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Tribocorrosion investigation of 316L stainless steel: the synergistic effect between chloride ion and sulfate ion

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Abstract

Tribocorrosion is a failure phenomenon which involves synergistic effect of electrochemical corrosion and mechanical wear. It usually results into early failure of mechanical components than simple wear and corrosion. Chloride (Cl−) and sulfate ions (SO42−) are often found together in corrosive media. In this study, the synergistic effect of Cl− and SO42− on tribocorrosion of 316L stainless steel was studied by changing the ratio of SO42−/Cl− in corrosive solution from 0.31 M : 0 to 0 : 0.62 M. The stainless steel was worn against with a ZrO2 sphere. The coefficient of friction (COF), material loss volume, surface micro-topographies and surface chemical composition in different solutions were compared to explore the synergism between SO42− and Cl−. The results indicated that the mix of Cl− and SO42− reduced material loss volume by a quarter when compared with that in pure Na2SO4 or NaCl solution. More than half of material loss was caused by the synergism between wear and corrosion in mixing solutions. The synergistic effect between SO42− and Cl− could promote the transmission of metal into oxides. This had two effects on tribocorrosion. First, the existence of oxides would cause abrasion which accelerated wear-affected corrosion and enhanced mechanical wear (corrosion-affected wear). On the other side, the transmission of metal into oxides benefited for the formation of tribo-film. The flexible stainless steel needed to coordinate deformation with the tribo-film which had relatively low deformability. This aggravated deformation of stainless steel and promoted surface work-hardening effect. It was helpful for stainless steel to resist wear, thus, the corrosion-affected wear was decreased.

1. Introduction

Tribocorrosion is a failure phenomenon which involves synergism between electrochemical corrosion and mechanical wear. It usually results into rapid degradation of metallic materials [1, 2]. During the tribocorrosion, the depassivation caused by wear could directly accelerate corrosion (called as wear-accelerated corrosion) [3]. Then, the passive film is reformed. In most cases, the passive films are composed of oxide or hydroxide. Thus, they are usually brittle and would be easier removed than the flexible metallic substrate (called as corrosion-accelerated wear) [4]. In some cases, the corrosion/wear products would be transformed to tribo-films which avoids the direct contact between frictional pairs. Some tribo-films even have lubricating effect and can relief wear [5]. Thus, the property of corrosion product plays a key role in tribocorrosion and it strongly depends on corrosive medium.

Chloride (Cl−) and sulfate ions (SO42−) are often found together in corrosive media such as seawater, industry water and physiological environment [6, 7]. Combined effect of their presence has been under investigation for several decades. Normally, increasing the Cl− concentration will shift pitting potential negatively, and the pitting potential is shifted positively by addition of SO42− which acts as pitting corrosion inhibitor [8–10]. It is widely accepted that the competitive adsorption of SO42− and Cl− on metal surface is the controlling factor of pit growth kinetics [11]. Cl− has strong depassivation ability, it could destroy passive film...
and accelerate anodic dissolution. It was found that 316L stainless steel showed higher corrosive current and larger material loss when worn in 0.62 M NaCl solution than that in 0.31 M Na2SO4 solution [12]. This was due to the strong depassivation effect of Cl\(^-\). At high potential, Cl\(^-\) could even resulted to pitting corrosion which caused local stress concentration. As a result, corrosion and wear were both accelerated. Further, it was found that the mix of SO\(_4^{2-}\) and Cl\(^-\) obviously influenced the tribocorrosion behavior of ferritic stainless steel [13, 14]. Interestingly, the smallest material loss appeared in the mixing solution (0.02 M Na2SO4 + 0.02 M NaCl) when compared with that in pure NaCl and pure Na2SO4 solutions. The passive film formed in mixing solution showed higher film resistance than the pure solutions, no matter before wearing of after wearing. Based on above introduction, the property of passive film could influence the tribocorrosion behavior of the stainless steel. Clearly, there is synergism exists between SO\(_4^{2-}\) and Cl\(^-\) in tribocorrosion. However, the synergism between the two anions on tribocorrosion has not be concerned and is remained unclear.

