

Full Length Article

Passive film growth on carbon steel and its nanoscale features at various passivating potentials



Yuan Li, Y. Frank Cheng*

Department of Mechanical & Manufacturing Engineering, University of Calgary, Calgary, AB T2N 1N4, Canada

ARTICLE INFO

Article history:

Received 3 August 2016

Received in revised form 20 October 2016

Accepted 5 November 2016

Available online 6 November 2016

Keywords:

Passive film

Carbon steel

Nanoscale features

Atomic force microscopy

X-ray photoelectron spectroscopy

ABSTRACT

In this work, the passivation and topographic sub-structure of passive films on a carbon steel in a carbonate/bicarbonate solution was characterized by electrochemical measurements, atomic force microscopy and X-ray photoelectron spectroscopy. When passivating at a potential near the active-passive transition, the film contains the mixture of Fe_3O_4 , Fe_2O_3 and FeOOH , with numerous nanoscale features. As the film-forming potential shifts positively, the passive film becomes more compact and the nanoscale features disappear. When the film is formed at a passive potential where the oxygen evolution is enabled, the content of FeOOH in the film increases, resulting in an amorphous topography and reduced corrosion resistance.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Studies on metal surface passivity and passive film formation are not new. Substantial efforts have been made in the past to investigate the thermodynamics and kinetics of the formation and growth, as well as the breakage of passive films [1–5]. In addition to the metals that are passivated in most environments, such as stainless steels, passivation can also be developed on carbon steels in certain environments. For example, carbon steels can be passivated in concentrated carbonate-bicarbonate solutions, which are typically generated under disbonded coatings which are permeable to cathodic protection current on buried pipelines [6–8].

Generally, the passivity is investigated on metals which are covered with a stable passive film. There has been limited work attempting to characterize the early stage of passivation. This is primarily attributed to the incapability of conventional electrochemical and surface analysis techniques for *in-situ* characterization of passivating processes, especially the early stage [9,10]. At the same time, the topography and chemical composition of passive films are closely related to the corrosion resistance of passivated metals [11–16]. Thus, characterizations of the topographic and compositional features of passive film growth, especially at the early stage, are able to analyze the corrosion behavior of the metal in environments.

Electrochemical atomic force microscopy (ECAFM) is able to image a metal electrode at the nanometer scale, and monitor the real-time topographic features while the electrode is under electrochemical controls in aqueous environments [17–21]. This avoids the potential contamination and degradation of passive film taking place during *ex-situ* characterization and analysis. Moreover, the high spatial resolution of the ECAFM enables characterization of passive films that are usually nanometers in thickness. It is expected that the results obtained by ECAFM provide mechanistic information on passive film growth, especially at its early stage. The uniqueness of the work is to characterize the evolution of nanoscale features on passive film formed at various potentials on a carbon steel, which has rarely been studied to date.

In this work, the passivation of an X100 pipeline steel was investigated in a concentrated carbonate/bicarbonate solution by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve measurements. The topography of the passive films formed at different film-forming potentials over various time periods was *in-situ* characterized by ECAFM, and the chemical composition of the films was determined by X-ray photoelectron spectroscopy (XPS). The surface roughness and sub-structure of passive films formed at the early stage were analyzed.

2. Experimental

2.1. Material and solution

Specimens used in this work were cut from a X100 steel plate, with a chemical composition (wt.%): C 0.07, Mn 1.76, Si 0.1, Ni 0.154,

* Corresponding author.

E-mail address: fcheng@ucalgary.ca (Y.F. Cheng).

Cr 0.016, Mo 0.2, V 0.005, Cu 0.243, Al 0.027, S 0.005, P 0.018, and Fe balance. The microstructure of the steel contains ferrite and bainite. The specimens used for ECAFM imaging were machined into a quadrangular shape with a dimension of $1\text{ mm} \times 1\text{ mm} \times 10\text{ mm}$, and were then painted with a primer and embedded into epoxy resin, leaving an exposed area of 1 mm^2 . The specimens were sequentially ground by emery papers up to 1200 grit, polished by $0.5\text{ }\mu\text{m}$ diamond paste, and degreased in ethanol using an ultrasonic bath, rinsed with deionized water, and dried by highly purified nitrogen. The specimens used for electrochemical measurements and XPS analysis were painted with a primer and then sealed in epoxy resin, leaving a work face of $10\text{ mm} \times 10\text{ mm}$. The test solution contained $0.05\text{ M Na}_2\text{CO}_3 + 0.1\text{ M NaHCO}_3$, with a pH of 9.5. All solutions were prepared using analytical grade chemicals and deionized water. All tests were performed at ambient temperature ($\sim 20^\circ\text{C}$) and open to air.

2.2. Electrochemical measurements

Electrochemical measurements were performed through a Solartron 1280C electrochemical system on a three-electrode cell, where the steel specimen was used as working electrode (WE), a carbon rod as counter electrode (CE), and a saturated calomel electrode (SCE) as reference electrode (RE). A salt bridge was used to avoid the chloride contamination from the RE to the solution. Prior to measurements, the freshly prepared specimen was cathodically polarized at -1.0 V(SCE) for 5 min to remove air-formed oxide. The potentiodynamic polarization curve was measured from -1.0 V(SCE) to 1.0 V(SCE) at a potential scanning rate of 0.167 mV/s . Prior to EIS measurements, the specimen was pre-polarized at various film-forming potentials (*i.e.*, passive potentials), which were chosen from the measured polarization curve, for 1 h. The EIS measurements were conducted, with a disturbance signal of 10 mV and the frequency range from $2 \times 10^4\text{ Hz}$ to 10^{-2} Hz . Each test was repeated at least three times to ensure the reproducibility of the results.

