



Surface Treatment of 304L Stainless Steel for Improving The Pitting Corrosion Resistance by Inhibitor

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(Received 23 December 2002 ; accepted 27 April 2003)

Abstract

Electrochemical techniques were used to study the surface treatment for improving the pitting corrosion resistance of 304L stainless steel by inhibitors in chloride medium. Sodium molybdate (in concentration range: 0.005–80 g/l), sodium nitrite (in concentration range: 0.001–50 g/l) and their mixture were used for this study. It was found that, molybdate and nitrite were good passivators for 304L stainless steel, but molybdate was not able to prohibit the pitting; nitrite prevented pitting corrosion of 304L stainless steel only at the concentration more than 25 g/l. The relationship between pitting potentials and concentrations of inhibitors in the logarithm expression obeyed the linear function.

It was found that the surface treatment by mixture of two inhibitors enables stainless steel to have increased the corrosion resistance; the pitting corrosion of 304L stainless steel was completely prohibited by the mixtures of molybdate and nitrite in ratio m/n , with $m \geq 3$ and $n \geq 10$. The interesting cases on electrochemical measurement of threshold of inhibitors concentration combination for optimum surface treatment were described.

Keywords : Surface treatment, Pitting corrosion, Inhibitor, Inhibition efficiency, Corrosion resistance, Electrochemical technique.

1. INTRODUCTION

Many attentions were paid for the pitting corrosion study of stainless steel¹⁾. A lot of authors have studied the application of inhibitors for surface treatment in order to improve the pitting corrosion resistance of stainless steel in different media. It was found that the addition of molybdate ions into a neutral chloride solution inhibits the pitting of stainless steel. Inhibition efficiency increases with the increasing the temperature and ratio of molybdate/chloride ions²⁾. Inhibition by molybdate is dependent on the presence of oxygen. Al. Borno et al [4] were studied inhibitors system for recirculating

cooling water system and showed that the best inhibitor for this medium is mixture of four constituents. Optimum ratio of them is nitrite/molybdate/polyphosphate/orthophosphate = 3/2/1/1. Others showed that in water medium, molybdate and nitrite are synergistic combination with molybdate/nitrite ratio = 3/2 or 1/1⁵⁾.

Nowadays, molybdate has been widely used in the field of corrosion protection as alternative for chromate, because of its low-toxicity and high effectiveness³⁾.

Nitrite is not only an effective agent for surface passive treatment of steel, because of its strong oxidation, but also is active in the repressing aggressive property of chloride ion⁴⁾.

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The effect of each inhibitor on the improving the pitting corrosion resistance of 304L stainless steel was studied, but an attempt to search a better protective effectiveness for the pitting corrosion of stainless steel in chloride medium was performed by combination of these two inhibitors.

The aim of our work thereby was to make clear the effect of inhibitors on the pitting corrosion resistance of stainless steel in order to provide the guideline in field application.

2. EXPERIMENTAL

2.1 MATERIALS

304L stainless steel was used as a substrate. Its composition (in percentage) is 0.03C, 0.2Mn, 0.03S, 0.045P, 18.0 Cr, 8.0 Ni, and Fe: rest. 304L steel was chosen because there is no molybdenum in its composition and is a susceptible to pitting by chloride ion

Electrodes with working surface about 0.5 cm² made of this steel were mounted in epoxy, polished by grit SiC paper 80-1200 and cleaned by ethanol and acetone.

Chemicals used in this study, including inhibitors, were PA grade made in Jansson, Belgium. The initial concentration of inhibitors was prepared by gravimetric method; thereafter lower concentrations were made by diluting with artificial seawater.

2.2 SOLUTION

Pitting corrosion study was carried out in chloride containing medium (artificial seawater)⁶⁾ with the following compositions (g/l): NaCl-28, MgCl₂-2.3, MgSO₄-3.5, CaCl₂-1.2, NaHCO₃-0.2, pH = 8.2, Salinity (S%) = 3.5, at room temperature, (20°C), in naturally aerated condition.

2.3 METHODS

Cyclic polarization scan was used for pitting corrosion study and potentiodynamic for surface passivation. Potential intervals were controlled from -600 to 1000 mV. For cyclic polarization, forward scan rate was 0.1 mV/s; reverse was 0.05 mV/s; for potentiodynamic it was 0.1 mV/s. Used equipment was computerizing EIZO 9052S with Gamry CMS 100 software. Measuring cell was set up by three electrodes with silver-silver chloride as reference.

