

Research on Pitting Behavior of DH32 Steel in Presence of Thiosulfate and Chloride Ions

Li Zhang^a, Xianpeng Ouyang^b, Yuanyuan Shen, Xiafei Zhang, Xucheng Dong

College of Ocean Science and Engineering, Shanghai Maritime University, 1550 Haigang Av.
Lingang New City, Shanghai 201306, China

^aemail: zhangli@shmtu.edu.cn, ^bemail: billouyang@foxmail.com

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Abstract. The pitting behavior of DH32 steel was studied by using the potentiodynamic polarization method. The results showed that the passivation zone narrowed as the concentrations of chloride ions and thiosulfate ions ($S_2O_3^{2-}$) increased. At high $S_2O_3^{2-}$ ions concentrations, there was a more potential shift to the positive. At high chloride concentrations, i.e. 10% mass NaCl solution, it is noticeable that the pitting corrosion rates had a reverse nature with the increase in concentration of $S_2O_3^{2-}$ ions. These findings also concur with the metallographic examination of the specimens after polarization tests.

Introduction

Currently, the development of ocean energy has been in a popular research around the world. There are huge ocean engineering marketing demands to high strength structural steels with good performance under marine environmental, especially the upsizing, high speed ship and the development of offshore oil and gas fields^[1-2]. Meanwhile, in order to ensure the reliability of safe navigation and use of the ship, higher requirements are put forward in term of strength, toughness, fatigue property, weld ability and corrosion resistance.^[3] Lots of investigations show that during the engineering process explored in marine, high strength structural steels have to served in a much more tough environments compared with the land environment. Most of the time, worked under seawater contains large amounts of chlorine and sulfur^[4-5]. High concentration chlorine can cause serious material localized corrosion damage, even lead to fracture of the whole material. Therefore, the corrosion resistance property becomes one of the key index to evaluate a material's marine-engineering suitability^[6]. At present, the pitting corrosion resistance behavior and its affections of a high strength steel DH32 in tough seawater was developed by using a mimic aqueous solution with various concentrations of sodium chloride and sodium thiosulfate.

Material and Experimental Procedure

The chemical composition (wt. %) of DH32 steel in this work is: 0.03C, 1.1Mn, 0.05Al, 0.4Si, 0.03 P, 0.02 S, and Fe balanced. Coupons of sizes 10mm×10mm×1mm were cut. For microstructure analysis, the coupons were abraded using a series of silicon carbide papers from 400#-1000# and some were rubbed against a smooth cloth using alumina (2.5μm) till reaching mirror bright surface, rinsed in water and sterilized, then stored in ethanol ready for use. For morphological examination, some coupons were etched by swabbing with a 10% solution of ferric nitrate to reveal microstructure. And to facilitate electrochemical monitoring, an electrical connecting wire was soldered to the back face of coupons then encapsulated in a temperature resistant epoxy resin.

The medium were NaCl solutions of various concentrations (0.01% mass, 0.1% mass, 1% mass, 10% mass), $Na_2S_2O_3$ solutions of various concentrations (0.001 mol/L, 0.01mol/L, 0.1mol/L, 1 mol/L) and NaCl solutions added $Na_2S_2O_3$ solutions of various concentrations. The solutions used in the tests mixed by deionized water and analytical grade NaCl, $Na_2S_2O_3$. The experimental temperature is 25°C.

A conventional three-electrode glass corrosion cell with a capacity of 500 ml was used to carry out the potentiodynamic polarization measurements. A saturated calomel electrode (SCE) was used

as the reference electrode, a platinum slice with an area of 2.25 cm^2 was used as the counter electrode and the DH32 was used as working electrode. Test medium is various of sodium chloride solution with or without various concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ addition. All electrochemical measurements were carried out using an Autolab work station (AUT83924) controlled by GPES Nova 1.8 software. Before the potentiodynamic polarization measurements, the specimens were maintained in the potential of -2.0V for 600s first, for cleaning the surface of the cathode. When the open circuit potential was steady for 400s, polarization curves were measured as a scanning rate of 1 mV/s . The workstation scanned from -2.0V to $+1.0\text{V}$. After all specimens were measured for the polarization curve, corrosion morphology of the surface was observed by optical microscope (METAM 1V).

