Corrosion Science 93 (2015) 80–89

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Effects of cyclic stress on the metastable pitting characteristic for 304 stainless steel under potentiostatic polarization

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ARTICLE INFO

Article history:
Received 17 September 2014
Accepted 4 January 2015
Available online 13 January 2015

Keywords:
A. Stainless steel
B. Potentiostatic
C. Pitting corrosion
C. Corrosion fatigue

ABSTRACT

The effects of the cyclic stress on the metastable pitting corrosion for 304 stainless steel have been investigated under potentiostatic polarization. The results show that cyclic stress with peak stress above yield strength (PSAY) can significantly increase the metastable pitting events and promote the growth of large pits, while those with peak stress below yield strength have no obvious effect. It also reveals that PSAY can decrease the stable pitting potential. These results indicate that cyclic plastic deformation plays more important role on the metastable pitting behaviour than cyclic elastic deformation.

1. Introduction

Corrosion fatigue failures of materials and structures have been found widely in industries and laboratories. It is generally believed that these failures are attributed to the well-known mechano-chemical and chemomechanical effect [1]. Compared with elastic deformation, plastic deformation was found to have more influence on the anodic activity of metals [2,3]. For example, Bockris et al. [4] reported that the iron-dissolution rate in the elastic region exhibited no change for iron wire in 0.1 M H_2SO_4 solution, while the anodic current density (at constant potential) underwent a remarkable rise at the beginning of plastic deformation. For film covered alloy, such as aluminium alloys and stainless steel in oxidizing aqueous solutions, the film rupture was regarded as a cause for increased dissolution rate on yielding. In engineering practice, these alloys are vulnerable to pitting corrosion. The corrosion pits often initiate and grow in the early stage of corrosion fatigue process [5,6]. A final failure of specimen can occur once a crack initiates from the grown pit and propagates to a critical length.

Metastable pitting as a precursor state to stable pitting has been investigated for decades [7–10]. Analysis of the transient current generated during metastable pitting has been proven to be a valid approach to study the formation, growth, and repassivation of a microscopic pit [11–13]. The metastable pitting rate and the characteristic parameters are closely related to potentials [14,15], environment conditions [16–19] and alloys microstructure [20,21]. To date, little is understood about the mechanical factor dependence of the metastable pitting, which is an important issue to be investigated since the pits have been identified as the potential origins for fatigue crack nucleation.

Li et al. [22] have systematically studied the correspondence between plastic strain waveform and transient current curve at active, passive and intermediate potentials. They found that transient current recorded during cyclic deformation can effectively assess the fatigue/environment interaction, which can provide valuable information of the damage mechanisms of corrosion fatigue. Tada et al. [23] have studied the current response induced by cyclic elastic stress. They concluded that the crack initiation and corrosion fatigue damage can be monitored and evaluated by analysing the current response. However, no current response related to metastable pitting has been reported during the cyclic loading.

Ma et al. [24] have investigated the growth of stable pits under cyclic stress for A537 steel. They found that cyclic stress promoted 3D growth of pits initiated at MnS inclusions, which is mainly due to the localized stress and plastic strain around a pit. However, this work mainly concerns about the stable pitting without providing specific relationship between the metastable pitting characteristic and the synchronous cyclic stress. Zhang et al. [25] have studied the effect of mechanical factors on the generation rate and size of metastable pit under potentiodynamic polarization and potentiostatic conditions. But they only concern the role of constant hydrostatic pressure.

In present work, the effects of cyclic stress on the metastable pitting have been investigated for 304 stainless steel (SS) in 1 M

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http://dx.doi.org/10.1016/j.corsci.2015.01.009
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NaCl solution (pH = 3). This study focuses on the comparison and quantification of metastable pitting initiation rate, growth behaviour by using current transient analysis during potentiostatic polarization under cyclic loading control. The peak stresses both under and above the yield strength are chosen for comparative analysis with the aim to understand the roles of cyclic plastic and elastic deformations on metastable pitting behaviour.

2. Experimental

2.1. Specimen preparations

Specimens used in this study were made from a 304 SS with the following chemical composition (in wt.%): 17.56 Cr, 8.11 Ni, 0.96 Mn, 0.05 Mo, 0.03 N, 0.044 C, 0.43 Si, 0.026 P, 0.003 S, and balance Fe. The 304 SS in the present study was hot-rolled into plates with thickness of 5 mm. The 0.2% proof stress of the material is 270 MPa.

The specimen for potentiodynamic polarization with the size of 10 × 10 × 5 (mm) was cut from the 304 SS plate tests. The specimen was electrically connected to a copper wire with conductive silver adhesive and mounted in the epoxy resin. Dumbbell-shaped fatigue specimens with gauge section size of 50 mm long, 5 mm wide and 2 mm thick were used for cyclic loading experiments. The loading axis is along the rolling direction.

