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Electrochemical behaviour of martensitic stainless steel after immersion in a H_2S-saturated solution

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ABSTRACT

Time dependent experiments were carried out to study the corrosion behaviour of Super 13Cr martensitic stainless steel after immersion in a H_2S-saturated solution. The Point Defect Model was employed to obtain key parameters. With increasing immersion time, the corrosion product layer thickened, but displayed a defective structure. The thickness of the barrier layer decreased with extending the H_2S-exposure time, which notably lowered the corrosion resistance. The presence of the corrosion scale resulted in a thinner barrier layer in contrast to that without the scale. With/without the corrosion scale, no semi-conductivity and no passive region was observed for Super 13Cr after 96 h-immersion. The hydrogen ingress during H_2S-exposure lowered the passivity of the bare alloy substrate.

1. Introduction

The corrosion of tubular goods in the oil and natural gas industry in wet H_2S environments has resulted in extremely high costs and sometimes even to the loss of life and property. It is generally believed that H_2S is aggressive to carbon and low-alloy steels by accelerating the anodic dissolution reactions, resulting in severe weight-loss [1–3]. In addition, the cathodic process in wet H_2S environments (e.g., hydrogen evolution) may also be catalysed on iron sulphide surfaces and lead to hydrogen embrittlement (HE), hydrogen induced cracking (HIC), and sulphide stress cracking (SSC) [4–6], all of which result from the entry of hydrogen into the alloy. In order to lower the risk of corrosion failure, compared with the low-grade steels, stainless steels have been widely employed in H_2S-containing environments, due to their better corrosion resistance, although the presence of H_2S also changed the semiconductor properties of passive film and increased the susceptibility of stainless steels to pitting corrosion [7–12]. Several investigations have contributed to developing an understanding of the influence of various corrosive media containing H_2S on the passive behaviour of stainless steels [7,9]. In comparison, because of the high formation rate of corrosion products on the surface of electrodes in H_2S-containing media [1,9], the often-neglected effect of the corrosion products on the electrochemical properties of steel should be explored.

Moreover, sulphide ions act as a hydrogen atom recombination poison, and the recombination process of atomic hydrogen can be significantly retarded, leading to the increased concentration of hydrogen absorbed by the substrate material [1]. Therefore, it is necessary to analyse the influence of hydrogen absorption on the passivity of stainless steels. The pre-charging method of cathodically polarizing the working electrode to a potential, at which hydrogen is evolved on the surface, was commonly applied in an acidic solution. Yang and Luo [13] found that hydrogen enhances the pitting susceptibility of Type 304 austenite stainless steel, which was rationalized by the authors in terms of "the enhanced substitution of chloride ion generated from the increase of hydrogen-containing species in the passive film" [14]. However, it is more likely that, due to recombination of hydrogen atoms within the blisters that are precursors to passivity breakdown, the blister ruptures at a shorter time after the initiation of cation vacancy condensation at the metal/barrier layer (m/bl) interface than would be the case in the absence of blister pressurization via hydrogen. Ningshen and Mudali [15] reported that hydrogen increased the passive current density and concentrations of the point defects in the passive film of

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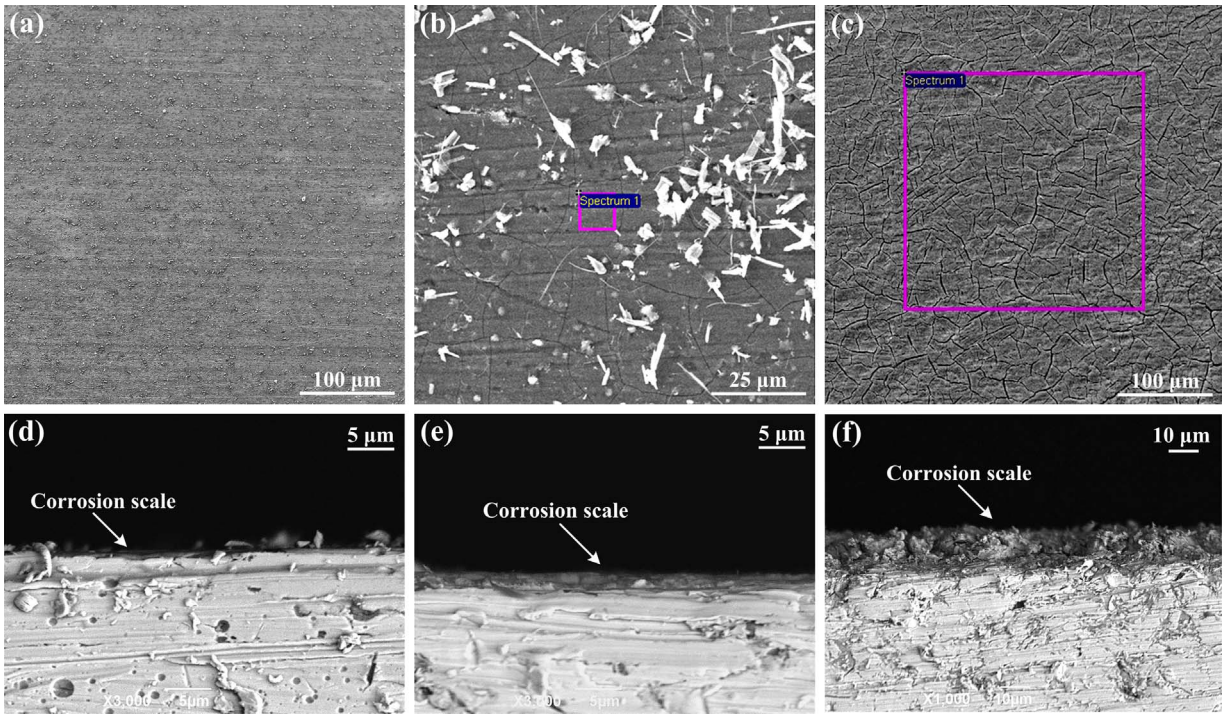

