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Quasi-in-situ ex-polarized TEM observation on dissolution of MnS inclusions and metastable pitting of austenitic stainless steel

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ABSTRACT

The pit initiation and growth processes occurring in austenitic stainless steel are included in the passive region of polarization curve. However, polarization measurements do not yield surface morphological insights, which limit the ability to provide a comprehensive picture of the corrosion process. A quasi-in-situ ex-polarized TEM observation method is designed to elucidate the microstructural evolution corresponding to the characteristic regions of the electrochemical polarization curve. This work shows the potential and advantage of combining TEM technique and the traditional electrochemical methods in investigating the initiation of localized corrosion.

1. Introduction

Stainless steels, as typical passive metallic materials, are susceptible to pitting corrosion in the presence of aggressive anionic species. The pitting corrosion of stainless steel is generally believed to originate from the local dissolution of MnS inclusions [1–10]. The dissolution of MnS may involve both electrochemical [2,3,11,12] and chemical dissolution [13] processes in aqueous media. Wranglen [2] proposed a model wherein MnS is primarily electrochemically oxidized to elementary sulfur through the reaction: $MnS = S + Mn^{2+} + 2e$. This model has been further verified by other studies [3,11] in which the sulfur was detected experimentally in neutral solution, albeit via different electrochemical reaction paths. One such path involves the oxidation of MnS to HSO_3^- [3] or $S_2O_3^{2-}$ [11] firstly, and subsequent production of S by cathodic reduction of HSO_3^- or the decomposition of $S_2O_3^{2-}$. Lott and Alkire reported that, thiosulfate was the only product of MnS dissolution in neutral NaCl electrolyte [12]. On the other hand, MnS was found to undergo chemical dissolution at OCP in acidic NaCl solution [13]. Webb et al. [14], through voltammetric response experiment, concluded that MnS inclusions dissolve chemically to HS^- at low anodic potentials under acidic conditions, but dissolve electrochemically at high potentials at neutral pH.

Our previous work using in-situ ex-environmental TEM method [15], gave direct evidence that pitting initiated from the local dissolution of MnS at the interface of the MnS and $MnCr_2O_4$ nano-octahedron embedded in the MnS. The dissolution occurring in the neutral NaCl should be through the electrochemical path as mentioned above. Under anodic polarization, such electrochemical dissolution events of MnS and the subsequent metastable pitting should be reflected in the anodic polarization curve. For austenitic stainless steels, the potentiodynamic polarization curve is typical and representative. Characteristic regions corresponding to active, active–passive, passive and stable pitting events are well known and generally accepted. Observation of corrosion morphologies corresponding to characteristic regions in a polarization curves provide useful insights into some corrosion events reflected in the curve. It is known that pit initiation and metastable pitting, occurring before stable pitting corrosion, overlap the passive region [16,17]. However, the characteristic features indicating pit initiation and metastable pitting in polarization curves are uncertain since polarization curves do not provide information on surface microstructural evolution, e.g., the tiny variation in microstructure resulted from the corrosion process.

Features of the passive region corresponding to the dissolution of MnS inclusions and metastable pitting have been studied using microelectrochemical probe method [9,10,18–23]. Webb

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et al. compared the polarization curves of inclusion-containing and inclusion-free regions and noticed that a steep rise in current was associated with the dissolution of the MnS inclusions [9,22]. Muto et al. [10,23], using a microcell technique combined with SEM and CLSM, observed that MnS dissolution occurred within the passive potential range and attributed the gradual increase in current density and transient current peak appearing within the passive region to the electrochemical dissolution of sulfide inclusions and metastable pitting events, respectively. It is thus obvious that there is as yet no consensus on the microstructural evolution corresponding to characteristic positions in the passive region of polarization curve. This is in spite of extensive studies [16,24–28] focusing on pit nucleation and growth mechanisms using electrochemical noise analysis methods. The corresponding microstructural evolution is undoubtedly necessary to support the electrochemical mechanisms, but this is still lacking due to the difficulty associated with obtaining the microstructural information at the scale dictated by polarization measurements. The present report describes a quasi-in-situ ex-polarized TEM method to investigate microstructural evolution associated with characteristic features of a polarization curve.

2. Experimental procedures

A commercial hot-rolled 316F austenite stainless steel (Nippon Steel and Sumikin Stainless Steel Corporation) was chosen. Compositions (in wt.%) of the 316F steel are given in Table 1. Hot-rolling made the MnS inclusions needle-shaped, and parallel to the rolling direction.

