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Effect of Chloride Salt Bath on Electrochemical Behavior and Morphology of 304L and 316L Stainless steels



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Abstract

Stainless steels (SSs) are highly valued for their exceptional properties, making them suitable for a wide range of applications. This study investigates the corrosion behavior of SS304L and SS316L in a chloride salt bath using chemical methods (weight loss) and electrochemical techniques (potentiodynamic polarization). The SS304L and SS316L undergo immersion in a chloride salt bath mixture consisting of 50% KCl and 50% NaCl at temperatures of 250, 350, and 450°C for 3h. Also, the immersion time at 350 °C for both stainless steels was investigated from 0.5 h to 3 h with an interval of 0.5 h. The potentiodynamic polarization (PDP) assessment was conducted at room temperature to assess the samples' corrosion behavior after exposure to the salt bath. Corrosion rates (CR) were then determined under different conditions to evaluate the samples' susceptibility to corrosion. The SEM and EDX analyses were employed to examine the corrosion products under various conditions. It was observed that the existence of Mo, Ni, and Cr content after PDP testing contributed to the protective layer formation and so inhibited further degradation. Before immersion, SS316L alloys exhibited the lowest corrosion rate (0.107 mm/y) but the CR values increased with an increase in the temperature of the salt bath before the PDP test. However, the SS316L samples for different conditions have lower CR values than SS304L. The SEM images confirmed the results of the PDP test.

Keywords: Corrosion behavior; Chloride salt bath; 304L Stainless steel; 316L Stainless steel; Surface morphology.

1. Introduction

Stainless steels (SSs) are a group of iron-based alloys that have different amounts of Cr and Ni to enhance their resistance to heat and corrosion [1]. A notable advantage of SSs is their ability to develop a protective and adherent Cr₂O₃ scale at elevated temperatures, effectively thwarting further corrosion [2, 3]. In oxidizing environments with high temperatures, SS typically demonstrates resilience against corrosion over extended periods. However, the existence of condensed molten salts, particularly alkali chlorides and sulfates, can lead to hot corrosion, even when temperatures are moderate, in contrast to the usual maximum operating temperature [2]. Researchers have investigated the corrosion behavior of SS in alkali molten salts, as documented by studies conducted by Tsaur et al. [4], Arivazhagan et al. [5], and Gonzalez-Rodriguez et al. [6]. While the SSs typically exhibit corrosion resistance in ordinary atmospheric conditions, they are susceptible to hot corrosion in the existence of chlorine or chlorides, as opposed to alkali sulfates. Additionally, Skrifvars et al.'s research [7] showed that pure alkali salts containing potassium or sodium, when tested in the absence of chlorine, showed no corrosion in the samples. However, when chlorine was present in the alkali salt, low-alloy and austenitic steels exhibited signs of iron volatilization from the steel surface [7]. Previous studies on hot corrosion of SS have primarily focused on oxidizing and molten salt environments. Yet, it's important to note that synergistic effects on corrosion may arise when both molten salt and oxygen are present in the same high-temperature environment [6, 7].

Materials such as austenitic steels are favored for their superior resistance to high-temperature corrosion and oxidation. However, it is important to note that austenitic steels generally come at a higher cost and exhibit reduced thermal conductivity

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[8]. One of the biggest problems with working with biomass at high temperatures in co-firing power plants is that it contains a lot of aggressive elements and a lot of variation because these aggressive media are always changing [8]. It investigated the biomass's richness in chlorine and alkali metals, including potassium and sodium [9]. Chlorine-induced "active oxidation" which is a mechanism that accelerates corrosion [10, 11]. The SSs' high-temperature behavior and CRST are particularly dependent on their various constituents, especially their chromium content. Notably, SS304 contains more than 17% Cr and 8% nickel, which enhances its resistance to both creep and corrosion. As a result, SS304 has a higher maximum service temperature than ferritic steels because of its superior corrosion and creep resistance. The formation of protective chromium-rich oxides, such as (Fe, Cr)₃O₄ and (Fe, Mn)Cr₂O₄, is responsible for SS304's exceptional resistance to oxidation [12]. However, the fluxing of the protective scales in corrosive environments may compromise the effectiveness of this protection. It is expected that the corrosion rate (CR) will significantly increase in the existence of chloride-rich ions [13]. Despite numerous investigations emphasizing fireside corrosion in environments resembling biomass [14, 15, 16, 17], none have specifically focused on the contribution of chromium content to steel degradation mechanisms concerning the composition of chloride-rich salt mixtures under accelerated testing conditions [13].