Fig. 1. The surface and cross-sectional morphologies of Super 13Cr specimens after immersion for (a, d) 5 h, (b, e) 20 h, and (c, f) 96 h in NACE Solution A. The surface and cross-sectional images were obtained by using secondary and back-scattered electrons, respectively.

316L austenite stainless steel. Guo et al. [16] revealed that hydrogen promotes the initiation and growth of pits in 2507 duplex stainless steel, and the pits tended to nucleate at austenite phase or austenite/ferrite interface. Thus, from these studies, we infer that the absorbed hydrogen, which is generated by cathodic reaction in H_2S-containing solutions, should have a significant impact on the electrochemical behaviour of stainless steel. However, to the best of our knowledge, few studies related to the impact of hydrogen ingress on the passivity of martensitic stainless steel in H_2S environments have been reported.

This paper presents a study of the corrosion behaviour of Super 13Cr martensitic stainless steel in a 3.5% NaCl solution after immersion into a saturated H_2S solution. Study of the immersed specimens, without/with removing the corrosion scale, not only reveals the impact of corrosion scale on the corrosion behaviour of Super 13Cr stainless steel in H_2S environments, but also unravels the impact of hydrogen ingress that is induced by H_2S on the electrochemical properties of Super 13Cr substrate.

2. Experimental

The chemical composition of the Super 13Cr specimen was (wt.%): 0.027C, 12.87 Cr, 5.32 Ni, 2.20 Mo, 0.18 Si, 0.47 Mn, 0.022 P, 0.004 S and balance Fe. The working electrode (WE) with dimensions of Φ15 × 5 mm was spot-welded to copper wires and embedded in two-component epoxy resin, leaving an exposed area of 1.766 cm^2. Before immersion, the WE was ground to 1500 grit, rinsed with deionized water, degreased in ethanol, and finally dried with a stream of cold air. Subsequently, the WE was immersed into a NACE Solution A [17], which comprises 5% NaCl and 0.5% CH_3COOH in aqueous solution at ambient temperature and pressure. The solution was deoxygenized with high purity N_2 gas for 4 h, then purged with H_2S gas until saturated (approximately 2 h), and kept purged with H_2S gas throughout the experiment. During the immersion process, the buffering effect of acetic acid [12] was used to ensure that the pH remains constant (equal to 2.7). The experimental temperature was 25 °C, and the immersion times were 5, 20, and 96 h. After immersion, the WE was rinsed with deionized water, dipped into ethanol, and dried with a stream of cold air. The surface and cross-sectional morphologies of the specimens after immersion were observed by using a Vega3 Easyprobe SEM with an EDS attachment.

It was found that corrosion scales were generated on the surfaces of the WEs after immersion. For a detailed comparison of the scales formed under different conditions, the electrodes were divided into two groups to analyse the electrochemical behaviour of the stainless steel with and without corrosion scale. The specimens without corrosion scale were obtained by gently polishing the immersed WEs with a 1500 grit SiC paper. The criteria for stopping the polishing process was when the metal substrate was fully exposed. Note that all the "specimens without scale" mentioned in this study refer to this group of WEs.

An aerated 3.5% NaCl aqueous solution was used to investigate the electrochemical properties of the H_2S-immersed specimens. The experimental temperature was controlled at 40 °C by using a recirculating water bath. Potentiodynamic polarisation curves were recorded by using a CS370 electrochemical workstation produced by CorrTest Instruments Corporation in China. EIS and Mott-Schottky experiments were carried out using an EG&G M273A potentiostat/galvanostat attached with an M5210 lock-in amplifier. Two graphite electrodes and a saturated calomel electrode (SCE) were used as the counter electrode (CE) and the reference electrode (RE), respectively. Before the measurements, the WEs were immersed in the electrolyte and stabilized for 30 min. The EIS data were then measured from 10 kHz to 0.05 Hz with potential amplitude of 10 mV. The Mott-Schottky experiment was carried out with an applied potential from −0.2 V_{SCE} to 0.15 V_{SCE}, and the potential was swept at a rate of 12.5 mV/s. This procedure ensures that the barrier layer thickness remains constant and the point defect structure remains "frozen" over the duration of the experiment, thereby more accurately conforming to the assumptions behind Mott-Schottky theory. The potentiodynamic polarisation test was started from −0.2 V (vs. OCP) with a sweep rate of 1 mV/s.