In-situ characterization of initial marine corrosion induced by rare-earth elements modified inclusions in Zr-Ti deoxidized low-alloy steels

Wenzhi Wei a, Kaiming Wu a, Xian Zhang a,*, Jing Liu a, Ping Qiu b, Lin Cheng a,∗

a The State Key Laboratory for Refractory Material and Metallurgy, Hubei Province Key Laboratory of Systems Science in Metallurgical Process, Collaborative Innovation Center for Advanced Steels, Wuhan University of Science and Technology, Wuhan 430081, China
b Department of Materials Science and Engineering, China University of Petroleum (Beijing), Beijing 102249, China

Original Article

ARTICLE INFO

Article history:
Received 10 July 2019
Accepted 27 November 2019
Available online 19 December 2019

Keywords:
Low-alloy steels
Initial marine corrosion
Inclusions
Rare-earth elements
Zr-Ti deoxidation
SVET

ABSTRACT

In the present research, the effects of rare-earth (RE) elements modified inclusions on initial marine corrosion of Zr-Ti deoxidized low-alloy steels were studied by first principle modeling and a variety of analytical methods including in-situ scanning vibrating electrode technique (SVET), scanning electron microscopy with x-ray microanalysis (SEM/EDS), and confocal Raman microscopy (CRM). The obtained results revealed that two types of complex inclusions with intertwined components of RE2Zr2O7, RE2Zr2O7S and RE2Zr2O7RE2O5S-TiN were formed. RE2O5S preferentially dissolved in 0.5 wt% NaCl solution, whereas the dissolution of RE2Zr2O7 propagated from the periphery to the middle of the inclusions and subsequently, formed stable pits on the steel surface. TiN was stable in the marine environment and finally, became detached from the substrate. Moreover, in-situ SVET results demonstrated the local current density change during corrosion process was influenced by single and multiple inclusions, indicating that the dissolution of inclusions induced the electrochemical activities of pitting corrosion and further inhibited the propagation of local corrosion. Furthermore, the corrosion tendency of inclusions and the Fe matrix was examined by first principle modeling. Finally, two schematic models were proposed to demonstrate the effects of inclusions on initial marine corrosion of low-alloy steels.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Low-alloy steels, as one of the most important construction materials, are widely used in various industrial applications including electrical transmission towers and bridges due to their low costs and excellent ductility and formability [1,2]. However, low-alloy steels are susceptible to localized corrosion in marine environments. Localized corrosion is considered as one of the most dangerous forms of corrosion that causes steel failure [12,14–17]. Generally, pitting corrosion is preferentially triggered by surface heterogeneities, such as inclusions, defects, and precipitates [3–9]. Due to different chemical compositions and sizes, the effects of inclusions on low-alloy...
steels range from strongly negative to highly positive [10,11]. The mechanism pitting corrosion has been elaborately investigated in the previous literature [6,7,10–24].

Rare-earth (RE) elements are often used as microalloying agents to enhance the purification, solidification, and corrosion resistance properties of low-alloy steels [10,23,25–28]. The formation of inclusions in steels could be significantly modified by RE microalloying, which can effectively produce small, spheroid-shaped inclusions [6,10,18,29]. Due to the high ratio of [S]_{init}/[O]_{init}, the (RE)O₂ inclusions are not easily formed in steels, whereas RE-oxo-sulfides and RE sulfides easily precipitate in low-alloy steels [12,27,30–33]. Liu et al. [23] indicated that the complete dissolution of (RE)₂O₃S-(RE)₂S₃ was the main cause of pitting corrosion in low-alloy steels. Soon-Tae Kim et al. [26] reported that the formation of RE oxides decreased the size of preferential interface areas and improved the resistance to pitting corrosion.

In recent years, the method of Zr-Ti deoxidation has been extensively applied to industrial steels in order to achieve better grain refinement in coarse-grained heat-affected zones [34,35]. However, the inclusions of fine Zr-Ti complex oxides are generally formed in Zr-Ti deoxidized steels [34–36]. Du et al. [36] noted that the corrosion behavior of Zr-Ti deoxidized steels was mainly influenced by the inclusions of different types and sizes. However, few studies have elaborately investigated the impacts of RE element-modified inclusions on local corrosion of Zr-Ti deoxidized low-alloy steels in marine environments.

