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Short Communication

Effect of Sulfate and Chloride Ions on Pitting Corrosion Behavior of 2Cr12MoV Steel at pH 6 and 90 °C

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The effect of SO_4^{2-} on the pitting corrosion behavior of 2Cr12MoV Steel in early condensates containing Cl^- was studied by electrochemical measurements, scanning electron microscopy and energy dispersive X-ray spectroscopy. The potentiodynamic polarization results show SO_4^{2-} suppressing the pitting corrosion initiation on 2Cr12MoV steel. Potentiostatic polarization, SEM and EDS analysis results show SO_4^{2-} has effect on suppressed pits initiated by competitive absorption with Cl^- and pits growth by forming low solubility salts with metal ions inside the pits and covered on the pit mouths. The effect of SO_4^{2-} on suppressed pits growth reduced with 10 ppm SO_4^{2-} added into test solution compared to 5 ppm SO_4^{2-} added due to cracks appeared on the corrosion products film, which enabled pit growth to continue.

Keywords: Blade steel, pitting corrosion, SO_4^{2-}, Early condensate

1. INTRODUCTION

In low pressure (LP) steam turbines of power plants, corrosive impurities such as SO_4^{2-} and Cl^- in the steam are concentrated in early condensates which is the first liquid phase formed in the phase transition zone (PTZ) of LP steam turbine, the liquid phase formed due to steam cools and partitions into liquid and vapor phases during adiabatic expansion [1-3]. As the concentration of SO_4^{2-} and Cl^- in early condensates may 1000 times higher than that in inlet steam [1-2], early condensates can cause significant corrosion damage to PTZ of LP steam turbine materials, such as pitting corrosion and stress corrosion cracking (SCC) of blades, discs, and rotors [4-7].

It is well known that Cl^- not only destroys the passive film and lead to the occurrence of pitting corrosion but also promotes the growth of pitting corrosion [8-13]. On the other hand, the effect of SO_4^{2-} on pitting corrosion has different conclusions in different environment: L.J. Yang, et al., found SO_4^{2-} has an inhibitory effect on the pitting corrosion [14], Z.P. Zhu, et al., found SO_4^{2-} can induce carbon steel pitting corrosion[15], S.H. Xiong, et al., also found SO_4^{2-} accelerates pitting corrosion of boiler water-wall tubes [16]. The ratio of SO_4^{2-}/Cl^- has observed to influence the effect of SO_4^{2-} on the pitting corrosion by Li-Bin Niu, et al., they founded the presence of 50 ppm SO_4^{2-} suppressed 13Cr steel pitting corrosion in simulated boiler water containing 100 ppm Cl^-. However, when the concentration of SO_4^{2-} is 100 ppm, SO_4^{2-} promoted pitting corrosion [17]. Y.L. Chou, et al., founded when SO_4^{2-}/Cl^- higher than 0.5, SO_4^{2-} has has an inhibitory effect on the pitting corrosion [18]. Thus, the combined effect of SO_4^{2-} and Cl^- on the pitting corrosion behavior of 2Cr12MoV Steel, which used for LP steam turbine blades, in early condensates has not clarified.

In the present work, the effect of SO_4^{2-} on the pitting corrosion behavior of 2Cr12MoV Steel in early condensates containing Cl^- was studied by electrochemical measurements, pit morphology analyses and energy dispersive X-ray spectroscopy to clarify influence and mechanism of SO_4^{2-} on pitting corrosion, which improving the understanding the effect of SO_4^{2-} on corrosion and can help plants better assess the risks of PTZ of LP steam turbine corrosion and control steam turbine corrosion.

2. EXPERIMENT

2.1 Materials And Solution

The work electrodes was prepared by 2Cr12MoV blade steel, with a chemical composition (wt%): 0.20% C, 0.21% Si, 0.76% Mn, 0.012% P, 0.011% S, 11.89% Cr, 0.83% Mo, 0.45% Ni, 0.32% V, 0.16% Cu, and Fe balance, and the work electrodes embedded in epoxy resin with exposed working area of 1.0 cm^2. Prior to testing, working surface of electrodes were polished on successively grades of metallographic sandpaper up to 1200 grit, and then washed by deionized water and degreased with acetone, alcohol successively.