Various factors, including composition, microstructure, and immersion temperature, influence the CRST of austenitic SSs. Elevating the temperature widely recognized leads to a more uniform microstructure, thereby enhancing the CRST of SSs. Researchers have extensively examined the effects of temperature on the corrosion characteristics of duplex stainless steels [18, 19, 20]. They have noted a considerable enhancement in the CRST of these alloys with increasing temperature up to a certain threshold [18]. While a lot of research has been done on how SS304L and SS316L alloys react to NaCl corrosion, not as much has been done on how they react to solutions like 50%KCl+50%NaCl at normal and high temperatures and for different lengths of time. This study examined the corrosion characteristics of SS304L and SS316L in a solution consisting of 50%KCl and 50%NaCl at room temperature (RT). Both types of stainless steel were submerged in a salt bath mixture of 50%KCl and 50%NaCl at temperatures of 250, 350, and 450 °C for 3.0 h before conducting the potentiodynamic polarization (PDP) test. Additionally, SS304L and SS316L underwent immersion for varying durations of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h at 350 °C, followed by the PDP test at RT. The surface morphology and elemental composition analysis of the corroded SS304L and SS316L at different immersion temperatures were assessed using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), respectively.

1. Experimental procedure

The chemical constituents of SS304L and SS316L are detailed in Table 1. Before analysis, the samples' flat surfaces were meticulously ground using sandpapers down to a 1200 grade to achieve a smooth finish, followed by polishing with 0.3 μ m alumina paste.

Alloys	С	Cr	Ni	Mn	Мо	Si	Fe
SS304L	0.03	19.1	8.3	1.5	0.0	0.4	Bal.
SS316L	0.02	17.4	11.2	1.9	2.1	0.5	Bal.

Table 1. Chemical constituents of SS304L and SS316L in wt.%.

Salt bath tests were conducted using a crucible furnace with an electric power of 5kW, featuring a temperature control accuracy of ± 5 degrees Celsius. Specimens measuring 2x2 cm² were utilized for the tests. A salt bath comprising 50% KCl and 50% NaCl was maintained at temperatures of 250, 350, and 450 °C for 3 h. The SS304L and SS316L samples were immersed for varying durations: 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h at 350 °C. Subsequently, the PDP test was conducted. The CR using the weight loss (WL) procedure was calculated using Eq. (1) [21, 22].

$$CR (mm/y) = 87.6 x (W/DAT)$$
 (1)

Where W represents the weight loss in milligrams, D represents the density in g/cm^3 , A donates the sample area in cm^2 , and T indicates the time at which the metal sample was exposed in hours.

Corrosion characteristics of the two types of stainless steel with/without exposure to the salt bath were assessed using the PDP test in a solution consisting of 50%KCl and 50%NaCl, conducted at RT. A PGZ 100 potentiostat was utilized for the test. A

calomel electrode served as the reference electrode, while a platinum electrode acted as the auxiliary electrode. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were established by analyzing Tafel plots of potential. The CR values were calculated by Eq. (2) [23, 24]:

$$CR (mm/y) = \frac{0.00327 * i_{corr} * Eq.wt}{D}$$
 (2)

The I_{corr} , Eq. wt., and D represent the corrosion current density (μ A/cm²), equivalent weight (grams), and specimen density (g/cm³), respectively.

The metallographic examination and elemental analysis of SS304L and SS316L samples, both with and without exposure to the salt bath, were performed using Quanta FEG 250 scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX).

