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Investigation of stress-enhanced surface reactivity on Alloy 800 using scanning electrochemical microscopy

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ABSTRACT

Scanning electrochemical microscopy (SECM) was used to simultaneously investigate the impact of tensile and compression stress on reactivity of the same Alloy 800 sample in ferrocenemethanol solution containing thiosulfate. Strong surface reactivity was observed on the stressed regions. Both tensile (the exterior edge) and compressed (inner edge) regions showed higher reactivity than the region between these. Hence both tensile stress and compression stress increased the localized surface reactivity, indicating potential for acceleration of corrosion susceptibility of Alloy 800 under stress in thiosulfate-contained chemistries.

1. Introduction

Stress causes localized microstructure deformation, which could enhance the localized corrosion [1–3]. Ghosh et al. revealed that surface machining of 304 L stainless steel results in extensive grain refinement, strain induced martensite transformation and a high magnitude of plastic deformation near the surface [4]. Many efforts have been made to correlate structure deformation and corrosion susceptibility, and to determine mechanisms. Corrosion mechanisms have been investigated using many different surface characterization methods, such as SEM [5], EDX [6], AFM [7], and Kelvin probing method [8]. However, these techniques rarely provide *in-situ* localized electrochemical information at micro- or submicro-scale. SECM has been found to provide a direct *in-situ* experimental method to study the relationship between electron-transfer rates, oxide conductivity and localized corrosion [6,7,9,10]. Sun et al. studied stress effects on heterogeneous electron transfer (ET) on a stainless steel and found that the electron transfer rate decreased with an increase in the applied stress. This technique provided insights into the mechanism of the impact of stress on corrosion.

In this paper, the effects of tensile and compression stresses on heterogeneous ET are simultaneously described using SECM. It is the first time to apply SECM to study the distribution of surface reactivity of both the tensile and compression stressed regions of a single sample in thiosulfate-containing solution.

2. Experimental

2.1. Chemicals and specimen preparation

The 0.9 mmol/L ferrocenemethanol (Fc, 97%, Aldrich) solution with 0.65 mol/kg KCl (Certified ACS, Fisher Scientific) and 0.075 mol/kg thiosulfate (Certified ACS, Fisher Scientific) was prepared by dissolving Fc, KCl and $Na_2S_2O_3$ into distilled water.

Alloy 800 tube (from Sandvik, Heat #: 516809) which contains Fe (43.2 wt.%), Ni (32.78 wt.%), Cr (21.87 wt.%) and other low-content elements (Si, Mn, P, S, Co, Ti) had the dimension of 15.88 mm outside diameter and 1.13 mm average wall thickness. The constant-strained sample (change of OD: 0.356 mm) is illustrated in Fig. 1a. In accord with GB38-01 [11], the applied stress was significantly higher than the Alloy 800 yield stress [12]. Specimens were cut from the long tube into ~2 cm lengths, connected with copper wire and sealed in epoxy. The end surface of the ring (Fig. 1b) was mechanically polished with wet silicon carbide paper (Buehler Ltd.) down to 1200 grit to expose the end surface of C-ring, then rinsed with copious deionized water, and dried in air.

2.2. SECM experiments

During the SECM experiments, a specimen was sandwiched between two pieces of Teflon to build an electrolyte cell. This cell was mounted on the SECM stage (CHI, USA). An ultramicroelectrode (UME) with a radius of 5 μm and RG of 5 was used as the SECM probe. An Ag/AgCl electrode (saturated with KCl, CHI) was used as the reference electrode and a Pt wire was the counter electrode. The potentials in this paper are presented in SHE scale. The probe was