The aim of this study is to investigate the synergistic effect between SO\(_4^{2-}\) and Cl\(^-\) on tribocorrosion. A 316L stainless steel was worn against with a ZrO\(_2\) sphere in corrosive solutions with different ratios of SO\(_4^{2-}\)/Cl\(^-\). The coefficient of friction (COF), material loss volume, surface micro-topographies and surface chemical composition after worn in different solutions were compared to explore the synergism between SO\(_4^{2-}\) and Cl\(^-\) in tribocorrosion. Besides, surface work-hardening effect was concerned and the interface microstructure was observed. This study will be helpful to understand the degradation mechanism of metallic materials in tribocorrosion further and guide the proper use of stainless steel.

2. Experimentation

2.1. Specimen preparation
AISI 316L austenite stainless steel rolling sheet having a thickness of 2 mm (provided by BAOWU Co., Ltd China) was used for the specimen preparation. Rectangular specimens were machined from this sheet having dimensions of 20 mm × 6 mm × 2 mm. The specimens was welded with wire and then embedded in a plastic ring with epoxy resin. The exposed area was 20 mm × 6 mm. The exposed side of specimen was first sanded with SiC sandpapers from 400# to 2000#, and then polished with diamond paste to obtain a smooth surface finish.

2.2. Tribo-electrochemical tests
The schematic diagram of tribo-electrochemical test setup was showed in figure 1. A ball-on-disk tribometer and an electrochemical working station were combined, thus, the frictional and electrochemical signals could be record simultaneously. The specimen was fixed on a Teflon cell then assembled on the reciprocating pedestal of the tribometer. A ZrO\(_2\) ball with 6 mm diameter was used as slider. The specimen, a platinum foil and an Ag/AgCl electrode were connected to the electrochemical workstation and worked as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively.

Five solutions with different SO\(_4^{2-}\)/Cl\(^-\) ratios were used as corrosive media. It was worth noting that electroconductibility was another important factor in corrosion. NaCl solution with concentration of 0.62 mol·L\(^{-1}\) (3.5 wt.%) was used as reference solution. To keep the charge concentration consistent in different solutions, the Na2SO4/NaCl ratio was adjusted and showed in table 1. The solutions were prepared with same de-ionized water (not deoxidized).

In tribocorrosion test, 150 ml solution was first added into cell to immerse specimen, then open circuit potential (OCP) measurement was started. Twenty minutes later, a load of 5 N was applied on ZrO\(_2\) ball to contact stainless steel surface. According to the Hertz contacting model, the initially contacting pressure was 1109 MPa. Then, cell started to reciprocate with frequency of 1 Hz and the stroke length on stainless steel surface was 8 mm. After worn for 1 h, the load was removed and the ball was left from stainless steel surface. OCP measurement was stopped 20 min later. Each test was repeated for three times.

The tribocorrosion tests were also carried out under the potentiodynamic condition. The potentiodynamic measurements were carried out in the five different solutions with wear and without wear. Under wearing condition, the load was 5 N and reciprocating frequency was 1 Hz. In the measurement, the stainless steel specimen was worn at OCP for 1800 s. Then, the potential scan started from −300 mV versus OCP with the scanning rate of 1 mV·s\(^{-1}\). Under the condition without wear, the load was not applied and the other parameters were the same with that in wearing condition.

2.3. Surface and subsurface characterizations
The three-dimensional contour of wear tracks were characterized using a white light interferometer (ContourGT-K1, Bruker). Field emission scanning electron microscopy (FE-SEM, SUPRA 55, Zeiss) was used to acquire the micro-topographies of the wear tracks. The chemical compositions were characterized by x-ray...
energy spectrometer (EDS). The surface micro-hardness of the wear tracks were measured with a Vickers hardness tester (load was 0.01 kg). To observe the interface microstructure, longitudinal cross-sections on the wear track were prepared by using focused ion beam (FIB, Helios Nanolab 600, FEI). The region of interest was located in the centre of the wear track. A platinum layer was first deposited on the top surface of the areas of interest before the cutting process to avoid exposure to Ga\(^{+}\) beam. After that, a cross-section specimen which was perpendicular to the wear direction was obtained. Then, the cross-section specimen was observed in a transmission electron microscope (TEM, Tecnai F20, FEI) with an accelerating voltage of 200 kV. To investigate the influence of solution composition on surface chemical composition, the polished stainless steel was immersed in 0 M or 0.1 M solution for 5 min. Then, the stainless steel was flushed with deionized water and dried with cool air. The surface chemical composition was characterized by x-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos).