3. Results and discussion

3.1 Weight loss (WL) method

The CR values for SS304L and SS316L were calculated using the WL technique in a 50% KCl and 50% NaCl solution at various temperatures, as shown in Fig. 1. Fig. 2 illustrates the CR values of SS304L and SS316L at 350 °C with immersion times from 0.5 to 3.0 h, in 0.5 h increments. At 250 °C and 350 °C, SS316L exhibits lower CR values compared to SS304L, while the CR value is versed at 450 °C for 3.0 h. Meanwhile, the effect of the exposure time of SS304L and SS316L is almost the same as shown in Fig. 2. Additionally, it was observed that the CR value of SS304L and SS316L was initially high at 0.5 h, followed by a decrease at 1.0 h, which could potentially be attributed to the formation of oxides providing surface protection against further corrosion. Subsequently, the immersion time increasing from 1 h to 2.5 h led to a rise in CR values, possibly due to the development of new oxide protective layers. In all immersion times, S316L samples have lower CR values than SS304L. Interestingly, after 3 h at 350 °C, the CR value decreased for SS316L, suggesting the establishment of a more effective protective oxide layer.



Fig. 1. The CR by WL method for SS304L and SS316L at different temperatures for 3h in 50% KCl+50% NaCl.



Fig. 2. The CR by WL method for SS304L and SS316L at 350 °C for different times in 50% KCl+50% NaCl.

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3.2 Potentiodynamic polarization (PDP)

The electrochemical parameters, as detailed in Table 2 and illustrated in Fig. 3, highlight notable differences between SS316L and SS304L. Initially, it was observed that the CR of SS316L (0.107 mm/y) was lower than that of SS304L (0.694 mm/y) without immersion in the salt bath. Table 3 shows the electrochemical parameters for SS304L at 350 °C in a chlorine solution at RT, while Table 4 presents the electrochemical parameters for SS316L under the same conditions. Figs. 4 and 5 show the PDP curves for SS304L and SS316L, respectively. At 450 °C, SS316L displayed a higher resistance polarization (Rp) value (2.21 k Ω .cm²), as depicted in Fig. 5. In contrast, the CR values of both SS304L and SS304L initially increased with the increased temperature of the salt bath before PDP test. Interestingly, for both SS316L and SS304L immersed at 350 °C, the variation in the immersion time of the salt bath did not show a significant impact, as illustrated in Figs. 6 and 7, respectively. The lowest CR value is 0.109 mm/y for SS316L at 350 °C for 0.5 h while the lowest CR value for SS304L is 0.658 mm/y for SS304L at 350 °C for 1.0 h.

Conditions		E _{corr} , mV	I _{corr} , mA/cm ²	Rp Kohm.cm ²	CR mm/y
	Without heating	-439.7	0.089	1.13	0.694
SS304L	2° • °C −3.0 h	-478.9	0.081	0.29	0.645
	۳۰۰ °C -3.0 h	-650.5	0.119	0.32	0.932
	450 °C – 3.0 h	-450.7	0.216	0.85	1.714
SS316L	Without heating	-391.0	0.014	3.13	0.107
	250 °C - 3.0 h	-470.2	0.075	1.95	0.297
	۳۰۰ °C -3.0 h	-458.9	0.047	1.48	0.374
	4° • °C −3.0 h	-349.6	0.054	2.21	0.431

Table 2. The electrochemical parameters for SS304L and SS316L for different conditions.



Fig. 3. The PDP curves of the corroded SS304L and corroded 316L without salt bath at RT.



Fig. 4. The PDP curves of SS304L after 3 h in the salt bath for different temperatures.

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Fig. 5. The PDP curves of SS316L after 3 h in the salt bath for different temperatures.

Conditions	E _{corr} , mV	I _{corr} , mA/cm ²	Rp Kohm.cm ²	CR mm/y
°° · °C −0.5 h	-404.0	0.009	2.39	0.109
°°∙ °C -1.0 h	-704.1	0.098	0.259	1.149
°° · °C −1.5 h	-695.4	0.097	0.254	1.139
۳۰۰ °C -2.0 h	-830.0	0.262	0.131	3.067
۳۰۰ °C -2.5 h	-758.5	0.122	0.211	1.421
۳۰۰ °C -3.0 h	-650.5	0.119	0.31	0.932

Table 3. The electrochemical parameters for SS304L-350 °C in chlorine solution at RT.



