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Critical conditions for pit initiation and growth of austenitic stainless steels

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ABSTRACT

The pitting behaviour of 316 stainless steel in NaCl solution was investigated using potentiodynamic (PD) and potentiostatic (PS) polarization. Tests with the mode change from PD to PS at potentials close to the pitting potential showed that the potential could play a role in the stable pitting by maintaining the pit stability product. The metastable pit growth was studied by changing the mode at potentials far below the pitting potential and by characterizing the first current density spikes. The results suggested that the cumulative electric charge density governs the metastable pit initiation as a critical condition.

1. Introduction

In predicting design life of a component against pitting, it is essential to know the critical conditions for different stages of pitting. The evolution of pitting on stainless steel in chloride containing solutions occurs in three stages [1,2]: (i) pit nucleation, (ii) metastable growth of pit, and (iii) stable pit growth. For the stable pit growth which is characterized by the pitting potential (E_{pit}) [3], several critical conditions (criteria) have been proposed as described below. When the critical conditions are not satisfied, pits will repassivate without further growth, which is called metastable pit growth. Hakkarainen [4] experimentally showed that pits repassivated at decreasing potentials when the concentration of the solution at the dissolving surface was decreased below a critical value, which was of the order of 0.8 times the saturation value of metal and chloride ions. Assuming the hydrolysis of metal ions and the transport of corrosion products by diffusion, Galvele [5,6] developed a pit model and suggested a pit stability product, '$x{\cdot}i$' where x is pit depth and i is current density. Galvele [5] used the critical condition to explain the existence of the pitting potential and protection potential determined in potentiodynamic measurements. The pit stability product has been well accepted as a critical condition for the stable pit growth by other investigators [2,7].

Concerning passive film breakdown followed by pit initiation, several theories have been proposed such as penetration mechanism [8] or adsorption theory [9]. Despite a number of studies on surface characterization [10–13], it seems that the exact nature of the chloride interactions with the oxide film of stainless steels remains unclear [14]. A stochastic approach has been used for analyzing the induction time of pit generation, metastable pitting, pitting potential [15–18]. This stochastic model has been found to be most appropriate to explain the characteristics of the pitting phenomena as localized corrosion, but it could not be simply applied to a life-prediction model of material degradation by pitting which identifying possible service life of a component. This study aims at identifying critical conditions or critical factors that govern the pit nucleation and growth that could be used for developing a material degradation prediction model by pitting. For this purpose, electrochemical polarization tests with potentiodynamic (PD) and potentiostatic (PS) modes were performed on 316 stainless steel in 0.6 M NaCl solution.

2. Experimental

Chemical compositions of AISI type 316 SS (UNS S31600) are given in Table 1. The samples connected to a wire were cold-mounted in epoxy resin and used as a working electrode. Sample surfaces were abraded up to #2400 using SiC papers and ultrasonically cleaned and dried just before they were introduced into the electrochemical set-up. To prevent crevice corrosion, the gap between the metallic sample and resin was covered by a manicure, leaving an exposed surface area of ~1 cm^2. All the electrochemical tests with the conventional three-electrode set up (graphite rod as counter electrode and saturated calomel electrode as reference electrode) were performed in aerated 0.6 M NaCl solution

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Table 1
Chemical compositions of AISI type 316 stainless steel (wt%).

Type	C	Fe	Cr	Ni	Mo	Cu	Mn	Si	S	P
316 SS	0.05	67.9	17.34	10.73	2.15	0.25	0.64	0.6	0.005	0.02

(~800 ml) at 22 ± 2 °C. Being measured before and after tests, the pH of the solution was 6.4 ± 0.1. Before all the types of polarization explained below, samples were cathodically conditioned at −500 mV vs. E_{OCP} (open circuit potential) for 5 min to remove air-formed surface oxide. Then, they were polarized from the cathodic conditioning potential in the positive direction. Three test types of polarization were adopted: (i) potentiodynamic (PD) and cyclic potentiodynamic (Cyclic-PD) tests; (ii) potentiodynamic and potentiostatic at high potentials (PDPS-HP) tests; (iii) potentiodynamic and potentiostatic at low potentials (PDPS-LP) tests, which are summarized in Table 2. The data sampling rates were 1 Hz for PD and PDPS-HP tests and 20 Hz for PDPS-LP tests.

2.1. Potentiodynamic (PD) and cyclic potentiodynamic (Cyclic-PD) tests

To measure the basic polarization behaviour of 316 stainless steel in NaCl solution, potentiodynamic polarization tests were performed at a scan rate of 1 mV s^{-1} and stopped when the current density reaches 5 mA cm^{-2}. The PD test was conducted for ten different samples, which were then ultrasonically cleaned in pure water and their surfaces were examined using an optical microscopy. In Cyclic-PD tests, cyclic potentiodynamic polarization was performed by reverse scans back to the starting potential when the samples reached a current density value of 5 mA cm^{-2}. The procedures before the reverse scan are the same as PD tests.