Most of these earlier studies mainly focused on morphological changes in inclusions at different corrosion stages. Very few studies have specifically investigated the mechanism of micro-electrochemical activities during inclusion-induced corrosion. The micro-electrochemical activities of inclusions can be monitored by in-situ scanning vibration electrode technique (SVET) [37–40], which can visually and accurately characterize the nature of cathodic or anodic reactions during corrosion.

In the current paper, the initial corrosion behavior of RE-bearing low-alloy steels under Zr-Ti deoxidation was investigated in detail. In-situ SVET measurements were performed to measure the changes in current density during electrochemical reactions induced by inclusions. Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) was adopted to analyze the changes in surface morphology and composition of inclusions before and after corrosion. Confocal Raman microscopy (CRM) was employed to identify the distribution of corrosion products. Finally, the impacts of inclusions on initial marine corrosion of low-alloy steels were demonstrated by two schematic models.

2. Methods

2.1. Materials preparation

Steel specimens were first prepared in a 50 kg vacuum melt induction furnace under Zr-Ti deoxidation, then rolled into 20 mm thick steel plates, and finally, air cooled to room temperature. In addition, RE elements were added to the samples as microalloying agents. The chemical composition of the experimental steel is presented in Table 1. The specimens were first cut into a dimension of 10 mm × 10 mm × 10 mm, then wet ground to 2000 grit by silicon carbide papers and polished to mirror surface, and finally, ultrasonically cleaned in ethanol and dried in a hot air stream. All SVET samples were sealed with insulating epoxy with an exposed area of 10 mm × 10 mm.

2.2. Initial corrosion tests

Initial corrosion tests were conducted in a 0.5% NaCl solution in order to simulate the characteristics of marine environments. After the completion of corrosion tests, 500 mL HCl, 500 mL deionized water, and 10 g hexamethylenetetramine were used to remove corrosion products from steel surfaces.

2.3. In-situ SVET measurements

In-situ micro-electrochemical measurements were conducted on an SVET system (Versascan, Ametek, Advanced measurement technology) in 0.5% NaCl solution. A scanning vibration probe (SVP, Pt-Ir) was used to measure the potential gradient distribution in the NaCl solution. The local corrosion properties during anodic and cathodic reactions were detected by measuring the surface potential gradient (current density was calculated by Ohm’s law: I = –ΔE/R, where R = d/k = 3.56E–4 Ω, d is the amplitude of SVP, k is the conductivity of the working solution (8.42 mS/cm for 0.5% NaCl solution) [40,41]). The positions of inclusions were marked by a microhardness tester (THV-1MD), and the probe was positioned to these marked areas with the help of a long focusing telescope. The needle tip was about 200 microns above the sample surface, and its amplitude was set to 30 Hz. In addition, in-situ line scans and area scans were performed with a step size of 2 μm and 150 μm, respectively.

2.4. SEM/EDS analysis

The changes in surface morphology and composition of inclusions before and after corrosion tests were analyzed by a Zeiss Auriga SEM equipped with an energy dispersive spectrometer (EDAX Genesis 2000). An accelerating voltage of 20 kV and a working distance of 10 mm were used to analyze secondary electron images.

2.5. CRM measurements

The formation of corrosion products after in-situ SVET measurements was analyzed by a Renishaw inVia Qontor CRM system equipped with a laser source of wavelength 532 nm operating under the scan range was 0–1000 cm⁻¹ and a spectral resolution of 1 cm⁻¹.

2.6. First principle modeling

The predictive calculation was performed to measure work functions (Φ) and surface energies (E_{surf}) of different low-indexed crystallographic planes of different inclusions and the Fe matrix [42]. In the present study, all calculations were carried out in the Vienna ab initio simulation package (VASP)
3. Results and discussion

3.1. Mechanical properties of the steel

The tensile tests were carried out by means of an electronic universal testing machine (CMT-5105) at room temperature, and the impact properties were obtained by using a Charpy impact testing machine (JB-300B) at different temperatures of −10, −20 and −40 °C. The yield strength, tensile strength, elongation and impact property of the experimental steel were shown in Table 2.

