



Passive film-induced stress and mechanical properties of α -Ti in methanol solution



Zhi Qin^a, Xiaolu Pang^a, Yu Yan^a, Lijie Qiao^{a,*}, Hai T. Tran^b, Alex A. Volinsky^{b,a}

^a Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, People's Republic of China

^b Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, United States

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ABSTRACT

Passive films play an important role in corrosion and stress corrosion cracking of titanium. Correlation between passive film-induced stress and film mechanical properties on α -Ti in methanol solution with varying water content was investigated. Film-induced stress in the methanol solution was measured by the flow stress differential method, and thin film fracture properties were determined by nanoindentation. For small amounts of water ($\leq 0.15\%$), both film-induced tensile stress and film fracture load were higher. However, the film-induced tensile stress and fracture load decreased significantly in more dilute solutions. Thus, water reduces Ti SCC susceptibility in methanol solution.

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1. Introduction

Stress corrosion cracking (SCC) of α -Ti occurs under anodic dissolution in a methanol solution, and a passive film forms during SCC, or natural corrosion [1,2]. However, adding more water into the solution decreased or ceased altogether α -Ti susceptibility to SCC. SCC of titanium and its alloys in methanol solution had been widely studied for a long time [3–6]. Some additions to the solution could influence the SCC susceptibility [7–9]. A large tensile stress, induced by the passive film, is a necessary condition for SCC of α -Ti in the methanol solution [10]. The film-induced stress variation with electrical potential is consistent with α -Ti susceptibility to SCC in the methanol solution. Both film-induced stress and SCC susceptibility in the methanol solution are reduced by increasing water content [11]. Similar experimental results are found in brass, where the variation of SCC susceptibility of brass in the ammonia solution under various applied potentials is consistent with that of the corrosion-induced stress for the same experimental conditions [12]. The pH value dependence of the susceptibility to SCC of brass in the ammonia solution also agrees with that of the

corrosion-induced stress [13]. Corrosion-induced or film-induced stresses act as additional mechanisms for the corrosion-enhanced dislocation emission and motion, in addition to the divacancies-enhanced dislocation climb. Transmission electron microscopy shows that the corrosion process can facilitate dislocation emission and motion during stress corrosion cracking of brass, 310 stainless steel, α -Ti and Ti₃Al + Nb [11,14–16]. SCC cracks will nucleate in a dislocation-free zone only when the corresponding stress level reaches the critical value. Moreover, the surface film provides an additional driving force, which can facilitate dislocation emission and motion during SCC.

Toshio [17] made a reasonable assumption that the initiation of a crack nucleation starts at a defect in the passive film on stainless steel. Sanderson confirmed that methanol can cause breakdown of the passive film on stressed Ti specimens [18]. Many experiments demonstrated that SCC of most metals started with the breakdown of the surface film [17–24]. It is obvious that surface film plays an important role in protecting metal from being attacked by the external environment during SCC. During SCC of α -Ti in methanol solution passive film forms and plays the following roles. First, passive film provides additional stress, and second, the intact passive film can protect Ti from the methanol solution. These two roles are mainly determined by the mechanical properties of the passive film, so they need to be studied to further reveal the SCC mechanism of α -Ti in the methanol solution.

Quantitative evaluations of the surface films' role did not flourish until the ultra-low load indentation systems (nanoindentation) have been developed. Nanoindentation can be used to probe the

* Corresponding author. Address: Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, People's Republic of China. Tel.: +86 10 6233 4499; fax: +86 10 6233 2345.

E-mail addresses: lqiao@ustb.edu.cn (L. Qiao), volinsky@usf.edu (A.A. Volinsky).

mechanical response of a surface layer by sensing displacements as low as 0.2 nm [25]. In general, most coated systems show a mixture of deformation comprising of both film and substrate effects [26]. Nanoindentation has been successfully used to measure mechanical properties of passive films on metals [27,28]. Two kinds of displacement discontinuity (excursion, or pop-in) were observed in load–displacement curves during load–controlled nanoindentation. The first type of excursion was found during nanoindentation of electropolished tungsten [29], single crystal Fe–3%Si [30], single crystal stainless steel [31], nickel [32], and austenitic stainless steel [33]. Prior to the excursion, indentation was fully recoverable, with no difference between the loading and the unloading. After the excursion, materials deformed plastically [29,34,35], thus, displacement excursion was associated with the beginning of plasticity in the oxide film on tungsten and Fe–3%Si single crystals [29,30]. The second type of indentation displacement excursion at low loads had also been observed in electropolished nickel [27], aluminum films [36], passive film on titanium [37] and air-formed film on single crystal Fe–3%Si [38]. These excursions were ascribed to film fracture, since the sample had already plastically deformed before the displacement excursion.