In this work, test solutions simulated early condensates in PZT of LP steam turbine [1-3], In order to study the effect of SO_4^{2-} and Cl^- on pitting corrosion, the test solution with a constant concentration of Cl^- and various concentration of SO_4^{2-}, thus the test solution containing 10 ppm of Cl^- and addition of 0 ppm, 5 ppm, 10 ppm SO_4^{2-}. Besides, the pH of test solution adjusted to 6 by acetic acid, and test temperature was 90°C. Before the tests, the solution was deoxygenated by purging pure N_2 until the concentration of dissolved oxygen below 5 ppb.

2.2 Electrochemical Measurements

Electrochemical measurements, including potentiodynamic polarization, potentiostatic polarization, were performed in a three-electrode cell using a CS350 electrochemical workstation. 2Cr12MoV steel was used as working electrode, both Pt electrodes were used as the counter electrode and reference electrode. Pt electrode adopted as reference electrode in this work is due to the impurities concentration and conductivity of test solution in this work is low, if saturated calomel electrode or Ag/AgCl electrode adopted as the reference electrode, chloride ions would contamination test solution due to the diffusion of chloride ions from the reference electrode chamber to the test cell occurred during the test. Prior to electrochemical measurements, the test solution was deoxygenated by purging pure N_2 for 1 h. Electrode was then immersed into solution and N_2 purging was continued throughout the tests at a low flow rate at the headspace but (to avoid flow effects) not bubbled through the electrolyte.

Potentiodynamic polarization tests were begun at a potential 300 mV below the open circuit potential and with a scan rate of 0.2 mV/s in anodic direction until the current density reached 100 $\mu A/cm^2$. The potential where continuous current increase starts on a potentiodynamic polarization curve is considered as pitting potential E_b, which is an important parameter for occurrence of pitting corrosion. The values of E_b potentials for 2Cr12MoV steel in different test solution were investigated by potentiodynamic polarization tests.

Potentionstatic polarization tests were conducted for 24 h in the different test solution. The applied potentials were the E_b potential obtained in the 10 ppm Cl^- and 10 ppm SO_4^{2-} test solution by potentiodynamic polarization test.

2.3 SEM and EDS analysis

After the potentionstatic polarization tests, SEM observations and elemental analyses with EDS were also conducted on the pits found on specimens. For the EDS analyses, point analysis was performed on the corrosion products inside the pit. SEM and EDS analysis using a SEM equipped with EDS, FEI QUANTA 200.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization

Figure 1 shows the potentiodynamic polarization curves for 2Cr12MoV steel in the different test solutions at 90 ^oC. The E_b potentials of 2Cr12MoV steel in test solution with 10 ppm Cl^- and added different concentration of SO_4^{2-} obtained form Figure 1, and the values of E_b of 2Cr12MoV steel in different test solution shown in Table 1. The E_b potential is related to occurrence of pitting corrosion, it shifted to noble values in the test solution with added SO_4^{2-} and increased with SO_4^{2-} concentration increasing indicated SO_4^{2-} has the effect of suppressing the pitting corrosion initiation on 2Cr12MoV steel.

