Tribocorrosion behaviours of AISI 310 and AISI 316 austenitic stainless steels in 3.5% NaCl solution

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Abstract

In this paper the tribocorrosion behaviours of AISI 310 and AISI 316 stainless steels have been studied under reciprocating sliding condition in 3.5% NaCl solution, using a pin-on-disk tribometer integrated with a potentiostat for electrochemical control. Different sliding loads were used at a constant rotational speed of 60 rpm. The results show that sliding load has significant effect on the tribocorrosion behaviour of both materials. Corrosion attack was severe at sliding load conditions in both materials suggesting corrosion-induced wear as the dominant of the two synergistic components. However, at low sliding load, anodic dissolution and pit formation in AISI 316 was accelerated by sliding action causing wear-induced corrosion to be dominant.

Keywords: Metals; Electrochemical techniques; Corrosion; Tribology; Friction

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1. Introduction

Austenitic stainless steels are extensively used in nuclear reactors, biomedical implants, as well as in components for chemical and food industries. They are the most popular corrosion-resistant materials used in various applications due to their excellent corrosion resistance and good mechanical properties. These materials derive their corrosion resistance from the formation of a thin passive film of less than 10 nm thick on the surface in various environments. However, austenitic stainless steels exhibit poor wear resistance and their use may result in material transfer between sliding bodies, mechanical mixing, oxidation and strain-induced martensitic transformation [1-3]. In many situations, austenitic stainless steel components are subjected to combined corrosion and wear actions, such as in off-shore, mining, power generation, biomedical and food processing applications, where the components are subjected to scratching, abrasion, erosion, and other forms of wear damages in a corrosive environment. These can lead to the damage or even complete removal of the passive film from the contact surface, resulting in accelerated metal dissolution, which in turn can in many cases lead to accelerated wear [4-6].

The tribocorrosion and corrosive-wear behaviour of stainless steels under combined chemical, electrochemical and mechanical actions have been studied extensively [7-15]. Investigators have conducted tribocorrosion study mostly in H_2SO_4 [7, 8, 16, 17] and NaCl solutions [6, 17-20]. In H_2SO_4, stainless steels form a passive film of oxide layer which protects the material from further degradation. In NaCl, however, stainless steels are susceptible to localised corrosion. The corrosive-wear behaviour of stainless steel in a NaCl environment has been reported by Abd-El-Kader and El-Raghby [21]. In their studies they found that at anodic potentials, chemical reactions led to increased wear rate which was almost as twice as that under cathodic protection. Tao and Li [22] also conducted research on the corrosive-wear behaviour of stainless steels in similar environment. However, the effect of wear on corrosion or vice versa was not reported. Iwabuchi et al. [23] studied the sliding wear behaviour of stainless steel in sea water and found that the enhancement in mass loss is due to wear-induced corrosion, which is different from the findings of several other investigators [24, 25]. Recently, Sun and Rana [26] investigated the tribocorrosion behaviour of AISI 304 in 0.5% NaCl environments. They found out that sliding speed and load have significant effects on the cathodic shift of open circuit potential induced by sliding and there were good correlations between coefficient of friction, total material loss from the wear track and applied potential. Both wear-induced corrosion and corrosion-induced wear were reported as the mechanisms of degradation of this material. Thus, the fundamental mechanism that determines the wear-corrosion synergism in tribocorrosion of stainless steels in chloride containing solutions is complex and has not been fully understood. The processes that occur during friction interaction of contacting materials in aggressive media have not been adequately studied. Most of the published works on tribocorrosion of austenitic stainless steels have focused on AISI 304 and AISI 316. Additionally, most of the reported works on tribocorrosion employ potentiostatic and open circuit potential techniques. Other techniques such as potentiodynamic polarisation are rarely used. This method allows one to observe the effect of friction on the different electrochemical reactions taking place depending on potential and hence the focus of this work. To the authors' knowledge, there has not been any reported work on the tribocorrosion behaviour of AISI 310. The knowledge of the tribological behaviour in the absence of corrosive medium and that of the electrochemical behaviour in the absence of wear is not sufficient to predict the tribocorrosion behaviour of passive systems. Even though AISI 316 is more resistance to pitting corrosion in chloride environments than AISI 310 due to the combined effect of chromium and molybdenum additions to AISI 316 [27-30], the tribocorrosion behaviour could be different and needs to be investigated. The interaction between mechanical and chemical factors governing tribocorrosion of these materials is not well understood and thus the need to gain a better insight into the mechanisms and to identify critical mechanical, material and chemical factors that could affect their tribocorrosion behaviour.