Fig. 6. The PDP curves of SS304L after the salt bath at 350 $^\circ$ C for different times.

Table 4. The	electrochemical	parameter	s for SS316L-	-350 °C in ch	ilorine solution	1 at RT.

Conditions	E _{corr} , mV	I _{corr} , mA/cm ²	Rp Kohm.cm ²	CR mm/y
°°∙ °C -0.5 h	-472.9	0.103	0.31	0.803
°° • °C −1.0 h	-574.0	0.083	0.83	0.658
°°∙ °C -1.5 h	-631.3	0.923	0.24	0.724
°°∙ °C -2.0 h	-578.9	0.102	0.74	0.806
°° · °C −2.5 h	-603.1	0.133	0.31	1.056
°°∙ °С -3.0 h	-458.9	0.047	1.48	0.374

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Fig. 7. The PDP curves of SS316L after the salt bath at 350 °C for different times.

3.3 Surface morphology (SM)

The SEM images and EDX results under different conditions are presented in Fig. 8 and Table 5, respectively. For SS304L and SS316L, an increase in the temperature of the salt bath before corrosion was found to increase the CR values, potentially attributed to fall out of the accumulation of protective oxide layers that inhibit corrosion, as illustrated in Fig. 8 (b). However, the buildup of these oxides may lead to the depletion of Cr, Ni, and Mn, as indicated in Table 5, potentially compromising the stability of the protective layers over time. In the case of SS316L, the highest polarization resistance among the immersed samples was observed at 450 °C for 3 h in the salt bath, as depicted in Fig. 8(f). The existence of Mo in SS316L enhances the formation of protective layers of Cr, Ni, Mn, and Mo oxides, as shown in Table 5. The tendency to form a protective layer at 450 °C for SS316L is greater compared to SS304L due to the existence of Mo. However, it's noted that the chlorides formed to attack the stainless steel through the grain boundaries [8].

Furthermore, the EDX analysis revealed that increasing the temperature of the salt bath led to an increase in potassium content after the PDP test. Generally, the Ni content in SS316L after corrosion was higher compared to SS304L. The oxygen content tended to increase with the rise in the temperature of the salt bath before corrosion in both cases, except for SS316L at 350 °C, where it decreased. This decrease may be attributed to the increase in chromium content, suggesting the protective layer formation mitigating further degradation. The SEM images represent uniform corrosion and galvanic corrosion due to the depletion of elements especially for SS304L.

Conditions	К	Na	Cl	0	Cr	Ni	Mn	Мо	Fe
SS304L-250 °C	0.1	1.4	0.1	5.0	15.1	6.9	1.7		Bal.
SS304L-350 °C	0.3	1.9	0.3	6.0	15.1	6.9	2.0		Bal.
SS304L-450 °C	0.5	2.1	0.4	17.5	11.3	6.8	1.7		Bal.
SS316L-250 °C	0.4	2.1	0.3	5.6	13.0	8.3	1.8	1.5	Bal.
SS316L-350 °C	0.5	1.6	0.2	3.5	14.6	9.7	2.1	2.0	Bal.
SS316L-450 °C	0.6	1.1	0.2	7.4	13.8	9.5	1.9	1.9	Bal.

Table 5. EDX results after corrosion of SS304L and SS316L in different conditions in wt.%.



Fig. 8. The SEM morphologies of the corroded SS304L and SS316L at different temperatures for 3h.

3.4 Corrosion Mechanism

The SS as a family of metals is very corrosion resistant but changing the alloying elements increases the grade's ability to withstand harsh environments. The presence of certain alloying elements, notably Cr, holds significant importance in stabilizing the behavior of alloys against both general and localized corrosion. This is particularly crucial for Ni and Fe-based metals. Due to its remarkably low dissolution currents, chromium accumulates in the passive layer even in highly corrosive electrolytes. The anodic reaction that takes place within the crevice during the corrosion process involves the dissolution of iron, as outlined in Eq. (3):

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (3)

The electrons released during the subsequent cathodic reaction move from the anode to the cathode, which is the passivated surface, as shown in Eq. 4.