3.2. Characterization of inclusions

The morphologies and compositions of inclusions in the unexposed experimental steel were characterized by SEM/EDS (Fig. 1), and (RE, Zr)-oxy-sulfide inclusions were identified on the steel surface. It is evident from elemental mapping that the distribution of S was mainly connected to O and RE. Due to the high ratio of [Si]_{init}/[O]_{init}, the (RE)_{2}O_{2} inclusions were hardly formed, whereas RE_{2}O_{2}S easily precipitated in the steel [12,27,30–33]. Moreover, RE addition was also beneficial for the modification of inclusions [23,31–33,36]. In Al-killed steels, (RE)AlO_{3} are generally observed adjacent to RE_{2}O_{2}S [23,33]. In the present experiment, complex (RE, Zr)-oxy-sulfide inclusions were composed of two intertwined components of RE_{x}Zr_{y}O_{2} and RE_{2}O_{2}S; however, the spatial distribution of these two components varied in different inclusions. Fig. 2 reveals the size distribution of these inclusions and the area ratio of the S-containing part in them. It is noticeable that the size of these inclusions was in the range of 1–3 μm and the proportion of RE_{2}O_{2}S varied in different inclusions.

According to EDS analysis, the content of Ti was negligible in (RE, Zr)-oxy-sulfide inclusions; however, Ti was occasionally identified in other inclusions (Fig. 3). Nano-sized precipitates appeared as dark spots adjacent to (RE, Zr)-oxy-sulfide inclusions signify a relatively high content of Ti in EDS spectra. The content of N was hard to be distinguished due to its overlapped peak with O. Park et al. [47] reported the formation of TiN-MgAl_{2}O_{4} hybrid incluions and found that TiN grew epitaxially on the surface of MgAl_{2}O_{4} compound. Hence, it can be inferred that precipitates formed in the present experiment were possibly composed of TiN [47–49]. Therefore, besides RE_{x}Zr_{y}O_{2}-RE_{2}O_{2}S inclusions, complex RE_{x}Zr_{y}O_{2}-RE_{2}O_{2}S-TiN inclusions were also formed.

3.3. Initial corrosion induced by inclusions

In order to investigate the initial corrosion behavior of the experimental steel induced by (RE, Zr)-oxy-sulfide inclusions, immersion tests were conducted in 0.5% NaCl solution. Fig. 4 displays the morphologies of (RE, Zr)-oxy-sulfide inclusions after 0.5 h and 2 h immersion periods. It is discernible that the initiation of pitting corrosion was triggered by the dis-
Table 2 – Mechanical properties of the experimental steel.

<table>
<thead>
<tr>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Impact property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature /°</td>
</tr>
<tr>
<td>276</td>
<td>381</td>
<td>45.5</td>
<td>−10</td>
</tr>
<tr>
<td>−20</td>
<td>310</td>
<td>290</td>
<td>−20</td>
</tr>
<tr>
<td>−40</td>
<td>306</td>
<td>290</td>
<td>−40</td>
</tr>
</tbody>
</table>

Fig. 2 – Size distribution of inclusions (a) and area ratio of S-containing part in the inclusions (b) of the experimental steel.

solution of these inclusions. Fig. 4(a) reveals that micro-gaps were formed between the peripheries of two inclusions. After 2 h exposure, the produced micro-gaps were transformed into stable pits and consequently, the complete dissolution of inclusions occurred (Fig. 4b). According to Zuertel and Böhni et al. [50,51], the highest intensity of electrochemical reactivity was found at the interface between inclusions and the matrix. RE-containing inclusions manifested much higher corrosion tendency as compared to the Fe matrix [33], thus inducing selective dissolution from the interface of inclusions and the matrix.

