

Article

Tribocorrosion Behavior of Medium-Entropy Super Austenitic Stainless Steel in Acidic Environments

Chia-Chi Liu ¹, Shih-Yen Huang ¹, Yu-Ren Chu ¹ , Tzu-Hsien Yang ², Hung-Wei Yen ² , I-Chung Cheng ³, Peng-Wei Chu ⁴  and Yueh-Lien Lee ^{1,*} 

¹ Department of Engineering Science and Ocean Engineering, National Taiwan University, Taipei 106319, Taiwan; r07525099@ntu.edu.tw (C.-C.L.); f08525129@ntu.edu.tw (S.-Y.H.); zeeve.y.chu@gmail.com (Y.-R.C.)

² Department of Materials Science and Engineering, National Taiwan University, Taipei 106319, Taiwan; yangdavid180@googlemail.com (T.-H.Y.); homeryen@ntu.edu.tw (H.-W.Y.)

³ Department of Mechanical Engineering, National Taiwan University, Taipei 106319, Taiwan; ichungch@ntu.edu.tw

⁴ Department of Engineering and System Science, National Tsing Hua University, Hsinchu 300044, Taiwan; pengweichu@mx.nthu.edu.tw

* Correspondence: yuehlien@ntu.edu.tw

Abstract: Although extensive studies have examined the tribocorrosion behavior of stainless steels, the performance of medium-entropy austenitic super stainless steels (MEASS) under severe combined corrosion and mechanical wear conditions has not been fully established. This study systematically compares the tribocorrosion behavior of a newly developed MEASS with conventional S31254 super austenitic stainless steel (SASS) in a 1 M H₂SO₄ solution, aiming to explore innovative material designs for enhanced performance under these demanding conditions. Electrochemical tests were conducted under both open-circuit potential (OCP) and cathodic potential, with and without sliding wear, to assess the corrosion, wear, and synergistic effects influencing the tribocorrosion performance. Worn surface morphologies and hardness were analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and hardness measurements, respectively. The experimental results revealed that MEASS exhibits a superior repassivation capability compared to S31254, with a 34.3% lower total material loss after 24 h of tribocorrosion test, primarily attributed to enhanced strain hardening and improved wear resistance. These findings emphasize the strong potential of MEASS for use in corrosive environments, particularly in chemical processing industries, where high resistance to wear and corrosion is critically required.

Keywords: medium-entropy austenitic super stainless steel; tribocorrosion; potentiodynamic polarization curve; strain hardening



Received: 10 February 2025

Revised: 10 March 2025

Accepted: 13 March 2025

Published: 16 March 2025

Citation: Liu, C.-C.; Huang, S.-Y.; Chu, Y.-R.; Yang, T.-H.; Yen, H.-W.; Cheng, I.-C.; Chu, P.-W.; Lee, Y.-L.

Tribocorrosion Behavior of Medium-Entropy Super Austenitic Stainless Steel in Acidic Environments.

Lubricants **2025**, *13*, 125. <https://doi.org/10.3390/lubricants13030125>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Tribocorrosion is an irreversible degradation process that affects materials due to the combined chemical and mechanical interactions at their surfaces when exposed to corrosive solutions [1]. This synergy between corrosion and wear has a significant impact on the performance and safety of engineering materials and can be broadly classified into two mechanisms: wear-induced corrosion and corrosion-induced wear. In wear-induced corrosion, the wear process raises the surface temperature of the material, accelerating chemical reactions and increasing the corrosion rate. Mechanical wear causes plastic deformation on the material's surface, which raises its energy state and predisposes it to further corrosion.

Moreover, the wear process can damage the protective passivation film, significantly enhancing corrosion. Unlike wear-induced corrosion, corrosion-induced wear originates from chemical reactions that deteriorate the surface before any significant mechanical loading occurs. When a material is exposed to a corrosive environment, chemical reactions can lead to the formation of surface defects such as pits, cracks, or the deposition of corrosion products (e.g., oxides). These defects weaken the surface by reducing its hardness and altering its microstructure. For example, if the corrosion products formed are relatively soft, they may provide a lubricating effect that alters wear behavior. On the other hand, if corrosion renders the surface more brittle, the material is more susceptible to removal by wear. The dislodged corrosion products or oxides, once scattered in the solution, can participate in three-body wear with the substrate, further increasing material loss. These intertwined processes highlight the inherent complexity of tribocorrosion, making its management an inevitable challenge in engineering applications. López-Ortega et al. [2] investigated the tribocorrosion behavior of two types of materials: those that form a passive film and those that actively dissolve. For passivating materials, immersion in an electrolyte leads to the formation of a protective passive film on the surface. However, during sliding contact, this film is disrupted, exposing the unprotected substrate to the electrolyte and initiating galvanic corrosion. In contrast, for actively dissolving materials, immersion results in the formation of a rust layer, which offers poor protection. When sliding occurs, this rust layer is readily removed, thereby diminishing the galvanic effect.

Stainless steels are widely utilized in marine engineering due to their excellent corrosion resistance and mechanical strength. Their inherent ability to form a passive film helps protect against the corrosive effects of chloride ions present in seawater. However, in marine applications, components often experience not only corrosive attack but also mechanical wear. There are numerous studies that have examined tribocorrosion behavior of stainless steels in sodium chloride environments [3–9]. For example, Zhang et al. [3] investigated the tribocorrosion of S31254 steel in artificial seawater and found that sliding contact increases the corrosion current density by three orders of magnitude. This marked deterioration in corrosion resistance is attributed to the damage inflicted on the passivation film during sliding. Similarly, Obadele et al. [6] evaluated the tribocorrosion behavior of AISI 310 and AISI 316 austenitic stainless steels in a 3.5% NaCl solution. They observed that the corrosion potential (E_{corr}) decreased during tribocorrosion as a result of the removal or destruction of the oxide films, which in turn promoted wear-induced corrosion. The tribocorrosion performance of stainless steels is also strongly influenced by applied load and rotating speed [4,5,10]. Silva et al. [4] examined the effect of load on the tribocorrosion behavior of S32750 steel in a 3.5 wt.% sodium chloride environment. Their results indicated that higher applied loads lead to more unstable polarization curves, with both the corrosion current density and the current density within the passivation interval increasing. Additionally, a larger area of damaged passivation film was observed on the material's surface under higher loads. Complementarily, Zhang et al. [10] conducted intermittent OCP measurements under varying loads. They reported that heavier loads cause a more significant drop in the OCP, and although the potential recovers immediately once sliding ceases—indicating the reformation of the passivation film—the recovery takes longer when the load is higher due to more severe film damage. The pH value of the environment also affects tribocorrosion behavior. Zhang et al. [11] studied the tribocorrosion of 304 stainless steel (304SS) in solutions with different pH values and found that higher pH leads to lower corrosion currents and an increased pitting potential. This phenomenon is explained by the role of chloride ions, which react with metal ions in the passive film to form chloride salts that compromise film integrity, whereas hydroxide ions form protective hydroxides due to their superior metal ion bonding properties. Consequently, elevated pH conditions tend

to inhibit corrosion. Finally, the viscosity of the test solution is another factor influencing tribocorrosion performance. Cao et al. [12] demonstrated that increasing the solution's viscosity hinders the wear process, thereby reducing the material loss rate.

On the other hand, stainless steel components used in industrial applications are frequently exposed to highly aggressive acidic environments that promote both chemical corrosion and mechanical wear. Consequently, the corrosion and tribocorrosion behavior of stainless steels in acidic media has attracted considerable attention [13–20]. For instance, Wang et al. [15] investigated the abrasion–corrosion behavior of 304 stainless steel (304SS) in a 0.5 mol/L H_2SO_4 solution and observed that stirring significantly accelerates hydrogen evolution. Similarly, Zhang et al. [16] examined the tribocorrosion wear of duplex stainless steels in sulfuric acid solutions containing chloride ions, demonstrating that the presence of NaCl increases the overall mass loss rate and intensifies the synergistic effects between wear and corrosion. Therefore, understanding the underlying degradation mechanisms in acidic media is essential for ensuring the structural safety of stainless steel components.