According to the literature reports, passive films are the key in protecting titanium from corrosion and stress corrosion cracking. The present work contributes to the understanding of the mechanical behavior of the passive film formed on Ti in methanol solutions by studying the role of water. In this paper, the film-induced stress and the film breakdown load of commercially pure titanium immersed in methanol were investigated as functions of water content using the flow stress differential method and nanoindentation.

2. Experiment

All experiments were conducted with commercially pure titanium with the following composition: 99.9 wt.% Ti, 0.1% Fe, 0.008% N, and 0.006% H. The specimens were obtained from rod for tensile tests and nanoindentation measurements, respectively, as described in detail below. Before testing, the specimens were heat treated at 720 °C for 1 h in a vacuum furnace (less than 5 Pa pressure) and then furnace cooled. Solutions of pure methanol without water and with varying water content from 0.1% to 1% were used.

2.1. Film-induced stress

The flow stress differential method was used to measure the film-induced stress [12,13] at room temperature controlled by the air conditioning, about 25 °C. The foil specimens with dimensions of 0.3 mm × 3 mm × 20 mm were polished down to 1000 grit finish, and cleaned in deionized water and acetone. The flat tensile specimens were subjected to plastic strain above 1% in air with a displacement rate of 10⁻⁶ mm s⁻¹. After unloading, the specimens were immersed in the 1% HF+2% HNO₃ solution for 1 min to remove the oxide (the cross-sectional area dimensions of the tensile specimens were not changed by this operation) and then placed in the methanol solution with different water content for 3 h to form passive films. After that, the specimens with the passive film were again subjected to yield in air. The yield stress of a reloaded specimen without passive film must be equal to the flow stress of the specimen before unloading. The yield stress of the specimen with passive film, σ_f , is different than the flow stress of the specimen before unloading, σ_s^* . The difference between these two stresses, $\sigma_f - \sigma_s^*$, is defined as the film-induced stress, i.e. $\sigma_p = \sigma_f - \sigma_s^*$, as indicated in Fig. 1.

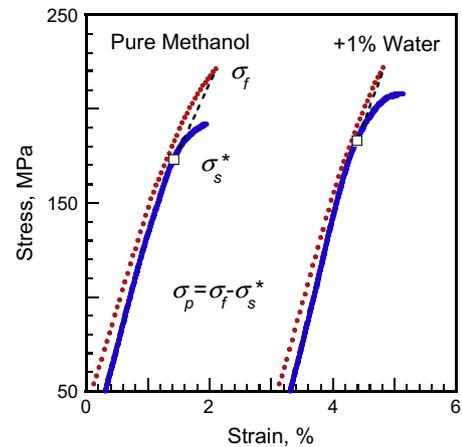


Fig. 1. Stress–strain curves before and after immersion in methanol solution. The stress–strain curves for 1% water are offset horizontally for clarity.

2.2. Nanoindentation test

The sectioned sample was vacuum annealed to achieve a primarily α hexagonal close packed phase structure, and then electropolished in a mixture of 60 vol.% H₂SO₄, 25 vol.% HF, and 15 vol.% glycerin at approximately 30 V with a titanium cathode to remove the mechanically deformed layer. Nanoindentation of the polished sample was carried out in ambient conditions after immersion in the methanol solution with different water content for 3 h, and the resulting passive film formation on the surface. Nanoindentation tests were performed right after passivation using the Hysitron Triboindenter with a Berkovich indenter tip at 35 μ N/s loading rate.