Results and Discussion

Effects of Chloride Ions Concentrations

The potentiodynamic polarization curves for DH32 in the presence of various concentrations of Cl^- ions in NaCl solution at room temperature are shown in Fig.1. It is clear that DH32 suffers from pitting corrosion at high Cl^- ion concentrations. At lower levels of Cl^- ions i.e. 0.01%, 0.1% and 1% NaCl the passivation zone is still wide enough to impede the current from reaching the surface of the metal. With the increase in Cl^- concentration to higher levels, the passivation zone is narrowed up to a level making DH32 prone to pitting corrosion.

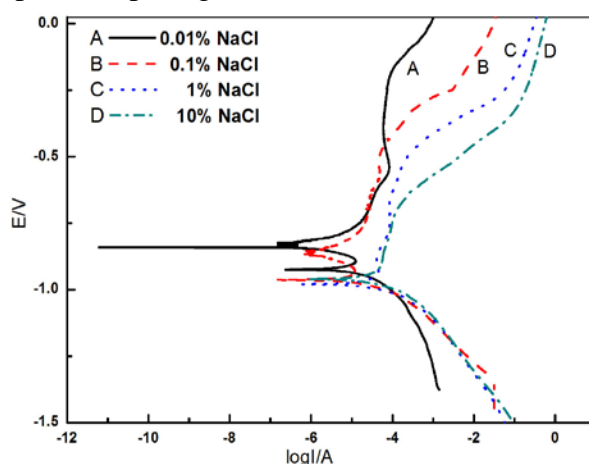


Fig. 1 Potentiodynamic polarization curves of DH32 steel specimens in NaCl solutions of various concentrations

Effects of Thiosulfate Ions Concentrations

The potentiodynamic polarization curves for DH32 in the presence of various concentrations of $\text{S}_2\text{O}_3^{2-}$ ions in $\text{Na}_2\text{S}_2\text{O}_3$ solutions at room temperature are shown in Fig. 2. It was found that corrosion potential (E_{corr}) values changed slightly towards active direction with the increase in $\text{S}_2\text{O}_3^{2-}$ ion concentration. While the pitting initiation potential of DH32 steel decreased with increasing concentration of $\text{S}_2\text{O}_3^{2-}$. Fig.3 showed the metallographic images of surfaces of the polarized specimens. It was confirmed no significant pitting occurred on all of tested specimens.

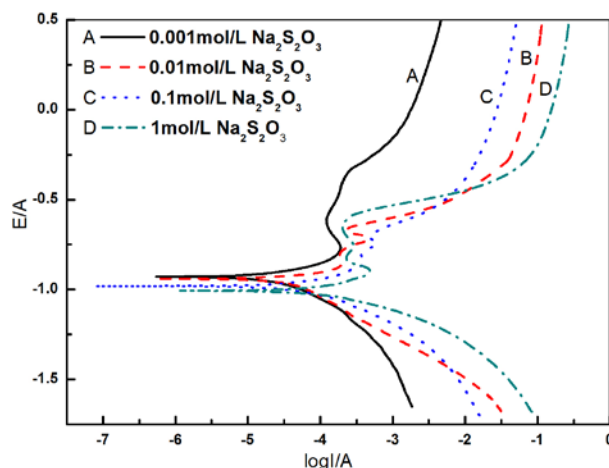


Fig. 2 Potentiodynamic polarization curves of DH32 steel specimens in $\text{Na}_2\text{S}_2\text{O}_3$ solutions of various concentrations