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$$
 (4)

Because of these reactions, the electrolyte enclosed within the pit acquires a positive electrical charge, in contrast to the negatively charged electrolyte surrounding the pit. According to Eq. (5), the negatively charged chloride ions are drawn towards the positively charged particles within the crevice, leading to an elevation in the acidity of the electrolyte.

$$FeCl_2 + 2H_2O \rightarrow Fe (OH)_2 + 2HCl$$
(5)

Due to the aggressive nature of ionic species, the CR is elevated. While manganese can serve as a cost-effective substitute element for alloys in moderately corrosive aqueous environments, its presence has a detrimental effect on the corrosion of stainless steel in aqueous environments containing chloride [25]. The corrosion process may result in the formation of manganese-rich compounds, such as hydroxides and oxides, derived from manganese, as illustrated in Eqs. (6)–(9). [25, 26].

$Mn^{2+} + 2FeOOH \rightarrow MnFe_2O_4 + 2H^+$	(6)
$2Fe_{3}O_{4} + 3Mn^{2+} + 4H_{2}O \rightarrow 3MnFe_{2}O_{4} + 8H^{+} + 2e^{-}$	(7)
$3Mn(OH)^{3-} + 2Fe_3O_4 + H^+ \rightarrow 3MnFe_2O_4 + 5H_2O + 2e^{-3}$	(8)
$MnFe_2O_4 + 4H_2O \rightarrow 6FeOOH + Mn_3O_4 + 2H^+ + 2e^-$	(9)

Nickel exists in a metallic state at the interface between the metal and oxide, which aids in mitigating dissolution. Compounds such as NiO and Ni(OH)₂ have the potential to form, as depicted in Eqs. (10) and (11). Elemental segregation reduces the passivation capability and makes alloys more susceptible to pitting corrosion. Conversely, SS promotes the even dispersion of constituents necessary for the permeation hypothesis, thereby enhancing its passivation capability. Cons equently, the surface of stainless steel tends to develop a uniform and dense passive coating. It's worth noting that while the high entropy effect does contribute to the enhanced protection provided by passive coatings formed on SS, it is not the sole contributing factor [27].

$$Ni + H_2O \rightarrow Ni(OH)_2 + 2H^+ + 2e^-$$
(10)

$$Ni(OH)_2 \rightarrow NiO + 2H^+ + 2e^-$$
(11)

The SS316L has enhanced corrosion resistance compared to other stainless steel grades due to the addition of molybdenum, making it suitable for use in aggressive environments like marine applications [7]. Apart from the formation of the Cr_2O_3 layer, which is primarily responsible for the passive behavior, Mo enhances the protective layer stability. This enhancement occurs through the Mo species precipitations on the surface, particularly at pH values higher than 8.0 [28, 29, 30].

$$Mo + 2H_2O \rightarrow MoO_2 + 4H^+ + 4e^-$$
(11)

The transmissivity of Mo arises through further oxidation at higher potentials [31, 32].

$$MoO_2 + 2H_2O \rightarrow MoO_4^{2-} + 4H^+ + 2e^-$$
(12)

The presence of Mo in SS316L significantly influences its corrosion performance by enhancing its passivation ability, thus preventing the onset of pitting corrosion. Molybdenum plays a significant role in the stability and formation of the passive layer in SS316L [28]. A correlation has been observed between acid concentration and changes in the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) . As the acidity increases, there is an upward trend in the corrosion potential and a

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downward trend in the corrosion current density. This phenomenon can be attributed to the formation of various molybdenum oxides (MoO₂, MoO₃, and Mo₂O₅) with increasing acidity.