3. Results

Film-induced stress, measured by the flow stress differential method, which is the average stress in the film along the thickness direction of the film, is listed in Table 1. The breaking load of the passive film, P_b , with the corresponding varied water content is listed in Table 2 (measured by nanoindentation). In the case of a small amount of water ($\leq 0.15\%$), both film-induced tensile stress and the film fracture load are the highest. The film-induced tensile stress and the film fracture load, however, decreased when more water was added to methanol. Therefore, the variation of film-induced stress with water content was consistent with that of the film fracture load, as shown in Fig. 2.

4. Discussion

4.1. Passivation mechanism

Ti oxidation reaction $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$ is thermodynamically favorable ($G^0 = -212.6$ kcal/mol), yielding a native oxide film [39]. The XPS results of titanium after immersion in methanol are consistent with this reaction, as seen in Fig. 3. The passive films formed in pure methanol without water, and in methanol with water consist mainly of TiO₂. The Ti 2p_{3/2}, 2p_{1/2} doublets are shown in Fig. 3. At the same time, in water and anhydrous alcohol solutions of electrolytes, the Ti surface undergoes unstable passivation.

Traces of metallic titanium can be dissolved in water. Water undergoes auto-dissociation following equilibrium:

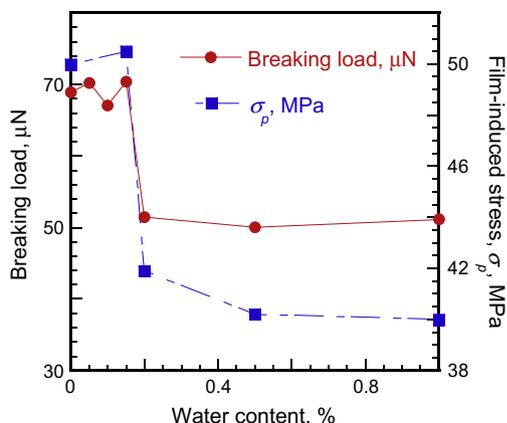
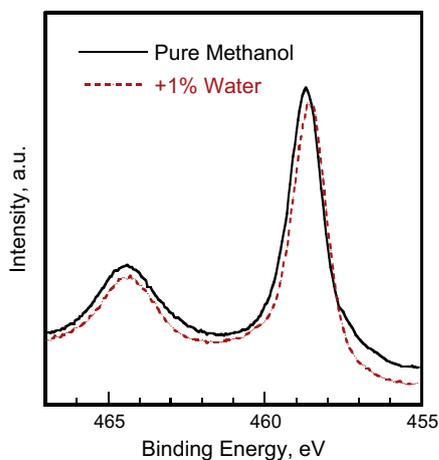


Table 1Film-induced stress, σ_p , in the sample immersed in methanol solution containing various amounts of water.

	Methanol	Methanol + 0.15% H ₂ O	Methanol + 0.2% H ₂ O	Methanol + 0.5% H ₂ O	Methanol + 1% H ₂ O
σ_p (MPa)	50	50.5 MPa	41.9 MPa	40.2 MPa	40 MPa

Table 2Average values of the passive film breaking load, P_b , with the corresponding varied water content.

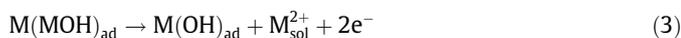
Water content (%)	0	0.05	0.1	0.15	0.2	0.5	1
P_b (μ N)	69	70	67	70	51	50	51

**Fig. 2.** Film fracture load and the film-induced stress vs. water content.**Fig. 3.** XPS spectra recorded from titanium after immersion in methanol with and without water.

At the very beginning, polar water molecule undergoes adsorption on the metal surface and, after that, undergoes thermal decomposition. OH⁻ groups are adsorbed on the metal surface.



Metal ions dissolve in water as the reaction continues:



The main product of Ti passivation in water is TiO₂, and the overall reaction is:



Methanol belongs to protogenic solvents and undergoes auto-dissociation, according to equilibrium:

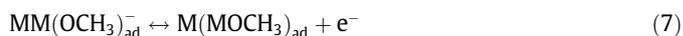


The electrochemical behavior of metals in this medium should be analogous to the behavior in aqueous environments, since the solvent exhibits similar dissolution properties as water. However, contrary to water, decomposition of methanol is a complicated process and can provide different surface adsorbed intermediates, depending on water content in methanol (CH₃O_{ad}, CH₂O_{ad} and CO_{ad}) [40–44].