In the present work, the tribocorrosion behaviour of AISI 310 and AISI 316 stainless steel under reciprocating sliding conditions in 3.5% NaCl solution, using a ball-on-disk tribometer integrated with a potentiostat for electrochemical control has been studied. The tribocorrosion behaviour has been investigated at varying applied load using potentiodyanmic polarisation technique. The results of the two materials have been compared and the tribocorrosion behaviour explained in terms of their chemical composition, effect of applied load and wear track morphology.

2. Experimental

2.1 Materials

Two grades of austenitic stainless steels were used in this study, namely AISI 310 and AISI 316. Materials were supplied by Columbus Stainless (Pty) Ltd., South Africa in hot rolled and annealed condition. The nominal chemical composition of the alloys is provided in **Table 1**. The experiments were conducted on as-received samples. The hardness profiles of the samples were measured using an EmcoTEST Durascan with a load of 100 g and dwell time of 15 s. Five indentations were made and an average value was taken. The AISI 310 recorded an average hardness value of 334.8 ± 0.8 HV whilst the AISI 316 recorded 340.6 ± 1.1 HV.

2.2 Wear testing

A ball-on-disk wear-testing tribometer (CETR-UMT-2) was employed to evaluate the friction and wear behaviour of the specimens in reciprocating dry sliding contact. Alumina ball with a diameter of 4 mm was used as the counter surface. Specimens for dry wear test were cut into 2 cm × 2 cm × 1.5 cm. Test surfaces of the specimens was ground to 1200 surface finish using a SiC paper and tests conducted at room temperature at a rotating speed of 60 rpm. Wear tests were carried out under a constant load of 2 N for 1000 seconds where coefficient of friction was continuously monitored. Test were conducted in triplicate and the average values taken.

2.3 Tribocorrosion testing

Specimen for tribocorrosion testing were cut into sizes of 2 cm × 2 cm × 0.3 cm and wet ground using a series of SiC grinding papers down to the 1200 grade, followed by cleaning with running water and then ethanol. The surface area of the sample exposed to the electrolyte was 1.54 cm^2. Sliding wear testing was conducted using a ball-on-disk tribometer with integrated potentiostat (UMT-2, Centre for Tribology Inc. Bruker Nano Inc. (CETR), Campbell, CA). Figure 1 shows a schematic diagram of the experimental setup [31]. During the test, specimens held in the test cell were rotating against a stationary ball slider, under controlled load and speed conditions. In order to electrically isolate the specimen from the tribometer and to facilitate tribocorrosion testing, the test cell, the specimen holder and the ball holder were made of an insulating and corrosion resistant material. The ball slider used in this work was an alumina ball of 4 mm in diameter. The stroke length was 2 mm. The electrolyte used for the tests was 3.5% NaCl solution, which was prepared from analytical grade NaCl and distilled water. The pH of the solution was 5.62. The test cell was filled with about 60 ml of the solution. A silver-silver chloride electrode (Ag/AgCl) filled with 3 M KCl was inserted in the test cell 5 mm above the test surface to serve as the reference electrode (RE), and a platinum rod was used as the counter electrode (CE). All the tests were performed at room temperature (22 ± 2 ^{o}C) and open to the air.

Potentiodynamic measurements were conducted on the samples which involved measuring the polarisation curves of the specimen during sliding and without sliding at a sweep rate of 1 mV/s. Under sliding condition, the polarisation curve was measured under a load of 2 N and 3 N, respectively and at a rotation speed of 60 rpm (contact frequency of 1 Hz). Under the condition without sliding, the specimen was rotating at a speed of 60 rpm without contact with the slider, which represents the condition of the unworn area outside the wear track during sliding tests. Before each polarisation measurement, the specimen was immersed in the solution for 5 min to obtain the stabilization of the open circuit potential before each test under the respective conditions. Polarisation scans were initiated from -0.5 to 0.5 V versus reference electrode. The corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rare were obtained using the Tafel extrapolation method. All tests were conducted in triplicate. The wear track after the test was examined using ultra high resolution scanning electron microscope (SEM JSM 7600F) equipped with EDX for elemental analyses.