For potentiodynamic study, electrodes were conditioned at -600mV for 4 hrs and measurements were repeated on the same electrode.

3. RESULTS AND DISCUSSION

3.1 SODIUM NITRITE

Nitrite concentration was controlled to range from 0.001 to 50 g/l.

Literal data showed that nitrite at 0.2 g/l begins to retard the corrosion of steels. In this study, the passivation of 304L stainless steel occurred at concentration of nitrite 0.005 g/l. Passive current density in this passive status was 10^{-6.5} A/cm²; potential interval was 150 mV. Unfortunately, at this low concentration, pitting took place easily. It was not difficult to see visually the pits on the electrode surface after measurement. The similar result was obtained in nitrite concentration range up to 25 g/l.

At nitrite concentration over 25 g/l, no pitting appeared on the steel surface. Cyclic polarization curve in this status is illustrated in the Fig. 1.

By increasing nitrite concentration, the passive potential intervals expanded and the pitting potentials increased as well. From many experimental data illustrated on Fig. 3, the relationship between sodium nitrite concentrations and

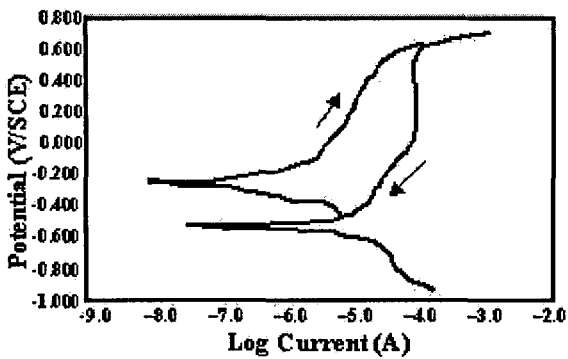


Fig. 1. Cyclic polarization curve of 304L stainless steel in chloride medium (S=3.5%) at 30.0 g/l of nitrite sodium.

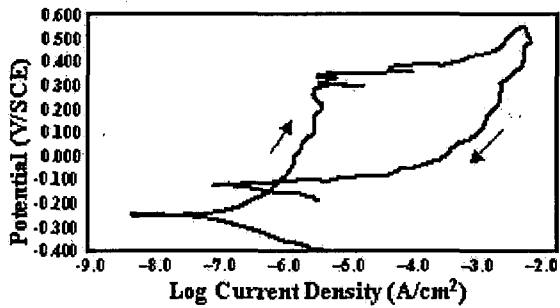


Fig. 2. Cyclic polarization curve of 304L stainless steel in chloride medium (S=3.5%) at 80.0 g/l of molybdate sodium.

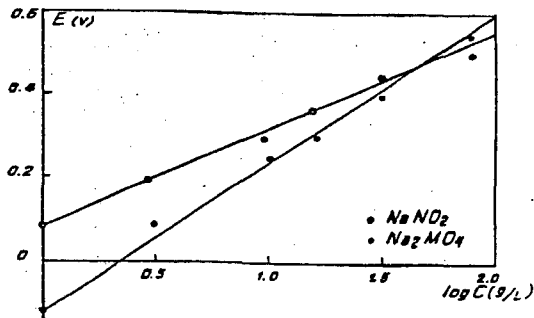


Fig. 3. Relationship between pitting potentials and concentrations of inhibitors in chloride medium (S=3.5%), 20°C.

pitting potentials could be found to fit the following equation:

$$E_{pit(V)} = 0.08 + 0.24 \log[C] \quad (1)$$

Where [C] is concentration of sodium nitrite in g/l.

In chloride containing medium such as artifi-

cial seawater, the nitrite concentration of 5 g/l is able to improve noticeably the corrosion resistance of 304L stainless steel, but for pitting prevention only at high concentration.

3. 2 SODIUM MOLYBDATE

The surface of 304L stainless steel was treated in sodium molybdate solution. At concentration 0.1g/l, the surface passivation was undergone at potential interval from -200 to 50 mV and current density $10^{-6.5}$ A/cm². The surface of 304L stainless steel was in good passivation, but its pitting corrosion was still recorded even after treatment at quite high molybdate concentration (up 80g/l) (Fig.2).