Fig. 5 exhibits SEM images of typical RE₂Zr₀.₇₇₀₂₀.₃₂₀₂S inclusion before and after 0.5 h exposure and also the corresponding EDS maps of the dissolved inclusion. It is evident that besides micro-gaps, micro-crevices were also gradually formed in the middle of the inclusion. It is worth noting that no sulfur was found in the inclusion after 0.5 h exposure, thus it does not comply with the results of unexposed inclusions (Fig. 1). Hence, it can be inferred that micro-crevices were probably formed due to the preferential dissolution of (RE)₂O₂S in the corrosive environment. It should be noted that this type of inclusion experienced two different dissolution mechanisms. The component of (RE)₂O₂S preferentially dissolved to form micro-crevices in the inclusion, and simultaneously, the interface between the inclusion and the matrix was dissolved, whereas the dissolution of RE₂Zr₇₇₀₂O₆ occurred from the periphery to the middle of the inclusion.

Fig. 3 – SEM image and the corresponding EDS spectra of the inclusions in the experimental steel.
Fig. 4 – SEM images of a typical pitting initiation site after 0.5 h (a) and 2 h (b) of immersion in 0.5% NaCl.

Fig. 5 – SEM image of a typical RE<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub>-RE<sub>2</sub>O<sub>2</sub>S inclusion before (a) and after (b) 0.5 h of immersion in 0.5% NaCl and the corresponding EDS maps after immersion.

Fig. 6 exhibits SEM images and EDS maps of a typical RE<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub>-RE<sub>2</sub>O<sub>2</sub>S-TiN inclusion before and after 0.5 h exposure. Similar to Fig. 5, the components of RE<sub>2</sub>O<sub>2</sub>S and RE<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> simultaneously dissolved in the corrosive environment. Moreover, the content of Ti was still high even though micro-gaps were formed around TiN, it implies that TiN was relatively stable in the corrosive environment. In contrast to RE<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub>-RE<sub>2</sub>O<sub>2</sub>S, TiN did not dissolve easily and, finally, became detached from the substrate due to the formation of micro-gaps and the complete dissolution of RE<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub>-RE<sub>2</sub>O<sub>2</sub>S.

3.4. In-situ SVET measurements

In order to further clarify the micro-electrochemical mechanism induced by inclusions in the low-alloy steel, in-situ SVET measurements were carried out in 0.5% NaCl solution. The localized current densities across inclusions on the
Fig. 6 – SEM image of a typical $\text{RE}_2\text{Zr}_2\text{O}_7$-RE$_2$O$_3$S-TiN inclusion before (a) and after (b) 0.5 h of immersion in 0.5% NaCl and the corresponding EDS maps after immersion.

steel electrode were measured after 0.5 h (black) and 2 h (red) exposure. Fig. 7a illustrates the scan lines of current densities across inclusions and the corresponding morphological changes, whereas Fig. 7b displays the scan direction. After 0.5 h immersion, a profound anodic current density peak was noticed across inclusions (black line in Fig. 7a); therefore, it confirms that pitting corrosion occurred due to the dissolution of inclusions and caused a major influence on local corrosion current density. Due to different electrochemical activities, the corrosion region and the surrounding Fe matrix acted as the anode and the cathode, respectively [33].

However, after 2 h exposure, the anodic current density peak was no longer observed in the same scanning area (red line in Fig. 7a), thus indicating the inhibition of electrochemical activities. Fig. 7c displays the surface morphology of the steel sample after the removal of corrosion products. The original inclusion was completely dissolved in NaCl solution and formed a stable pit.

Fig. 8 exhibits 3D current density maps of the experimental steel after 0.5 h, 1 h, and 2 h of exposure in 0.5% NaCl solution and presents a much larger corrosion region as compared to Fig. 7. It is observable that although the anodic area expanded at the early stage (Fig. 8a and b), it no longer propagated to a larger area at the later stage (Fig. 8c). The current density in the most anodic site dramatically dropped from 21.9 mA/cm$^2$ after 0.5 h exposure to 10.1 mA/cm$^2$ after 1 h and to 7.15 mA/cm$^2$ after 2 h. In comparison to a single inclusion (Fig. 7), multiple inclusions were present in the larger anodic region (Fig. 8); hence, pitting corrosion was initiated from the dissolution of these inclusions, subsequently, multiple electrochemical cells were formed in the corrosion region. The dissolution of inclusions continuously occurred, thus a decreasing trend in anodic current density was observed throughout the immersion test.

