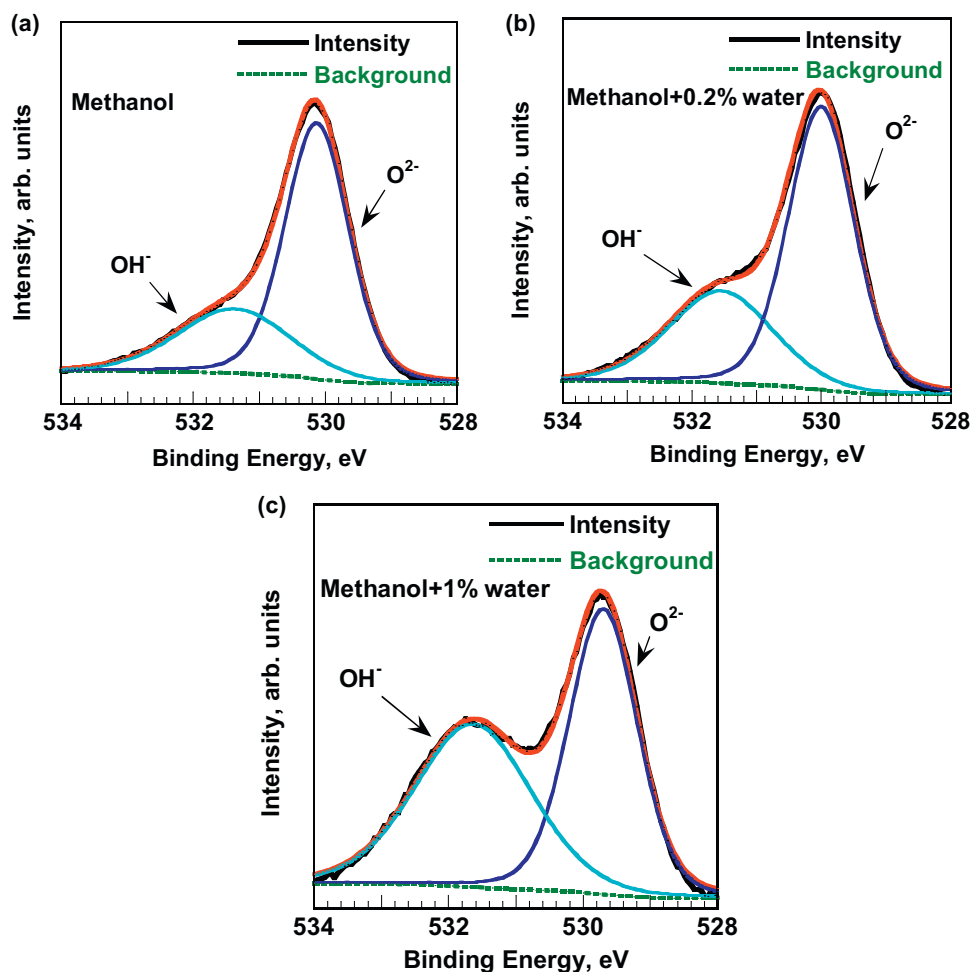


Fig. 10. Deconvoluted O 1s XPS spectra for pure Ti after immersion in methanol: (a) no water; (b) 0.2% water; (c) 1% water.

[47]. Thus, moisture contained in the methanol inhibits the SCC of titanium.

Fig. 10 shows that the O 1s band could be resolved into two peaks, which correspond to O^{2-} and OH^- , respectively, and that the relative amounts of these two species within the films varies with the water content. Fig. 11 shows that a higher percentage of

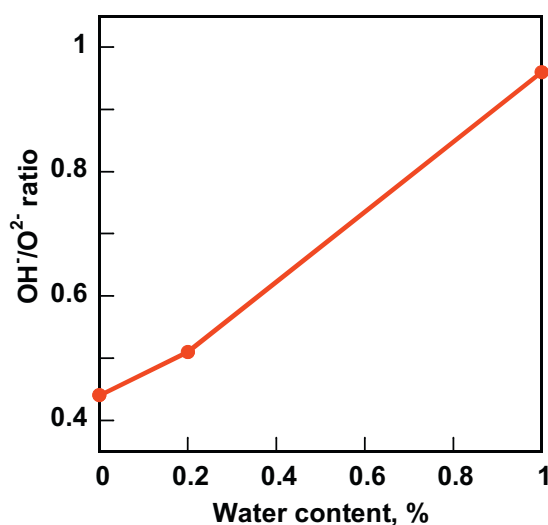


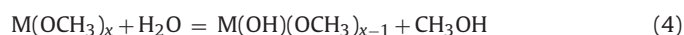
Fig. 11. OH^-/O^{2-} ratio as a function of water content.

OH^- groups was incorporated in the surface film with increased water amount. It is recognized that the high vacuum required for the XPS measurements would have resulted in some dehydration of the films; hence the absolute values for the OH^-/O^{2-} ratio reported in Fig. 11 are unlikely to reflect the true ratio in the oxide films. Nevertheless, the general trend of the increasing OH^- amount incorporated within the film with more water is believed to be valid.

Combining all the experimental results, the inhibition mechanism of water in methanol for pure Ti can be inferred. Once Ti is exposed to methanol, dissolution reaction starts. Ti forms alkoxides when reacting with methanol. In this specific case a methoxide will be formed, following this possible reaction [20]:



Ti dissolves as Ti^{3+} and Ti^{4+} in methanol and forms oxide film, stopping the reaction (3). However, Ti^{3+} is not stable enough and the film can be easily broken, so the film can be penetrated and the reaction will go on. Methoxides can be hydrolysed by water as:



The reaction (4) continues, until $M(OH)_x$ is formed. Thus, reaction (3) will not take place, and the exposed surface will be passivated once again. However, when enough water (here 0.2% is enough) is added, metal dissolution is stopped.

Ti has a very strong bond with oxygen atoms. CH_3OH molecules contain C–H, C–O, and O–H bonds, which all can be inserted with the Ti ion [48], and breaking of the C–H and O–H bonds are

both exothermic reactions. The formation of methoxide $M(OCH_3)_x$ makes it clear that the favorable path is inserting the O–H bond. It is reasonable due to the chemical reactivity order: $O-H > C-O > C-H$ [49]. Compared with methanol, water molecules are much simpler, and contain only one kind of O–H chemical bond that can be inserted. Since the polarity of water is greater than methanol, water is more easily absorbed and reacts preferentially.

4. Conclusions

The composition and the structure of the passive film formed on pure titanium immersed in methanol solution without water, and with different water content play an important role in the stress corrosion cracking process. In order to further reveal the SCC mechanism of pure titanium in methanol, XPS and EIS techniques were used to study the formed passive film. From the XPS and electrochemical studies the following conclusions can be drawn:

1. CP titanium undergoes spontaneous passivation due to spontaneously formed oxide film, passivating the metal surface in the methanol solutions. The passive film formed in methanol without water was predominantly TiO_2 , but contained small amounts of Ti_2O_3 suboxide. When water amount increased to 0.2%, there was only TiO_2 found in the passive film.
2. The EIS spectra can be interpreted in terms of the two-layer model for the oxide film, which consists of a thin barrier inner layer and a porous outer layer. The thickness of the barrier inner layer is no more than 3.6 nm and decreases with the increasing water content.
3. Water can improve the stability and the corrosion protection ability of the passive film by changing the relative values of the OH^-/O^{2-} and Ti^{3+}/Ti^{4+} ratios.

This work complements previous studies of pure titanium SCC in methanol solution. However, the real morphology of the passive film can hardly be observed due to its small thickness.

Acknowledgements

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