In acidic solutions, the passive film primarily consists of MoO_2 , accompanied by MoO_3 and $Mo(OH)_3$. The reduction of these compounds can be achieved using either Eq. (13) or Eq. (14) [33]:

$2MoO_3 + 2H^+ + e - \rightarrow Mo_2O_5 + H_2O$	(13)
$MoO(OH)_2 + H^+ + e - \rightarrow MoOOH + H_2O$	(14)

With increasing acid concentration, an oxide layer develops on the electrode surface. The findings suggest that, in comparison to neutral and basic media, the oxide layer on Mo demonstrates greater stability in acidic environments. This behavior can be attributed to the prevalent presence of MoO_2 in the passive film, with minimal amounts of MoO_3 and $Mo(OH)_3$. Depending on the solution's voltage and pH, these oxides may dissociate in aqueous solutions according to Eqs. (15, 16, and 17) [33]:

$MoO_2(s) + 2H_2O(l) \rightarrow HMoO_{(aq)}^{4-} + 3H_{(aq)}^{+} + 2e$	(15)
$MoO_2(s) + 2H_2O(l) \rightarrow + MoO_{2(aq)}^{4-} + 4H_{(aq)}^+ + 2e-$	(16)
$HMoO_{(aq)}^{4-} + H_{(aq)}^{+} \rightarrow MoO_3 + H_2O(l)$	(17)

.

In aqueous solutions, The Cr reacts to produce Cr_2O_3 according to Eq. (18): $4 Cr (s) + 3 O_2 \rightarrow 2 Cr_2O_3 (s)$ (18)

These oxides and hydroxides precipitate on the metal surface leading to the transfer of metal from an active state to a passive state [34, 35].

Chloride ions (Cl \neg) effectively attack the SS304L material, initiating pitting corrosion. The small size of Cl ions facilitates their penetration through the passive oxide film, influenced by an electric field. To maintain electrical neutrality, the electric field intensifies, leading to the hydrolysis of corrosion byproducts within crevices. This hydrolysis-induced acidification impedes repassivation during the migration of chloride ions. The acidity within the crevices accelerates the dissolution rate of this autocatalytic mechanism [34].

All free alkali metals can bind as chloride, potentially forming chloride-alkali complexes if all alkalis are free. This phenomenon poses a significant risk to alkaline sintering as it has the potential to induce salt adhesion, deposit formation, and the release of free corrosive acidic gases [36]. Cr is frequently preferred in Fe-based alloys for high-temperature applications due to its selective oxidation, which facilitates the formation of a dense and protective surface layer of Cr_2O_3 . Prior research indicates that a rise in Cr content generally leads to a decrease in CR values [17]. However, there are instances where increasing Cr content may adversely affect corrosion performance, particularly in environments containing chlorine, such as biomass combustion environments.

In such environments, steel may experience a combination of internal and external corrosion. High-chromium steels may experience exacerbated internal corrosion, while low-chromium steels typically exhibit more pronounced general corrosion. Although an increased chromium content promotes the formation of surface Cr_2O_3 , its higher affinity for chlorine compared to other alloying elements can worsen corrosion attacks [37]. Grain boundaries within the material act as pathways for both the inward diffusion of chlorine and the outward diffusion of chromium, respectively. As a result, grain boundary internal corrosion may be more pronounced in materials with higher Cr content. Moreover, elevated Cr concentrations lead to the formation of a greater number of chromium carbides along grain boundaries, which are more susceptible to preferential chlorine attack and subsequently cause intergranular corrosion [38, 39].

Given the complex nature of co-combustion environments, it is essential to develop a material selection strategy that is economically feasible. This should involve a comprehensive assessment of various factors, including temperature, chlorine concentration in the environment, alloying elements such as nickel and molybdenum, and chromium content. A study has revealed that the chromium-to-nickel ratio at the interface of the oxide layer and substrate may offer a more reliable indication of breakaway corrosion induced by chlorine-active oxidation [40], rather than solely relying on the initial Cr content in the alloy. Further strategies or criteria for establishing material selection guidelines in related fields should be proposed in future studies [1].