In recent years, the demand for cost-effective materials that offer superior corrosion resistance and excellent mechanical properties has increased, especially for applications in harsh environments. SASS have garnered attention as a viable substitute for traditional austenitic stainless steels. These advanced materials are formulated with higher amounts of critical alloying elements—specifically, chromium (20–24 wt.%), nickel (17–22 wt.%), molybdenum (4–8 wt.%), and nitrogen (0.15–0.5 wt.%)—which together deliver exceptional strength, enhanced toughness, and significantly superior resistance to both pitting and crevice corrosion when compared to standard grades such as AISI 304 and 316 [21–24]. Consequently, SASS is extensively utilized in a wide range of engineering applications, including those in the marine, chemical, mining, and nuclear industries [25,26]. Nonetheless, in highly corrosive environments, SASS components experience simultaneous corrosion and wear, leading to material degradation that far exceeds the simple additive effects of each process. Therefore, a comprehensive understanding of the tribocorrosion behavior of SASS is important to ensure its long-term reliability and performance. While extensive studies have examined the corrosion and tribocorrosion behaviors of conventional stainless steel [3,8,27,28], such as S31254 [3], our understanding of how advanced alloys perform under these harsh conditions remains limited. In our previous work, we introduced a novel MEASS that demonstrated comparable corrosion resistance in NaCl solutions and superior mechanical properties relative to the commercial S31254 [24]. Despite the promising potential of MEASS for extreme service environments, there is limited understanding of their tribocorrosion behavior under aggressive environments. This study provides the first comprehensive investigation of the tribocorrosion behavior of MEASS compared to S31254 in a H_2SO_4 solution, contributing to the development of advanced materials for aggressive, high-wear applications. Wear track microstructures that formed after the tests were characterized using SEM and TEM, and the study systematically discusses the corrosion, wear, and synergistic interactions between these degradation processes for both steels. This research aims to clarify the key mechanisms influencing the tribocorrosion performance of two steels in acidic environments, thereby supporting the development of more durable materials for demanding industrial applications.

2. Materials and Methods

2.1. Sample Preparation

Table 1 lists the chemical compositions of both S31254 and MEASS. The heat treatment for MEASS—specifically, isothermal aging at 700 °C for 4 h—was chosen based on our previous work [24]. Prior to each measurement, all specimens (15 mm × 15 mm × 1 mm) were mechanically ground using silicon carbide (SiC) papers with grit sizes ranging from

80 to 2000. After polishing, the specimen surfaces were cleaned in an ultrasonic bath with ethanol and then allowed to air-dry.

Table 1. Chemical composition (wt. %) of S31254 and MEASS.

	Fe	Cr	Ni	Mo	Cu	Mn	N
S31254	Bal	20	18.31	6.1	0.73	0.95	0.21
MEASS	Bal	24.9	21.5	5.5	4.1	0.6	0.3

2.2. Electrochemical Tests

The electrochemical tests were divided into three parts: (1) potentiodynamic polarization tests, (2) intermittent OCP measurements, and (3) potentiostatic tests. For the potentiodynamic polarization tests, the potential was scanned from -600 mV to $+1200$ mV vs. SCE at a rate of 1 mV/s, and polarization curves were obtained under both sliding and non-sliding conditions in a 1 M H_2SO_4 solution. Prior to the scan, the OCP was monitored for 1800 s to ensure that the specimens reached equilibrium. For the intermittent OCP measurements, the specimens were first maintained under non-sliding conditions for 1800 s, then subjected to sliding for 3600 s. Finally, the potential was continuously recorded for 100 s after sliding ceased. In the potentiostatic sliding tests, an applied passive potential of $+400$ mV vs. SCE was used for both S31254 and MEASS, as determined from the polarization curve data. Current measurements were initially taken under static conditions for 1000 s, followed by 4000 s of sliding. The current was then continuously recorded during the final 1000 s after sliding was stopped.

Tribocorrosion tests were carried out using a ball-on-disk tribocorrosion tester integrated with a potentiostat (Gamry Ref 600, Warminster, PA, USA), as illustrated in Figure 1. Both corrosion and tribocorrosion measurements employed a standard three-electrode electrochemical configuration, with the metallic specimen serving as the working electrode (WE), a carbon rod as the counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode (RE). In these tests, zirconia balls with a 10 mm diameter acted as the counterpart. All experiments were performed under consistent mechanical conditions—a load of 4.9 N and a rotational speed of 120 rpm—in a 1 M H_2SO_4 solution, with the metallic specimen exposing an area of 1 cm².

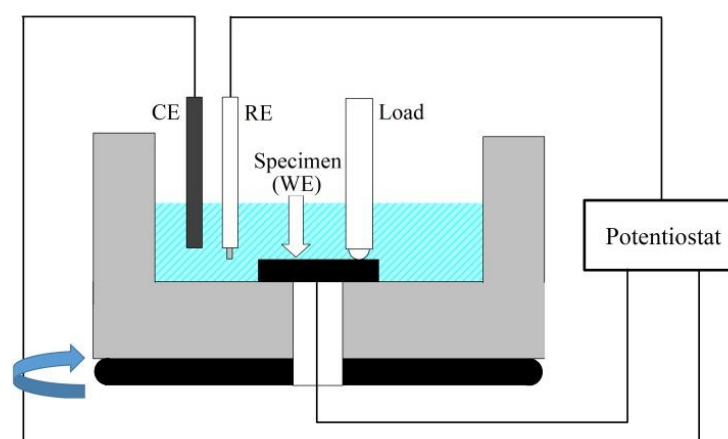


Figure 1. Schematic diagram of tribocorrosion ball-on-disk experimental setup.

2.3. Microstructure Characterization and Hardness Measurements

The surface morphology of the two stainless steels was examined using an SEM (JOEL JSM-6510, Tokyo, Japan). Their cross-sectional profiles were captured with a laser scanning microscope (KEYENCE VK-9710, Osaka, Japan). Hardness measurements were performed

using a Vickers hardness tester (FM-700e, Future-Tech Corporation, Tokyo, Japan) under a load of 0.5 kg for 10 s. For each specimen, the reported hardness values represent the average of 10 individual tests.

2.4. Material Loss Rate Analysis

In this study, the material loss rate was evaluated following the ASTM G119 standard [29], which outlines the calculation of the interaction between wear and corrosion. The total material loss rate, T , can be expressed as the sum of three components, as shown in Equation (1).

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

In this equation, the T value was determined by weighing the specimen before and after the tribocorrosion test conducted at OCP for 24 h; C_0 represents the corrosion rate without wear (pure corrosion), calculated from the corrosion current density obtained from the relevant potentiodynamic polarization curves under corrosion conditions; and W_0 denotes the wear rate without corrosion (pure mechanical wear), calculated from the volume of the wear tracks measured from cross-sectional profiles produced during potentiostatic tests at -500 mV vs. SCE for 24 h. Furthermore, the wear–corrosion synergistic factor (S) can be divided into two components, as defined in Equation (2).

$$S = \Delta C_w + \Delta W_c \quad (2)$$

where ΔC_w represents the increment in corrosion due to wear, while ΔW_c denotes the increment in wear due to corrosion. These parameters can be calculated using Equations (3) and (4), respectively [25].

$$\Delta C_w = C_w - C_0 \quad (3)$$

$$\Delta W_c = T - W_0 - C_w \quad (4)$$

C_w is calculated based on the corrosion current density extracted from the potentiodynamic polarization curves under wear conditions

3. Results

3.1. Potentiodynamic Polarization Test

Figure 2 illustrates the potentiodynamic polarization curves for both S31254 and ME-ASS specimens under sliding (tribocorrosion) and non-sliding (corrosion-only) conditions in a 1 M H_2SO_4 solution. The key electrochemical parameters—namely, the corrosion potential (E_{corr}), corrosion current density (i_{corr}), and passive current density (i_{pass})—extracted from these curves are summarized in Table 2. Under corrosion-only conditions, both steels exhibit typical passivation behavior in their anodic polarization curves, transitioning smoothly from active to passive and ultimately to transpassive states. Notably, the ME-ASS specimen shows similar E_{corr} and i_{corr} values to those of S31254, suggesting that its corrosion resistance is comparable.