Increasing molybdate concentration, the surface of 304L stainless steel moved to deeper passivation. Measurement showed that the passive potential intervals were 600 mV at 80g/l; 500 mV at 40g/l; 400 mV at 30g/l. The relationship between pitting potential and inhibitors concentration is illustrated in Fig. 3 and obeys the following equation:

$$E_{pit(V)} = -0.12 + 0.36 \log[C] \quad (2)$$

Where [C] is concentration of sodium molybdate in g/l.

After treatment in molybdate sodium solution, on the steel surface appeared a black-brown thick layer of corrosion product. This layer was very porous and low adhesive. However results showed that the treatment of 304L stainless steel surface in sodium molybdate increases its corrosion resistance, but do not completely prevent the pitting corrosion in chloride medium.

3. 3 MIXTURE OF NITRITE AND MOLYBDATE SODIUM

Fig. 4 represents one of typical curve among a number of the curves measured on 304L stainless steel surface treated in chloride solu-

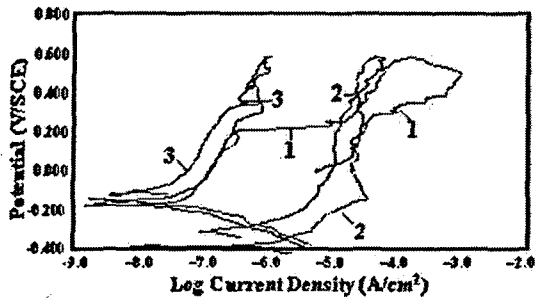


Fig. 4. Cyclic polarization curve of 304L stainless steel in chloride medium (S=3.5%) at molybdate/nitrite (g/l) : 3/10.

tion containing mixture of two inhibitors. In this mixture, the concentration of molybdate and nitrite is 3 and 10 g/l, respectively.

From data obtained in series of mixture of nitrite concentration ranging up to 50 and molybdate up to 80 g/l, a summary graph was constructed and shown on Fig.5.

When concentration of nitrite is lower than 10g/l, the pitting corrosion of steel in chloride medium still shows even concentrations of molybdate up to 80g/l.

In general, the pitting on surface of stainless steel was completely prohibited with molybdate and nitrite ratio m/n, here: $m \geq 3$; $n \geq 10$ (m is concentration of sodium molybdate and n is concentration of sodium nitrite). The mixture with ratio m/10 was selected, because, in practice, sodium nitrite at adequate concentration

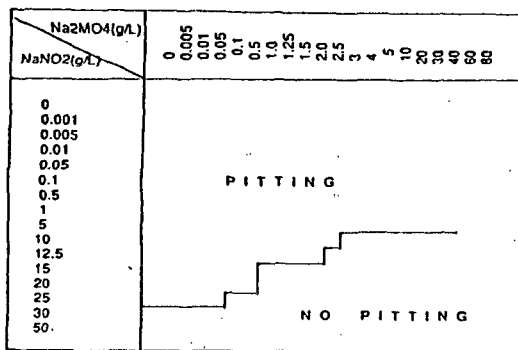


Fig. 5. Inhibitors combination for 304L stainless steel in chloride medium.

accelerates the cultivation of the sealivings in seawater.

The threshold of inhibitors concentration for the best surface treatment of 304L stainless steel, where the corrosion and pitting of steel is prevented completely and satisfied in practice is 2.5/12.5.

It was interesting to consider the electro-chemical behavior of this steel in the vicinity of the threshold concentration. Three cases were selected:

Case 1. The molybdate concentration was quite low (m=0.5); nitrite was high (n=20.0). The cyclic polarization scan is demonstrated on curve 1, Fig. 6. This curve has two portions: The first indicated the passivation of stainless steel at potential interval from -100 to 200 mV and passive current density $10^{-6.8}$ A/cm²; whilst second portion demonstrated the active dissolution of steel in solution studied.

Case 2. Molybdate concentration was low (m=2.0); nitrite was in the range of threshold concentration (n=12.5).