3. Results

Figure 2 shows the polarisation curve of the AISI 310 and AISI 316 in 3.5% NaCl without sliding load. It is observed that the corrosion potential (E_{corr}) of the AISI 316 was less than that of AISI 310. Thus, AISI 316 shows more susceptibility to corrosion in 3.5% NaCl than AISI 310. Figure 3 shows the SEM images of both samples after polarisation tests. Corrosion occurred mainly along the grain boundaries with formation of oxide films in both materials. Figure 4 shows the polarisation curves of AISI 310 and AISI 316 measured under reciprocating sliding load and rotating conditions. Polarisation curves measured without sliding load has been added for comparison. In the case of AISI 310, there was a cathodic shift in the E_{corr} at sliding load of 2 N (Figure 4a). At sliding load of 3 N, a positive shift in the E_{corr} was observed in relation to the E_{corr} at 2 N. The current densities at higher potentials was lower at 2 N compared to 3 N. The polarisation behaviour of the AISI 316 is shown in Figure 4b. The E_{corr} shifted cathodically when a sliding load of 2 N was applied. At 3 N, a positive shift of the E_{corr} was observed in relation to E_{corr} at 2 N, similar to that observed in AISI 310. The uniform corrosion rate of AISI 310 decreased strongly at 2 N and then increased marginally at 3 N (see Figure 5) whilst that of AISI 316 increased at 2 N and then decreased marginally at 3 N. Figures 6 and 7 show SEM images during tribocorrosion investigations of AISI 310 and AISI 316 at varying sliding loads, respectively. The measured wear track width of AISI 310 was about 280 µm at 2 N and 400 µm at 3 N sliding loads. In the case of AISI 316, the measured wear track at 2 N was 203 µm whilst 255 µm was recorded at 3 N. Figure 8 shows the evolution of coefficient of friction (COF) due to reciprocating sliding load at 2 N and 3 N, respectively for AISI 310 and AISI 316. The COF evolution due to dry sliding has been included for comparison. The COF of AISI 310 at the end of the dry sliding test was slightly higher than AISI 316. It could also be observed that the COF under dry sliding were lower in both materials compared to wet sliding under tribocorrosion studies. It is also observed that at higher load, the COF was higher in AISI 310 (Figure 8a); the reverse is true for AISI 316.

4. Discussion

The corrosion potential (E_{corr}) of the AISI 316 was less than that of AISI 310 (Figure 2). This is due to the high concentration of chromium and nickel in the AISI 310 compared to the AISI 316 causing the former to be more noble compared to the later. Weak passivation was observed in both materials which were expected in alkaline environments [32, 33]. The pitting potential was higher in AISI 316 compared to AISI 310 in the studied environment. This is due to the combined effect of chromium and molybdenum additions to AISI 316 [27-29]. It has been reported that stainless steels alloyed with chromium and molybdenum increase pitting corrosion resistance either in concentrated chloride solutions or in diluted ones [14, 30]. Molybdenum retards the corrosion by forming passive films containing molybdenum species or oxides [8]. The potential region within which general corrosion occurred was small in both materials indicating susceptibility to localised corrosion in NaCl. The weak passive region of AISI 316 was up to -0.18 $V_{Ag/AgCl}$ which is closed to the value (-0.08 $V_{Ag/AgCl}$) reported by Yamamoto *et al* [8] in 0.9% NaCl. It should be mentioned that the chemical composition of these two materials were slightly different with the sample used in their investigation with the samples used in this investigation having higher chromium and nickel contents. The uniform corrosion current density was lower in AISI 316 (0.045 mA/cm^2) compared to AISI 310 (0.232 mA/cm^2). One would have expected that AISI 310 with higher chromium content (24.4%) would have higher uniform corrosion resistance compared to AISI 316 (18.1%). However, this was not the case. From Figure 3, there were visible cracks in the oxides formed in AISI 310 compared to AISI 316. This could be due to thicker oxide layer formed on AISI 310 due to its relatively higher chromium and nickel contents which ruptured chemically [8]. This contributed to the higher corrosion current densities recorded in AISI 310.

