Effects of applied potential on stable pitting of 304 stainless steel

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ABSTRACT

Effects of applied potential on stable pitting corrosion of 304 stainless steel were studied by potentiostatic polarization and three-dimensional video microscope. The results showed that pit mouth morphologies and three-dimensional structures were dependent on potential. Higher potentials resulted in more open pits. Pit volume, depth, and width increased with potential. The ratio of pit depth to width continuously changed with time and potential. The pitting current density of a single pit increased with potential, indicating that an ohmic potential drop presented between the pit internal surface and the bulk solution, but stable propagation was still controlled by corrosion products diffusion.

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1. Introduction

Stainless steel 304 is used extensively in industry because of its good mechanical properties, good processability and excellent corrosion resistance [1,2]. However, it undergoes pitting corrosion, and thus becomes unavailable during servicing. Pitting corrosion is one of the most widespread and dangerous forms of localized corrosion in passive metals, and occurs commonly in a range of aggressive environments. The most common aggressive ion is the chloride anion, which is found in many natural and industrial environments [3]. The metal loss from pitting corrosion is lower than that from uniform corrosion, but this type of pitting usually occurs over a small area, and thus occurs to a greater depth. Pits are always covered by corrosion products, and generally cause devices to fail by perforation, or initiate stress corrosion cracks [4,5]. Thus pitting is one of the more destructive and undetectable forms of metal corrosion [6–9].

Pitting research is classified primarily into two categories. In one kind of research, pitting sensitivity, and the effects of environmental factors, such as ion types and content are studied by electrochemical methods to obtain the thermodynamic and kinetic parameters of pitting. Research objects include a large number of randomly generated corrosion pits, and passive films on a whole electrode. Experimental methods include potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), potentiodynamic electrochemical impedance spectroscopy (DEIS), and electrochemical noise (EN) [1,10–17].

In other research, which involves a diversity of experimental methods, the growth behavior of a specific pit is studied, and includes initiation and propagation. Burstein et al. [3,4,18–25] used a tiny specimen, a microelectrode to study pit nucleation and propagation, and obtained single and separated current transients. They demonstrated and proved that the pit stable or metastable growth is controlled by corrosion products diffusion, since the pitting current density is independent of the applied potential. As is well known, a chloride-induced pit must be either enriched in chloride, or of a lower pH, or both relative to the bulk solution, in order to sustain continuous propagation of pit [18–21,23,26]. This mechanism is also suitable for crevice corrosion [27,28]. Because the anodic reaction occurs inside the pit and the supporting cathodic reaction occurs on the passive metal surrounding the pits, the electroneutrality of the pit anolyte necessitates a local accumulation of chloride anions acting as the counter-ion, as a natural consequence of metal cations dissolving within the anolyte [11,19,21,23,29,30]. Local acidification also occurs from hydrolysis of the dissolving metal cations with the anolyte inside the pit. The diffusion of corrosion products controlled propagation can lead to an accumulation of metal cations and chloride, and significant local acidification [18–20,27–30]. Therefore, it is reasonable to believe the accuracy of diffusion controlled theories regarding pit propagation. The diffusion barrier can be lacy cover (metal plate), anodic salt film (metal chloride layer), residual passive film or pit depth, or both based on pit volume and morphology.

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Based on experiments with artificial pit electrodes (pencil and foil electrodes), Newman et al. [31–37] studied the anodic dissolution of stainless steel and the relevant kinetics of pit growth. They confirmed that at a high anodic potential, pit dissolution is diffusion controlled across a salt film, and pit growth in depth follows a parabolic law with time and is independent of the potential. They also found the formation of lacy covers, and interpreted the causes of this phenomenon. At the edge of a pit, the transport of metal cations from pit surface into bulk solution is relatively rapid, the local concentration of metal and chloride ions falls below the critical value, and metal repassivation occurs more easily. In contrast, deeper into the pit cavity, active dissolution continues such that pit growth undercuts the metal surface, and forms lacy cover that helps the pit to sustain a concentrated local chemistry [31–35]. In fact, many pits are entirely dependent on the anodic salt film per se is responsible for pit stabilization is partly correct, especially for stable or big pits, and the key event in pit stabilization is the onset of surface undercutting and the subsequent forming of lacy cover [33–35]. Metastable pits are unable to undercut the surface and achieve stability, and the anodic salt film may be their primary diffusion barrier. Newman's group also studied the critical pitting temperature (CPT) of stainless steel, and the relevant pitting behavior around the CPT [38–40]. The CPT is the lowest temperature at which stable pit growth is possible. It is affected by the environment, grain size and phase composition of metal, and the electrode surface state such as surface roughness [41–44]. The pit cavity shape obtained below the CPT is significantly different from the pit obtained above the CPT. The CPT also has a significant influence on the formation of lacy cover over the pit mouth [38,39].