3. Results

3.1. Tribocorrosion behaviours

Figures 2(a) and (b) were the potentiodynamic polarization curves of 316L stainless steel in different corrosive solutions without wear and with wear. Table 2 listed the corrosive parameters which were calculated from the potentiodynamic polarization curves by Tafel theory. Under the condition without wear, with the increasing ratio of SO\(_4^{2-}\)/Cl\(^-\), the corrosive current was decreased and the breakdown potential was increased. It demonstrated that SO\(_4^{2-}\) had corrosion inhibition effect in Cl\(^-\) containing medium and the inhibition efficiency was increased with the increasing ratio of SO\(_4^{2-}\)/Cl\(^-\). With the introduction of wear, corrosive currents were
enormously increased and corrosion potentials were decreased by mechanical depassivation. There was no significant effect on breakdown potential.

Figure 3(a) were the evolution of potential and COF during the tribocorrosion test under OCP. At the initially immersing stage, the potentials tended to be stable due to passivation. However, with the start of wear, all potentials were sharply dropped down due to mechanical depassivation [3]. The potentials were slightly decreased during wearing. This could be explained by the broadening of wear track [15]. At the same time, COFs were slightly increased. The stainless steel showed the highest COF when worn in pure Na₂SO₄ solution (0 M), and the COF was obviously decreased with the addition of NaCl. The average COFs in different corrosive solutions were showed in figure 4. Except that in pure Na₂SO₄ solution, the average COF was increased with the decreasing ratio of SO₄²⁻ / Cl⁻.

The three-dimensional contours of the worn surfaces were showed in figure 5. The width and depth of the wear track were both increased with the decreasing ratio of SO₄²⁻ / Cl⁻ in Cl⁻ containing solutions. The material loss volumes in different corrosive solutions were calculated from the contours and showed in figure 5(f). Except

![Figure 2. Potentiodynamic polarization curves of 316L stainless steel in different corrosive solutions (a) without and (b) with wear.](image-url)

### Table 2. Corrosion parameters from the potentiodynamic polarization curves.

|                     | 0 M       | 0.1 M     | 0.3 M     | 0.5 M     | 0.6 M     |
|---------------------|-----------|-----------|-----------|-----------|-----------|
| **Without wear**    |           |           |           |           |           |
| $i_{corr}/\mu\text{Acm}^{-2}$ | 0.02 ± 0.01 | 0.05 ± 0.02 | 0.06 ± 0.01 | 0.06 ± 0.02 | 0.07 ± 0.03 |
| $E_{corr}/\text{mV}$ | -173 ± 12 | -184 ± 19 | -160 ± 21 | -181 ± 24 | -159 ± 37 |
| $E_b$/mV            | 1197 ± 31 | 1212 ± 42 | 712 ± 54  | 555 ± 35  | 362 ± 24  |
| **With wear**       |           |           |           |           |           |
| $i_{corr}/\mu\text{Acm}^{-2}$ | 6.90 ± 0.35 | 9.27 ± 0.87 | 8.12 ± 0.54 | 5.46 ± 0.18 | 5.90 ± 0.58 |
| $E_{corr}/V$        | -385 ± 27 | -438 ± 15 | -366 ± 36 | -418 ± 35 | -330 ± 23 |
| $E_b$/mV            | 1285 ± 14 | 1198 ± 33 | 617 ± 27  | 468 ± 52  | 428 ± 31  |
that in 0 M solution, the lost volume was increased with the decreasing ratio of \( \text{SO}_4^{2-} / \text{Cl}^- \). Particularly, the addition of relatively low concentration of NaCl into Na\(_2\)SO\(_4\) solution could obviously reduce material lost volume.