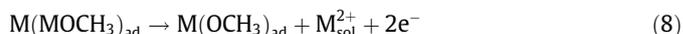
The –OCH₃ group plays a very important role in the reactions of anodic dissolution and cathodic deposition (similarly to the OH group). The presence of adsorbed oxygen or the surface oxide film promotes the surface methoxylation according to the reaction [40,41]:



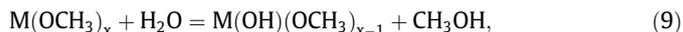
It seems that the surface of active metals is rapidly covered with –OCH₃ and the anodic oxidation in methanol proceeds according to the reaction:



Oxidation of (MOCH₃)_{ad} and activation of metal surface in methanol solution proceed according to the reaction:



Things change when water is added to methanol. Methoxides can be hydrolysed by water, following the hydrolysis reaction



which continues until M(OH)_x is formed. It is clear that the reaction of Ti in the methanol solution with water is more likely to occur, and the passivation products are more stable, compared to the reaction in pure methanol. Water affects passive film in two possible ways: it reacts with titanium surface directly and changes methanol dissolution properties.

As seen in Fig. 2, there is 0.2% critical water content, past which both the breaking load and the film-induced stress are substantially reduced. When water content is below 0.2%, titanium reacts with methanol. More water prevents the reaction continuation, according to reaction (9), and the formed more stable film has lower pop-in load and induces less stress.

4.2. Film-induced stress reduction mechanism

The origin of the film-induced stress should be discussed. Briefly speaking, there are two modes for film formation, which are inward or outward growth. In corrosion of metals, the Pilling–Bedworth ratio (R_{PB}) is the ratio of the volume of the elementary cell of a metal oxide to the volume of the elementary cell of the corresponding metal (from which the oxide is created) [45]:

$$R_{PB} = \frac{V_{\text{oxide}}}{V_{\text{metal}}} \quad (10)$$

The evidence is compelling that the tensile stress is generated at or near the metal/passive film interface by corrosion, i.e. metal ionization process. The passive film is an oxide, and its formation

involves either the inward diffusion of anions or outward migration of cations [46]. The anion transport number in the oxide rules the volume of the oxide formed at the metal/oxide interface. If only the anions move, as shown schematically in Fig. 4a, the anion transport number, β , is equal to 1, and a new passive film is generated at the metal/passive film interface, i.e. the passive film grows inward. Since the volume of the oxide (passive film) is greater than the volume available for ionization, i.e. $R_{PB} > 1$, the lattice of the surface layer expands. The metal matrix of the sample hinders the surface layer consisting of the passive film to elongate, resulting in compressive stress. If only cations move outward, as shown schematically in Fig. 4b, the anion transport number β is equal to 0, and a new passive film is generated only at the passive film-solution interface, and there are many free spaces (vacancies) left at the metal side of the inner interface produced by the oxidation of α -Ti. The other part of the sample hinders the ability of the metal layer containing vacancies to contract, resulting in a tensile stress at the inner interface.

If the transport number of the anion, β , is equal to a critical value β_c , the reciprocal of the Pilling–Bedworth Ratio is:

$$\beta_c = \frac{1}{R_{PB}}, \quad (11)$$

and no stress would be generated due to volume conservation. During corrosion of α -Ti in the methanol solution without water, $\beta < \beta_c$, so a tensile stress is generated. However, in the presence of water in the solution, the transport number after adding water, β_w ,

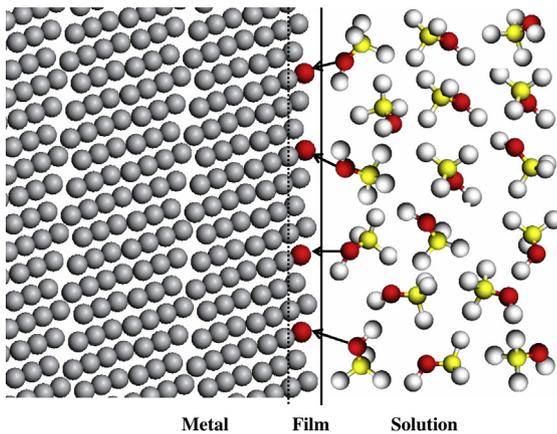


Fig. 4a. Schematic of the anions inward diffusion.