The growth of corrosion pit has been identified as occurring in three distinct steps: nucleation, metastable propagation and stable propagation [1]. The transition to stability occurs when the pit has grown sufficiently for its own depth to act as a diffusion barrier; this pit can propagate continuously without its perforated cover and is thus stable. The critical condition for transition from metastability to stability is characterized by the pit stability product [19,20], which is defined by the product of pit current density i and pit radius a (for a hemispherical pit). For 304 stainless steel in chloride solution, the critical value of the pit stability product is 3 mA/cm, and stable pit propagation occurs for 3 mA/cm < ia < 6 mA/cm as demonstrated by Pistorius and Burstein. The value of the critical stability product changes depending on different metals and environments [4,20,45]. Although Pistorius and Burstein characterized the transition condition, the distinction between metastable and stable growth is still unclear. Pits that survive for only a short period, such as less than 5–30 s, can be termed metastable pits [32]. Some researchers believe that metastable pits always have a diameter less than 30 μm, and no lacy cover [9,38]. In fact, many pits are dependent on the existence of covers for their continuous growth, since they repassivate when their covers are punctured, [46]. Therefore, stable pits always have a large diameter (volume) and a lacy cover [38]. Based on this characteristic of stable pits, Burstein's studies are focused mainly on metastable pits, whereas Newman's group studies mostly stable pits.

2. Experimental

2.1. Sample preparation

Specimens used in the study were made from 304 stainless steel, with a chemical composition (wt.%): C 0.035, Si 0.52, Mn 1.18, P 0.036, S 0.026, Cr 17.59, Ni 8.03, Fe 72.6. Heat treatment of this material included solutionizing and sensitizing. Solution heat treatment was conducted in an air furnace at 1060 °C for 0.5 h, followed by water quenching. The sensitization heat treatment was carried out in an air furnace at 650 °C for 2 h, followed by air cooling. Such a process facilitates pitting [9]. The 304 stainless steel was cut into 1 mm and 10 mm diameter cylinders to act as working electrode inlaid in phenolic resin. Electrical contact of the specimen was made by spot welding a copper lead on to the back of the specimen. The nonworking surface of the electrode was sealed using epoxy resin. The exposed surface of each electrode was finished by wet-grinding with a series of emery papers from 400 to 1200 grit, and then cleaned thoroughly with alcohol, acetone and deionized water in turn.

2.2. Electrochemical experiments

Before the electrochemical and pitting tests, electrodes were cathodically polarized for 5 min at −1.3 V (saturated calomel electrode, SCE) to remove the oxide film on the surface. Electrodes were then immersed in test solution for 3 h, so that the electrode surface could generate a stable passive film. In order to obtain the pitting current of a single stable pit, it was necessary to use an electrode of 1 mm diameter (area 7.85×10^{-3} cm^2), whereas a 10 mm diameter electrode was used to obtain statistical data of a large number of stable pits.

Electrochemical tests were provided by Autolab PGSTAT 302N. Tests were carried out using a three-electrode electrochemical cell with a SCE as reference and a platinum sheet as auxiliary electrode. All the potentials quoted in this work referred to the SCE. The applied potentials were 0.05 V (SCE), 0.15 V (SCE), 0.25 V (SCE) and 0.35 V (SCE). The electrochemical test system was mounted into an earthed Faraday cage to minimize interference from outside electrical signals. When the current density reached 100 μA/cm^2, this signaled the beginning of pitting. The test solution was 3.5% (mass fraction) sodium chloride solution, prepared with deionized water and analytical grade sodium chloride and without deoxygenation. Tests were performed at room temperature (20 ± 2 °C).

At least nine valid experiments were carried out for each condition, with a small variation in behavior of individual pits. An average of the results was not informative since the growth details would be lost. It was therefore decided to display only those results that showed the typical behavior based on the experimental conditions.

The observation and measurement of pit morphology were achieved using a KH-7700 three-dimensional video microscope. The KH-7700 could construct the three-dimensional pit structure, and thus obtain precise morphological parameters, such as pit volume, depth and diameter. The geometrical parameters of a stable pit are defined as shown in Fig. 1. Prior to the measurement of pit geometrical parameters, a dilute nitric acid ultrasonic bath was used to remove metal covers and corrosion products. The cleaning time for each electrode was 10 min.

2.3. Energy dispersive spectroscopy (EDS) analysis

A CamScan CS-3400 scanning electron microscope (SEM) was used to observe corrosion pits. Corrosion products composition was determined using combined quantitative energy dispersive spectroscopy (EDS). Prior to the SEM measurement, a layer of platinum was coated on the electrode surface to enhance the electrical conductivity. To reduce the loss of corrosion products inside the pit, the working electrode was removed rapidly from the testing cell prior to the polarization ceasing. The electrode surface was wiped using alcohol cotton to remove residual sodium chloride solution layer on the electrode. It was difficult to obtain EDS results of corrosion products from an occluded pit, because of signal shielding caused by the side wall and residual covers of a pit. Some