Enhancements of Passive Film and Pitting Resistance in Chloride Solution for 316LX Austenitic Stainless Steel After Sn Alloying

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Abstract

In the present work, the electrochemical behavior and properties of the passive film of a new Sn-alloyed 316LX austenitic stainless steel were investigated. With the increase in Sn content in 316LX austenitic stainless steel from 0 to 0.21%, the critical pitting temperature value increased from 32.6 to 38.8 °C, and the pitting potential increased from 0.252 V_{SCE} to 0.317 V_{SCE}. Electrochemical impedance spectroscopy results showed that the corrosion resistance of passive film rose with the increase in Sn content, indicating a more stable passive film. The Mott–Schottky measurement revealed an n-type passive film with a decreased carrier concentration on the 316LX austenitic stainless steel surface. The Cr, Sn²⁺ and Sn⁴⁺ (SnO, SnOHCl or SnO₂) enrichments were observed in the passive layer by X-ray photoelectron spectroscopy. The enrichment of Sn and Cr in the passive film can account for the enhanced pitting resistance of 316LX austenitic stainless steel in chloride solution.

Keywords Austenitic stainless steel · Sn alloying · Pitting · Chloride solution

1 Introduction

Austenitic stainless steels have been widely used in many industries, such as the petrochemical aerospace, transportation and acid production, due to their comprehensive mechanical properties and good corrosion resistance [1–3]. The excellent corrosion resistance mainly owes to the diverse alloying elements, i.e., chromium, nickel and molybdenum [4–6]. Cr plays an important role in the passivity of stainless steel [7]. Ni can stabilize the austenitic phase and improve the pitting resistance in moderation. The minor alloying element Mo is effective for reducing the pitting susceptibility in the presence of Cr. Mo may also be absorbed on the steel surface in the form of molybdate [8]. However, the prices of these as-mentioned alloying elements are rather high and can greatly increase the cost of stainless steels. In this case, other substitutes for

these elements, such as nitrogen [9], manganese [10] and tin [11], have attracted many attentions. Unlike the afore-said elements which present positive effects, Sn was acknowledged as a harmful impurity. Sn alloying could deteriorate the hot workability, tensile strength and hardness of steels and even lead to embrittlement [12–15].

However, Sn itself possesses high corrosion resistance, which can potentially improve the corrosion performance of stainless steel. A new Sn-alloying ferritic stainless steel (FSS) with high corrosion resistance has been firstly developed in 2012 [16]. After that, Nam et al. [17] have reported a decreased corrosion rate in an acid chloride solution for a low-alloy FSS with an increased Sn content. The formation of a protective SnO₂ layer and a more continuous and adherent rust layer on the steel surface due to the interactions of Sn with Cu and Sb could account for the improvement of corrosion performance. Li et al. [18] also found that the corrosion resistance of low-alloy FSS steel in sea water has increased after Sn alloying. The more uniform and adherent passive layer containing tin oxides (SnO and SnO₂) could inhibit the dissolution of steel and increase the impedance of passive film. Luo et al. [19, 20] pointed out that the Sn-rich oxide film formed on the FSS surface could act as a barrier against the elementary

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dissolutions in sulfuric acid solution. A better passive behavior in alkaline chloride solution was also reported for the Sn-alloyed FSS than the Sn-free ones [20]. Zhang et al. [21] reported the optimum Sn content for the ultra-purified FSS containing 17 wt% Cr.