In this case, the steel surface after treatment was still kept on a passive-active status, as cyclic polarization scan illustrated on the curve 2

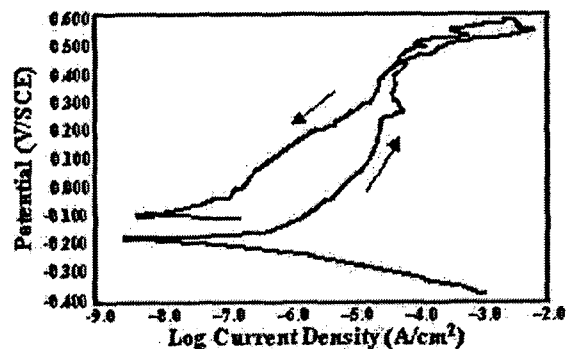


Fig. 6. Cyclic polarization curve of 304L stainless steel in chloride medium with different inhibitors concentrations,
 1. m=0.5; n=20.0
 2. m=2.0; n=12.5
 3. m=2.5; n=12.5

which path was placed around the second portion of curve 1.

Case 3. Concentrations of inhibitors were in the threshold range ($m=2.5$ and $n=12.5$). The polarization curve of case 3 was illustrated on the curve 3, which traced the same path with the first portion of the curve 1 and demonstrated the passive status of steel surface.

In fact, for pitting prevention, the inhibitors mixture enables to lower the dissolution current of steel to very small values - a hundreds times lower than passive current density.

In this study, the reverse scans often followed the path with lower current density indicating the presence of the passive layer on the metal surface.

To confirm above results, the electrochemical measurements on the 304L steel surface with different treatment concentration were carried out in parallel with surface morphology observation within the large range of concentration. Results were shown on Fig. 7. At threshold concentration of both inhibitors (curve 1, below and photograph 1, upper), passive potential expanded and no pits appeared on the metal surface. Far from threshold concentration (curve 2, below and photograph 2, upper), passive potential interval was very short and pits were very big. Around the threshold (curve 3 and photograph 3), electrochemical measurement and morphology observation both showed the acceptable understanding about the small pits.

4. DISCUSSION

It is well known that sodium nitrite is oxidizing agent as an anodic inhibitor. In its presence, the passivation of stainless steel occurs favorably and forms a surface passive layer containing chromium oxide. Nitrite enables the passivation

by moving the passive potential to positive direction. At low concentration of sodium nitrite, cathodic reaction speed is not high enough for shifting metal potential to completely passive region. Metal surface is still in "passive-active" state; passive film does not cover all active areas of metal surface. On any small anode, substrate is corroded with high current density enabling pits. At high nitrite concentration, cathodic process moves the metal surface towards deep passive status, passive oxide layer covers all surfaces, and pitting is thereafter prohibited.

By interaction with metallic cations, molybdate forms a surface covering layer impermeable to other anions, such as Cl^- and SO_4^{2-} . It is a kind of insoluble solid product, named as "metal-molybdate" layer, which prevents the pitting corrosion¹⁰⁾. Unfortunately, non-oxidizing agent is present in case of molybdate sodium solution, so molybdate does not fulfill its activity.

In the mixture of molybdate and sodium nitrite, nitrite plays a role of oxidant and molybdate contributes as film-forming agent. In the solution, molybdate anions react with metallic cations formed by oxidation of nitrite to produce a protective layer. If the concentration of nitrite is lower than a critical value, the amount of cations is not enough for constructing a layer covering all active areas on the surface and then pitting appears.

Further electrochemical measurement was conducted to reconfirm the role of metallic cations in the mixture of molybdate and sodium nitrite. A series of polarization curve was indicated on Fig. 8. Two kinds of surface preparation were made to differentiate the dissolution of metals in medium. One is mechanically polished by 1200 grit SiC paper, denoted as series-a, and the other electrochemically in polishing solution for stainless steel denoted as series-b.