Both the gauge section of the fatigue samples and electrochemical specimens were wet-ground manually with a series of emery papers from 800 to 5000 grit, then degreased with alcohol and rinsed with deionised water. The gauge sections of fatigue samples were covered with silicon resin. The exposed window with size of 0.5 cm^2 is located at the centre of gauge section on one of the 5 mm wide surface. To avoid crevice corrosion, the interfaces between specimen and resin were sealed with nail oil (containing nitrocellulose, butyl acetate and ethyl acetate) and dried in the air for 1.5 h before the fatigue tests.

2.2. Electrochemical tests during cyclic loading

Cyclic loading tests of the specimens were carried out on a Shimadzu fatigue machine (model: EHF-EB10-20L) under load control using a sinusoidal waveform with a frequency of 0.5 Hz and a stress ratio of 0. The cyclic peak stresses below yield strength (PSBY) were 0 MPa, 150 MPa and 250 MPa, respectively. For comparison, peak stress above yield strength (PSAY) of 350 MPa was chosen in the fatigue tests. The fatigue specimens are successively insulated from the fatigue machine using four pieces of thin steel plates coated with fusion-bonded epoxy powder coating.

Electrochemical measurements were carried out using a PARSTAT 4000 potentiostat. A platinum foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The electrolyte of 1 M NaCl (pH = 3) was made with analytical grade reagent and distilled water. The pH was prepared by adding appropriate amounts of hydrochloric acid and sodium hydroxide. The electrolyte was exposed in the air during all experiments. Prior to the electrochemical measurement and fatigue test, the specimen was allowed to stabilize in solution under free corrosion condition for 5 min, then fatigue tests and potentiostatic polarization were carried out simultaneously. The current transient measurements were conducted at constant applied potentials (0.05, 0.1 and 0.2 V (SCE)) in the passive range with a data collection frequency of 20 Hz at 19 ± 2 °C. All potentials are referred to saturated calomel electrode (SCE).

During cyclic loading, stress-induced cyclic current with the same frequency of the cyclic stress can form, which should be removed before the counting of the current transients associated with metastable pitting. The number of the transients was manually counted to calculate the metastable pitting initiation rate. In the present work, the criterion to identify the current transients is that peak current is at least two times higher than the background current noise amplitude with elapsing time of more than 1 s. The critical parameters are statistically calculated and compared, such as peak pitting current (I_{peak}) and pitting current density (i_{peak}). The pitting current density (i_{peak}) is obtained by dividing I_{peak} by the superficial area of a hemispherical pit [11]. All the parameters to characterize the metastable pitting are obtained from three repeated electrochemical measurements during cyclic loading. After the cyclic loading tests, the corrosion morphologies were observed by confocal laser scanning microscopy (CLSM, OLYMPUS LEXT OLS4000).

For the potentiodynamic polarization tests without cyclic loading, the scan rate was 0.5 mV/s.

3. Results

3.1. Potentiodynamic polarization curve

A typical potentiodynamic polarization curve of 304 SS in 1 M NaCl solution (pH = 3) is shown in Fig. 1. As can be expected, 304 SS shows passive behaviour in the anodic polarization curve. During the potentiodynamic polarization, current fluctuations have also been observed especially at anodic applied potential above 0 V (SCE) in the passive region, which can be regarded as the metastable pitting events [14,26]. At around 0.2 V (SCE), the stable pitting occurs suddenly with a sharp increase in the current density from the passive current density of 0.8 $\mu A/cm^2$.

3.2. Current response under cyclic loading

In order to exhibit the metastable pitting current in more detail, potentiostatic polarization tests with a data collection frequency of 20 Hz were carried out below E_{pit} determined from replicate polarization curve measurements. Fig. 2 shows the typical current densities versus time records for 304 SS in 1 M NaCl solution (pH = 3) at 0.05 V (SCE) under various cyclic loading conditions. In each case, discrete short spikes from pitting events are superimposed on a background current density as shown in Fig. 2. It is noted that the current densities as quoted here are obtained by dividing the current by the total area of the test sample, and therefore this value

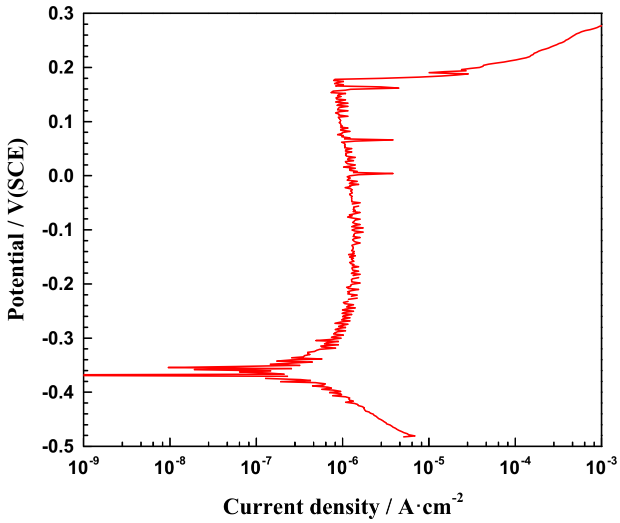

Fig. 1. A typical potentiodynamic polarization curve of 304 SS in 1 M NaCl solution (pH = 3) at a scan rate of 0.5 mV/s.