### 3.2. Surface and interface characterizations

Figure 6(a) to e were the SEM images of the stainless steel surface after worn in different solutions. Scratches which were parallel to the sliding direction appeared on all worn surfaces. The worn surfaces were partially covered by film-liked tribocorrosion products which were called as tribo-film [16]. The coverage ratio of the
tribo-film was decreased with the decreasing ratio of $\text{SO}_4^{2-}/\text{Cl}^-$. The stainless steel surface was almost completely covered by tribo-film after worn in 0.1 M solution. In comparison, the tribo-film was sporadic in 0.6 M solution. It was found the coverage ratio of tribo-film corresponded with COF: the surface with higher coverage ratio of tribo-film had the lower COF. It indicated that the tribo-film had lubricating effect [16]. The chemical compositions of the worn surfaces were analysed with EDS and the results were showed in figure 6(f). Generally, the O content on the tribo-film was much higher than that on the exposed region. This indicated that the tribo-film was consisted of oxides/hydroxides. The Fe content in the tribo-film was decreased and the Cr content increased with the decreasing ratio of $\text{SO}_4^{2-}/\text{Cl}^-$. The subsurface microstructure of the metallic materials would be changed by plastic deformation during the tribocorrosion [17]. The property of surface, such as hardness, is changed and in turn affect the tribocorrosion behaviour [18, 19]. The change of surface micro-hardness could reflect the change of subsurface microstructure. All the surface hardness were increased after the tribocorrosion tests, and that was widely known as work-hardening effect. Figure 7 was the increasing ratio of surface micro-hardness in different corrosive solutions. Clearly, the increasing ratio of the surface micro-hardness was obviously affected by solution composition. With the increasing ratio of $\text{Cl}^-$, the increasing ratio of surface micro-hardness went up to a peak value at 0.3 M and then dropped down. The stainless steel showed the lowest increasing ratio in pure NaCl solution (0.6 M).

The different increasing ratio of surface micro-hardness suggested that stainless steel should have different subsurface microstructures after worn in different solutions. To investigate this further, the worn surfaces from

![Figure 5](image-url)
**Figure 6** (a) to (e): SEM images of 316L stainless steel after worn in different corrosive solutions; (f) chemical compositions on the worn surfaces.

**Figure 7.** Increasing ratio of surface micro-hardness of 316L stainless steel after worn in different corrosive solutions.
0.3 M and 0.6 M were characterized by TEM because these two surfaces had the greatest difference in increasing ratio of surface micro-hardness. Figure 8 showed the TEM images of the cross-sections cut from the two worn surfaces. From figures 8(a) and (c), the gradient nanostructured microstructure was found on both two worn surfaces. The closer to the surface, the grains were finer and the dislocation density was higher. The grain boundary and dislocation could inhibit the motion and generation of dislocation, and then led to the increase of hardness [20]. The formation of gradient nanostructured microstructure was caused by the repetitive surface deformation under gradient strain [21]. The formation process of the gradient nanostructured microstructure mainly contained formation of planar dislocation arrays, grain subdivision, martensite transformation and formation of nanocrystallites [22]. From the high magnification images of the top-most region (figures 8(b) and (d)), the grain size in both two samples was smaller than 100 nm which was much smaller than the original grain (20–30 μm), and a large number of dislocations appeared in the nano-sized grains. Clearly, the sample from 0.3 M (figure 8(c)) had the smaller grain and higher dislocation density than that from 0.6 M (figure 8(d)). This was the reason that the stainless steel had the higher increasing ratio of the surface micro-hardness in 0.3 M than that in 0.6 M. The ring-like pattern in the selected area electron diffraction (SAED) indicated that the top region was nano-sized polycrystalline with random orientation. These nano-sized grains had two crystallographic structure: γ austenite (face centred cubic, FCC structure) and martensite (body centred cubic, BCC structure). The diffraction ring in SAED was more continuous in 0.3 M than 0.6 M. This indicated that the difference in crystal orientation was greater in 0.3 M than 0.6 M. Above TEM results indicated the 316L stainless steel had severer surface deformation after worn in 0.3 M solution than that in 0.6 M solution.