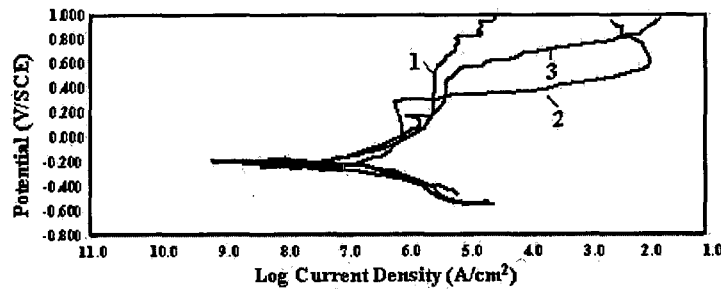
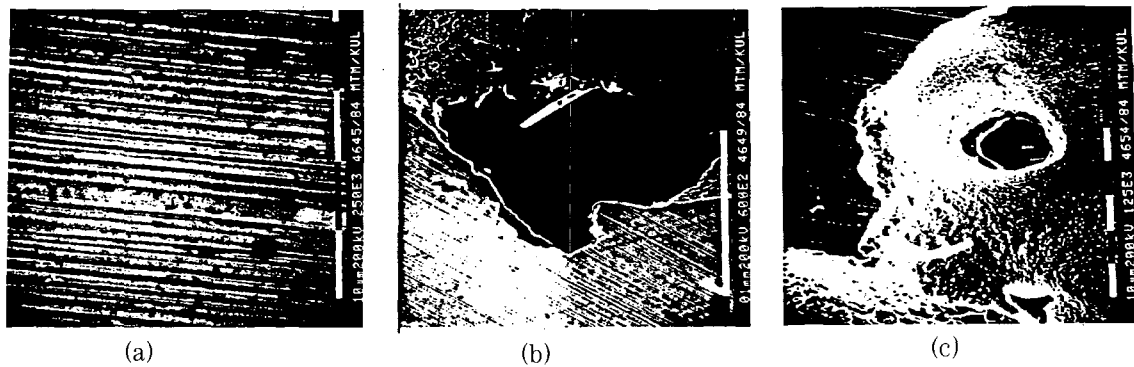


Fig. 7. Potentiodynamic curves of 304L stainless steel in chloride medium, at 20 °C (below) 1- $m=2.5$; $n=12.5$, 2- $m=80.0$; $n=0.0$, 3- $m=0.6$; $n=12.5$ and corresponding photomicrographs (upper),
 (1) : at threshold concentration - no pits
 (2) : far from threshold concentration - big pits
 (3) : near threshold concentration - small pits.

In the first curve (a-a), the surface was rather uneven, the metal dissolution took place easier, and a lot of cations could be thrown into solution, composed with molybdate to construct the protective layer. In the second curve (a-b),

oppositely, surface was smoother thereby the dissolution process was slow, the metal cations were not enough to form the completely passive layer, then pitting corrosion undergone.

5. CONCLUSION

1) Surface treatment with sodium nitrite within wide range of concentration (from 0.001 to 50.0 g/l), the passivation of 304L stainless steel is promoted, but pitting corrosion prevention in chloride medium only at nitrite concentration more than 25 g/l. Oppositely, molybdate is an adequate passivator for 304L stainless steel in chloride solution but is not able to protect the pitting corrosion in this medium (in the concentration range from 0.005 to 80 g/l).

2) The relationship between pitting potentials and inhibitor concentrations for surface treat-

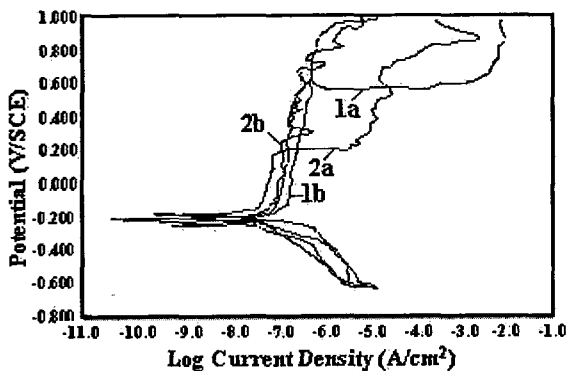


Fig. 8. Potentiodynamic curves of 304L stainless steel in chloride medium, at 20 °C with different ratio of inhibitors,
 1: $m = 5.0$; $n = 12.5$
 2: $m = 40.0$; $n = 12.5$
 a- Polished by 1200 SiC Paper
 b- Polished by electrochemical.

ment with both nitrite and molybdate in the logarithm expression obeys the linear functions.

3) The surface treatment by mixture of molybdate and nitrite enables to improve the pitting corrosion resistance of 304L stainless steel in chloride medium. The specific mixture of molybdate and nitrite for pitting prevention of 304L stainless steel in chloride medium is m/n with $m \geq 3$ and $n \geq 10$, the best is $m/10$.

4) Sodium nitrite plays a role of oxidant and molybdate, a film-forming agent. They made a synergistic effect for prevention of 304L stainless steel against pitting corrosion in chloride medium.

ACKNOWLEDGEMENT

This work was supported by the National Science Council of Vietnam. The Authors wish to express their thank to this Organization.

The authors truly thank also KISTEP for financial support for international scientific cooperation.

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