In contrast, under tribocorrosion conditions, the E_{corr} values shift slightly in the cathodic direction, while the i_{corr} values increase by at least an order of magnitude relative to those observed in polarization measurements under corrosion-only conditions. A distinct feature in these curves is the emergence of a passive-like region—a plateau of constant current—in the anodic branch for all steels. However, due to the relatively high current density values in this region, it is more accurately described as pseudo-passivation rather than true passivation (which is typically characterized by a passive current density below 10^{-5} A/cm² [26,30]). It should be noted that in Figure 2b, a small current peak is observed

under tribocorrosion conditions, which we speculate can be attributed to the selective dissolution of Cu-rich precipitates in the MEASS substrate. Our previous study [24] identified spherical Cu-rich nanoparticles in MEASS. Based on the Pourbaix diagram for copper, under our experimental conditions (1 M H₂SO₄, pH $\approx$ 0–1, and potentials of 0 mV to +50 mV vs. SCE/+241 mV to +291 mV vs. SHE), these Cu-rich phases become unstable and dissolve into Cu²⁺ ions, causing a transient current peak. Accordingly, from the data in Table 2, the MEASS specimen demonstrates a higher E_{corr} and a lower i_{corr} compared to S31254, indicating that MEASS possesses superior resistance to tribocorrosion.

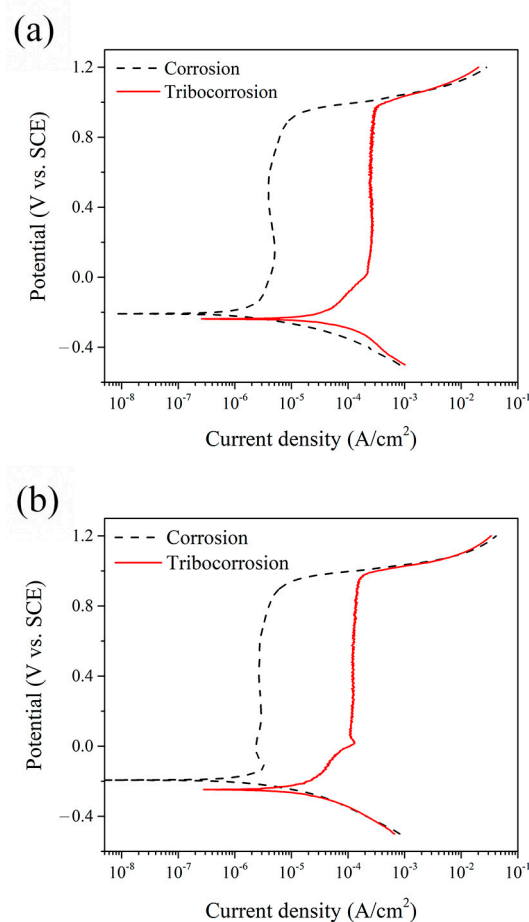


Figure 2. Potentiodynamic polarization curves of (a) S31254 and (b) MEASS.

Table 2. Electrochemical parameters extracted from potentiodynamic polarization curves of S31254 and MEASS.

S31254	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	i_{pass} ($\mu\text{A}/\text{cm}^2$)
Corrosion	-210 ± 2.3	1.7 ± 0.17	3.87 ± 0.2
Tribocorrosion	-236 ± 1.7	30.9 ± 8.82	247 ± 14.2
MEASS	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	i_{pass} ($\mu\text{A}/\text{cm}^2$)
Corrosion	-199 ± 19.4	3.3 ± 1.5	2.78 ± 0.1
Tribocorrosion	-248 ± 7.1	15.6 ± 2.6	137 ± 11.9

3.2. Intermittent OCP Measurements

OCP measurements provide valuable insights into the changes in alloy surface conditions, particularly regarding passivation and depassivation phenomena. In this study, we monitored the evolution of the OCP for both steels before, during, and after sliding in a 1 M H₂SO₄ solution. As illustrated in Figure 3, both steels followed a similar trend in OCP

evolution throughout the tests. After an initial immersion period of 1800 s under unloaded conditions, all specimens stabilized at a constant potential, confirming the formation of passive films on their surfaces [31]. Notably, the MEASS specimen exhibited a more noble stable potential (-50 mV vs. SCE) compared to the S31254 specimen (-100 mV vs. SCE), indicating that the passive film on MEASS has enhanced corrosion resistance.

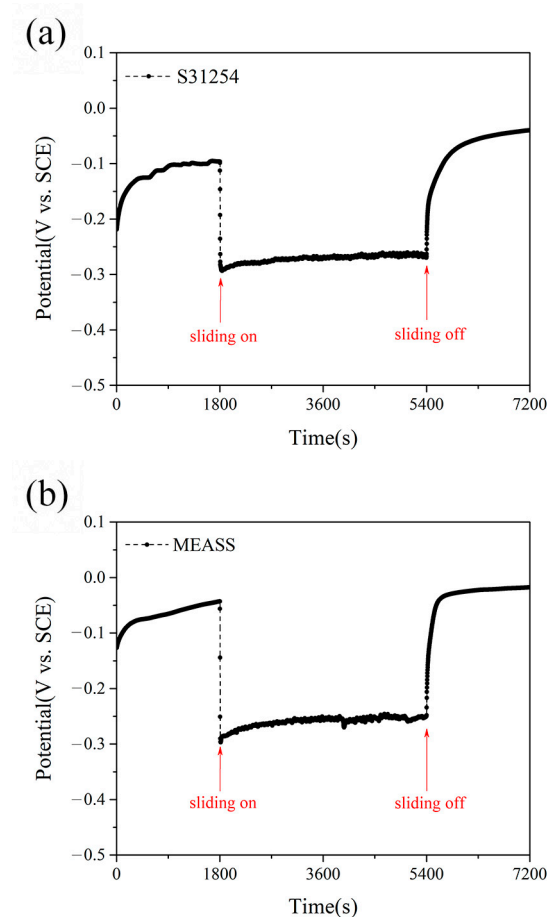


Figure 3. Evaluation of OCP in 1 M H_2SO_4 with and without sliding: (a) S31254 and (b) MEASS.

Upon the initiation of sliding, both steels experienced a rapid shift toward more negative potentials, a change attributed to the disruption of the passive film by fretting motion, which exposed the underlying metal to more active corrosion conditions. During the sliding phase, fluctuations in the OCP were observed, reflecting the ongoing competition between passivation and depassivation reactions. Once sliding ceased, the potentials of all specimens quickly shifted back toward more noble values and gradually returned to their pre-sliding levels, indicating effective repassivation of the worn areas. Significantly, the MEASS specimen recovered its initial potential much faster than the S31254 specimen, demonstrating that MEASS exhibits superior repassivation capability in the H_2SO_4 solution—likely due to its higher chromium and nickel content.

3.3. Potentiostatic Test

The potentiostatic test is essential for assessing the tribocorrosion performance of metallic substrates. It enables effective monitoring of passive film formation and the dynamic changes that occur during wear processes, providing valuable information into the stability and repassivation behavior of the protective films formed on metallic surfaces. Therefore, the evolution of current density over time was monitored at an applied passive potential ($+400$ mV vs. SCE for both S31254 and MEASS, as determined from prior polariza-

tion curve results) in the H_2SO_4 solution. Figure 4 displays these results. During the initial 500 s—prior to sliding—the current density remained near zero, confirming the presence of intact passive films on the steel surfaces. Once sliding began, an abrupt increase in current density was observed for all specimens, signaling accelerated corrosion as the passive films were disrupted or removed in the contact areas. Throughout the sliding phase, both steels exhibited a gradual increase in current density with noticeable fluctuations, reflecting the ongoing dynamic interplay between the formation and degradation of the passive film. By the end of the sliding period, the S31254 specimen reached a current density of $275 \mu\text{A}/\text{cm}^2$, whereas the MEASS specimen recorded a lower value of $189 \mu\text{A}/\text{cm}^2$. This consistently lower current density for MEASS under anodic conditions indicates a reduced degree of depassivation, thereby demonstrating its superior repassivation ability compared to S31254.