2.1. TEM specimen preparation

The steel rod was first cut into sections of 1 cm using a linear precision saw. Pieces parallel to the rolling direction were sliced with the thickness of 300 μm. The steel piece was ground using grit silicon carbide papers to 120 μm and then was die-cut into disks with diameter of 3 mm. The samples were ground using variant grit silicon carbide papers, polished with diamond paste to 1 μm finish, and finally thinned by ion-milling. After the first-round of TEM observations, some of the specimens were plasma-cleaned and then anodic polarized in NaCl electrolytes at 28 °C. The TEM specimens which underwent electrochemical polarization were quickly cleaned (in distilled water and methanol), dried, and transferred into the TEM for further investigation, designated quasi-in-situ ex-polarized TEM method. A Tecnai G2 F30 transmission electron microscope, equipped with a high-angle angular-dark-field (HAADF) detector and X-ray energy-dispersive spectrometer (EDS) systems, was used at 300 kV in TEM characterization.

2.2. HAADF–STEM imaging technique

HAADF (High Angle Annular Dark Field)–STEM (Scanning Transmission Electron Microscopy) imaging is a newly developed technique in TEM, in which an electron beam (with atomic scale) scans the specimen point to point and an annular detector collects the high-angle scattered electrons (~50 to 200 mrad). The high-angle scattering is predominantly incoherent and roughly proportional to the square of the atomic number, Z, of the scattering atom, which yields HAADF–STEM image [29]. Even small changes in chemical composition and/or thickness are easily distinguished. Therefore this imaging mode has the advantage of studying the initial stage of localized corrosion.

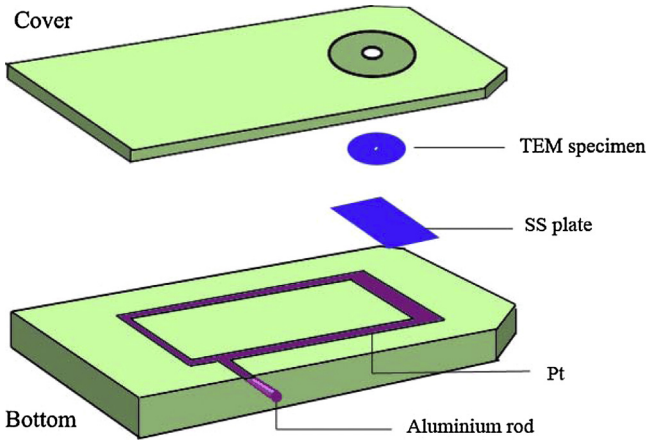

Fig. 1. Schematic diagram of the setup that allows positioning of a TEM specimen as working electrode.

2.3. Electrochemical experiments

In quasi-in-situ ex-polarized TEM observations, obtaining the electrochemical polarization curves of the TEM specimens is key, but quite challenging to accomplish. A traditional three-electrode system was used in electrochemical experiment. The working electrode is the TEM specimen, Pt counter electrode and SCE (saturated with KCl) reference electrode.

A plastic-shelled fixing plate was designed (shown in Fig. 1) to facilitate mounting the TEM specimen as working electrode. The specimen is linked through a Pt slice, which is connected with the outer aluminum rod and fixed by a plastic cover. A 316F stainless steel plate (same material with TEM specimen) is placed between the Pt slice and the TEM specimen in order to avoid electrolyte contact. The specimen was exposed to the electrolyte via the hole in the cover, with diameter 2 mm. Gaps in the setup were coated with thread sealing tape and olefin resin.

It should be noted that all the potential values reported have been normalized with respect to the standard hydrogen electrode (vs. SHE). The electrolyte was NaCl solution with concentrations of 0.5 mol/L and 0.1 mol/L. The electrochemical treatments include potentiodynamic and potentiostatic polarization. In the potentiodynamic polarization measurements, the potential scan began from −250 mV versus OCP and the scan rate was 0.33 mV/s. In the potentiostatic polarization experiments, a potential of 240 mV (vs. SHE) located in the passive region was selected and the current response recorded once every 0.5 s. The electrolytes were maintained at 28 °C with electric-heated thermostatic water bath. The working area of TEM specimen is estimated to be about 0.03 cm^2 and the bulk counterpart is about 0.1 cm^2. AUTOLAB PGSTAT302N electrochemical workstation was used in electrochemical polarization experiments.

3. Results and discussion

3.1. Dissolution of MnS inclusions and metastable pitting under potentiodynamic polarization

A TEM specimen of type 316F stainless steel (316F SS) was polarized in 0.5 mol/L NaCl electrolyte and a potentiodynamic polarization curve was recorded, as shown in Fig. 2a. A polarization curve obtained on a bulk counterpart specimen is also shown in Fig. 2a. The TEM specimen is qualitatively of the same character with the bulk specimen, thus confirming the reliability of the polarization response of the TEM specimen, as well as validating the corresponding microstructural evolution. The polarization measurement was stopped at 345 mV (vs. SHE) below the pit-