Effects of elastic deformation on the anodic dissolution of X70 carbon steel in sulfuric acid solution

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ABSTRACT

Effects of elastic deformation on the anodic dissolution of X70 steel have been investigated in $0.5 \, mol \, dm^{-3}$ H_2SO_4 solution. In the active region, the elastic stress exerts no obvious influence on the active dissolution rate of the specimen. However, in the oscillatory region, it leads to a marked increase in the frequency of current oscillations, while the mode remains essentially the same. In the passive region, it induces oscillations at the initial stage, but shows no significant effect on the passive current when the potential is controlled at the more positive stage. Two explanations are postulated: the elastic deformation degrades the stability and increases the defects of the passive film; it increases the surface energy (ΔG_S), causing the effective potential (E_V) to move negative.

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1. Introduction

During the anodic dissolution of metallic materials, potentiostatic current oscillations are often observed in acidic solutions, such as iron/acid systems [1–8]. The oscillatory electrodissolution arises from such intricate processes as surface reactions, mass transfer, film formation and dissolution [6]. Therefore, current oscillations contain abundant information about the dynamics of electrode processes, the study of which will yield insight into the mechanisms of anodic dissolution, prepassive and passive processes of metallic materials. Despite the amount of work done in this area, the mechanisms of current oscillations are far from being fully understood.

The current oscillation is a typical non-linear phenomenon resulting from the periodic formation and dissolution of the surface film at the electrode/electrolyte interface [4]. The oscillatory electrodissolution processes are mainly determined by the physicochemical microenvironment at the interface, which is very sensitive to external and/or internal perturbations. Three main types of possible perturbation sources can be identified: changes in the electrolyte, such as pH, the nature and the concentration of chemical species, the stirring and the viscosity of the solution; changes of the electrode, such as hydrogen charged and tensile stress applied; changes involving both electrolyte and electrode, such as the application of the potential and the existence of the magnetic field.

Studies concerning the changes caused by electrolyte variables are the richest. According to the model developed by Franck and Fitzhugh, the Flade potential

$$E_F = 0.58 - 0.058 \, pH \, (E \, vs. \, SHE \, at \, 20 \, °C) \tag{1}$$

and the current oscillations are related to the spontaneous passivation–activation triggered by the concentration wave of H^+ ions in the vicinity of the iron electrode surface [1]. The research of Podesta et al. indicated that when the concentration of sulfuric acid was more than $2 \, mol \, dm^{-3}$, the passive effect was apparently produced by a precipitated ferrous sulfate salt film, while the passive layer might be composed of hydroxide when the concentration of sulfate acid was less than $2 \, mol \, dm^{-3}$ [2]. Sazou et al. discussed perturbation of the passive–active transition state of the Fe/$0.75 \, mol \, dm^{-3}$ H_2SO_4 system by adding a low concentration of halide ions, and found that halide ions triggered local dissolution by an adsorption mechanism [6]. They also discussed the effects of nitrate ions on the breakdown of the passive film and current oscillations of iron in the chloride-containing sulfuric acid solution [7]. Ferreira et al. studied the effects of solution viscosity on the current oscillations of Fe/H_2SO_4 system at the beginning of the plateau of polarization curves. The increase in solution viscosity eliminated the oscillations by a change in the hydrodynamic condition [9]. The

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necessary electrode potential for oscillations increased as the stirring speed of the solution rose, until it reached a critical point above which stable limit cycle oscillations could not appear during the anodic dissolution of iron in sulfuric acid solution [10].

The solution injection method has been found to be convenient and effective in exploring how the system behaves when the electrode/electrolyte interface is disturbed by solutions different from the bulk solution. An et al. found that when the chemical environment near the surface of an iron electrode was changed artificially, potentiostatic current oscillations in the Fe/H_2SO_4 system were generated [11]. In a partially-closed environment (PCE), with the precise control of the amount of the solution injected, the physico-chemical microenvironment at the electrode/electrolyte interface is manipulated. Artificial oscillations of Fe/H_2SO_4 system were induced when different chemical materials were injected into the PCE periodically and the periods of the artificial oscillations could be changed as designed [12].

Studies concerning the changes in both electrolyte and electrode are paid more and more attention to. Wang and Chen [13] found the current oscillations of Fe/H_2SO_4 system appeared to be quite sensitive to the strength of the magnetic field (MF). The existence of the MF enhanced the mass transport by the magnetohydrodynamic (MHD) flow which changed the current oscillatory behavior. The opposite effect to that of the MF caused by the addition of glycerol in the solution provided further support to the influence of the MF on the current oscillations. According to Yu et al., a fairly low magnetic field of about 0.030 T could affect the period and the amplitude of current oscillations; however, only the magnetic field intensity above 4 T could affect the Flade potential of the iron electrode in sulfuric acid solution [14].