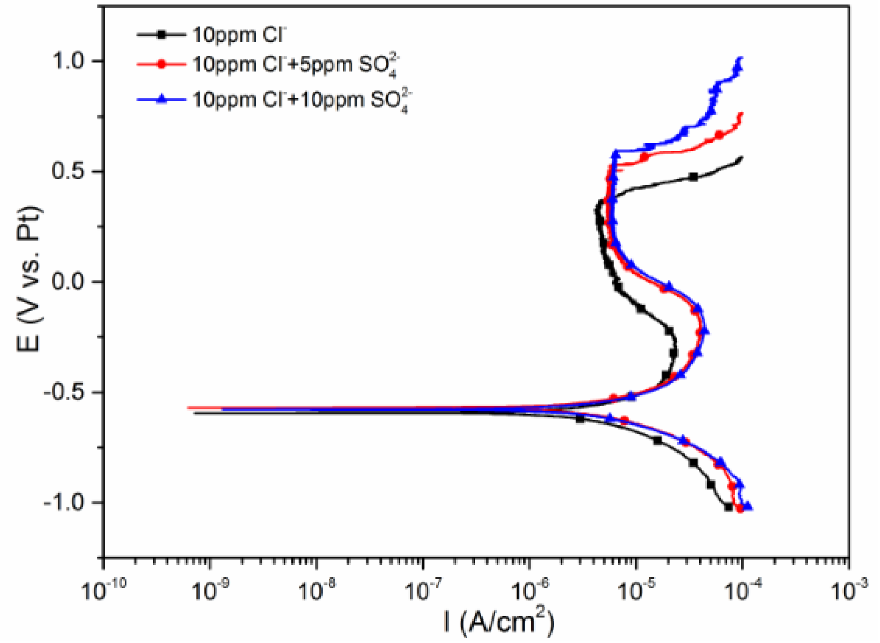


Figure 1. Polarization curves of 2Cr12MoV steel in the test solution with 10ppm Cl^- and added different concentration of SO_4^{2-}

Table 1. The values of E_b of 2Cr12MoV steel in the test solution with 10ppm Cl^- and added different concentration of SO_4^{2-}

SO_4^{2-}/(ppm)	E_b/ (V)
0	0.37
5	0.53
10	0.59

It is well known that Cl^- are aggressively ions can breakdown passive film and lead to pitting corrosion, according to local acidification theory [19-22]: Cl^- adsorbed on passive film and migrated to the steel/passive film interface, then accelerating metal ions hydrolysis, acidity inside the pit and lead to pitting corrosion. When SO_4^{2-} added on the solution, SO_4^{2-} has a competitive absorption effect with Cl^-, a part of steel interface where Cl^- absorbed displaced by SO_4^{2-}. By the reason of SO_4^{2-} has a lager ionic radius than Cl^-, thus SO_4^{2-} more difficult to migrate to steel interface than Cl^-, thus SO_4^{2-} has the effect of suppressing the pitting corrosion initiation on 2Cr12MoV steel [23]. Besides, insoluble salts, such as $FeSO_4$, $Cr_2(SO_4)_3$, formed on the 2Cr12MoV steel surface by SO_4^{2-} and metal ions when SO_4^{2-} added into solution, which impeding aggressively ions migrated to the steel/passive film interface lead to pitting corrosion, thus pit initiation inhibited. Consequently, SO_4^{2-} has the effect of suppressing the pitting corrosion initiation on 2Cr12MoV steel.

3.2 Potentiostatic polarization

Potentionstatic polarization tests were conducted in test solution at the applied potentials of 0.59 V (vs. Pt) which corresponding to E_b potentials of 2Cr12MoV steel in the test solution with 10 ppm Cl^- and 10 ppm SO_4^{2-} . Figure 2 shows the current density varies with time for 2Cr12MoV steel in different test solution during potentiostatic polarization at applied 0.59 V (vs. Pt).