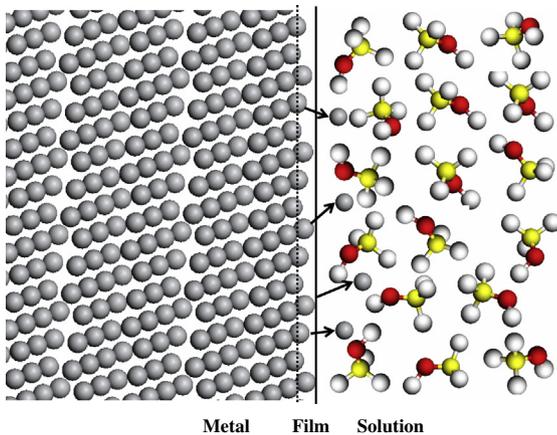


Fig. 4b. Schematic of the cations outward movement.

decreases. When the moisture content reaches 1 vol.%, β_w is still less than β_c . Since $\beta < \beta_w < \beta_c$, water reduces film-induced tensile stress.

4.3. Film residual stress and fracture load

Residual stress in a film is a key characteristic related to its mechanical properties. Yuan et al. [47] examined the novel method to measure the residual stress in the film formed on a metallic substrate using tensile tests, and pointed a way to calculate the residual stress in the surface film. During the loading, unloading and reloading process of metallic materials, the yield stress for the reloading process is equal to the flow stress prior to unloading. When a film is deposited on an unloaded metallic substrate, an additional stress, σ_b^{sub} will be generated in the substrate to balance the residual stress in the film, σ_r^{film} . According to the force balance (assuming that the stresses are uniformly distributed), the derivation process is simplified as follows [47]:

$$\sigma_b^{sub} = -\frac{d\sigma_r^{film}}{t} \quad (12)$$

where d and t are the thicknesses of the film and the substrate, respectively. The reduced Young's modulus of the substrate with the surface film, E_t , is:

$$E_t = \frac{d}{d+t}E_{film} + \frac{t}{d+t}E_{sub}, \quad (13)$$

where E_{film} and E_{sub} are the Young's modulus of the film and the substrate, respectively. The residual stress in the surface film can be derived through a series of transformations, as:

$$\sigma_r^{film} = -\frac{t}{d} \left(\sigma_Y^{sub} - \frac{E_{sub}}{E_t} \sigma_Y^{*sub} \right), \quad (14)$$

where σ_Y^{sub} is the yield stress of the substrate, σ_Y^{*sub} is the measured yield stress of the substrate with the surface film.

For a thin foil sample, two surfaces on both sides contribute to the residual stress, ignoring the lateral edge, since the side edge is very small compared to the surface. To obtain the residual stress of a single side passive film, the formula in equation 14 needs to be multiplied by 1/2. For the passive film on the α -Ti surface immersed in the methanol solution with different water content, the residual stress, σ_r^{film} , is approximately at the 1 GPa level, as shown in Table 3.

To minimize the substrate effect on the measurements, the indentation depth is often limited to less than 10% of the film thickness [48]. Thus, the hardness and modulus of the passive film of titanium immersed in methanol solution cannot be obtained exactly. The indentation of a hard film on a deforming substrate material [49] can be approximated by the spherical loading of a hard elastic plate on a soft yielding foundation. Under contact pressure, the plate undergoes elastic deformation until brittle fracture happens. The nanoindentation has been successfully used previously to study passivation film fracture [50]. The titanium oxide/titanium system can be modeled as a hard elastic plate on a soft yielding substrate under contact, as it has a thin stiff ceramic coating on a more compliant and ductile metal substrate [25]. The

Table 3

Values of the passive film residual stress, σ_r^{film} , breaking stress, σ_b , with the corresponding varied water content.

