Corrosion Science 82 (2014) 347–355

Contents lists available at ScienceDirect

Corrosion Science

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

The passive behaviour of 304 stainless steels in saturated calcium hydroxide solution under different deformation

Xingguo Feng [a,*], Xiangyu Lu [b], Yu Zuo [c], Da Chen [a,*]

[a] Key Laboratory of Coastal Disaster and Defence, Ministry of Education, College of Harbour, Coastal and Offshore Engineering, Hohai University, Nanjing 210098, Jiangsu, China
[b] School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China
[c] School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 22 November 2013
Accepted 25 January 2014
Available online 1 February 2014

Keywords:
A. Concrete
A. Stainless steel
B. Polarization
B. XPS
C. Passive films
C. Interfaces

ABSTRACT

The passive behaviour of deformed 304 stainless steel samples in saturated calcium hydroxide solution has been studied by electrochemical technologies and X-ray photoelectron spectroscopy (XPS). The passive films on seriously deformed stainless steel become heavily doped. The donor and acceptor densities increase with increasing degree of deformation. The space-charge layer is thinned as the substrate is progressively deformed. The degree of deformation has an obvious influence on the composition of Fe^{II}/Fe^{III} cations, but do not have a significant influence on the content of Cr cations. Compared with an elastically deformed sample, the passivity of a plastically deformed stainless steel is more significantly affected.

1. Introduction

The use of stainless steel rebars is one of the most effective methods for ensuring the durability of concrete structures in highly aggressive environments [1,2]. Castro-Borges et al. [3] reported that a stainless steel rebar constructed pier still performed satisfactorily after more than 60 years of service. Dimitri and Stewart [4] and Cramer et al. [5] concluded that using stainless steel rebar will reduce the cumulative costs by 50% for a concrete bridge exposed to a marine environment over 120 years.

Concrete structures are always subjected to a number of loads, which will ultimately degrade them. Anhvu et al. [6] studied stress corrosion cracking of precast steel wires and found that their service life was significantly reduced as the magnitude of the stress was increased. In addition, the results indicated that high stress increases mass loss in comparison to unstressed samples. On examining a cracked pre-stressed concrete line for water supply, Valiente [7] found that the strength and ductility of the steel wires were obviously diminished, whereas those of the concrete materials were not significantly degraded. Clearly, stress affects the corrosion behaviour of rebar in concrete.

Some authors also studied the effects of stress on the passive behaviour of metals in neutral or acid solutions. Yang and Luo [8] studied the passive behaviour of 304 stainless steel under tensile stress in a borate buffer solution. The results suggested that the critical chloride concentration, corresponding to rupture of the passive films, decreased with increasing tensile stress. Vignal et al. [9] studied the semiconducting behaviour of 316L stainless steel under elastic stress in an acid solution at pH 3 containing 0.02 M sodium chloride and found that high elastic stress caused the passive films to be heavily doped. In addition, the heavily doped films were sensitive to pitting corrosion. In another report, Zhang and Cheng [10] investigated the passive behaviour of pre-cracked X70 pipeline steel in carbonate/bicarbonate solution under tensile stress. The authors proposed that both the crack-tip and the region ahead of the cracks could be passivated. However, the results also indicated that the passive films at the crack-tip were less stable and susceptible to pitting corrosion. Studying the micro-electrochemical behaviour of 304L stainless steel in 0.5 M K_2SO_4 solution containing 10 mM $K_3Fe(CN)_6$, Sidane et al. [11] found that the kinetic constant for oxidation of the mediator on the substrate increased significantly with increasing stress magnitude. Zhu and Luo [12] studied the activity of Alloy 800 under stress in a ferrocenemethanol solution containing potassium chloride and thiosulfate, and found that both tensile stress and compression stress enhanced the surface activity. Phadnis et al. [13] studied the passive behaviour of cold-rolled 304 in 3.5 wt% NaCl solution and

* Corresponding authors. Tel./fax: +86 25 83786611.
E-mail addresses: fengxingguo@hhu.edu.cn (X. Feng), chenda@hhu.edu.cn (D. Chen).

http://dx.doi.org/10.1016/j.corsci.2014.01.039
0010-938X/

found that the Cr/Fe ratio of the passive film increased as the cold-rolling procedure. After investigating the metastable pitting of 17–4 precipitation hardening stainless steel in 3.5 wt% NaCl solutions, Nakhaie and Moayed [14] reported that the pit peak current and pit growth rate increased with increasing degree of cold working. Díaz et al. [15] studied the passivation of high-strength steel wires under constant stress in alkaline solutions containing different chloride ions. Their results indicated that stress will provoke the breakdown of passive films, even at low chloride concentrations solutions.

To the best of our knowledge, there has been little study on the effects of stress or strain on the passivation of stainless steel in alkali solutions. In the present study, the passive behaviour of deformed 304 stainless steels has been studied in saturated calcium hydroxide solution. The results suggest that the passive films on seriously deformed samples become heavily doped, and the space charge layers are thinned with increasing degree of deformation. Moreover, XPS results suggest that high deformation provokes oxidation of Fe^{2+} ions to Fe^{3+} ions in the passive films, whereas it does not visibly affect the oxidation state of the Cr cations.