The results of in-situ SVET characterization demonstrate that the dissolution of inclusions induced the electrochemical activities of initial corrosion in the anodic and cathodic regions. However, the electrochemical activities of local corrosion were inhibited after the complete dissolution of inclusions.

3.5. Characterization of corrosion products

After in-situ SVET tests, the surface morphologies of corrosion sites were analyzed by SEM (Fig. 9). Fig. 9(a) displays a clear corrosion ring, thus indicating the existence of the anodic region in SVET maps. Etched microstructures of ferrite and pearlite separated by grain boundaries were observed in the anodic region. The magnified micrograph in Fig. 9b reveals that most inclusions were completely dissolved in NaCl solution and corrosion products were randomly distributed in grains. However, the cathodic region surrounded by the corrosion ring demonstrated a completely different morphology of corrosion products. It was found that a film of corrosion products covered the substrate, and the thickness of this film is around
Fig. 7 – SVET lines measured on the steel electrode across the inclusion after 0.5 and 2 h immersion in 0.5% NaCl and the corresponding SEM image (a); The optical image showing the scanning line (b) and an SEM view of the inclusion (marked in (a)) after 2 h of immersion in 0.5% NaCl (c).

Fig. 8 – SVET current density maps of low-alloy steel after immersion in 0.5% NaCl solution: (a) 0.5 h, (b) 1 h, (c) 2 h.
Fig. 9 – SEM images showing the surface morphology after SVET test in Fig. 8. (a) An overview of the corrosion site; (b) the magnified anodic region; (c) the microstructure of the corrosion products in the cathodic region; (d) the microstructure of the corrosion products in the anodic region; (e) the magnified pit after completed dissolution of inclusions; (f) the microstructure of corroded pearlite.

2–5 μm by SEM observation of the cross-section. At the interface between anodic and cathodic regions, a part of corrosion products was possibly detached from the surface, thus revealing the exposed substrate. Magnified SEM images of corrosion products presented in Fig. 9(c and d) demonstrate flower-like microstructures with a lamellar morphology. It is obvious that the microstructures of corrosion products in the anodic region were much finer than those in the cathodic region.

After the removal of corrosion products (Fig. 9e), a stable pit was observed on the steel surface. João Victor de Sousa Araujo et al. [52] reported that the deposition of corrosion products possibly hindered ionic fluxes and led to a decrease in current density value in the SVET curve. However, after SVET measurements, it was found that non-uniform corrosion products were dispersed across the anodic corrosion region, it indicates that ionic fluxes over the corrosion pit were mainly influenced by electrochemical reactions instead of corrosion products. The morphology of pearlite after immersion is presented in Fig. 9f. It is evident that a lamellar structure composed of cementite was formed due to the selective dissolution of ferrite; hence, pearlite possibly had a relatively higher corrosion tendency [12].

CRM measurements after the in-situ SVET test were conducted to identify the distribution of corrosion products in corrosion sites. The Raman spectra in Fig. 10 reveal the formation of different corrosion products in anodic and cathodic regions. It is observable that corrosion products in the anodic region mainly consisted of lepidocrocite (γ-FeOOH; associated with the bands at 250 cm⁻¹ and 380 cm⁻¹) [53] and magnetite (Fe₃O₄; associated with the shifted bands at
Table 3 – Work function and surface energy of La$_2$O$_2$S$_2$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.14</td>
<td>~0.21</td>
<td>6.35</td>
<td>2.53</td>
</tr>
<tr>
<td>110</td>
<td>5.55</td>
<td>1.80</td>
<td>3.75</td>
<td>0.97</td>
</tr>
<tr>
<td>111</td>
<td>5.59</td>
<td>1.87</td>
<td>3.72</td>
<td>1.36</td>
</tr>
</tbody>
</table>

566 cm$^{-1}$ and 656 cm$^{-1}$ [54] (Fig. 10a). Further, the corrosion products in the cathodic region were possibly composed of hematite ($\alpha$-Fe$_2$O$_3$; associated with the bands at 218 cm$^{-1}$ and 282 cm$^{-1}$) [55], goethite ($\alpha$-FeOOH; associated with the bands at 282 cm$^{-1}$ and 292 cm$^{-1}$), and Fe$_3$O$_4$ (associated with the shifted bands at 588 cm$^{-1}$ and 686 cm$^{-1}$) [54] (Fig. 10b).