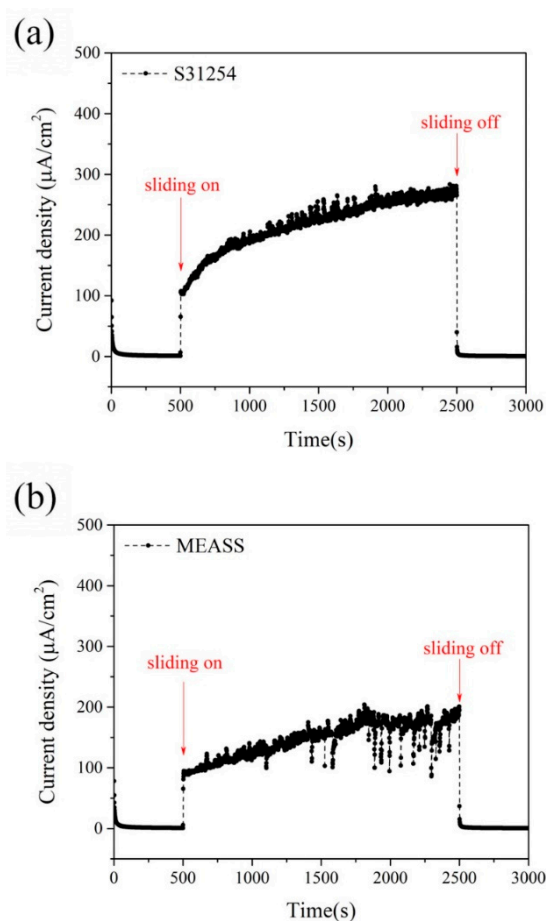


Figure 4. Evolution of current density recorded before, during, and after sliding tests under anodic polarization conditions (+400 mV vs. SCE): (a) S31254 and (b) MEASS.

3.4. Microstructure Characterization of Wear Track and Evaluation of Material Loss After Tribocorrosion Test

Figures 5 and 6 present SEM images of the worn surface morphologies on the wear tracks, along with their corresponding cross-sectional profiles, for both steels after 24 h of tribocorrosion tests at OCP conditions. Figure 5a,b shows plowing grooves aligned with the sliding direction on both samples. However, when comparing the enlarged SEM images, Figure 5(b-1) reveals more pronounced peeling marks on the S31254 surface than those seen in Figure 5(a-1), suggesting a higher susceptibility to tribocorrosion-induced degradation. The EDS spectra obtained from the areas labeled 1–4 in Figure 5(a-2,b-2), as quantified in Table 3, reveal that the composition of the worn surface closely resembles that of the base substrate. The wear track dimensions summarized in Table 4 correspond to

the cross-sectional profiles presented in Figure 6. The data clearly indicate that the S31254 specimen exhibits considerably wider and deeper wear tracks than the MEASS specimen, implying a greater volume of material removal. These findings align with the earlier SEM image observations.

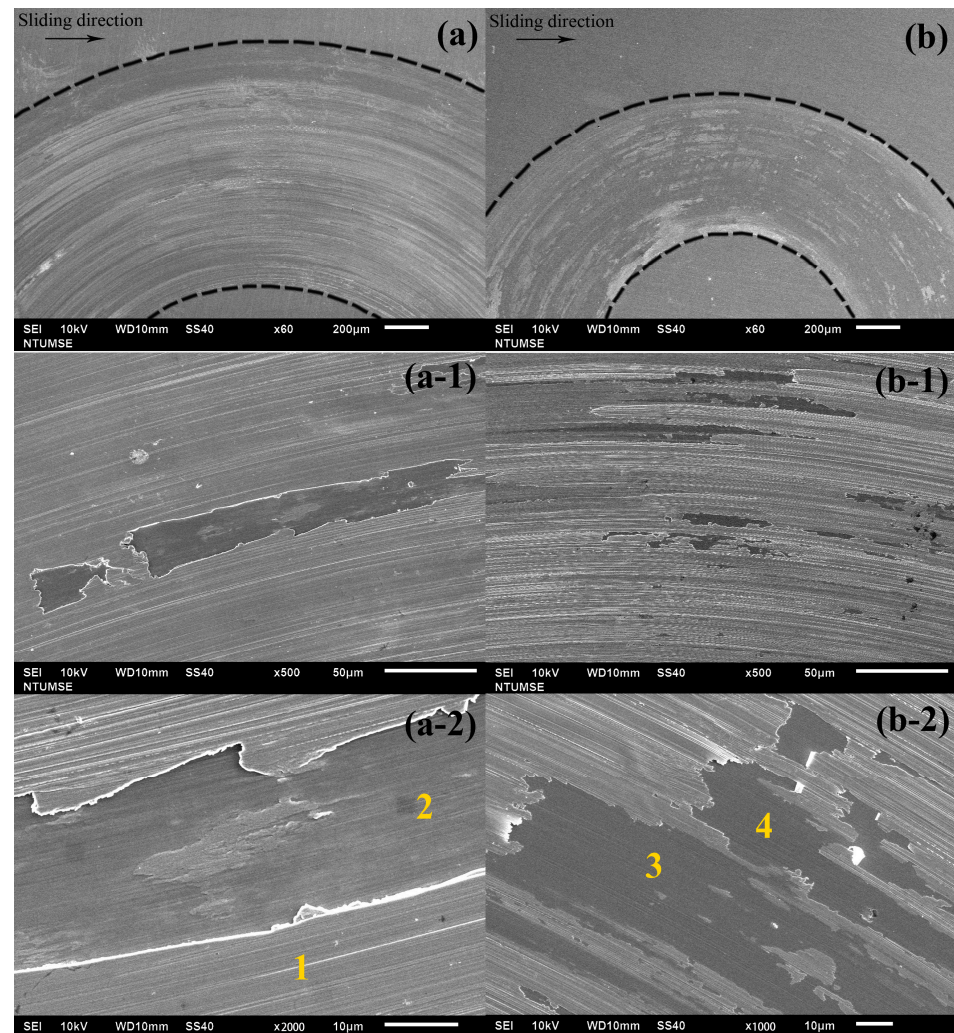


Figure 5. Surface morphology observation of worn surface after tribocorrosion test for 24 h. (a) S31254, (b) MEASS, (a-1), (b-1) are enlarged images in (a), (b), respectively, (a-2), (b-2) are enlarged images in (a-1), (b-1).

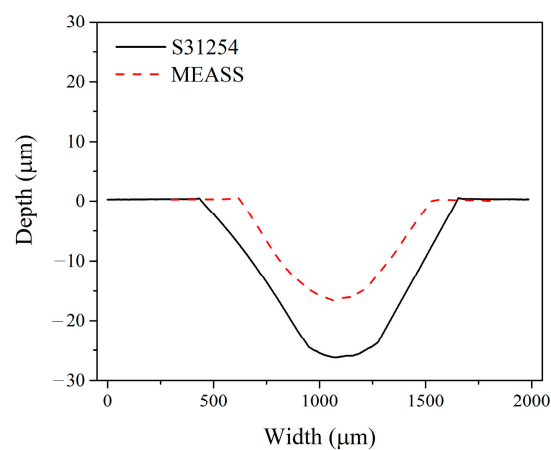


Figure 6. Cross-sectional profiles of wear tracks produced after tribocorrosion test for 24 h.

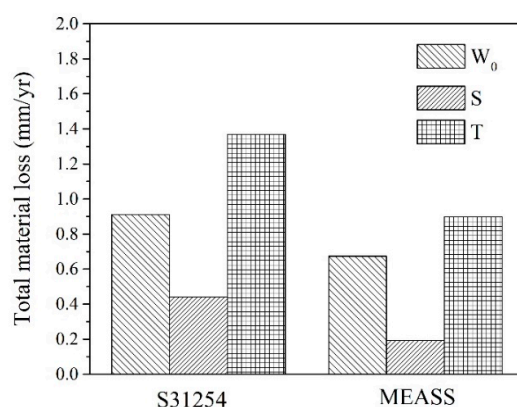
Table 3. EDS analysis results of worn surface after tribocorrosion test for 24 h.