Figure 8. Bright-field TEM images and SAED (inserted in top right corner) of the cross-sections of stainless steel after worn in different corrosive solutions: (a) (b) 0.3 M and (c) (d) 0.6 M.
To observe the finer interface microstructure, high revolution TEM (HR-TEM) was applied. Figures 9(a) and (b) showed the HR-TEM images of the interface of worn stainless steel from 0.3 M. The twisty matrix indicated that the surface was evidently deformed (figure 9(a)). From the image with higher magnification (figure 9(b)), dislocations could be found. The fast Fourier transform (FTT) result of the deformed metallic matrix showed that the diffraction spots were prolonged, which indicated the appearance of misorientation. These results proved that the stainless steel surface was seriously deformed in tribocorrosion. The metallic matrix was covered by a thin film with thickness of ∼50 nm. Most part of the film was amorphous, but some crystalline particles were embedded in it. The crystalline interplanar spacing demonstrated that the embedded particles were Fe₂O₃. On the interface from 0.6 M, there was an ultra-thin film covered on metallic matrix (figure 9(c)) and the matrix was regular (figure 9(d)). The FTT result with regular pattern also proved it. It meant that the deformation was slighter in 0.6 M than 0.3 M.

Figures 10(a) and (b) were the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the EDS element line scanning results of the worn interfaces from 0.3 M and 0.6 M, respectively. In figure 10(a), the tribo-film could be easily distinguished from stainless steel substrate for its deeper colour and higher O content. The O was also detected on the stainless steel substrate, it may be caused by the oxidation of the cross-section sample during the transportation from SEM to TEM. The interface from 0.6 M did not show such element distribution due to the relatively thin film (figure 10(b)).
4. Discussion

4.1. Calculation of material loss components

The experimental results confirmed that the synergism between Cl\(^-\) and SO\(_4^{2-}\) did exist in tribocorrosion. It obviously influenced the tribocorrosion behavior of 316L stainless steel. To investigate this, the material loss components were calculated. The material loss caused by tribocorrosion could be described as following equation [23]:

\[ V_T = V_w + V_c + V_s \]  

(1)

where \( V_T \) was the total material loss volume, \( V_w \), \( V_c \) and \( V_s \) were the lost volume caused by pure wear, pure corrosion and synergistic effect between wear and corrosion, respectively. Further, \( V_s \) could be devised into two parts:

\[ V_s = V_{w-c} + V_{c-w} \]  

(2)
$V_{w-c}$ was the material loss caused by wear-affected corrosion and $V_{c-w}$ was the material loss caused by corrosion-affected wear.

In this study, $V_{w}$ was obtained from the tribocorrosion test under cathodic protection potential ($-800 \text{ mV}$) [24], $V_{c}$ was calculated from the potentiodynamic polarization test without wear, and $V_{w-c}$ was calculated from the potentiodynamic polarization test with wear [1]. The calculated results were showed in figure 11. The $V_{w}$ was the highest in pure Na$_2$SO$_4$ solution, and it was decreased with the addition of Cl$^-$, but then increased with the increasing ratio of Cl$^-$. The $V_{c}$ was very low when compared with other components and was neglected. The $V_{w-c}$ and $V_{c-w}$ were positive value in all solutions. This indicated that wear and corrosion had synergistic effect and could promote each other. In the Cl$^-$ containing solutions, the $V_s$ (sum of $V_{w-c}$ and $V_{c-w}$) had been the main factor (more than 50%) to cause material loss.

4.2. Synergistic effect between SO$_4^{2-}$ and Cl$^-$ on wear-affected corrosion ($V_{w-c}$)

The passive film on metallic materials in pure Na$_2$SO$_4$ solution was formed by following reactions (11):

$$\begin{align*}
(MOH)_{ads} + SO_4^{2-} &\rightarrow (MOH \cdot SO_4^{2-})_{ads} \\
(MOH \cdot SO_4^{2-})_{ads} &\rightarrow (MOH)_{pas} + H^+ + SO_4^{2-} + e
\end{align*}$$

The passive film in pure NaCl solution was formed by following reactions:

$$\begin{align*}
(MOH)_{ads} + Cl^- &\rightarrow (MOH \cdot Cl^-)_{ads} \\
(MOH \cdot Cl^-)_{ads} + OH^- &\rightarrow (MOH \cdot OH^-)_{ads} + Cl^- \\
(MOH \cdot OH^-)_{ads} &\rightarrow [M(OH)_2]_{ads} + e \\
[M(OH)_2]_{ads} &\rightarrow (MO)_{pas} + H_2O + e
\end{align*}$$

