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The effect of deformation on metastable pitting of 304 stainless steel in chloride contaminated concrete pore solution

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1. Introduction

Stainless steel reinforcements constitute an economical and reliable solution for ensuring the durability of concrete structures in extremely aggressive environments [1]. These steels fail most frequent as a result of pitting corrosion [2]. In fact, pitting corrosion accelerates the failure of stainless steels that are subjected to stress. Many researchers have estimated the service life of stainless steel, determining the effect of stress or strain on the initiation of pitting corrosion. For example, in separate studies, Štefec et al. [3] and Peguet et al. [4] investigated the pitting corrosion of coldworked stainless steel in a 0.1 M NaCl solution. Stefec et al. [3] found that the area of the pitted region, current density, and the number of pits increased with increasing magnitude of the deformation; the growth rates of pitting increased significantly with increasing deformation. In addition, Peguet et al. [4] found that maximum metastable pitting occurred at 10% tensile deformation or 20% cold-rolling reduction. Cold-working led to reduction in the repassivation potential as well as an increase in the depassivation pH and the number of stable pits. Mudali et al. [5] and Zhang et al.

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ABSTRACT

Metastable pitting of tensile-stressed 304 stainless steel in a simulated concrete pore solution was studied via potentiostatic polarization and Mott–Schottky plots. The results revealed that the carrier density of passive films increases significantly with increasing magnitude of the strain. In addition, the lifetime of metastable pitting increases with the strain and secondary metastable pitting always occurred in the severely deformed samples. The growth rates of individual metastable pits were only slightly influenced by the strain level and carrier density. However, the repassivation rates of pitting dramatically decreased with deformation and carrier density when the strain is below 10%.

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[6] also investigated the influence of cold-working on the pitting corrosion resistance of stainless steel in a neutral chloride medium. The authors found that the resistance increased with increasing cold-working level of up to 20%, and decreased thereafter. Suter et al. [7] compared the pitting corrosion of 304 stainless steel in a NaCl solution with and without an applied mechanical stress, by using a microelectrochemical cell. The results indicated that the stress had no effect on the pitting corrosion behaviour of the MnSinclusion-free regions. In regions containing these inclusions, the applied stress shifted the MnS dissolution more negative potentials, compared to that of the non-stressed material, and increased the dissolution rate. Wang and Han [8] simulated the development of metastable pitting under mechanical stresses and found that the growth rate of the pits was significantly higher than that determined in the stress-free state. Similarly, Guan et al. [9] studied the effect of cyclic stresses on the metastable pitting of 304 stainless steel in a chloride-containing acidic electrolyte. The results showed that a cyclic stress, whose peak value was higher than the yield strength, could significantly increase the occurrence of metastable pitting events and promote the growth of large pits. In contrast, stresses with peak values lower than the yield strength, had only a negligible effect on the pitting. Contradictory results have been reported regarding the effect of stress (or strain) on the pitting corrosion of stainless steel. Some studies [3,4,8,9] have shown that the

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ARTICLE IN PRESS

X. Feng et al. / Corrosion Science xxx (2015) xxx-xxx



Fig. 1. Geometry of the 304 stainless steel specimens used in the tensile state.

strain promotes pitting corrosion, whereas others [5,6] suggested that the low levels of deformation hinder this corrosion.

Many researchers [1,10,11] have also studied the corrosion behaviour of stainless steel in simulated concrete pore solutions. For example, Fajardo et al. [1] compared the corrosion behaviour of the conventional AISI 304 and a low-nickel stainless steel in a carbonated alkaline solution (pH 8). The results suggested that the corrosion potential (E_{corr}) became slightly more noble, compared to its initial value, and the pitting potential (E_{pit}) decreased, with increasing chloride concentration of the solution. Moreover, the steels exhibited similar corrosion behaviour in the simulated carbonated pore solution. Freire et al. [10] studied the passivation and depassivation of AISI 304 in pore solutions with differing pH values; in that work, the Epit increased by approximately +0.5 V when the pH increased from 9 to 13. When chlorides were added to the simulated pore solutions, the film resistance and charge transfer resistance also increased with the pH value. This indicates that, compared to that occurring in mild solutions, more significant pitting activity occurs in aggressive carbonated pore solutions. Similarly, Li et al. [11] studied the pitting corrosion in the weldment of a 304L joint with 308L austenitic stainless steels in simulated concrete pore solutions with differing pH (i.e., with pH ranging from 10.5–13.5); there, the pitting corrosion resistance of the austenite stainless steel weld improved with increasing pH value of 10.5-13.5. This indicates that, the pH value of the concrete pore solution plays an important role in the pitting corrosion of stainless steel bars. In fact, the pitting corrosion resistance of stainless steel increases with increasing pH of the pore solution.

Previous studies have focused on the effect of strain on the pitting corrosion of stainless steel in acidic [9] and neutral media [3–8], or on the pH-dependence of the pitting corrosion resistance [1,10,11]. To the best of our knowledge, the effect of stress or strain on the metastable pitting of stainless steel in alkali solutions has scarcely been investigated. As such, this work focuses on the semi-conductivity and metastable pitting behaviour of 304 stainless steels in a simulated concrete pore solution. The results reveal that the repassivation rate of individual metastable pits decreases significantly with the increasing strain level. However, the growth rate is only modestly influenced by the magnitude of the strain. The relationship among the growth rate, the repassivation rate and the density of carrier is also discussed.

2. Experimental methods

2.1. Materials

A traditional austenitic stainless steel, AISI 304, was used in this study. The chemical composition of the steel was as follows (wt.%): 0.075% C, 0.32% Si, 1.3% Mn, 0.0068% S, 0.020% P, 18.1% Cr, 8.2% Ni, 0.16% Mo, and Fe balance. Samples having the dimensions shown in Fig. 1 were used for tensile testing. These samples were ground by using a series of emery papers, down to grade 1000. The samples were degreased with acetone and then coated with silica gel, leaving an exposed area of 0.12 cm² in the middle. The cement

Table 1

The concentration of ions in the cement extract solution (mol/L).

Iron	K ⁺	Ca ²⁺	Na ⁺	SO_4^{2-}	Cl-
Concentration	5.37×10^{-5}	2.71×10^{-5}	9.62×10^{-5}	$\textbf{2.08}\times10^{-5}$	$7.52 imes 10^{-1}$

extract solution was prepared by adding 1000 g of ordinary Portland cement (P.O 42.5) to 5 L of distilled water. The resulting liquid was stirred for 30 min, held for 4 h, and then filtered [12,13]. The filtered liquid, with a pH of 12.5, was taken as the concrete pore solution. Moreover, the anions and cations in the solution were analyzed by using an ICS3000 (Dionex, USA) ion chromatography system and an ICP-MS7500CE (Agilent, USA) inductively coupled plasma mass spectrometer, respectively. The resulting concentrations are listed in Table 1. The pH of the filtered liquid was adjusted to a value of 9 by using a dilute nitric acid solution as the carbonated concrete pore solution. An electrolyte consisting of 0.05 M (0.292 wt.%) aggressive ions (Cl⁻) was prepared from analytical grade sodium chloride.

2.2. Experiments

An in-house setup (Fig. 2), was used to control the deformation of the samples. The stress-strain curve of the materials indicated that plastic deformation occurred at the strain higher than 0.83% [14]. Various engineering strains, elastic deformation including 0%, 0.4%, 0.8%, and plastic deformation including 2.0%, 5.0%, 10%, 20%, and 40%, were chosen to study the effect of deforma-



Fig. 2. Illustration of tensile-stressed 304 stainless steel samples and the electrochemical test model.

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