In comparison, investigation into the perturbation on the electrode has been scarce. Li et al. observed the oscillatory electrodissolution of metals to study the hydrogen-promoted corrosion of iron in phosphoric acid solution, and the primary results proved that it is an effective method for investigating the effect of hydrogen on both the formation and the dissolution of a passive film [15]. Few researchers have reported the effects of tensile stress, especially elastic stress on current oscillations. According to the experimental results of Lu et al. [16], the elastic deformation could affect the frequency of the current oscillations of carbon steel in 5 mol dm^{-3} H_3PO_4 solution but the oscillatory mode was essentially unchanged; after the tensile stress exceeded the yield strength, the mode changed into a chaotic one with high frequencies.

In this paper, the elastic stresses are applied during the anodic polarization processes, and the effects of the elastic deformations on the anodic dissolution of X70 steel in sulfuric acid solution are discussed.

2. Experimental

X70 steel was used as the test material. It has the yield strength of 483 MPa and the chemical composition (in wt%) of 0.22 C, 1.65 Mn, 0.24 Si, 0.015 S, 0.025 P and Fe balance. The tensile specimen was used as the working electrode, which was 25.6 mm in gauge length and 2.5 mm in diameter, as shown in Fig. 1. In the electrochemical measurement, only 5 mm of the working segment was exposed to the solution and the rest was sealed with epoxy resin. The specimen was abraded with a series of wet sand paper of different grit sizes (1200 and 2000), and then cleaned by alcohol and triply distilled water in an ultrasonic bath before each experiment. In the submerged test, a sheet of X70 steel with the size of 0.20 mm × 3.0 mm × 70 mm was used as the working electrode. One side of the specimen was coated with 705 silicon rubber, and the other side exposed to the solution. One end of the specimen was
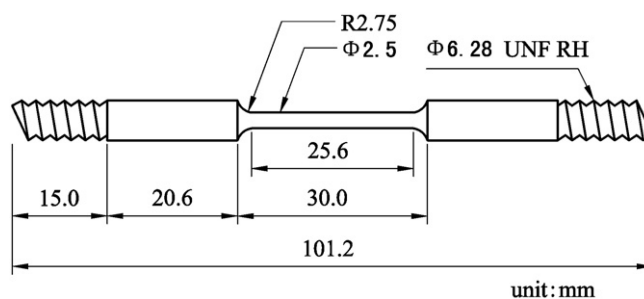

Fig. 1. The illustration of the specimen used in the slow strain rate test and the electrochemical measurements.

fixed, and the other free. The counter electrode was a platinum net with a size of 10 mm × 5 mm and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary tip set at 2 mm from the working electrode. All potentials reported here are referred to SCE. The test solution was 0.5 mol dm^{-3} H_2SO_4 prepared from reagents of analytical grade and triply distilled water.

The electrochemical experiments were carried out by CHI 660 electrochemical analyzer. The scan rate of the j–E curves was 0.002 V s^{-1}. The stresses were applied by a Stress Corrosion Testing Machine (Letry, produced by Lichuang Machine Company, Xi'an, China). In the slow strain rate test (SSRT), the strain rate was 3.33×10^{-6} s^{-1}. The tensile stresses used in the electrochemical experiments were 150 MPa, 300 MPa and 450 MPa respectively. All the experiments were carried out at room temperature.

3. Results

3.1. The stress–strain curve of X70/H$_2$SO$_4$ system

The tensile stress–strain curve of X70 steel in 0.5 mol dm^{-3} H_2SO_4 solution is presented in Fig. 2, from which the tensile properties can be obtained. The X70 steel did not show the yield point phenomenon when the SSRT was carried out, and the tensile strength was about 640 MPa. The tensile stresses used in the electrochemical experiments were about 30%, 60% and 90% of the nominal yield strength of X70 steel.

3.2. The j–E curves of X70/H$_2$SO$_4$ system with various elastic deformations

The polarization curves of X70/0.5 mol dm^{-3} H_2SO_4 system with various elastic stresses, shown in Fig. 3(A–D), can be roughly divided into three regions: the active region (I), the oscillatory
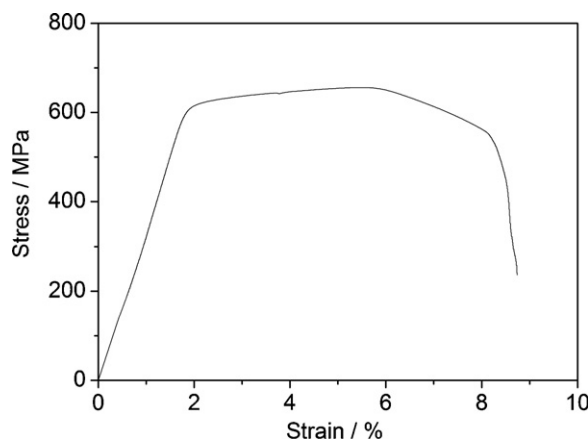

Fig. 2. The stress–strain curve of X70 steel in 0.5 mol dm^{-3} H_2SO_4 solution.