However, depassivation reaction would occur in Cl$^-$ containing solution:

$$(MOH \cdot Cl^-)_{ads} \rightarrow (MOHCl)_{rem} + e$$

In the mixing solution, the competitive adsorption between Cl$^-$ and SO$_4^{2-}$ would occur:

$$\begin{align*}
(MOH \cdot Cl^-)_{ads} + SO_4^{2-} &\rightarrow (MOH \cdot SO_4^{2-})_{ads} + Cl^- \\
(MOH \cdot SO_4^{2-})_{ads} + Cl^- &\rightarrow (MOH \cdot Cl^-)_{ads} + SO_4^{2-}
\end{align*}$$

Due to the decrease of reactant of (MOH \cdot Cl$^-)$_{ads} in the depassivation reaction by competitive adsorption of SO$_4^{2-}$ through reaction 10. The corrosive current was decreased and the breakdown potential was increased with the increasing ratio of SO$_4^{2-}/Cl^-$ in the potentiodynamic polarization tests. With the introduction of wear, all the corrosive currents were sharply increased due to mechanical depassivation [25]. However, the corrosive current was increased with the increasing ratio of SO$_4^{2-}/Cl^-$ in the mixing solutions. During the tribocorrosion, Cl$^-$ could contact with the fresh steel surface, then following reactions may occur and led to the dissolution of the steel:

$$\begin{align*}
M + Cl^- &\rightarrow (MCl)_{ads} + e \\
(MCl)_{ads} + H_2O &\rightarrow (MOH \cdot Cl^-)_{ads} + H^+ + Cl^- + H_2O
\end{align*}$$

Reaction (9)
For the strong electronegativity and complexation ability of Cl\(^{-}\), the corrosive current was increased when it was added into Na\(_2\)SO\(_4\) solution. However, on the other side, SO\(_4^{2-}\) could replace Cl\(^{-}\) in (MOH \cdot Cl\(^{-}\))\(_{ads}\) by competitive adsorption (reaction (10)) to form (MOH \cdot SO\(_4^{2-}\))\(_{ads}\), then, passivation reaction (4) could occur. In other words, though the presence of Cl\(^{-}\) promoted the oxidation/dissolution of the stainless steel, then the presence of SO\(_4^{2-}\) could react with the product formed in the previous reaction by competitive adsorption. As the result, the mix of SO\(_4^{2-}\) and Cl\(^{-}\) promoted the transmission of metal into oxides. To improve this speculation, XPS was used to analyse O element on stainless steel surface. Figure 12 showed the XPS spectra (O 1s) of 316L stainless steel after immersed in different corrosive solutions for 5 min: (a) 0 M and 0.1 M.

4.3.4 Synergistic effect SO\(_4^{2-}\) and Cl\(^{-}\) on corrosion-affected wear (V\(_{c-w}\))
The mix of SO\(_4^{2-}\) and Cl\(^{-}\) showed relatively complicated influence on V\(_{c-w}\). Normally, the positive V\(_{c-w}\) was caused by the formation of brittle corrosive products, such as oxide and hydroxide which were easier to be removed than the flexible metal (Roscoe effect) [25]. This could explain the decrease of V\(_{c-w}\) value from 0.1 M to 0.3 M because the amount of solid product was increased with the increasing ratio of Cl\(^{-}\) (figures 6(b) and (c)). With the continually increase of Cl\(^{-}\) ratio, though the solid product was disappearing, the V\(_{c-w}\) began to rise. Roscoe effect could not explain this phenomenon. Thus, the surface hardness became the focus because surface work-hardening effect could enhance wear resistance of material [27] and it was influenced by the ratio of SO\(_4^{2-}\)/Cl\(^{-}\) in corrosive solution. The relation between V\(_{c-w}\) with the ratio of SO\(_4^{2-}\)/Cl\(^{-}\) (figure 11) was consistent with the trend of increasing ratio of surface micro-hardness (figure 7). The weakening of work-hardening effect might be the main reason to lead to the increase of V\(_{c-w}\) in the solution with low ratio of SO\(_4^{2-}\)/Cl\(^{-}\).