Figure 4 presents the results of the polarisation curves of AISI 310 and AISI 316 measured under varied conditions. Cathodic shifts in the corrosion potential have been reported in passive systems when sliding load is used and the reason has been attributed to the destruction of the passive state by its partial or complete removal and the activation of the material inside the wear track [6, 9, 11, 13, 34]. The positive shift in the E_{corr} in both materials at higher sliding load is due to the smoothening of the oxide layer formed making it less susceptible to corrosion attacks.

From Figure 5, the uniform corrosion rate of AISI 310 decreased strongly at 2 N due to the smoothening of corrosion products formed on the surface as the normal force was increased at constant sliding speed. However, as the sliding load increased to 3 N, the corrosion current density increased marginally, possibly due to crack initiation and removal of corrosion products within the wear track. Also, the pitting potential increased marginally at 2 N compared to 3 N. However, in the case of AISI 316, at higher load of 3 N, lower corrosion current densities were recorded compared to 2 N. This is due to the ability of AISI 316 to repassivate quickly when the passive film breaks down due to the presence of combined action of chromium and molybdenum [27, 28]. It is observed that at sliding load of 2 N, higher current densities were measured compared to sliding load of 3 N and without sliding load. The reason for this behaviour is explained below.

From Figure 6, the corrosion attack inside the wear track was severe at 3 N with formation of larger pits compared to 2 N. This is due to the destruction of oxide film formed. Corrosion attacks outside the wear track were similar with attack being severe along the grain boundaries. Comparing Figures 3 and 6, it could be concluded that corrosion attack was severing at sliding load conditions compared with samples tested without sliding load condition. This is so because of the galvanic interaction between the active area inside the wear track and the surrounding area. Thus at reciprocating sliding load conditions, localised corrosion of AISI 310 in 3.5% NaCl is enhanced. Pitting corrosion is the dominant form of corrosion under test conditions which is typical in chloride containing environments. That is even though the general corrosion rate of AISI 310 decreased at applied sliding loads, the localised corrosion increased under same conditions.

The measured wear tracks of AISI 316 at varying loads were less than what was recorded in AISI 310 due to the relatively higher hardness of AISI 316 sample. The relatively lower wear width of AISI 316 at 2 N increased the cathode-to-anode area ratio increasing the corrosion current densities measured as reported by Mischler and Ponthiaux. Wear debris were observed inside the wear track in AISI 316 which was absent in AISI 310. Additionally, fewer pits were formed inside the wear track of AISI 316 compared to AISI 310. The reason could be due to the effective repassivation mechanism in AISI 316 compared to AISI 310. It could be observed that pits distribution inside the wear track was uniform at 2 N compared to 3 N which was concentrated along the centre of the wear track where the highest force was applied. The oxides formed at higher load were effectively smoothened sealing the pits closer to the edge of the wear tracks and therefore recording lower current densities. Thus at 2 N, anodic dissolution and pit formation are therefore accelerated by the sliding action which is attributed to wear-induced corrosion (i.e. corrosion rate is higher compared to sliding without load as shown in Figure 5).

The COF of AISI 310 was higher than AISI 316 during dry sliding due to the lower hardness value of the former. The COF under dry sliding were lower than wet sliding which is an indication of corrosion-induced wear in both materials. Whereas the COF decreased from start of cathodic potential sweep to about 380 sec in AISI 316, that of AISI 310 increased gently within the same period. The decrease in COF in AISI 316 is due to stable oxide film formation whilst the increase in COF is due to either pits or weak oxide formation which increased the surface roughness (Figures 6 and 7). The trend in the evolution of COF in AISI 310 was different from AISI 316. The variation is due to the varying fractions of pits inside the wear tracks as could be seen from the SEM results shown in Figures 6 and 7. From 400 sec to 700 sec, the COF increased sharply and then decreased for both materials under the different sliding loads. The sharp increase in COF is due to increased roughness of the surface of the wear track due to increased pits formation whilst the decreased is due to repassivation and/or smoothening of the pits under applied load. The maximum COF reached was about the same for AISI 310 under different loads (~0.48) whilst for AISI 316, the maximum COF reached (~0.55) was at sliding load of 2 N; at 3 N load, the maximum COF was about 0.46.