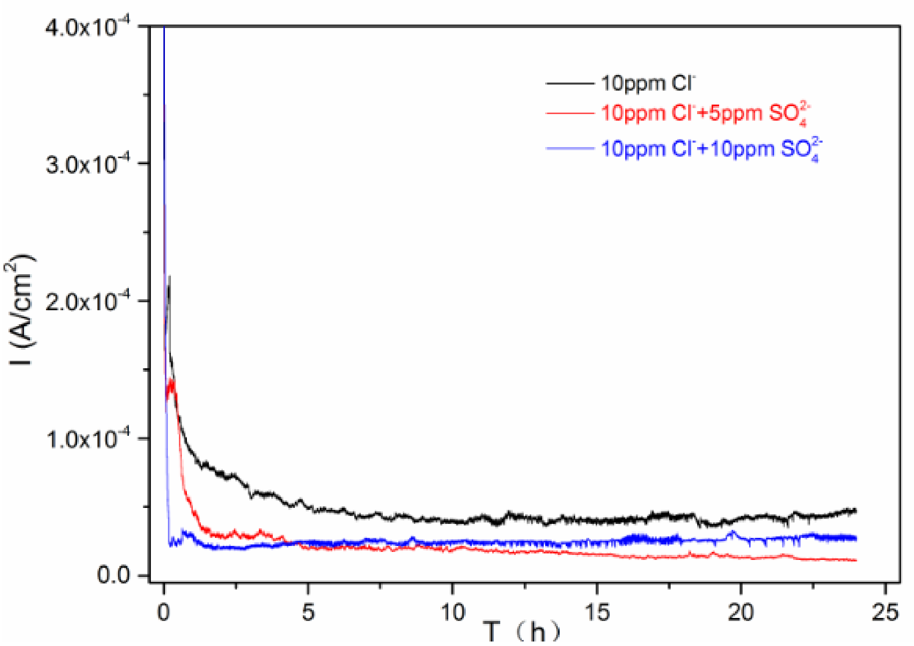


Figure 2. Current density varies with time for 2Cr12MoV steel in different test solution during potentiostatic polarization at applied 0.59 V (vs. Pt).

As we can see form Figure 2, the tendency of current density varies with time can be divided into three different stages: current density quickly decreases, current density increases, current density decreases slowly again and then remained about constant. The tendency of current density varies with time due to the surface of electrode changed with time during potentionstatic polarization process. As the applied potential is 0.59 V (vs. Pt) which higher than E_b in all test solution, the current density varies with time during potentiostatic polarization influenced by the growth of passive film, pit initiated and propagated. Therefore, the tendency of current density varies with time divided into three different stages. At the first stage of potentiostatic polarization, passive film gradually formed on the electrode surface, thus current density quickly decreases with time. With polarization going on, after pits nucleation period, pits initiated on the electrode surface and grow to become stable pits [24-27], so current density increases with time. Then pits started propagating, as the propagation of pits is diffusion controlled, so pits grow suppressed due to corrosion products gradually formed inside the pits and covered the pit mouths serves as a barrier to the diffusion of metal cation. Therefore, the current density gradually decreases with time [17,28-29]. But salts products can't suppress the pits propagated absolutely, pits will still propagated at a constant low growth rate after some time or even increased again, so current density decreases to a steady state values or firstly decreased and then increased. In addition, the values of current density on this stage related to growth rate of pits propagated.

As shown in Figure 2, Current density varies with the concentration of SO_4^{2-} in the test solution, which indicated SO_4^{2-} has effect on the pitting corrosion. At first stage of polarization process, i.e., pits nucleation period, passive film gradually formed on the electrode surface, the pits nucleation period prolonged with SO_4^{2-} concentration increasing indicate SO_4^{2-} suppressing the pitting corrosion initiation on 2Cr12MoV steel. After nucleation period, pitting corrosion initiated, the current density of 2Cr12MoV steel less increased with SO_4^{2-} concentration increasing indicate SO_4^{2-} suppressing the pitting corrosion. SO_4^{2-} suppressed pits initiated due to SO_4^{2-} more difficult to migrate to steel interface than Cl^- and formed insoluble salts with metal ions impeding aggressively ions migrated to the steel/passive film interface. Then on the third stage, the pits started propagating, as corrosion products, such as $FeSO_4$,$Cr_2(SO_4)_3$, formed by SO_4^{2-} and metal ions is sparingly soluble which with much lower solubility than chlorides, more protective salts cover formed on the surface of 2Cr12MoV steel in the solution with added SO_4^{2-}. As propagation of pits is diffusion controlled and pits growth suppressed by corrosion products gradually formed inside the pits and covering the pit mouths, so the current density decreased with SO_4^{2-} concentration increasing due to SO_4^{2-} formed protective salts suppressing the pits propagated. However, the current density of 2Cr12MoV steel in the solution with 10 ppm SO_4^{2-} added higher than 5 ppm SO_4^{2-} added after potentiostatic polarization 5h, this phenomenon suggests that the pit growth rate in the solution added 10ppm SO_4^{2-} higher than added 5 ppm after 5h.