2. Materials and experiments

Type 304 stainless steel, with the chemical composition listed in Table 1, was used in this study. Samples of the size shown in Fig. 1 were adopted for tensile testing. The stress–strain curve of the studied stainless steel is shown in Fig. 2. As can be seen, plastic deformation occurred when the strain exceeded 0.83%. The deformations presented in Table 2 were chosen to study the influence of the degree of deformation on the passivation of stainless steel. The designed deformations were obtained by using a universal testing machine (LETRY, Machine Company, Xi'an, China) at a strain rate of 1 mm/min. Samples were ground with emery papers up to No. 600 and degreased with acetone. Thereafter, the samples were covered with a coating of silica gel, leaving an exposed area of 1 cm^2 in the middle. The saturated calcium hydroxide solution, at pH 12.5, was used to simulate concrete pore solution.

After achieving the designed deformation, electrochemical tests were performed on the deformed samples using the apparatus shown in Fig. 3. All electrochemical tests were performed with a CS350 workstation (Corrtest Instrument, China). Using a platinum plate as the counter-electrode and a saturated calomel electrode (SCE) as the reference electrode, a classical three-electrodes cell was used in the electrochemical measurements. Each experiment was performed in triplicate, with a new sample each time. To reduce the oxide film formed by aerial oxidation, all samples were cathodically polarized at a potential of $-1.0\,V_{SCE}$ for 5 min [16] before testing. At a scan rate of 2 mV/s, potentional dynamic polarizations were carried out after immersion of the deformed sample in saturated calcium hydroxide solutions for 1 h. To determine the optimal applied frequency, the frequency dependence of the measured capacitance was measured over a wide frequency range from 100 Hz to 5000 Hz after the samples had been stabilized for 2 h in solution. Using a 10 mV superimposed AC signal and a potential step of 50 mV from $-1.2\,V_{SCE}$ to $1.2\,V_{SCE}$, capacitance measurements were also performed after different immersion times. Finally, capacitance measurements of the differently deformed samples are made at a frequency of 1000 Hz after passivation for 2 h in solution. In addition, after stabilization for 1 h in saturated calcium hydroxide solution, potential step tests were performed to record the current transients during the initial passivation of the stainless steel. The potential was maintained at $-0.8\,V_{SCE}$ for 100 s, then suddenly stepped up to $0.5\,V_{SCE}$ and the current was recorded against time [17].

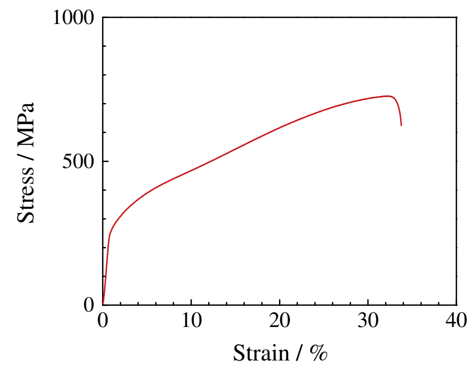

Fig. 2. Stress–strain curve of the tested 304 stainless steel.

The composition of the passive films was analyzed by means of an ESCALAB 250 X-rays photoelectron spectrometer (XPS). Monochromatized Mg Kα radiation (1253.6 eV) was used as the excitation source. After being exposed to the saturated calcium hydroxide solution for 24 h, the samples were dried and transferred to the XPS instrument for analysis. The binding energy values were calibrated with reference to the C 1s peak at 285 eV, and the narrow scan spectra were fitted with XPSPEAK 4.1 software.

3. Results and discussion

3.1. Potential dynamic polarization curves

Potentiodynamic polarization curves of differently deformed samples are depicted in Fig. 4. As can be seen, the magnitude of

Table 1
Chemical composition of the studied 304 stainless steel.

Element	C	Si	Mn	S	P	Cr	Ni	Mo	Fe
Percentage (%)	0.075	0.32	1.3	0.0068	0.020	18.1	8.2	0.16	Balance

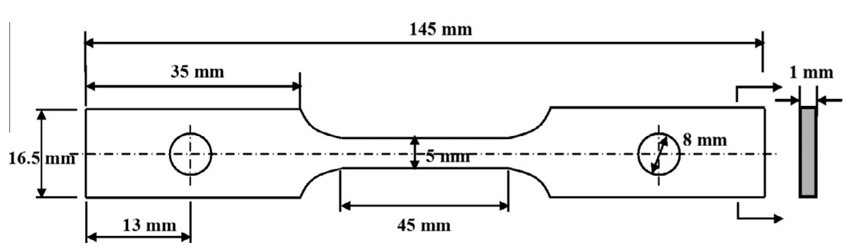

Fig. 1. Geometry of specimens used in tensile state.