SVET, SEM, and CRM results revealed that the initial corrosion of the low-alloy steel in NaCl solution separated local anodic and cathodic areas and demonstrated different mechanisms of corrosion product formation. The central area had higher Cl$^-$ concentration and lower pH as compared to its surrounding areas, and the dissolution of inclusions easily triggered pitting corrosion. Consequently, the anodic reaction occurred, thus causing the etched corrosion morphology in the corrosion ring. The cathodic reaction occurred around the corrosion ring. Fe$^{2+}$ ions generated at pits diffused outwards and reacted with OH$^-$ to form Fe(OH)$_2$ [55]. As Fe(OH)$_2$ is not stable, it is usually transformed into other corrosion products. FeOOH$_2$ was initially formed in the corrosive environment [53-55]. Fe$_3$O$_4$ was also formed at the very beginning of corrosion due to the oxidation of Fe(OH)$_2$ [54]. Furthermore, when FeOOH was exposed to dry air, it was transferred into $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH during the drying process after the immersion test [54].

3.6. First principle modeling

Work function ($\Phi$) and surface energy ($E_{surf}$) are two fundamental factors that manifest profound influences on electrode potential and current density in the anodic dissolution process [42]. A low work function value usually suggests a higher probability to lose electrons and also a higher tendency of corrosion initiation [42]. Corrosion generally occurs at a certain crystal surface, and crystallographic orientation has a significant influence on corrosion behavior [42]. In the current study, the slab models of three low-indexed crystallographic planes [(100), (110), and (111)] for different inclusions, the Fe matrix, and TiN were established (Fig. 11). The work functions and the surface energies of La$_2$O$_2$S, La$_2$Zr$_2$O$_7$, TiN, and Fe matrix are presented in Tables 3–6, respectively.

It is evident that different low-indexed crystallographic planes yielded different work functions and surface energies. However, the determination of the exposed surface to the corrosive environment was difficult. Therefore, the average work function of two crystallographic planes with lower surface energy was used to compare the corrosion tendencies of different inclusions and the Fe matrix. La$_2$Zr$_2$O$_7$ manifested the highest work function followed by the pure...
Fe matrix; however, La$_2$O$_2$S and TiN had much lower work function as compared to the Fe matrix. Therefore, the theoretical corrosion tendencies of different inclusions and the Fe matrix could be arranged in the descending order as follows: TiN > (RE)$_2$O$_2$S > Fe > (RE)$_2$Zr$_2$O$_7$. Hence, RE$_x$Zr$_y$O$_z$ and TiN inclusions manifest different theoretical corrosion tendency when compared to experimental results. The explanation will be discussed in the next section.
3.7. Mechanism of initial corrosion induced by inclusions

The mechanisms of initiation and propagation of pitting corrosion by \( \text{RE}_x \text{Zr}_y \text{O}_z \)-(\( \text{RE}_2 \text{O}_3 \))\text{S-TiN} inclusions in marine environments are illustrated in Fig. 12. In the initial stage, \( \text{RE}_2 \text{O}_3 \) preferentially dissolved into NaCl solution due to its weak stability [23] and induced pitting corrosion, which further led to the accumulation of \( \text{H}^+ \) ions in inclusions [23]. The interface between inclusions and the matrix simultaneously dissolved and created local micro-gaps. Subsequently, \( \text{RE}_x \text{Zr}_y \text{O}_z \) started to dissolve from the periphery to the middle of the generated inclusions although it exhibited a lower corrosion tendency as compared to the Fe matrix. It happened because the accumulation of \( \text{H}^+ \) ions created an acidic environment in the pit and caused the further dissolution of \( \text{RE}_x \text{Zr}_y \text{O}_z \) [23]. In the later stage, corrosion products, inclusions, and the matrix formed catalytic occluded cells [52], which accelerated the dissolution of inclusions to form stable pits on the steel surface. Hence, weak electrochemical activities in corrosion sites significantly reduced the local pitting susceptibility of the low-alloy steel.