In the case of SS304, it can develop spinel oxides primarily composed of (Ni, Fe, Mn) Cr_2O_4 . The presence of corrosion products like NaFeO₂ confirms the formation of FeCl₂(s) on the steel surface, beneath the Fe₂O₃ and Fe₃O₄ oxide layers. This

occurs because sodium ferrite is accompanied by the generation of $Cl_2(g)$ according to Eq. (19). The $Cl_2(g)$ then diffuses through the metal oxide layer and reacts with the Fe, as depicted in Eq. (20), resulting in the formation of volatile FeCl₂(s) [8].

$$\begin{array}{rcl} 2NaCl~(l)~(s)+Fe_2O_3(s)~+0.5O_2~~\rightarrow~~2NaFeO_2(s)+Cl_2(g) & (19)\\ Fe(s)+Cl_2(g)~~\rightarrow~~FeCl_2(s)~~\rightarrow~~FeCl_2(g). & (20) \end{array}$$

 $FeCl_2(g)$ is generated through the transformation of $FeCl_2(s)$, which then diffuses through the oxide layer. Once the oxygen partial pressure reaches a sufficient level, the iron chloride destabilizes and converts into Fe_2O_3 and $Cl_2(g)$. Due to the presence of voids and fissures within the oxide layer, lateral diffusion of $Cl_2(g)$ and $FeCl_2(g)$ is facilitated. Additionally, the occurrence of intergranular corrosion at elevated temperatures in SS304L via grain boundaries has previously been attributed to either the accelerated diffusion pathways created by these boundaries or the selective degradation of chromium carbides segregated at these interfaces. Therefore, the comprehensive mechanisms proposed in this study are consistent with prior research that extensively elucidated the mechanisms of combined active and direct oxidation.

While the high-Cr steels encountered comparatively less damage, they were still subjected to substantial erosion from the aggressive salt deposits. In addition to non-protective Fe_2O_3 , protective Cr-rich oxides compose the oxide layer that forms. Intergranular attack through the grain boundaries causes the depletion of Cr from the steel surface because of outward diffusion caused by the growth of this multilayer. Furthermore, the reaction between alkali metals and chromium oxides produces corrosion byproducts, namely $NaCr_2O_4$ or KCr_2O_4 , which undermine the steel's protective oxide layer. The compromised protective barrier enables chlorides to permeate and attack the Cr-depleted layer present on the surface of the steel. These phenomena become even more pronounced in steels containing intermediate chromium.

The presence of NaCl–KCl deposits caused the most severe corrosion in all tested steels, with SS304L exhibiting the highest CRST. Various corrosion byproducts were identified, including Na_2FeO_4 in low-chromium steel, and K_2CrO_4 and Na_2CrO_4 in intermediate and high-Cr steels, initiating concurrent damage mechanisms such as active oxidation induced by chlorine and direct oxidation. These findings emphasize the challenge of accurately determining the CRST of steels in the presence of molten salts, given the significant influence of the composition of aggressive deposits [8].

Conclusions

The corrosion characteristics of SS304L and SS316L were evaluated in a chloride solution comprising 50% KCl and 50% NaCl using electrochemical methods at RT. Both types of stainless steel were subjected to immersion in a salt bath at temperatures of 250°C, 350°C, and 450°C before the PDP test. The SS316L and SS304L at 350 °C are examined for different exposure times from 0.5 h to 3 h with intervals of 0.5 h. In the absence of immersion, SS316L exhibited a higher corrosion resistance compared to SS304L in the chloride media. Similarly, immersion in the salt bath at 450°C for 3 h yielded consistent results. The presence of Mo, Cr, and Ni contributed to the maintenance of protective layers, thereby decreasing the corrosion rate values. Surface analysis revealed evidence of general corrosion, pitting, and grain boundary attack on both SS types. The SS316L exhibits a lower CR (0.107 mm/y) compared to SS304L (0.694 mm/y) without immersion, primarily attributable to the existence of Mo. The immersion temperature led to an increase in the CR value for SS304L, peaking at 1.714 mm/y at 450°C. The SEM images indicate the corrosion is due to uniform corrosion and galvanic corrosion, especially for SS304L.

Conflict of interest

The authors declare that they have no conflicts of interest.

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