Elements (wt %)	Fe	Cr	Ni	Mo	Cu
Spectrum 1	55.83	19.29	18.03	6.85	--
Spectrum 2	53.36	19.06	21.13	6.45	--
Spectrum 3	40.81	21.73	25.70	6.46	5.30
Spectrum 4	41.39	19.94	26.54	6.94	5.20

Table 4. The size of the wear track of S31254 and MEASS after the tribocorrosion test for 24 h.

Specimen	Width (μm)	Maximum Depth (μm)
S31254	1149.0 ± 14.7	26.1 ± 1.1
MEASS	876.4 ± 15.6	16.4 ± 0.8

Figure 7 compares the total material loss (T) for both specimens tested under identical experimental conditions. As is consistent with previous cross-sectional profile observations, the S31254 specimen exhibits a significantly higher total material loss than the MEASS specimen, which indicates its lower resistance to tribocorrosion under the tested conditions. Moreover, W_0 contributes more than 50% to the total material loss for both steels, demonstrating that mechanical wear plays a dominant role in their overall tribocorrosion behavior. To better understand this influence, a detailed investigation of the microstructural evolution within the wear tracks following the W_0 test is necessary to further clarify the tribocorrosion performance differences observed between these two steels.

**Figure 7.** Mechanical wear, synergistic factor, and total mass loss of S31254 and MEASS.

3.5. Microstructure Characterization of Wear Track and Evaluation of Material Loss After W_0 Test

Figures 8 and 9 display SEM images of worn surface morphologies and the corresponding cross-sectional profiles of the wear tracks for both steels after 24 h of the W_0 test. Figure 8a,b illustrates that, while plowing grooves remain visible, they are significantly less pronounced compared to those observed in Figure 5a,b—particularly for the MEASS specimen. High-magnification SEM images taken from the track centers (Figure 8(a-1,b-1)) reveal clear differences in wear characteristics under cathodic conditions. For the S31254 specimen, distinct plowing grooves aligned parallel to the sliding direction can be clearly observed. These grooves result from harder asperities on the zirconia balls gouging into the relatively softer metal surface [32]. In contrast, the MEASS specimen exhibits notably shallower grooves, indicating a harder and more wear-resistant surface. Although the differences in surface morphologies might appear subtle, cross-sectional images obtained after the W_0 test reveal a notable difference in wear volume between the two steels. As

shown in Figure 9 and wear track dimensions summarized in Table 5, the MEASS specimen exhibits narrower and shallower wear tracks, indicating a substantially lower wear volume caused by pure mechanical wear compared to S31254. To further elucidate the superior mechanical wear resistance of MEASS in H_2SO_4 solution, TEM characterization was conducted to investigate the microstructural differences between the two steels after the W_0 test.

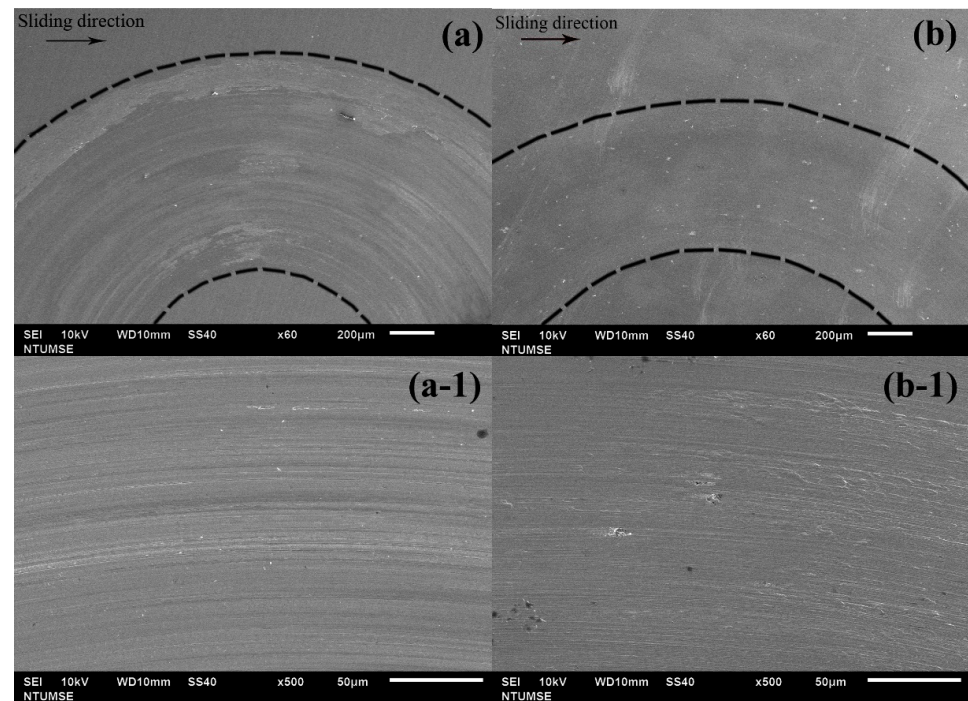


Figure 8. Surface morphology observation of worn surface after W_0 test. (a) S31254, (b) MEASS, (a-1), and (b-1) are enlarged images in (a) and (b), respectively.

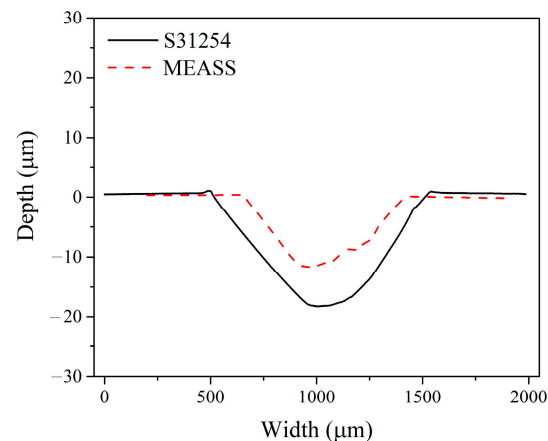


Figure 9. Cross-sectional profiles of wear tracks produced after W_0 test.

Table 5. The size of the wear tracks of S31254 and MEASS after the W_0 test.

Specimen	Width (μm)	Maximum Depth (μm)
S31254	988.1 ± 10.2	18.6 ± 1.5
MEASS	711.7 ± 9.8	11.2 ± 1.3

Figure 10a illustrates the microstructure from the surface to the volume in 31254SS after 24 h of wear, showing a gradient of plastic strain. Figure 10b,c reveals a heavily deformed

microstructure, including dislocation debris and deformation bands. In addition, ultrafine grains (UFGs) and nanograins (NGs) are present in only certain areas of the surface, as shown in the subpanel of Figure 10b. As the depth goes into the volume, i.e., the strain level decreases, only dislocation debris is observed, as seen in Figure 10d. Importantly, based on the worn microstructure in Figure 10, the dislocations appear wavy and entangled.