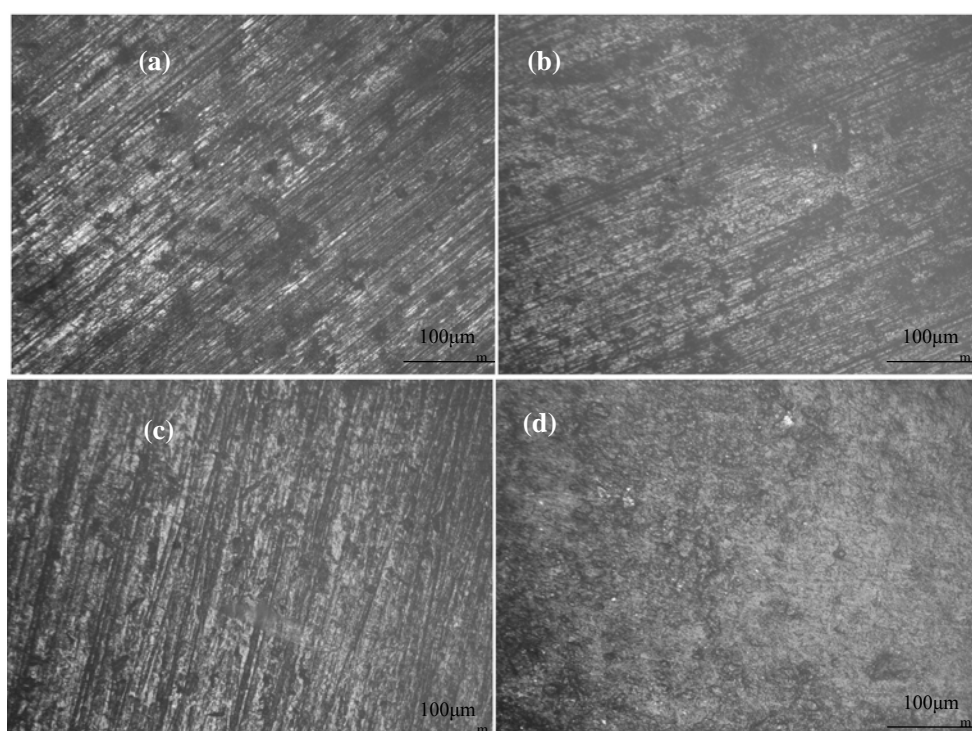


Fig.3 Micrographs of DH32 steel specimens after polarization testing in $\text{Na}_2\text{S}_2\text{O}_3$ solutions of various concentrations: (a) 0.001mol/L $\text{Na}_2\text{S}_2\text{O}_3$, (b) 0.01mol/L $\text{Na}_2\text{S}_2\text{O}_3$, (c) 0.1mol/L $\text{Na}_2\text{S}_2\text{O}_3$, (d) 1mol/L $\text{Na}_2\text{S}_2\text{O}_3$

Effects of Thiosulfate Ions in the Presence of Chlorine Ions

Potentiodynamic polarization curves of DH32 steel in the presence of various concentrations of $\text{S}_2\text{O}_3^{2-}$ ions (0.01M, 0.1M and 1M) in varying concentrations of Cl^- (1% mass and 10% mass) solution at room temperature are shown in Fig.4. For low concentrations of chloride ions i.e. 1% mass NaCl solution, the corrosion rates increased with the increase in $\text{S}_2\text{O}_3^{2-}$ ions concentrations. At high chloride ions concentrations i.e. 10% mass NaCl solution, the corrosion rates had a reverse nature with the increase in concentration of $\text{S}_2\text{O}_3^{2-}$ ions. In the presence of high $\text{S}_2\text{O}_3^{2-}$ ions concentration, there was a noticeable corrosion inhibition. This signifies reduced corrosion rates. This was again confirmed from the metallographic images in Fig. 5. No “pits” were recorded.