The mechanisms of initiation and propagation of pitting corrosion by \( \text{RE}_x \text{Zr}_y \text{O}_z \)-(\( \text{RE}_2 \text{O}_3 \))\text{S-TiN} inclusions in marine environments are depicted in Fig. 13. Similar to Fig. 12, \( \text{RE}_x \text{Zr}_y \text{O}_z \)-(\( \text{RE}_2 \text{O}_3 \))\text{S} followed the same dissolution mechanism. Some previous researchers [56–58] investigated the effects of TiN inclusions on corrosion initiation of alloys, and expressed that TiN possessed excellent electrochemical stability and usually behaved as the cathode under corrosive environments [56–58]. Meng et al. [58] found no stress corrosion cracking (SCC) initiation occurred in small, submicron-sized TiN inclusions; however, SCC occurred in broken micron-sized TiN inclusions. In the present study, the average size of TiN inclusions was in the range of 100–500 nm. Hence, although the results of first principle modeling indicated a lower corrosion tendency for TiN, it was actually quite stable in the corrosive environment. Local micro-gaps between inclusions and the Fe matrix were created during the dissolution of \( \text{RE}_x \text{Zr}_y \text{O}_z \) and lowered the adhesion between TiN and the substrate. After the completion of \( \text{RE}_x \text{Zr}_y \text{O}_z \)-(\( \text{RE}_2 \text{O}_3 \))\text{S} dissolution, TiN became detached from the substrate and stable pits were formed on the steel surface which inhibited the electrochemical activities in the corrosion site, and the local pitting susceptibility of low-alloy steel was significantly reduced.

4. Conclusions

1) Two types of complex inclusions with intertwined components of \( \text{RE}_x \text{Zr}_y \text{O}_z \)-(\( \text{RE}_2 \text{O}_3 \))\text{S} and \( \text{RE}_x \text{Zr}_y \text{O}_z \)-(\( \text{RE}_2 \text{O}_3 \))\text{S-TiN} were formed in the low-alloy steel.

2) Pitting corrosion was initiated by the dissolution of inclusions. \( \text{RE}_2 \text{O}_3 \) preferentially dissolved in NaCl solution, whereas the dissolution of \( \text{RE}_x \text{Zr}_y \text{O}_z \) propagated from the
periphery to the middle of the inclusions and formed stable pits on the steel surface. TiN was quite stable in the corrosive environment and finally, became detached from the substrate.

3) The results of in-situ SVET indicate that the dissolution of inclusions induced the electrochemical activities of pitting corrosion, revealing a profound anodic current density peak. The complete dissolution of inclusions caused a significant drop in the local current density and, consequently, inhibited the propagation of local corrosion.

4) The corrosion products were characterized after SVET measurements and were mainly composed of lepidocrocite (γ-FeOOH), magnetite (Fe₃O₄), hematite (α-Fe₂O₃), and goethite (α-FeOOH).

5) The work functions of low-indexed crystallographic planes of different inclusions and the Fe matrix were calculated based on the first principle modeling and indicated their possible corrosion tendencies.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The financial support from the National Nature Science Foundation of China (No. 51601138, 51601137), the State Key Laboratory of Refractories and Metallurgy (No. 2018QN118), and the 111 Project (No. D18018) is highly acknowledged. The authors are also grateful to the support from Excellent Young and Middle-aged Science and Technology Innovation Team in Colleges and Universities of Hubei Province (No. T201903).

REFERENCES


[40] Liu ZY, Li XG, Cheng YF. In-situ characterization of the electrochemistry of grain and grain boundary of an X70 steel in a near-neutral pH solution. Electrochim Commun 2010;12(7):936–8.