Clearly, the difference in surface hardness was originated from different subsurface microstructures. According to the TEM results (figure 8), the gradient deformation microstructure was formed on stainless steel surface in tribocorrosion. The densities of grain boundary and dislocation in the deformation microstructure were higher in 0.3 M than that in 0.6 M, thus the former showed higher surface micro-hardness. In normal condition, surface work-hardening effect mainly depended on stress (normal and shear). Larger stress normally resulted in severer surface deformation and more remarkable work-hardening effect (higher hardness) [28, 29]. In this study, the normal stress was constant and the frictional shear stress in 0.6 M was even higher than that in 0.3 M (figure 4). However, the stainless steel showed higher increasing ratio of surface micro-hardness in 0.3 M solution. This indicated that the surface plastic deformation was influenced by other factors.

It had been reported that corrosion condition could influence surface deformation in tribocorrosion by changing surface chemistry [30–32]. There was a tribo-film with thickness of ~50 nm covered on stainless steel...
surface after worn in 0.3 M solution. As discussed above, this film was formed with the help of the synergistic effect between $\text{SO}_4^{2-}$ and $\text{Cl}^-$. The tribo-film and the stainless steel surface under it would be repeatedly deformed during the tribocorrosion. The tribo-film which was mainly consisted of oxide and hydroxide was harder to be deformed than the relatively flexible stainless steel [33]. When they were suffered from plastic deformation, the soft phase (stainless steel) needed to coordinate deformation with the hard phase (tribo-film) [34]. This would lead to deformation concentration in the soft phase [35]. Dislocations would be nucleated in the film/steel interface and glide to the steel [36]. This could be proved by the TEM image (figure 8(a)). Further, the presence of tribo-film could inhibit annihilation of dislocations at steel surface [30, 37]. As the result, the deformation of steel surface was aggravated. In 0.6 M solution, the film was ultra-thin, thus, the stainless steel was not required to coordinate deformation and the annihilation of dislocations would be relieved. Finally, the stainless steel worn in 0.3 M had the higher dislocation density and finer grain in the deformed subsurface, then, showed higher hardness than that in 0.6 M. It was helpful for the stainless steel to resist mechanical wear, thus, the component of $V_{\text{corr}}$ was decreased. In 0.1 M solution, the coverage of tribo-film was higher than that in 0.3 M, but the increasing ratio of surface hardness was lower. This might be due to the lowest COF in 0.1 M. Even so, the increasing ratio of surface hardness in 0.1 M was higher than that in 0.6 M. This indicated that the influence of tribo-film on surface deformation still existed.

5. Conclusions

In this study, 316L stainless steel was worn in five different corrosive solutions with different ratios of $\text{SO}_4^{2-}/\text{Cl}^-$ (from 0.31 M: 0 to 0: 0.62 M) to investigate the synergistic effect of $\text{Cl}^-$ and $\text{SO}_4^{2-}$ on tribocorrosion. Following conclusions could be drawn:

1. The mix of $\text{Cl}^-$ and $\text{SO}_4^{2-}$ (0.25 M: 0.1 M) could reduce 25.5% and 26.3% material loss of stainless steel in tribocorrosion when compared with that in pure Na$_2$SO$_4$ solution (0.31 M) or pure NaCl solution (0.62 M) with same charge concentration, respectively.

2. The synergism between wear and corrosion was the main factor (more than 50%) to cause material loss in the mixing solution.

3. The corrosive current during the tribocorrosion was increased with the increasing ratio of $\text{SO}_4^{2-}/\text{Cl}^-$. The mix of $\text{SO}_4^{2-}$ and $\text{Cl}^-$ could promote the transmission of metal into oxides. The existence of large amount of oxides might cause abrasion, then the wear-affected corrosion was accelerated by the enhanced depassivation.

4. The mix of $\text{Cl}^-$ and $\text{SO}_4^{2-}$ promoted the formation of tribo-film on stainless steel surface. The flexible stainless steel needed to coordinate deformation with the tribo-film which had relatively low deformability. This enhanced the surface work-hardening effect which was helpful for the stainless steel to resist corrosion-affected wear. When the ratio of $\text{SO}_4^{2-}/\text{Cl}^-$ was 0.15 M: 0.3 M, the synergistic effect between the two anions on the surface work-hardening was the most significant and the increasing ratio of surface hardness was 90.8%.

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Data availability statement

No new data were created or analysed in this study.

Conflict of interest

The authors declare that they have no conflict of interest.
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