2.3. In-situ ECAFM characterization

An ECAFM (Keysight 5500 scanning probe microscope system) was used for topographic characterization on the steel specimens which were passivated at film-forming potentials of -0.1 V(SCE) , 0.5 V(SCE) and 0.7 V(SCE) , respectively, for 60 min. A scanner carrying a long rectangular cantilever with a spring constant of 0.2 N/m (apex radius $<10\text{ nm}$) was placed above the specimen. The scanning mode was configured to contacting, with a scanning rate of 4 Hz and resolution of $512 \times 512\text{ pixel}$. The working electrode was installed at the bottom of a homemade solution container, with 30 mm in diameter, 10 mm in height and 7 mL in volume. The size of the cell was sufficient to avoid evaporation of the solution during testing. Electrochemical controls were applied with a three-electrode setup, where the steel WE was installed at the bottom of the cell and a platinum wire was used as the RE, which was calibrated versus SCE in the same solution. The potential of the WE was controlled by a build-in potentiostat assembled with an AFM controller. The obtained images were processed by supplied software to remove tilt, and the topographic profile of the specimen was derived along the surface-finishing direction to diminish the effect of original topographic fluctuations.

2.4. XPS characterization

The XPS characterization was performed using a PHI VersaProbe 5000 spectrometer operating at a fixed pass energy of 23.5 eV and working in vacuum ($<10^{-7}\text{ Pa}$). The spectra were taken using a monochromatic Al source (1486.6 eV) at 50 W and a beam diam-

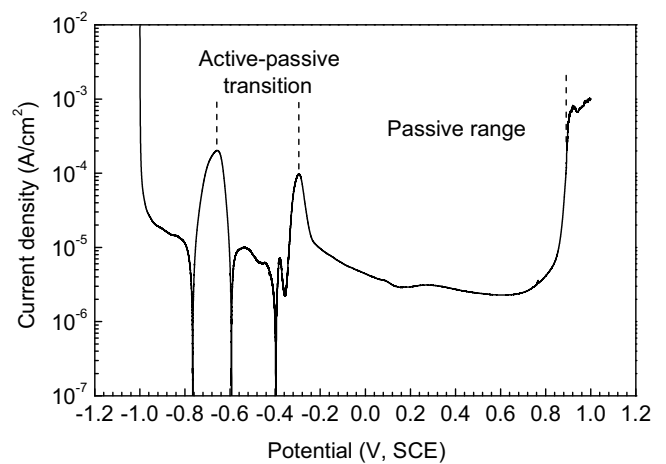


Fig. 1. Potentiodynamic polarization curve measured on the steel specimen at a potential scan rate of 0.167 mV/s in the test solution.

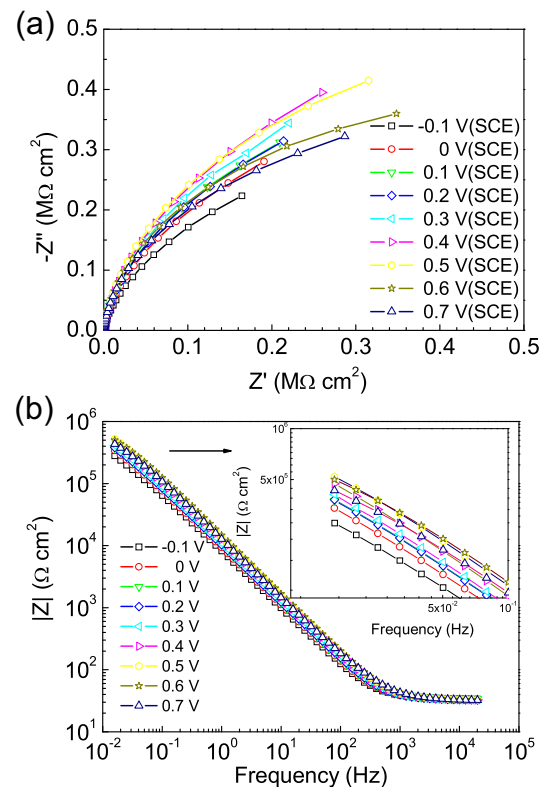


Fig. 2. Nyquist diagrams (a) and Bode modulus plots (b) measured on the steel specimen at various film-forming potentials, which are determined from the polarization curve in Fig. 1, after 1 h of immersion in the test solution.

eter of $200\text{ }\mu\text{m}$ with a take-off angle of 45° . The specimen was fixed with a double-sided tape, and spectra were taken with double neutralization. The binding energies were reported relative to C 1s at 284.8 eV . After 60 min of polarization at various film-forming potentials in the test solution, the specimen was rinsed with deionized water, dried by highly purified nitrogen, and was ready for XPS characterization.

Download English Version:

<https://daneshyari.com/en/article/5352689>

Download Persian Version:

<https://daneshyari.com/article/5352689>

[Daneshyari.com](https://daneshyari.com)