



Influence of microstructure evolution on tribocorrosion of 304SS in artificial seawater



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ABSTRACT

The influence of microstructure evolution on tribocorrosion of 304SS was investigated for the first time in artificial seawater. Strain-induced α' -martensite and twinning occurred during sliding friction at room temperature. The volume fraction of transformed martensite decreased with increasing load, making the dominant corrosion mechanism changed from α' -martensite to austenite as the dissolved anode during sliding. Meantime, the extent of transformed twinning peaked at 125 N, which controlled the wear resistance of 304SS. Quantitative calculation showed the role of microstructure evolution playing in the interplay of mechanical and electrochemical reactions, which eventually resulted in accelerated degradation of 304SS.

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1. Introduction

As one of the familiar materials, austenitic (γ , face-centered cubic, fcc) stainless steels perform excellent corrosion resistance, but their relatively low hardness and poor wear resistance seriously restrict their actual application. A number of investigations have shown that the strain hardening behavior of austenitic steels often strongly relates to deformation induced by, e.g. twinning, dislocation slip, ϵ (hexagonal-close packed, hcp) and α' (body-centered cubic, bcc) phases, at near room-temperature [1–4].

It is well established that the deformation mechanism and the mechanical properties of fcc metals are strongly related to their stacking fault energy (SFE). For materials, low SFE ($<18 \text{ mJ m}^{-2}$) favors the $\gamma \rightarrow \epsilon$ or $\gamma \rightarrow \epsilon \rightarrow \alpha'$ phase transformation, whereas higher SFE suppresses this mode of phase transformation but avails to the transformation $\gamma \rightarrow$ twinning $\rightarrow \alpha'$ phase [5]. Twinning is reported to be dominant in the course of plastic deformation for fcc materials with SFE at a range of $18\text{--}45 \text{ mJ m}^{-2}$, which is very important for material strengthening [6–8]. Moreover, the higher the SFE within this range, the more difficult the transformation twinning $\rightarrow \alpha'$ phase. When SFE is higher than 45 mJ m^{-2} , the plastic deformation mechanism may change from twinning to dislocation slip under progressing strain. At this point, the strain hardening is controlled solely by the slip of dislocation.

Up to date, although great efforts have been made to study the effect of strain-induced microstructure evolution on the mechanical properties of austenitic steels [9–11], little refers to those steels operating in corrosive environment. For example, when metallic materials, especially passive metals, are subjected to frictional motion in corrosive solution, it includes a synergistic effect between mechanical, chemical and electrochemical actions [12–17]. Because rubbing/sliding can destroy the protective passive film and the regeneration of complete passive film is difficult to take place, at which galvanic corrosion is established between the mechanically depassivated areas and the surrounding passive areas [18,19]. On the other hand, the occurrence of corrosion will degrade the nature of contact surface (such as roughness [20], hardness [21], and second phase content [22]), so that the wear resistance decreases and presents an accelerated wear rate.

Moreover, steels often suffer from corrosion and wear (namely, tribocorrosion) simultaneously in a wide variety of practical engineering and industrial contexts where the synergetic effect causes irreversible damage to installations, machines and devices. Regrettably, till now this synergistic effect is still incompletely understood, because under electrochemical control the tribocorrosion behavior of sliding contacts depends on many factors, such as the electrochemical parameters, the mechanical conditions, and the solution properties. Among the constraints above, the materials and surface particularities are of the utmost importance. It is well known that the microstructure peculiarity of materials, including phase evolution and distribution, grain size and orientation, and dislocation density, is critical for the mechanical behavior. It is

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therefore reasonable to infer that the same parameters must also have an important influence on the synergistic effect in tribocorrosion, although few data are available at this time. Hence, a targeted study of the microstructure evolution of contacting surfaces and its influence on tribocorrosion behavior is greatly important and valuable for both academia and industry.

In the present work, the friction-induced microstructure evolution characteristic of 304 austenitic stainless steels (304SS) and its influence on tribocorrosion behavior were investigated in detail in artificial seawater. Particularly, special attention was paid to the transformed volume fraction of α' -martensite after sliding wear under different loading conditions. This work is beneficial to have profound knowledge on the influence of microstructural evolution, and provides a more comprehensive view of investigating the mechanism of tribocorrosion in seawater.

2. Experiments

2.1. Materials

The material used in the present work is 304SS and its chemical composition is listed in Table 1. The ring samples of 304SS with outer diameter of 54 mm and inner diameter of 38 mm were annealed at 1050 °C for an hour before tribocorrosion experiments to relieve internal stresses. Before experiments, each specimen was ground mechanically using a series of SiC papers up to 1500 grit, then degreased with acetone and dried with nitrogen gas. Before immersed into tribocorrosion cell, all surfaces except the upper-surface were sealed with insulating glue. During the tests, a rotating alumina pin with a diameter of 4 mm slid against stationary 304SS specimen.