Besides the researches focused on the corrosion behavior of Sn-alloying ferritic stainless steel, the effect of Sn alloying on the corrosion performance of austenitic stainless steel (ASS) in acid solutions was also investigated. Pardo et al. [22] reported that Sn had a beneficial effect on the corrosion resistance of AISI 304 and 316 ASSs in 30 wt% H_2SO_4 , and the Cu–Sn synergy was more positive than Sn or Cu singly added. Itzhak and Harush [23] found that the addition of 0.5–3 wt% Sn would enhance the corrosion resistance of hot-pressed sintered 316 ASS in H_2SO_4 . However, there are few studies focused on the pitting behavior of Sn-alloying ASS in chloride solutions. In our previous work, the critical pitting temperature (CPT) and impedance values were compared for the 316L and B316LX-0.08% Sn samples in NaCl solution [24]. However, a systematic study of Sn-added austenitic stainless steel on its pitting behavior in chloride solution is still lacking. And the composition and semi-conductive properties of the passive films formed on the Sn-added ASS in chloride solution are not yet clear.

This work aims at investigating the effect of tin addition on the pitting corrosion and passive film of 316LX austenitic steel in chloride solution. The pitting resistance of specimens was examined by the CPT and potentiodynamic polarization tests. The electrochemical impedance spectroscopy (EIS), Mott–Schottky measurements (MS) and X-ray photoelectron spectroscopy (XPS) were used to study the structure and composition of passive films. All the results were discussed on the basis of the above electrochemical experiments and microscopic characterizations. The present work is beneficial to better understand the relationship between the properties of passive film and the corrosion behavior of Sn-alloying ASS in chloride solution.

2 Experimental

2.1 Sample Preparation

The materials for test were 316LX ASS with different contents of Sn provided by Baosteel Research Institute. The chemical compositions of these materials are shown in Table 1. The experimental samples were cut into 10 mm × 10 mm from the cold-rolled sheets with a thickness of 1 mm. Specimens were embedded in epoxy resin, ground mechanically from 600 to 2000 grit, polished

with a diamond paste of 2.5 μm , degreased with ethanol and blow-dried successively.

2.2 Electrochemical Tests

The electrochemical tests were carried out with a CHI660 electrochemical system in a three-electrode cell. The 316LX ASS sample was used as the working electrode, a saturated calomel electrode (SCE) was served as the reference electrode, and a platinum sheet was used as the counter electrode. All the potentials in this paper were referred to SCE. The tests were repeated for three times to guarantee the repeatability.

The CPT values of specimens were obtained through potentiostatic measurements according to ASTM G 150-99. The tests were carried out in 1 mol/L NaCl solution deaerated by nitrogen gas. Before the CPT measurements, a cathodic polarization at $-900 \text{ mV}_{\text{SCE}}$ was performed for 120 s to deoxidize the working electrodes. Then, the open-circuit potential test was carried out to form the passive film on the sample surface. In order to get the CPT results, an anodic potential of $300 \text{ mV}_{\text{SCE}}$ was applied on the samples and the solution was heated at a rate of $1^\circ\text{C}/\text{min}$. The current density was continuously recorded with the increase in temperature until it reached $100 \mu\text{A}/\text{cm}^2$. The CPT was defined as the temperature at which the current density was equal to $100 \mu\text{A}/\text{cm}^2$. The potentiodynamic polarization measurement was carried out from -600 to $400 \text{ mV}_{\text{SCE}}$. The potential at which the current reached $100 \mu\text{A}/\text{cm}^2$ was identified as the pitting potential (E_{pit}). A constant potential of $+100 \text{ mV}_{\text{SCE}}$ was applied on the specimens for 5400 s to study the metastable pitting process. This potential of $+100 \text{ mV}_{\text{SCE}}$ was selected based on the results of the potentiodynamic polarization curve.

The EIS measurements were run in 1 mol/L NaCl solution for samples passivated at OCP for 3600 s in the same solution. A perturbation of $10 \text{ mV}_{\text{SCE}}$ was applied at the OCP, and the test frequencies ranged from 100 kHz to 10 mHz. The semi-conductive properties of the passive film on stainless steels were measured by Mott–Schottky tests. The MS measurements were taken in the potential range from -0.3 to $0.2 \text{ V}_{\text{SCE}}$ with a $10 \text{ mV}_{\text{SCE}}$ amplitude. The frequency was set at 1000 Hz, and the scanning rate was $50 \text{ mV}/\text{s}$. Before the MS measurements, the specimens were stabilized at 0 V_{SCE} for 5400 s.