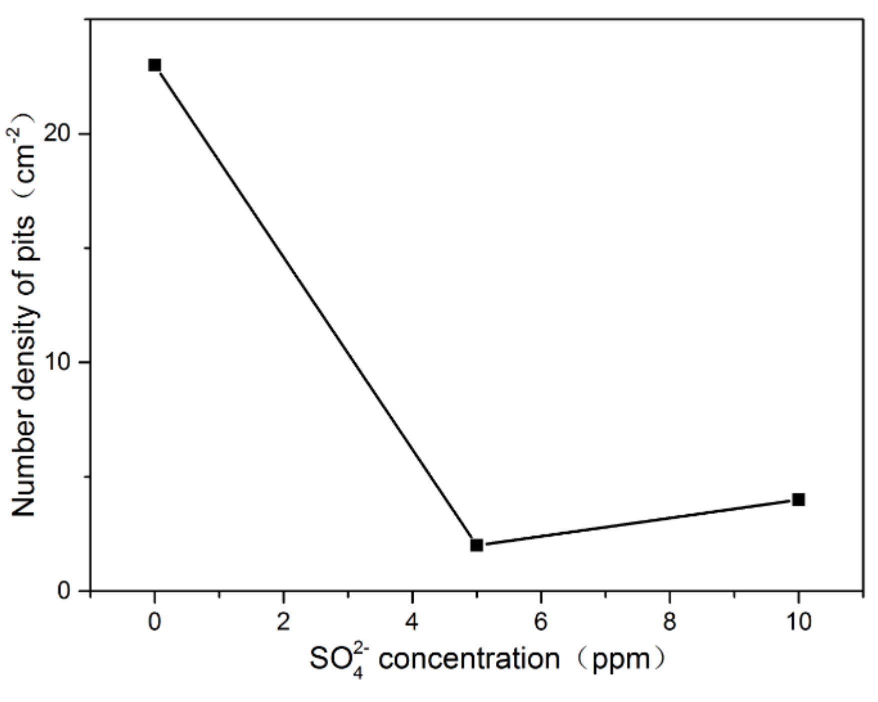


Figure 3. Number density of pits on specimens after potentiostatic polarization in the test solution with 10ppm Cl^- and added different concentration of SO_4^{2-}

This phenomenon can explained as the osmotic pressure between inside and outside of pitting hole increased during potentiostatic polarization in the solution high concentration of SO_4^{2-}, slats film covered on the pitting hole may appeared cracks due to the effect of osmotic pressure after 5h. Because the cracks in slats film decreased diffusion resistance, so the pits growth rated increased in the solution with 10 ppm SO_4^{2-} added after 5h, even higher than in the solution with 5 ppm SO_4^{2-} added [30-31]. Therefore, the current density of 2Cr12MoV steel in the solution with 10 ppm SO_4^{2-} added higher than 5 ppm SO_4^{2-} added after potentiostatic polarization 5h.

Figure 3 shows the relationship of the pitting number density with different concentration SO_4^{2-} added in the test solution. As we can see form Figure 3, the pitting number density of 2Cr12MoV steel in the SO_4^{2-} free test solution biggest indicated SO_4^{2-} suppressing the pitting corrosion of 2Cr12MoV steel. The pitting number density of 2Cr12MoV steel in the test solution with 10 ppm added bigger than with 5 ppm added inconsistent with the result of potentiodynamic polarization, this is because of with SO_4^{2-} concentration increase to 10 ppm, the effect of SO_4^{2-} on suppressing the pits initiated strengthen, but the effect on suppressing pits propagated weaken.