H ₂ O (%)	σ_r^{film} (GPa)	σ_b (GPa)
0	1	0.82
0.15	1	0.8
0.2	0.85	1.1
0.5	0.8	1.13
1	0.8	1.11

plate is assumed to undergo elastic deformation until brittle fracture. Both bending and membrane stretching cause nonlinear deformation of the plate. Therefore, the load actually carried by the plate can be approximated as the sum of the partial loads resisted by the bending and the membrane stretching actions. The applied load during the surface film breakdown can be related to the tensile stress in the membrane as [51]:

$$\sigma_b = 0.357E_f \frac{\delta^2}{c^2} + 2.198E_f \frac{\delta h_f}{c^2}, \quad (15)$$

where δ (nm) is the displacement at the beginning of the pop-in excursion, E_f (GPa) is the elastic modulus of the film, h_f (nm) is the film thickness, and c is the plastic zone in the underlying metal. The behavior of the film and the substrate in this model is reported in reference [25]. The mechanical reaction of the substrate is assumed to be Hertzian-like [25], based on the previous study, which found that the actual pressure distribution for a bilayer system is quite similar to the Hertzian distribution for the film and the substrate elastic modulus ratio less than 4 [52] ($E_{oxide} = 300$ GPa [53], $\nu_f = 0.3$, $E_{Ti} = 110$ GPa).

To simplify the model, the following assumptions are also proposed:

1. Due to the bluntness of the Berkovich tip used in the current study, a spherical tip is assumed in the contact regime.
2. The oxide/metal interface is perfectly bonded. No frictional stresses are involved.
3. As a first order approximation, the size of the plastic zone developed in the substrate is given by [54]:

$$c = \sqrt{\frac{3P_s}{2\pi\sigma_f}}, \quad (16)$$

where P_s is the load carried by the deformed materials and σ_f is the flow stress of the substrate.

The stress in the film is rather difficult to quantify, given the very thin nature of the passive film (usually in the range of several nanometers), and it is challenging to directly measure the passive film thickness. However, the film thickness can be estimated by electrochemical impedance spectroscopy (EIS). A simple parallel RC circuit can be used to represent the oxide film, and the capacitance of the film given by:

$$C_p = \frac{\epsilon\epsilon_0 r}{d}, \quad (17)$$

where C_p is the oxide film capacitance, ϵ_0 and ϵ are the permittivity of free space (8.9×10^{-14} F cm⁻¹) and the relative permittivity of the oxide, r is the oxide film surface and d is the oxide film thickness. Therefore, the thickness of the passive film could be determined by using EIS to monitor the capacitance:

$$d = \frac{\epsilon\epsilon_0 r}{C_p} \quad (18)$$

With the estimated film thickness (10 nm approximated conservatively), the estimated value of the breaking stress at film fracture is reasonable (shown in Table 3). The passive film could be fractured more easily if the residual stress, σ_r^{film} , is greater than or close to the breaking stress, σ_b . Water in the methanol solution could change the composition and/or the thickness of the passive film, and make the passive film more difficult to be broken. If the passive film can be easily broken, the metal would be more susceptible to SCC [50], while on the contrary, stronger passive film reduces metal SCC susceptibility.

When metals are anodized to form barrier oxide films, growth of these films is generally accompanied by a development of internal stresses in the oxides. These stresses are often quite large

and may exceed the strength of the film, resulting in cracking, interfacial and delamination. The chemical reactions that are likely to occur can be simply stated. First, the protective film must be penetrated and second, the metal must be attacked by the environment [18]. There is a general notion that the water molecule plays an important role in passivity of the transition metals and alloys in acid solutions [55]. Small amounts of moisture contained in the methanol inhibit the SCC of titanium and its alloys [56]. Water plays an inhibitory effect on SCC by changing the mechanical properties of the passive film growth on α -Ti immersed in the methanol solution.

5. Conclusions

From the flow stress differential method and nanoindentation tests the following conclusions can be drawn:

1. An additional tensile stress can be generated at the metal/passive film interface during α -Ti corrosion in the methanol solution.
2. The variation of film-induced stress with water content is consistent with that of the film mechanical properties.
3. Passive film-induced stress and film mechanical properties of α -Ti in a methanol solution are reduced by water.

Acknowledgements

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