2.3 Characterization

To investigate the compositions of passive films on the specimen surface in 1 mol/L NaCl solution, the tested samples were passivated at 0 V_{SCE} for 5400 s. Then, the chemical composition of the passive film was examined by

Table 1 Chemical compositions of 316LX ASS with different Sn addition (wt%)

Material	C	Si	Mn	S	P	Cr	Ni	Cu	Mo	N	Sn	Fe
316L–0Sn	0.027	0.49	1.37	0.004	0.009	16.20	10.19	0.17	2.11	0.024	–	Bal.
316L–0.062Sn	0.024	0.51	1.33	0.005	0.009	16.49	9.90	0.19	2.06	0.030	0.062	Bal.
316L–0.21Sn	0.022	0.45	1.36	0.003	0.009	16.33	10.05	0.19	2.07	0.026	0.21	Bal.

XPS using a PHI5300 instrument with a monochromatic Mg radiation source (14 kV). The recorded XPS spectra were fitted using the Avantage software to analyze the type and content of various compounds in the passive films. Gaussian–Lorentzian functions and Shirley background subtraction were used for curve fitting [25, 26]. The morphology of specimens after the potentiodynamic polarization test was characterized by the Philips XL30 FEG scanning electron microscope (SEM).

3 Results and Discussion

3.1 CPT Test

Figure 1 illustrates the typical CPT curves of current density for 316LX ASS with different Sn contents. In the beginning, the current density stayed at a value lower than $1 \mu\text{A}/\text{cm}^2$, suggesting that the specimen was in a well-passivated condition. Some current glitches were observed with further increasing the solution temperature, which was related to the formation of metastable pits caused by the film breakdown [27, 28]. When the temperature further increased to a value near CPT, the current density raised sharply as a result of the formation of stable pits [29, 30]. It could be seen that the least current glitches were presented for the 316L–0.21Sn sample, indicating the most stable passive film and the best pitting resistance associated with this specimen. The average CPT value of specimen

increased from 32.6 to 38.8 °C as the Sn content increased from 0 to 0.21%, revealing a positive effect of Sn addition on the pitting resistance of 316LX ASS.

3.2 Potentiodynamic Polarization Measurement

Figure 2 exhibits the typical polarization curves of Sn-added 316LX in 1 mol/L NaCl solution. Some current fluctuations were found in the polarization curve, suggesting the formation of metastable pits during the measurements. The passive current density (i_p) was obtained from the middle-passive region in the polarization curves. The value of i_p decreased from $1.46 \mu\text{A}/\text{cm}^2$ to $1.15 \mu\text{A}/\text{cm}^2$ with the increase in Sn content. The i_p could reflect the dissolution rate of a passive film [31]. The higher i_p suggests the higher dissolution rate. Hence, with increasing the Sn addition the dissolution rate of passive film decreased. Furthermore, a higher i_p means a less stable passive film formed on the surface. The corrosion potential (E_{corr}) increased with the increase in Sn content. The E_{pit} , which demonstrates the pitting resistance of stainless steel [32, 33], is $0.252 \text{ V}_{\text{SCE}}$, $0.273 \text{ V}_{\text{SCE}}$ and $0.317 \text{ V}_{\text{SCE}}$ for the 316L–0Sn, 316L–0.062Sn and 316L–0.21Sn samples, respectively. It could be concluded that the susceptibility of pitting corrosion gradually decreased with increasing Sn addition. Meanwhile, the pit nucleation resistance ($E_{\text{pit}} - E_{\text{corr}}$) increased from 547 to 560 mV, revealing the decreased possibility for pitting nucleation. The

Fig. 1 **a** Typical current density curves for 316LX specimens in 1 mol/L NaCl solution, **b** derived CPT values with error bars for 316LX specimens with different Sn contents

Fig. 2 Potentiodynamic polarization curves for 316LX samples in 1 mol/L NaCl solution (i current density)

potentiodynamic polarization results were consistent with the CPT researches.