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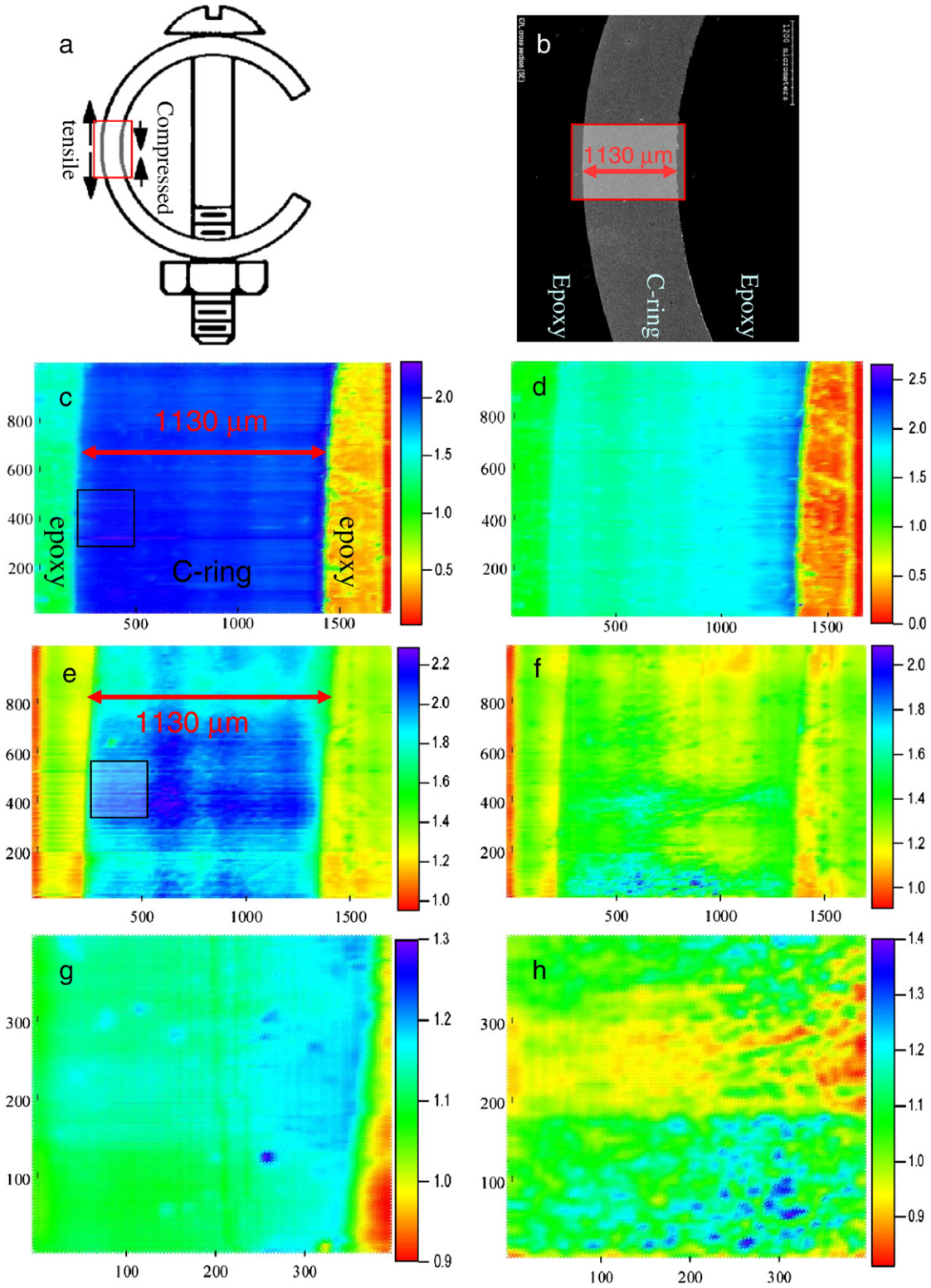

Fig. 1. The illustration (a) and SEM image (b) of a stressed C-ring, and SECM images of a non-stressed specimen (c and d) and a stressed specimen (e and f) in thiosulfate-contained Fc solution at different potentials (E_S) on specimen (c and e: 0.0 V, d, f, g and h: 0.4 V). The distance between tip and specimen: 6 μm for Images c, d and g, and 9 μm for Images e, f and h.

biased at a potential of 0.65 V to obtain steady-state current, and then the probe was driven to the epoxy region on specimen surface in order to accurately determine the gap distance between the probe and the specimen [13]. When the UME current (i_T) reached the prescribed value, the tip stopped automatically. The normalized current (I_T, the real tip current over the tip current in bulk solution) vs. normalized distance (L, the real distance between tip and specimen over the radius of UME) was plotted as the probe approach curve (PAC). The real gap distance between tip and specimen was estimated by comparing experimental PACs with simulated/theoretical PACs. The UME gap distance was maintained constant and scanned above the specimen to obtain the SECM images of the C-ring surface.