3.3 SEM and EDS analysis

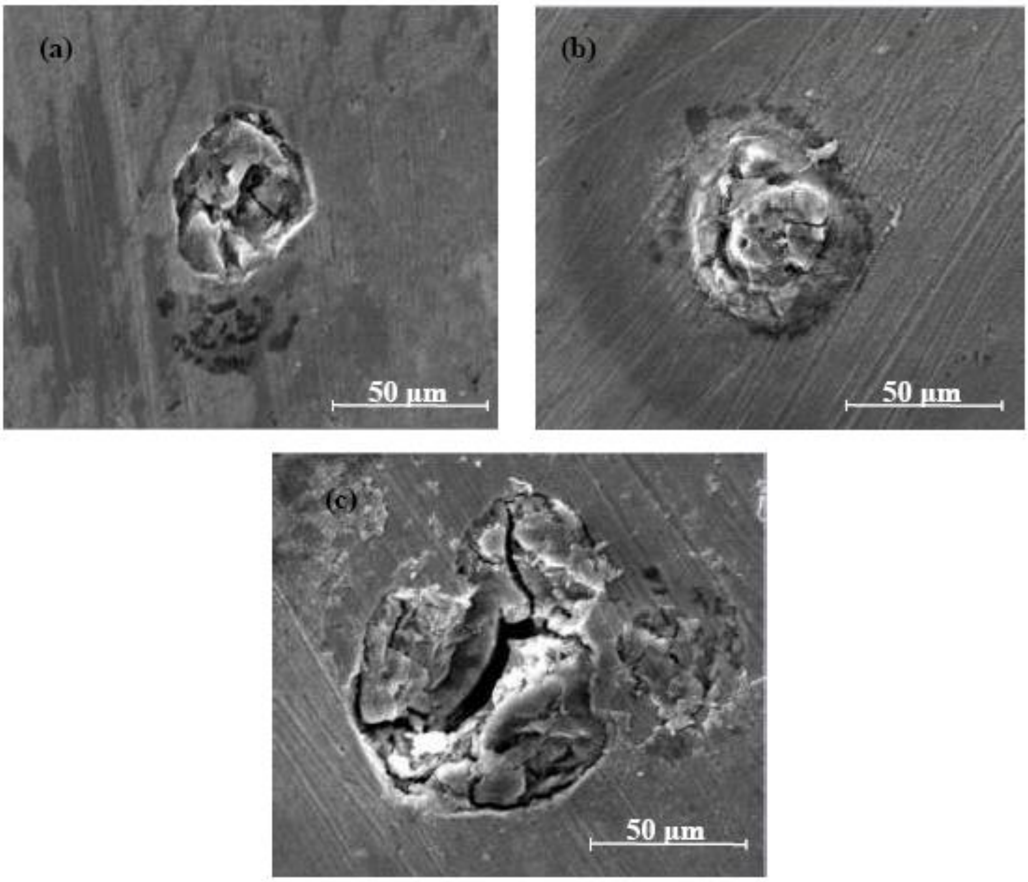
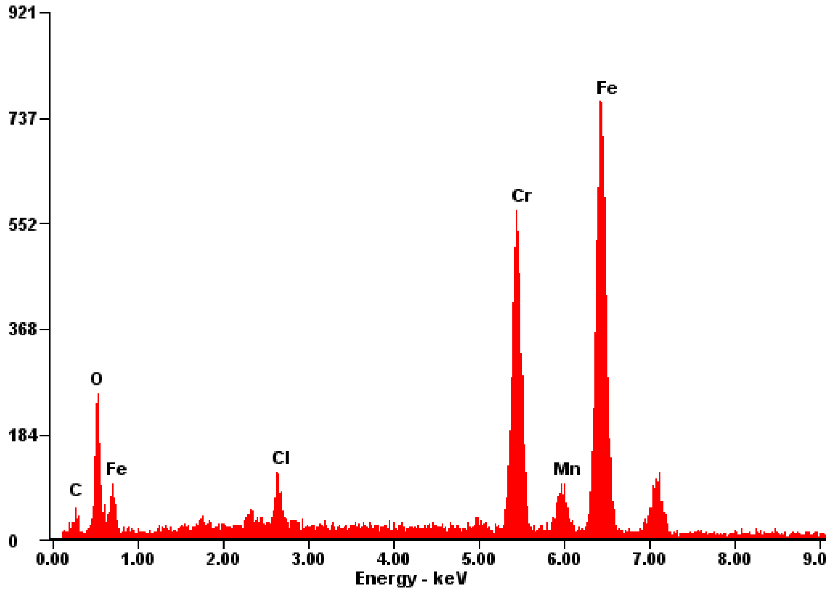
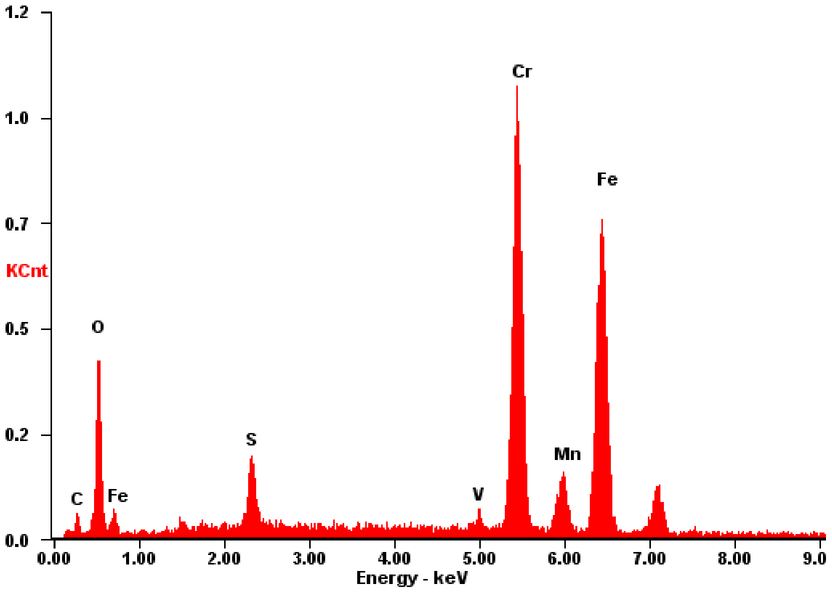