The morphologies of specimen after potentiodynamic polarization were observed with SEM as exhibited in Fig. 3. A few corrosion pits were present on the specimen surface which displayed the typical stable pitting morphology of a round shape.

3.3 Current–Time Transient Measurement

The current–time transient measurements were taken at 100 mV_{SCE} for 5400 s in 1 mol/L NaCl solution at 30 °C. The recorded curves are shown in Fig. 4. It could be seen that the current density decreased sharply at first since the growth rate of the passive film was faster than the dissolution rate for all specimens. Afterward, the current density diminished gradually until reaching a constant value. The current transient can reflect the metastable pitting corrosion process [34]. The dissolution of the passive film at metastable pits would increase the number and amplitude of current glitches. In Fig. 4, three samples displayed different metastable pitting behaviors. The number and amplitude of the metastable pitting current transient changed with the content of Sn. With the increase in the Sn content, the number and amplitude of current glitch

Fig. 4 Current density curves versus elapsed time of 316LX samples in 1 mol/L NaCl solution at 100 mV_{SCE}

decreased significantly. These results coincide with the CPT and potentiodynamic polarization data. It suggested that the addition of Sn could inhibit the nucleation of metastable pits, which was consistent with the point of Pardo et al. [35]. It might be related to the changes of passive film after Sn addition.

3.4 Electrochemical Impedance Spectroscopy Measurements

Figures 5 and 6 show the Nyquist and Bode plots of 316LX specimens. The Nyquist plot of the tin-free sample had a

Fig. 3 Surface morphologies of pits on 316LX samples after potentiodynamic polarization test in 1 mol/L NaCl solution: **a** 316L–0Sn; **b** 316L–0.062Sn; **c** 316L–0.21Sn

Fig. 5 Nyquist plots of 316LX samples in 1 mol/L NaCl solution (Z' real part of impedance; Z'' imaginary part of impedance)

Fig. 6 Bode plots of 316LX samples in 1 mol/L NaCl solution (f frequency; Z impedance)

similar shape with that of the tin-containing ones. However, the semicircle diameter increased with increasing the Sn content. The semicircle diameter can be used to represent the corrosion resistance of stainless steel. The larger diameter represents the better corrosion resistance. Therefore, the corrosion resistance increased with the increase in Sn content. This result matched well with the tendency in potentiodynamic polarization and CPT measurements. As mentioned in Ref. [19], in the high-frequency region, the phase angle value was close to 0° and the $\log|Z|$ ranged at $1\text{--}10\ \Omega\ \text{cm}^2$ (Z impedance), which indicated that the impedance was caused by the electrolyte. For the intermediate frequencies, the phase angle reached the maximum and the $\log|Z|$ was linear with the logarithm of frequency, suggesting that a stable passive film was formed on the sample surface [36, 37].

Many equivalent electric circuit (EEC) models can be used to fit the EIS data. As seen in Fig. 6, the impedance spectra appeared to include two time constants. Therefore, the EEC shown in Fig. 7 was selected to fit the impedance spectra of specimens. In Fig. 7, R_s was the solution resistance. On account of the dispersion effect of surface roughness, the pure capacitance element was replaced by the constant phase element Q to reflect the capacitance behavior. Q_1 was the double-layer capacitance, and R_1 is the charge-transfer resistance. The values of Q_2 and R_2 were related to the reactions that occurred in the passive film. The parameter Q_2 represented the capacitive behavior of passive film, and R_2 was the resistance of ionic paths through the passive film. n_1 and n_2 are equal to 1 for an ideal capacitor and less than 1 for the non-uniform surfaces. The fitted results of EIS data for 316LX ASS in 1 mol/L NaCl are listed in Table 2. The values of Chi square were around 10^{-3} , showing a good correspondence between the experimental and simulated data. The polarization resistance R_p (the sum of R_1 and R_2) has been widely used to reflect the corrosion resistance of samples [38]. It could be seen from Table 2 that R_p value for the 316L-0Sn sample was slightly smaller than 316L-0.062Sn sample. The R_p of 316L-0.21Sn sample was higher than the other two, indicating a higher corrosion resistance. It would be also found that R_2 increased and Q_2 decreased with the increasing content of Sn, manifesting a more uniform and stable passive film with the reduced surface physical defects. According to Ref. [39], the values of Q_2 decreased because of the formation of a stable passive film. The EIS results were consistent with that of the potentiodynamic polarization and CPT measurements.