This is rather an interesting observation since the variation in COF gives an indication of pitting and passive formation behaviour in the wear track of these materials. Initiation of pits of AISI 310 inside the wear track at higher load (3 N) occurs faster than at lower load (2 N). This agrees very well with the polarisation curves shown in Figure 4. Additionally, even though pits initiation was faster at 3 N, the maximum COF reached were the same at both sliding load conditions. At higher loads, any passive film formed is removed faster due to the higher contact force. The removal of the oxide layer causes galvanic interaction between the fresh surface and the passivated surface.

In the case of AISI 316, pits initiation only starts after anodic potential; hence the decrease in COF during cathodic polarisation. Also at higher load (3 N) the maximum COF reached was lower than at 2 N. The COF recorded in this case was higher than in AISI 310. The increase in friction of the AISI 316 at 2 N could be explained by third-body effects at the contact interface [35]. This is because at lower load, higher current densities and higher COF values were measured as observed in Figures 5 and 8. Thus more corrosion products were formed during this period. Corrosion products formed inside the wear track could increase the COF due to abrasive wear (Figure 7b). Figure 8b reveals a decrease in the coefficient of friction with increasing normal force at constant frequency and constant sliding time, due to smoothening of the surface at high load as reported elsewhere [36].

An interesting correlation between coefficient of friction (COF) and current densities arising from anodic branch of the polarization was observed during sliding as shown in Figure 9. The friction curve can be divided into three zones. During the initial 400 sec, the COF decreased sharply from 0.7 becoming stable at a value around 0.38 (zone I). This zone occurred at the cathodic branch of the polarization curve. With the onset of anodic branch of the polarization, starting at the E_{corr} (-100 mV), the COF experienced a sudden rise reaching a peak of about 0.57 and then decreased to a value of 0.38 (zone II) before becoming stable again after about 700 sec (zone III). The highest COF value was observed when the slope of the polarization curve changed slightly. It is clear from Figure 9 that the development of an oxide film was responsible for the decreased in COF values observed in zone I. The reduced friction at higher anodic potential could be due to the smoothening of oxides films in the wear track sealing off pits (zone III). The formation of stable corrosion pits in the anodic region (zone II) increased the COF values and the repassivation of pits resulted in the decreased in COF values. Pits formation can increase friction in two folds. Firstly, pit formation will increase the surface roughness of the wear track and thus would lead to increased friction due to increased contribution from mechanical interlocking. Secondly, pit formation will reduce the real contact area inside the wear track and thus would lead to reduced friction due to reduced contribution from adhesive junction shearing [35]. It appears that during zone II, at a potential ranging from about -100 mV to about 0.75 mV, the first effect outweighs the second effect and thus the COF is increased. Similar observation was made in AISI 310 and at higher load. The strong correlation between COF and current densities measured during polarization test was also observed by Sun and Rana [26].

5. Conclusion

The tribocorrosion behaviour of AISI 310 and AISI 316 has been investigated in 3.5% NaCl and the results compared. The corrosion potential (E_{corr}) and corrosion current density of AISI 316 were lower than AISI 310. Cathodic shifts in the E_{corr} were observed in both materials during tribocorrosion due to the removal and/or destruction of oxide films. Corrosion attacks inside the wear tracks were more severe in AISI 310 than in AISI 316. This is due to the ability of AISI 316 to repassivate quickly when there is passive film breakdown. There was a strong correlation between coefficient of friction and current densities arising from anodic branch of the polarization curve during unidirectional sliding loads in both materials. Whereas the degradation of AISI 310 was mainly due to corrosive-induced wear while that of AISI 316 was both corrosive-induced wear and wear-induced corrosion.

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