Figure 4. SEM micrographs of pits on the specimens after potentiostatic polarization in the different test solution: (a) 10 ppm Cl^-, (b) 10 ppm Cl^- + 5 ppm SO_4^{2-}, (c) 10 ppm Cl^- + 10 ppm SO_4^{2-}

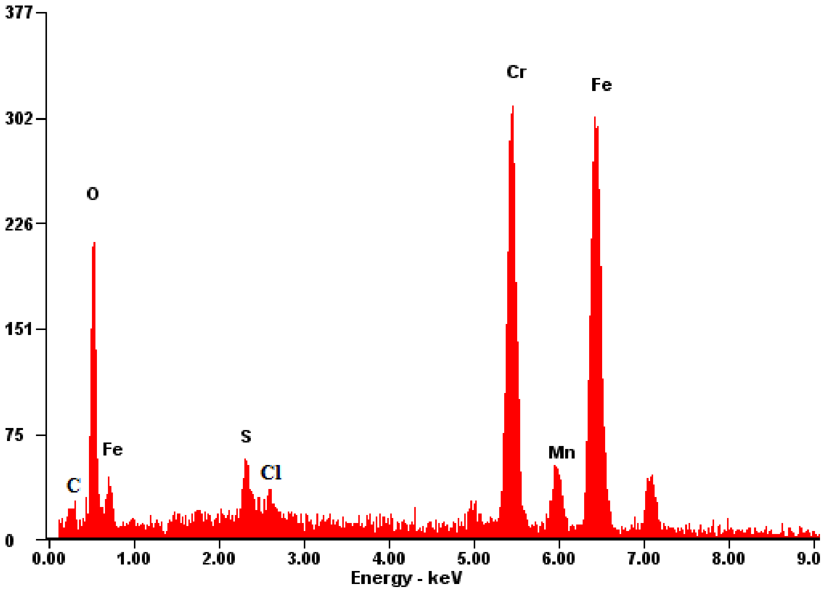
SEM and EDS analysis for specimens after potentiostatic polarization at the applied potential of 0.59 V (vs. Pt) in the different test solution to investigated the effect of SO_4^{2-} on the pitting corrosion of 2Cr12MoV steel in early condensates containing Cl^-. The SEM micrographs of typical pits on the 2Cr12MoV steel electrode after potentiostatic polarization at the applied potential of 0.59 V (vs. Pt) in the different test solution shown in Figure 4. As we can see form Figure 4, the pits formed in the SO_4^{2-} free solution hardly any corrosion products covered (Figure 4(a)). Nevertheless, in the test solution with 5 ppm SO_4^{2-} added pit mouth completely covered by corrosion products (Figure 4(b)). The pit mouth also covered by some corrosion products (Figure 4(c)) in the test solution with 10 ppm SO_4^{2-} added, but cracks appeared on the corrosion products film.