3.5 Mott–Schottky Measurement

The semi-conductive properties of the passive film on stainless steels are often measured by Mott–Schottky analysis. The relationship between the space charge layer capacitance (C) and the applied potential (E) can be calculated by the Mott–Schottky equation [40], which could be used to calculate the donor concentration and flat-band potential:

Fig. 7 Equivalent electric circuit model for interpretation of impedance spectra of 316LX samples in 1 mol/L NaCl solution

Table 2 Fitted results of impedance data for 316LX ASS samples in 1 mol/L NaCl solution

Material	R_s (Ω cm ²)	Q_1 (Ω^{-1} cm ⁻² s ⁻ⁿ)	n_1	R_1 (Ω cm ²)	Q_2 (Ω^{-1} cm ⁻² s ⁻ⁿ)	n_2	R_2 (Ω cm ²)	R_p (Ω cm ²)
316L-0Sn	11.46	4.389×10^{-5}	0.88	5.707×10^5	8.084×10^{-5}	1	1.135×10^5	6.842×10^5
316L-0.062Sn	10.56	1.264×10^{-4}	1	7.198×10^4	3.954×10^{-5}	0.89	6.126×10^5	6.846×10^5
316L-0.21Sn	9.574	1.394×10^{-4}	1	2.012×10^4	3.059×10^{-5}	0.909	9.314×10^5	9.515×10^5

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 e N_d A^2} (E - E_{fb} - kT/e) \quad (\text{For n-type}), \quad (1)$$

$$\frac{1}{C^2} = -\frac{2}{\varepsilon \varepsilon_0 e N_a A^2} (E - E_{fb} - kT/e) \quad (\text{For p-type}), \quad (2)$$

where e is the electron charge (1.602×10^{-19} C), ε_0 is the vacuum dielectric constant (8.854×10^{-14} F/cm), ε is the dielectric constant of passive film which is adopted as 15.6 [41], A is the exposed area of the working electrode (1 cm^2), N is the charge carrier density: the donor density (N_d) for n-type semiconductor and the acceptor density (N_a) for p-type semiconductor, k is the Boltzmann's constant (1.38×10^{-23} J/K), E_{fb} stands for the flat-band potential, and T is the absolute temperature. According to the following equation:

$$N = 2/(m\varepsilon\varepsilon_0e), \quad (3)$$

the value of N_d or N_a can be obtained from the slope of C^{-2} versus E since m stands for the slope of linear region in the Mott-Schottky plot.

Figure 8 shows the Mott-Schottky plots of passive films on the passivated 316LX stainless steels in 1 mol/L NaCl solution. It could be found that the Mott-Schottky plots of the specimen showed the same trend. The slopes of the fitting lines were all positive, indicating that the passive