2.2. Tribocorrosion tests

The tribocorrosion tests were carried out using a MMW-1 vertical universal friction and wear tester (Jinan Shijin Testing Machine Group, PR China) which was connected with a CHI 760C electrochemical workstation (Shanghai CH Instruments, PR China), and the schematic view of components of tribocorrosion tester is shown in Fig. 1. The tribocorrosion behavior of 304SS was studied in artificial seawater (chlorinity is 19.38, and pH is 8.20), which was prepared referenced to ASTM D1141-98 and a Teflon cell filled with 400 mL of the corrosive solution was employed for tribocorrosion measurements, connecting with a classic three electrode system. The system comprised 304SS as the working electrode, cylindrical Pt gauge of 2 cm in height and 9 cm in diameter as the counter electrode, and Ag/AgCl (3.5 M KCl filled) as the reference electrode. All friction tests, in the absence or presence of corrosion, were carried out under a fixed velocity of 100 R min⁻¹ but a varying load ranging from 25 N to 150 N. In addition, cathodic protection technology, an applied potential which is 0.7 V cathodic to the open circuit potential of passive film, was performed to eliminate the electrochemical corrosion during sliding. That is, the mass loss obtained under cathodic protection was absolutely from pure mechanical wear.

The electrochemical measurements were carried out to investigate the effect of wear on corrosion for 304SS. Open circuit potential (OCP) variation curves were monitored before, during and after

sliding to assess how the sliding action affected the depassivation and repassivation within the contact area. Potentiodynamic polarization measurements were performed by changing the potential automatically from -350 to +1200 mV versus OCP with a scan rate of 2 mV s⁻¹. Before each measurement the electrodes were immersed in the test solution at OCP for 20 min. All the tests were conducted at room temperature (17 °C) and open to the air. Upon the electrochemical experimental results several electrochemical parameters, such as the corrosion potential (E_{corr}), the pitting potential (E_{pit}), and the corrosion current density (i_{corr}), were calculated and listed in Table 2.

All tests were performed a minimum of three times under the identical conditions, and the average results were reported in this paper.

The mass loss during tribocorrosion was calculated according to ASTM G119-09. The total wear-corrosion degradation (T) is expressed by the following equation:

$$T = W_0 + C_0 + S \quad (1)$$

where W_0 is the wear rate without corrosion, mm y⁻¹; C_0 is corrosion rate without wear, mm y⁻¹; S is the sum of the interactions between corrosion and wear, which is determined by Eq. (2).

$$S = \Delta W_C + \Delta C_W \quad (2)$$

where ΔW_C is the increment in wear rate due to corrosion, mm y⁻¹; ΔC_W is the increment in corrosion rate due to wear, mm y⁻¹.

Based on Eqs. (1) and (2), the Eqs. (3) and (4) can be derived to calculate the total wear rate (W , mm y⁻¹) and total corrosion rate (C , mm y⁻¹) during tribocorrosion.

$$W = W_0 + \Delta W_C \quad (3)$$

$$C = C_0 + \Delta C_W \quad (4)$$

Thus,

$$T = W + C \quad (5)$$

Three dimensionless factors are used to depict the degree of corrosion-wear synergism. The total synergism factor is:

$$\frac{T}{T - S} \quad (6)$$

The corrosion augmentation factor is:

$$\frac{C_0 + \Delta C_W}{C_0} \quad (7)$$

The wear augmentation factor is:

$$\frac{W_0 + \Delta W_C}{W_0} \quad (8)$$

2.3. Microstructure characterization

The morphologies of the worn surfaces and the cross-sections of the 304SS were examined by scanning electron microscope (SEM, JEOL 5600, Japan). The metallographic surfaces of worn specimens were studied by BX53T-12F01 optical microscope (OLYMPUS, Japan) in order to distinguish martensite (α' phase) from austenite (γ phase) after polishing and etching. The etching solution was composed of 3 mL HCl, 12 mL H₂O and 1 g FeCl₃. The polished samples were immersed into the etchant for 15 s. Thin foil specimens for transmission electron microscopic (TEM) investigations were manual ground to a thickness about 80 μ m, and then electropolished to perforation by using the double jet technique in a polishing solution of 8% (V/V) perchloric acid and 92% ethanol at 25 V. Transmission electron microscope (TEM) were performed using a TECNAI G2 TF20 apparatus (FEI, USA) operated at 200 kV. X-ray dif-

Table 1
Chemical composition of 304SS.

| Elements | Cr | Si | Mn | Ni | Mo | C | P | S | Fe |
|-----------------|-------|------|------|------|------|------|-------|-------|------|
| Content/ wt% | 18.50 | 0.59 | 0.88 | 8.12 | 0.30 | 0.05 | 0.015 | 0.028 | Bal. |

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