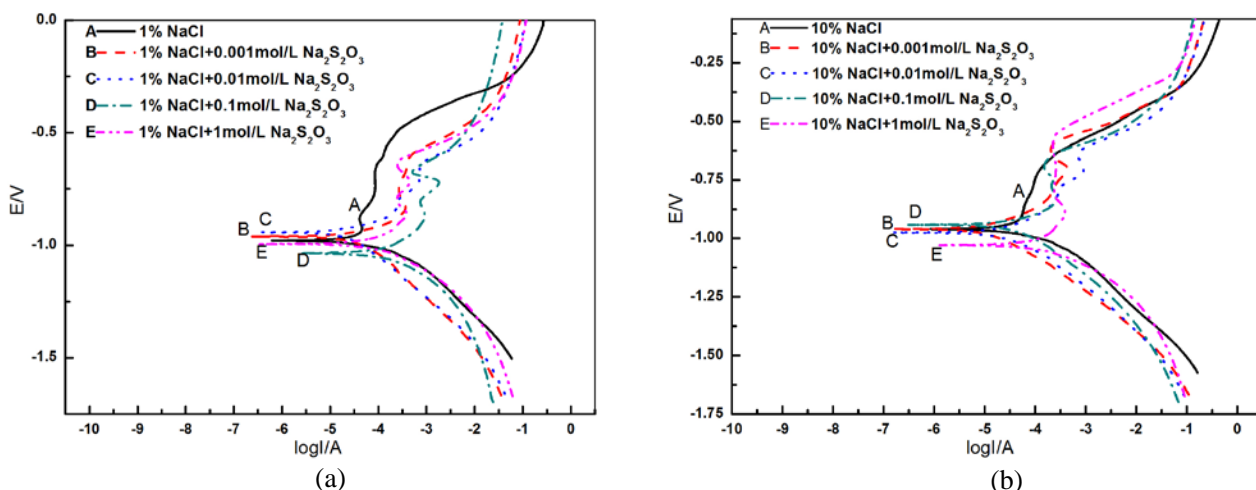


Fig. 4 Potentiodynamic polarization curves of DH32 steel in NaCl solutions added $\text{Na}_2\text{S}_2\text{O}_3$ solutions of various concentrations. (a) 1% mass NaCl, (b) 10% mass NaCl.

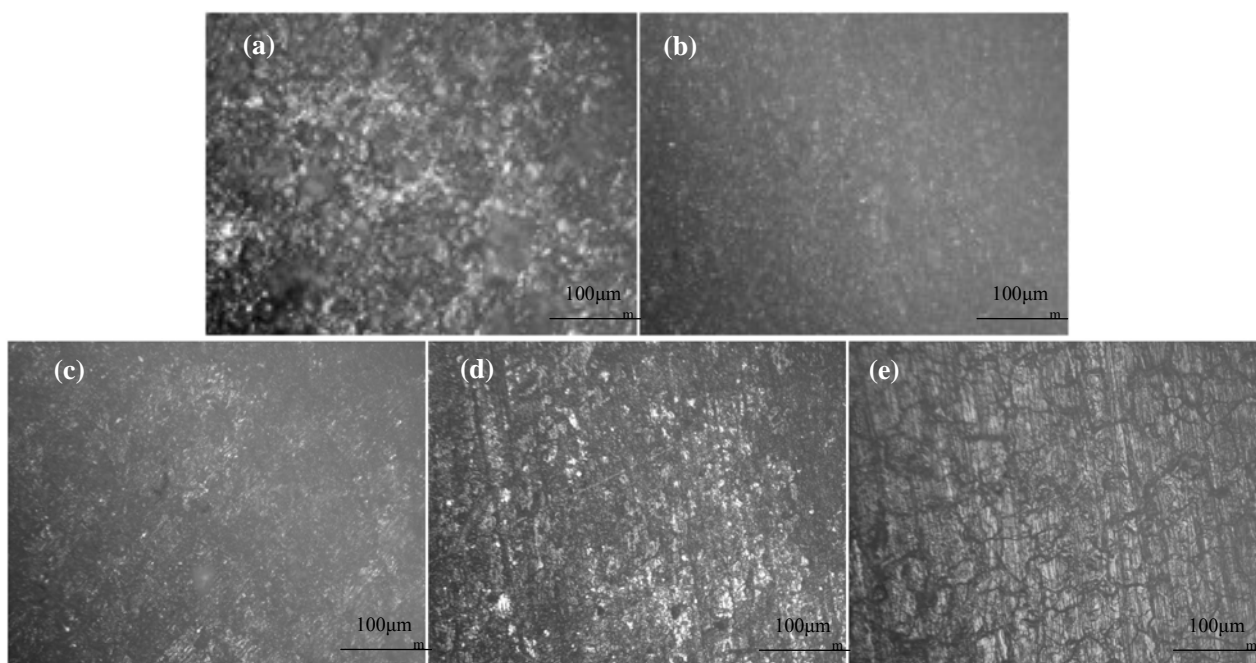


Fig.5 Micrographs of DH32 steel samples after polarization curves testing in 10% mass NaCl solutions added $\text{Na}_2\text{S}_2\text{O}_3$ solutions of various concentrations: (a) 0 mol/L, (b) 0.001 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, (c) 0.01 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, (d) 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$, (e) 1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$

Conclusions

In the case of seawater environment simulated by NaCl aqueous solution, with the increase in Cl⁻ concentration to higher levels, the passivation zone is narrowed up to a level making DH32 prone to pitting corrosion. When $\text{Na}_2\text{S}_2\text{O}_3$ solution of higher concentration (>0.1 mol/L) was added into NaCl solutions, the passivation zone enlarged and pitting susceptibility of DH32 steel decreased. At higher chloride concentrations, i.e. 10% mass NaCl solution, it is noticeable that the pitting corrosion rates had a reverse nature with the increase in concentration of $\text{S}_2\text{O}_3^{2-}$ ions. The pitting behavior was inhibited significantly.

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