films of tested specimens were n-type semiconductors. The slope value increased with the addition of Sn. N_d was calculated from the slopes of the linear regions. The carrier densities for the specimens were 5.50×10^{20} , 4.22×10^{20} and $3.20 \times 10^{20} \text{ cm}^{-3}$, respectively, which was within the reported value ranges of carrier concentration for the passive films on stainless steels [42, 43]. The carrier concentration was related to the conductivity of passive film. The higher dopant density suggests more ongoing electrochemical reactions, leading to a higher passive current density. It could be seen from Table 3 that the 316L-0Sn sample had the highest N_d value compared with the 316L-0.062Sn and 316L-0.21Sn samples, implying the more disordered structures and higher defect densities. The decrease in N_d with increasing Sn additions might be attributed to the neutralization of dopants by Sn. N_d also represents the adsorption affinity of chloride ions, which can reflect the pit nucleation ability in the passive films [37, 44]. Thus, the 316L-0Sn specimen had the highest sensitivity to pitting nucleation. The thickness of passive film (L_{ss}) for each sample also increased with increasing the addition of Sn. It was shown in Table 3 that E_{fb} shifted to negative direction as the Sn contents increased. The Nernstian equation for semiconductor flat-band potential is:

$$E_{fb} = -E_F^0/q + \Delta\Phi_H, \quad (4)$$

where the E_F^0/q is the voltage drop of the space charge layer and $\Delta\Phi_H$ is the potential difference between the electrode surface and the Helmholtz layer. The change of E_{fb} reflects the potential difference of the Helmholtz double layer. Anion adsorbing on the film resulted in a decrease in the Helmholtz potential drop, which leads to a negative shift of

Fig. 8 Mott-Schottky plots of passive films on 316LX samples surface in 1 mol/L NaCl solution**Table 3** Semi-conductive parameters derived from Mott-Schottky plots for passive films obtained at 0 V_{SCE} in 1 mol/L NaCl solution

Material	N_d (cm ⁻³)	E_{fb} (V)	L_{ss} (nm)
316L-0Sn	5.50×10^{20}	-0.4460	1.183
316L-0.062Sn	4.22×10^{20}	-0.4740	1.392
316L-0.21Sn	3.20×10^{20}	-0.490	5.142

E_{fb} . It might be caused by the adsorption of CrO_4^{2-} generated by the following reaction:

The passive film changed from anion-selective to cation-selective because of the adsorption of CrO_4^{2-} on the film [45]. It partly prevented the Cl^- adsorbing on the passive film and inhibited the breakdown of film, consequently improving the corrosion resistance.

3.6 Chemical Composition of Passive Films

The chemical compounds of the passive films have great influences on their semi-conductive properties and the corrosion behavior of stainless steel. The XPS results for passive films on the 316LX samples after pre-passivation at 0 V_{SCE} for 5400 s are shown in Figs. 9 and 10. After background removal according to Shirley, the XPS results could be separated into different oxidation states. Figure 9a and b shows the Fe and Cr spectra of 316L–0Sn samples. The spectra could be separated into several constituent peaks. The peaks correspond to the states of Fe^0 (705.9 eV), Fe^{2+} (709.6 eV) and Fe^{3+} (710.8 eV). As such, it could be concluded that the main iron oxides in the passive film for Sn-free specimen are Fe_2O_3 and FeO . Figure 9b reveals that three states of Cr exist in the passive film: Cr^0 (572.6 eV), Cr_2O_3 (575.9 eV), and $\text{Cr}(\text{OH})_3$ (578.0 eV). The amount of $\text{Cr}(\text{OH})_3$ was very little in films, and the content of Cr_2O_3 was much greater than $\text{Cr}(\text{OH})_3$. These species are the basic components of passive film. Figure 10 plots the XPS spectra for the passive film formed on 316L–0.21Sn specimen in 1 mol/L NaCl solution. The passive film also included the Fe^0 , Fe^{2+} and Fe^{3+} species, which was same as the 316L–0Sn sample. However, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreased after Sn alloying, which might be resulted from the decomposition of