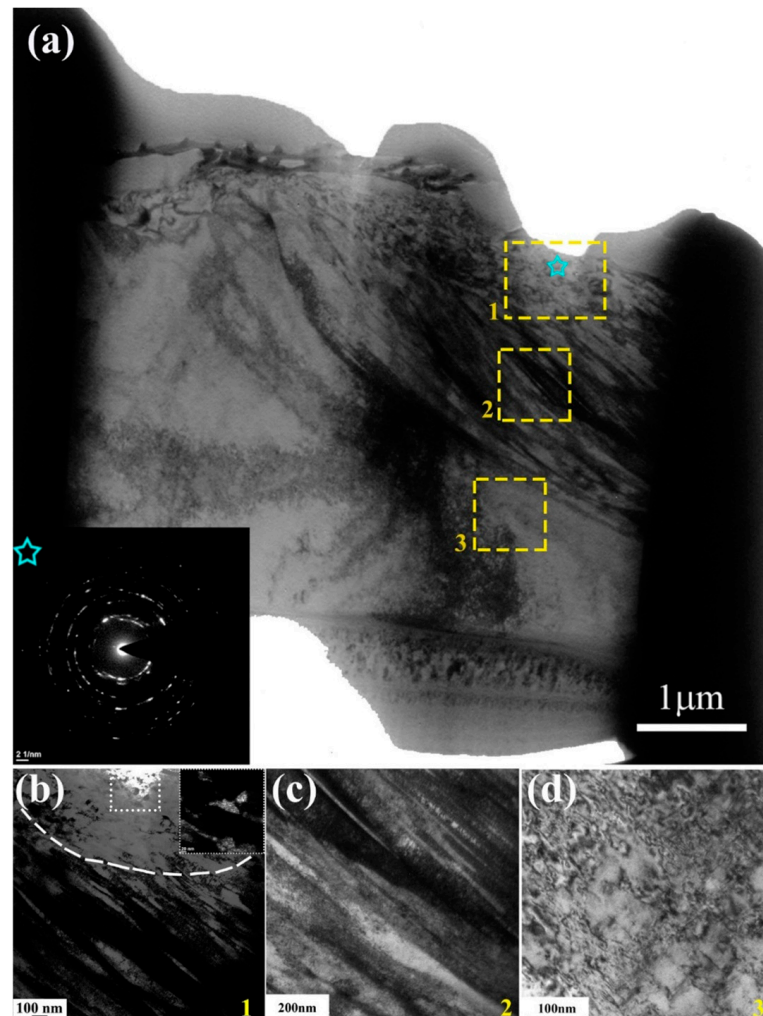


Figure 10. Bright-field TEM images of S31254 after 24 h of the W_0 test: (a) an overview of the worn S31254, with the star marking the location of the selected-area diffraction; (b) a magnified view of the dashed square 1 in (a); (c) a magnified view of the dashed square 2 in (a); and (d) a magnified view of the dashed square 3 in (a).

Figure 11a illustrates the microstructure from the surface to the volume in MEASS after 24 h of the W_0 test. Unlike S31254, Figure 11b shows that a uniform UFG/NG layer has developed in the surface layer, which is a product microstructure of dynamic recrystallization. Figure 11c depicts a high dislocation density forming a Taylor lattice, indicating planar slip of dislocations. Figure 11d clearly demonstrates that dislocations undergo planar slip even at lower strain levels. Therefore, plastic deformation occurs through wavy slip in S31254 but through planar slip in MEASS. This result also confirms that MEASS exhibits low stacking fault energy.

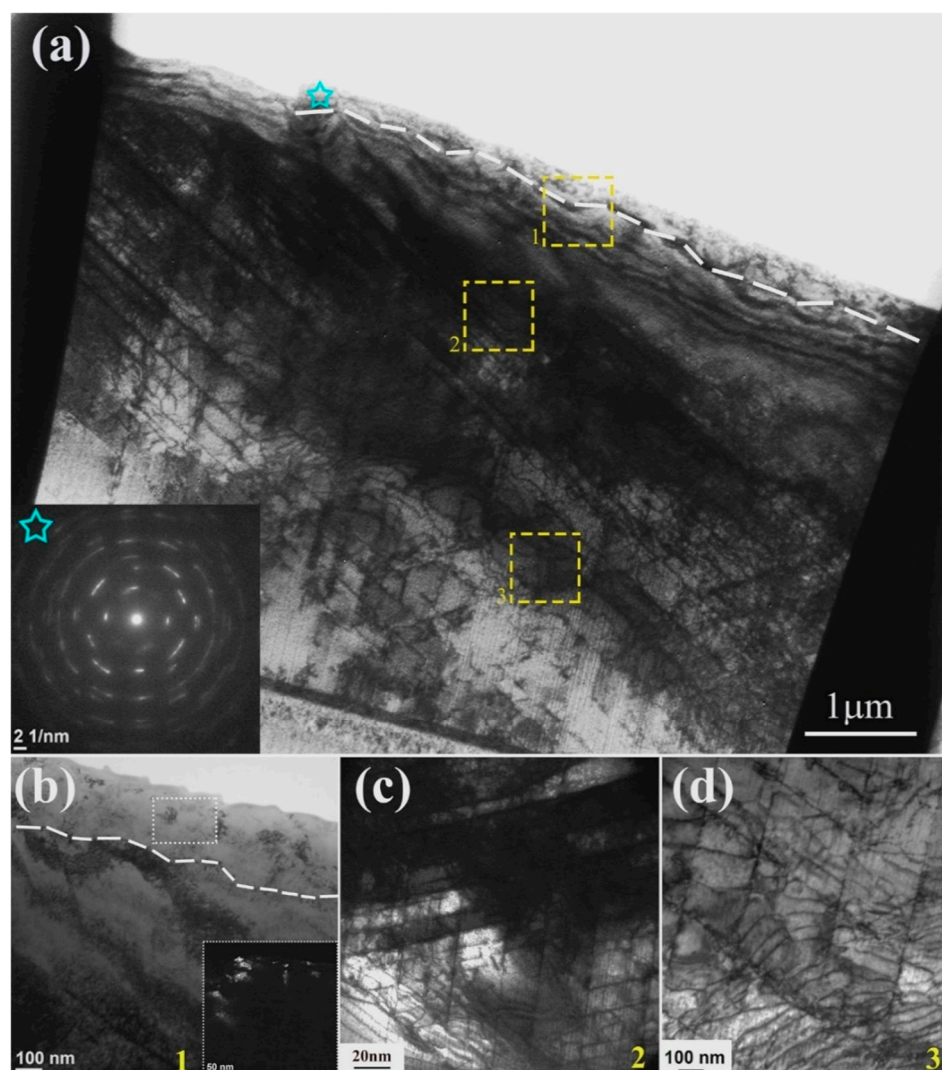


Figure 11. Bright-field TEM images of MEASS after 24 h of the W_0 test: (a) an overview of the worn MEASS, with the star marking the location of the selected-area diffraction; (b) a magnified view of the dashed square 1 in (a); (c) a magnified view of the dashed square 2 in (a); and (d) a magnified view of the dashed square 3 in (a).

4. Discussion

Tribocorrosion is the surface reaction behavior resulting from the combined effects of mechanical, chemical, and electrochemical processes during sliding contact friction in corrosive environments. In addition to the individual effects of wear and corrosion, their interaction plays a crucial role in determining the performance and safety of engineering materials and can be classified into two mechanisms: wear-induced corrosion and corrosion-induced wear. In wear-induced corrosion, mechanical wear elevates the surface temperature, accelerates chemical reactions, and damages the protective film, thereby promoting corrosion. The other mechanism, corrosion-induced wear, occurs when chemical reactions create surface defects—such as pits and cracks—that weaken the material and modify its wear behavior by either lubricating or embrittling the surface. The continuous interaction between these processes accelerates material degradation and leads to premature failure. Therefore, in this study, we not only measure the total material loss by weighing samples before and after the tribocorrosion tests (see Figure 7) but also quantify the contributions of pure mechanical wear and the combined effects of wear and corrosion on steels operating under tribological contact in corrosive environments.

Accordingly, the material loss rates attributed to pure mechanical wear, pure corrosion, wear-induced corrosion, and corrosion-induced wear were calculated following the ASTM G119 standard, with the results summarized in Tables 6 and 7. In these tables, the S value represents the combined synergistic effects ($\Delta C_w + \Delta W_c$), while C and W denote the total corrosion components ($C_0 + \Delta C_w$) and wear components ($W_0 + \Delta W_c$), respectively. The data in Tables 6 and 7 reveal that, although both steels have similar C_0 values, the MEASS specimen exhibits a lower ΔC_w value compared to S31254. This difference is attributed to the superior repassivation capability of MEASS when its passive film is disrupted by wear. Wear-induced corrosion typically arises from additional corrosion occurring on the freshly exposed metal surface following the mechanical removal of the passive film. The enhanced repassivation ability of MEASS promotes a more rapid reformation of the passive film in the worn areas, thereby reducing the ΔC_w value during the tribocorrosion test. Furthermore, while the corrosion components ($C_0 + \Delta C_w$) account for approximately 20% of the total material loss rate for both steels, their contribution is significantly lower than that of the wear components ($W_0 + \Delta W_c$) under tribocorrosion conditions in 1 M H_2SO_4 . Given the negligible contribution of ΔW_c to the overall wear components, it is evident that pure mechanical wear is the dominant factor governing the total material loss rate—contributing about 67% for S31254 and 75% for MEASS during tribocorrosion tests conducted at OCP.