(a)



(b)



(c)

Figure 5. EDS spectra for corrosion products of inside pits on the specimens after potentiostatic polarization in different test solution：(a) 10 ppm Cl^-, (b) 10 ppm Cl^- + 5 ppm SO_4^{2-}, (c) 10 ppm Cl^- + 10 ppm SO_4^{2-}

As the propagation of pits is diffusion controlled, so pits grow suppressed due to corrosion products gradually formed inside the pits and covered the pit mouths serves as a barrier to the diffusion of metal cation [29,32]. Obvious, the more corrosion products and higher density of corrosion products film formed, the stronger the inhibition on pits propagated. Therefore, we can conclude SO_4^{2-} suppressed the pitting corrosion of the pitting corrosion of 2Cr12MoV steel in the early condensates. However, because of cracks appeared on the salts film in the test solution added 10 ppm SO_4^{2-}, so the effect of SO_4^{2-} on suppressed pitting corrosion weakened after cracks appeared, which consist with the results of potentiostatic polarization, i.e. the current density of 2Cr12MoV steel in the solution with 10ppm SO_4^{2-} added higher than 5ppm SO_4^{2-} added after potentiostatic polarization 5h.

Figure 5 is the EDS spectra of corrosion products inside the typical pits on the 2Cr12MoV steel electrode after potentiostatic polarization in the different test solution. As we can see form Figure 5, a generous amount of Fe, Cr, O elements and a small amount of Cl element inside the pits formed in the test solution in the absence of SO_4^{2-} (Figure 5(a)), it is indicate metal oxide formed and Cl^- concentrated inside the pits formed in the test solution in the absence of SO_4^{2-} [33]. However S element also inside the pits formed in the test solution with added SO_4^{2-} (Figure 5(b), Figure 5(c)), and Cl element disappeared inside the pits formed in the test solution with added 5 ppm SO_4^{2-}. As S element appeared inside pits formed in the test solution with added SO_4^{2-}, it is considered not only metal oxide formed, but also $Cr_2(SO_4)_3$ and $FeSO_4$ formed in the test solution with added SO_4^{2-}, which have relatively low solubility, and Cl element disappeared indicated Cl^- migrate to inside pits impeded in the test solution with added 5 ppm SO_4^{2-}.

The chemical element composition of corrosion products inside pits formed in different test solution changed with the concentration of SO_4^{2-} due to SO_4^{2-} influenced the pit growth. The principle of SO_4^{2-} influenced the pit growth to changed chemical element composition of corrosion products inside pits can interpreted as follow: As the pit growth is controlled by the diffusion of metal ions, so the pit geometry determines the pit growth. In the stage of pits propagation, the inside of pit are anodic sites where metal dissolution takes place, metal ions migrate from pits inside to bulk solution, and anions would migrate from bulk solution into keep electric neutrality. Because of hardly any corrosion products covered over pits mouths in the SO_4^{2-} free test solution due to corrosion products formed has large solubility, so the pit growth high. Therefore, more Cl^- migrate to inside pits and participation in corrosion products formation, thus a generous amount of Fe, Cr, O elements and a small amount of Cl element inside the pits formed in the test solution in the absence of SO_4^{2-}. In the test solution with 5 ppm SO_4^{2-} added, low solubility salts, such as $Cr_2(SO_4)_3$ and $FeSO_4$, formed, thus S elements appeared in the corrosion products. In addition, low solubility salts covered on the pits mouth, ions diffusion was impeded by corrosion products film and pits growth was suppressed. As pits growth is low, Cl^- migrate to inside pits impeded. Therefore, Cl element disappeared in corrosion products in the test solution with added 5 ppm SO_4^{2-} due to pits growth very low.

4. CONCLUSIONS

(1) The potentiodynamic polarization results show E_b potential shifted to noble values in the test solution with added SO_4^{2-} and increased with SO_4^{2-} concentration increasing. SO_4^{2-} suppressed the pitting corrosion initiation on 2Cr12MoV steel in early condensates containing Cl^- by competitive absorption with Cl^-.

(2) The potentiostatic polarization, SEM and EDS analysis results show SO_4^{2-} has effect on suppressed pits initiated by competitive absorption with Cl^- and pits growth by forming low solubility salts with metal ions inside the pits and covered on the pit mouths. The effect of SO_4^{2-} on suppressed pits growth reduced with 10 ppm SO_4^{2-} added into test solution compared to 5 ppm SO_4^{2-} added due to cracks appeared on the corrosion products film, which enabled pit growth to continue.

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