2.2. Potentiodynamic and potentiostatic at high potentials (PDPS-HP) tests

In this type of tests, samples were first potentiodynamically polarized and then the potential mode was changed to the potentiostatic mode within the metastable potential region in Fig. 1. The polarization mode was changed when the amplitudes of the current density spikes by metastable pit growth bigger than 1 μA cm^{-2} were observed. After the tests samples were examined using OM to identify the localized corrosion types and count the number of pits.

2.3. Potentiodynamic and potentiostatic at low potentials (PDPS-LP) tests

The PDPS-LP test conditions were the same as the PDPS-HP except for the mode change potential. In this test, three potential values far below the pitting potential were arbitrarily selected: 50 mV, 150 mV, and 250 mV (vs. SCE). When the potential in the potentiodynamic polarization reaches the selected potentials, the mode was switched to potentiostatic. Three samples were tested at each potential condition. The data sampling rate was 20 Hz. On the potentiodynamic and potentiostatic polarization curves, current density spikes corresponding to metastable pit growth were examined and analyzed.

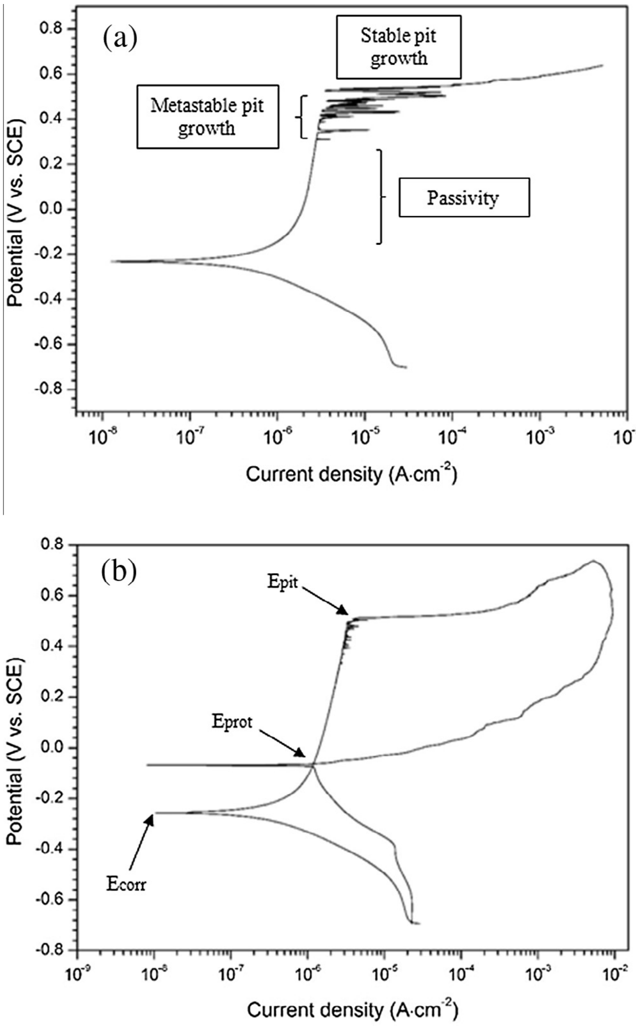

Fig. 1. Examples of potentiodynamic polarization curves of type 316 stainless steel in 0.6 M NaCl solution (a) PD and (b) cyclic PD tests.

3. Results

3.1. Potentiodynamic polarization (PD) and cyclic potentiodynamic (Cyclic-PD) tests

The potentiodynamic polarization was stopped when the current density by stable pit growth reached 5 mA cm^{-2}. Fig. 1(a) is

Table 2
Polarization test matrix.

Test Method	Description	Remarks
PD	Cathodic treatment at −500 mV vs. E_{ocp} and potentiodynamic polarization 1 mV s^{-1} scan rate until current density reaches 5 mA cm^{-2}	
Cyclic-PD	Cathodic treatment at −500 mV vs. E_{ocp} and potentiodynamic polarization 1 mV s^{-1} scan rate until current density reaches 5 mA cm^{-2} and then reverse scan at 1 mV s^{-1} down to −500 mV vs. E_{ocp}	
PDPS-HP	Cathodic treatment at −500 mV vs. E_{ocp}, potentiodynamic polarization up to a potential close to pitting potential at 1 mV s^{-1} scan rate and potentiostatic polarization at the potential	HP: high potentials
PDPS-LP	Cathodic treatment at −500 mV vs. E_{ocp}, potentiodynamic polarization up to a potential far below the pitting potential at 1 mV s^{-1} scan rate and potentiostatic polarization at the potential	LP: low potentials (50 mV, 150 mV, 250 mV vs. SCE)