Table 6. Contributions of various components to total volume loss in tribocorrosion for S31254.

S31254	Values (mm/yr)	Percentage (%)
T	1.369	100
C	0.312	22.79
C_0	0.017	1.24
ΔC_w	0.295	21.55
W	1.057	77.21
W_0	0.912	66.62
ΔW_c	0.145	10.59
S	0.440	32.14

Table 7. Contributions of various components to total volume loss in tribocorrosion for MEASS.

MEASS	Values (mm/yr)	Percentage (%)
T	0.899	100
C	0.154	17.13
C_0	0.033	3.67
ΔC_w	0.121	13.46
W	0.745	82.87
W_0	0.674	74.97
ΔW_c	0.071	7.90
S	0.192	21.36

Moreover, the W_0 value of MEASS is approximately 26% lower than that of S31254 under identical tribocorrosion test conditions. This reduction is likely due to the enhanced surface hardness of MEASS relative to S31254 during the tests. The results suggest that the pure mechanical wear rate—closely linked to the contact surface hardness—is the primary factor influencing the tribocorrosion behavior of both steels in H_2SO_4 . Figure 12 illustrates

the evolution of hardness for S31254 and MEASS, measured on the worn surfaces after various durations of the W_0 test in H_2SO_4 . As depicted, both steels exhibit a continuous increase in hardness with increasing pure wear time. This enhancement is attributed to strain hardening and the accumulation of deformation in the subsurface region [33]. Notably, the surface hardness of MEASS increased significantly—from 208 Hv before testing to 289 Hv after 6 h, representing a 38.9% increase. In contrast, the S31254 specimen showed a more modest improvement of 23.7%, suggesting that strain hardening occurs more prominently in the MEASS specimen. The pronounced strain hardening behavior observed in MEASS can be explained well by the TEM results described previously. Figures 10 and 11 demonstrate a gradient worn microstructure from surface to volume. As the strain decreases, the microstructure transitions from UFG/NG to deformation bands or Taylor lattice, and then to dislocation debris. During plastic deformation, an extremely high dislocation density can induce dynamic recrystallization, forming UFGs and NGs in the deformed microstructure [34]. Hence, MEASS is expected to exhibit a higher capacity for dislocation storage. This is supported by its uniform UFG/NG layer and higher hardness. It is well-known that planar slip and Taylor lattice structures can enhance the capacity for dislocation storage in face-centered cubic materials [35,36]. In summary, the planar slip of dislocations in MEASS contributes to a higher dislocation density and latter dynamic recrystallization of UFGs and NGs, resulting in its high hardness. Overall, although both steels follow a similar hardness evolution trend, MEASS consistently exhibits higher hardness than S31254 under all conditions, leading to its superior tribocorrosion performance in the H_2SO_4 acid solution.

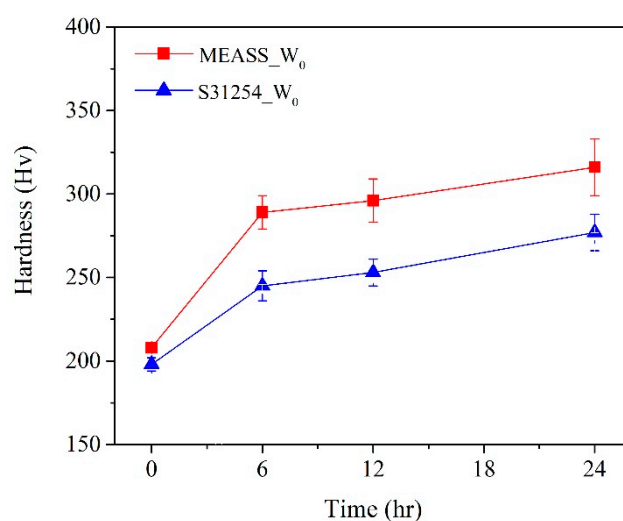


Figure 12. Evolution of hardness values of S31254 and MEASS specimens after various durations of W_0 test.

5. Conclusions

In this study, the tribocorrosion behavior of MEASS in a H_2SO_4 solution was investigated and compared with that of conventional S31254, with evaluations of material loss resulting from pure corrosion, pure wear, corrosion-accelerated wear, and wear-accelerated corrosion. Based on tribocorrosion measurements and microstructural characterization, it was found that both steels exhibited similar behavior in potentiodynamic polarization tests under sliding and non-sliding conditions; however, OCP measurements revealed that MEASS possesses a higher repassivation capability than S31254. After tribocorrosion tests, the wear track on the S31254 specimen showed a significantly greater width and depth compared to that on the MEASS specimen, and over 24 h, the total material loss for MEASS was lower than that for S31254. For the first time, the tribocorrosion behavior of MEASS in a H_2SO_4 solution was investigated and found to be predominantly governed by mechanical

wear, with the reduced wear in MEASS attributed to its higher hardness arising from superior strain hardening behavior. MEASS exhibits excellent tribocorrosion resistance, making it suitable for demanding applications requiring durability, minimal material loss, and low maintenance. Future research will focus on optimizing alloy composition and heat treatment to further enhance corrosion and wear resistance, as well as extending tests to diverse corrosive environments and long-term industrial conditions.

Author Contributions: Conceptualization, Y.-R.C. and Y.-L.L.; Methodology, C.-C.L.; Validation, S.-Y.H.; Formal analysis, C.-C.L. and S.-Y.H.; Investigation, C.-C.L. and T.-H.Y.; Resources, H.-W.Y.; Writing—original draft, C.-C.L.; Writing—review & editing, Y.-R.C., I.-C.C., P.-W.C., H.-W.Y. and Y.-L.L.; Supervision, Y.-L.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was sponsored by the Ministry of Science and Technology, R.O.C, under Grant No. MOST 108-2221-E-002-055-MY2 and MOST 109-2224-E-002-002.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author, Y.-L.L., upon reasonable request.

Acknowledgments: We especially thank I-Chung Cheng and Peng-Wei Chu for providing technical assistance and valuable contributions.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Landolt, D.; Mischler, S. *Tribocorrosion of Passive Metals and Coatings*; Elsevier: Amsterdam, The Netherlands, 2011.
- López-Ortega, A.; Arana, J.; Bayón, R. On the comparison of the tribocorrosion behavior of passive and non-passivating materials and assessment of the influence of agitation. *Wear* **2020**, *456*, 203388. [[CrossRef](#)]
- Zhang, Y.; Yin, X.-Y.; Yan, F.-Y. Tribocorrosion behaviour of type S31254 steel in seawater: Identification of corrosion—Wear components and effect of potential. *Mater. Chem. Phys.* **2016**, *179*, 273–281. [[CrossRef](#)]
- Silva, R.C.C.; Nogueira, R.P.; Bastos, I.N. Tribocorrosion of UNS S32750 in chloride medium: Effect of the load level. *Electrochim. Acta* **2011**, *56*, 8839–8845. [[CrossRef](#)]
- Sun, Y.; Rana, V. Tribocorrosion behaviour of AISI 304 stainless steel in 0.5 M NaCl solution. *Mater. Chem. Phys.* **2011**, *129*, 138–147. [[CrossRef](#)]
- Obadele, B.A.; Andrews, A.; Shongwe, M.B.; Olubambi, P.A. Tribocorrosion behaviours of AISI 310 and AISI 316 austenitic stainless steels in 3.5% NaCl solution. *Mater. Chem. Phys.* **2016**, *171*, 239–246. [[CrossRef](#)]
- Alkan, S.; Gök, M.S. Effect of sliding wear and electrochemical potential on tribocorrosion behaviour of AISI 316 stainless steel in seawater. *Eng. Sci. Technol. Int. J.* **2021**, *24*, 524–532. [[CrossRef](#)]
- Haruman, E.; Sun, Y.; Adenan, M. A comparative study of the tribocorrosion behaviour of low temperature nitrided austenitic and duplex stainless steels in NaCl solution. *Tribol. Int.* **2020**, *151*, 106412. [[CrossRef](#)]
- Alkan, S. Evaluation of pitting susceptibility and tribocorrosion behaviors of AISI 304 stainless steel in marine environments. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* **2023**, *237*, 808–823. [[CrossRef](#)]
- Zhang, Y.; Yin, X.; Wang, J.; Yan, F. Influence of microstructure evolution on tribocorrosion of 304SS in artificial seawater. *Corros. Sci.* **2014**, *88*, 423–433. [[CrossRef](#)]
- Zhang, Y.; Yin, X.; Yan, Y.; Wang, J.; Yan, F. Tribocorrosion behaviors of 304SS: Effect of solution pH. *RSC Adv.* **2015**, *5*, 17676–17682. [[CrossRef](#)]
- Cao, S.; Mischler, S. A lubricated tribocorrosion model incorporating surface roughness. *Biotribology* **2021**, *26*, 100181. [[CrossRef](#)]
- Sun, Y.; Haruman, E. Effect of electrochemical potential on tribocorrosion behavior of low temperature plasma carburized 316L stainless steel in 1 M H₂SO₄ solution. *Surf. Coat. Technol.* **2011**, *205*, 4280–4290. [[CrossRef](#)]
- Shtefan, V.; Kanunnikova, N.; Pilipenko, A.; Pancheva, H. Corrosion behavior of AISI 304 steel in acid solutions. *Mater. Today Proc.* **2019**, *6*, 150–157. [[CrossRef](#)]
- Wang, Z.; Yan, Y.; Su, Y.; Qiao, L. Effects of stirring action during friction on electrode processes of AISI 304 stainless steel in sulphuric acid. *Electrochim. Acta* **2019**, *298*, 756–769. [[CrossRef](#)]
- Zhang, T.; Jiang, X.; Lu, X.; Li, S.; Shi, C. Corrosion wear of duplex stainless steels in sulfuric acid solution containing chloride. *Corrosion* **1994**, *50*, 339–344. [[CrossRef](#)]

17. Priya, R.; Ningshen, S. The Tribocorrosion Behaviour and its Mechanisms of Type 304L Stainless Steel in Nitric Acid Media. *J. Mater. Eng. Perform.* **2023**, *32*, 5261–5272. [\[CrossRef\]](#)
18. Anburaj, J.; Nazirudeen, S.M.; Narayanan, R.; Anandavel, B.; Chandrasekar, A. Ageing of forged superaustenitic stainless steel: Precipitate phases and mechanical properties. *Mater. Sci. Eng. A* **2012**, *535*, 99–107. [\[CrossRef\]](#)
19. Hänninen, H.; Romu, J.; Ilola, R.; Tervo, J.; Laitinen, A. Effects of processing and manufacturing of high nitrogen-containing stainless steels on their mechanical, corrosion and wear properties. *J. Mater. Process. Technol.* **2001**, *117*, 424–430. [\[CrossRef\]](#)
20. Plaut, R.L.; Herrera, C.; Escriba, D.M.; Rios, P.R.; Padilha, A.F. A short review on wrought austenitic stainless steels at high temperatures: Processing, microstructure, properties and performance. *Mater. Res.* **2007**, *10*, 453–460. [\[CrossRef\]](#)
21. Lewis, A.; Bingert, J.; Rowenhorst, D.; Gupta, A.; Geltnacher, A.; Spanos, G. Two-and three-dimensional microstructural characterization of a super-austenitic stainless steel. *Mater. Sci. Eng. A* **2006**, *418*, 11–18. [\[CrossRef\]](#)
22. Wang, S.-H.; Wu, C.-C.; Chen, C.-Y.; Yang, J.-R.; Chiu, P.-K.; Fang, J. Cyclic deformation and phase transformation of 6Mo superaustenitic stainless steel. *Met. Mater. Int.* **2007**, *13*, 275–283. [\[CrossRef\]](#)
23. Li, H.; Zhang, B.; Jiang, Z.; Zhang, S.; Feng, H.; Han, P.; Dong, N.; Zhang, W.; Li, G.; Fan, G. A new insight into high-temperature oxidation mechanism of super-austenitic stainless steel S32654 in air. *J. Alloys Compd.* **2016**, *686*, 326–338. [\[CrossRef\]](#)
24. Chen, T.-E.; Huang, S.-Y.; Chu, Y.-R.; Chen, S.-C.; Tseng, M.-Y.; Yen, H.-W.; Lee, Y.-L. Investigating the effects of aging time on corrosion resistance and antibacterial property of newly designed medium-entropy super austenitic stainless steels. *Materialia* **2023**, *27*, 101687. [\[CrossRef\]](#)
25. Priya, R.; Mallika, C.; Mudali, U.K. Wear and tribocorrosion behaviour of 304L SS, Zr-702, Zircaloy-4 and Ti-grade2. *Wear* **2014**, *310*, 90–100. [\[CrossRef\]](#)
26. Konadu, D.; Van Der Merwe, J.; Potgieter, J.; Potgieter-Vermaak, S.; Machio, C.N. The corrosion behaviour of WC-VC-Co hardmetals in acidic media. *Corros. Sci.* **2010**, *52*, 3118–3125. [\[CrossRef\]](#)
27. Liu, Z.; Liu, E.; Du, S.; Zhang, J.; Wang, L.; Du, H.; Cai, H. Tribocorrosion behavior of typical austenitic, martensitic, and ferritic stainless steels in 3.5% NaCl solution. *J. Mater. Eng. Perform.* **2021**, *30*, 6284–6296. [\[CrossRef\]](#)
28. Parker, M.E.; Horton, D.J.; Wahl, K.J. Tribocorrosion behavior of 2205 duplex stainless steel in sodium chloride and sodium sulfate environments. *Tribol. Lett.* **2022**, *70*, 70. [\[CrossRef\]](#)
29. ASTM G119-09(2016); Standard Guide for Determining Synergism Between Wear and Corrosion. ASTM International: West Conshohocken, PA, USA, 2016.
30. Human, A.; Exner, H. The relationship between electrochemical behaviour and in-service corrosion of WC based cemented carbides. *Int. J. Refract. Met. Hard Mater.* **1997**, *15*, 65–71. [\[CrossRef\]](#)
31. Buciumeanu, M.; Araujo, A.; Carvalho, O.; Miranda, G.; Souza, J.; Silva, F.; Henriques, B. Study of the tribocorrosion behaviour of Ti6Al4V–HA biocomposites. *Tribol. Int.* **2017**, *107*, 77–84. [\[CrossRef\]](#)
32. Zhang, B.; Wang, J.; Liu, H.; Yan, Y.; Jiang, P.; Yan, F. Tribocorrosion properties of AISI 1045 and AISI 2205 steels in seawater: Synergistic interactions of wear and corrosion. *Friction* **2021**, *9*, 929–940. [\[CrossRef\]](#)
33. Tyfour, W.; Beynon, J.; Kapoor, A. The steady state wear behaviour of pearlitic rail steel under dry rolling-sliding contact conditions. *Wear* **1995**, *180*, 79–89. [\[CrossRef\]](#)
34. Sakai, T.; Belyakov, A.; Kaibyshev, R.; Miura, H.; Jonas, J.J. Dynamic and post-dynamic recrystallization under hot, cold and severe plastic deformation conditions. *Prog. Mater. Sci.* **2014**, *60*, 130–207. [\[CrossRef\]](#)
35. Sun, Y.-H.; Chen, S.-W.; Lai, Z.-H.; Lu, S.-L.; Lin, Y.-T.; Tu, J.-F.; Yen, H.-W. Strain-hardening resilience via the cooperation of geometrically necessary dislocations and deformation twins in a strong and ductile lightweight high-entropy steel. *Mater. Des.* **2024**, *244*, 113212. [\[CrossRef\]](#)
36. Lai, Z.-H.; Sun, Y.-H.; Lin, Y.-T.; Tu, J.-F.; Yen, H.-W. Mechanism of twinning induced plasticity in austenitic lightweight steel driven by compositional complexity. *Acta Mater.* **2021**, *210*, 116814. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.