magnetite [19]. The decreased ratio may influence the thickness of passive film [46, 47]. In Fig. 10b, there were three peaks in the $\text{Cr}2p_{3/2}$ spectra which could represent the Cr^0 , Cr_2O_3 and $\text{Cr}(\text{OH})_3$, respectively. And the concentration of Cr_2O_3 was higher than $\text{Cr}(\text{OH})_3$. As shown in Fig. 10c, the Sn spectra could be separated into three peaks, representing the Sn^0 , Sn^{2+} and Sn^{4+} species. The XPS test without sputtering proved that the outer layer of passive film was rich of Sn oxides [19]. A mixed passive film had formed on the Sn-added ASS sample. According to Table 4, the Cr/Fe ratio for 316L–0.21Sn was much greater than that of 316L–0Sn. This result suggested that the passive film was mainly composed of iron oxides for the 316L–0Sn sample, while the Cr and Sn were enriched in the passive film of 316L–0.21Sn sample, which could improve the pitting resistance of specimens [18, 19, 48]. This might be caused by the active dissolution of iron oxides and hydroxides in the passive film when the element Sn was alloyed. Compared with the 316L–0Sn sample, the formation of SnOHCl for the 316L–0.21Sn specimen led to a less aggressive environment around the sample surface, which might result in the different contents of Cr and Fe for different samples. The content ratio of Cr to Fe increased, indicating an improved pitting resistance [49].

In neutral media, the anodic reaction is principally the dissolutions of iron with some other elements, where the reaction is expressed as:

According to the Pourbaix diagram for the Sn/ H_2O -Cl system [34], the reaction of Sn in chloride solution is supposed to proceed as follows:

Fig. 9 XPS peak analysis for passive films on 316L–0 ASS in 1 mol/L NaCl solution: **a** Fe $2p_{3/2}$ spectra; **b** Cr $2p_{3/2}$ spectra

Fig. 10 XPS peak analysis for passive films on 316L-0.21Sn ASS in 1 mol/L NaCl solution: **a** Fe 2p_{3/2} spectra; **b** Cr 2p_{3/2} spectra; **c** Sn 3d_{3/2} spectra

Table 4 The derived composition data from XPS spectra for the 316L-0Sn and 316L-0.21Sn ASS samples (at%; the total atomic amounts of Cr, Fe, Sn and O elements have been set to 100 at%)

Material	O	Fe	Cr	Sn
316L-0Sn	64.98	30.49	4.53	—
316L-0.21Sn	67.10	14.85	12.01	6.04

The Sn(OH)₂ is unstable and may undergo both the dehydration to 2SnO·H₂O, 3SnO·H₂O, 5SnO·H₂O or SnO and the oxidation to SnO₂·nH₂O, where *n* can be 0, 1 or 2. SnO₂ can also be generated by the hydrolysis reaction:

And the Sn(OH)₄ can further dehydrate into SnO₂.

Sn is passivated in a moderately strong chloride solution, due to the formation of SnOHCl·H₂O [50],

As is known that the chloride ions can be absorbed on the surface as a result of the formation of a thin electrolyte layer in the chloride solution [24, 51], the chloride ions break down the passive film and lead to metastable pits firstly. The metastable pits will either grow up into stable pits and develop further in depth or be repaired by the re-passivation of metal. In this research, the reactions between Sn and the chloride solution produce the hydroxides and oxides of Sn and SnOHCl·H₂O. The mixed compounds of Sn, Fe and Cr form a stable passive film on the 316LX in chloride solution according to the XPS results. The compact and uniform passive layer that contained Sn oxides decreases the susceptibility of metastable pits, which was consistent with the conclusion of Luo et al. [19]. It could be explained by the pitting defect model. The absorbed Cl⁻ ions bind with the oxygen vacancy (V_o). When the concentration of V_o decreases, the equilibrium of reaction was broken and more V_o were

generated. In the present research, Cl⁻ preferentially formed the SnOHCl compound with Sn²⁺, which could reduce the probability for Cl⁻ to bind with V_o. The concentration of carriers decreased, and therefore, the passive film became more stable. At the same time, SnO₂ could block the aggressive ions that of high electronic conductivity and corrosion reactivity and thus improve the pitting resistance [52]. Meanwhile, it is shown in Table 4 that the Sn content in the passive film is more than that in the matrix. With the alloying of Sn to the austenitic stainless steel, the Fe content in passive film decreases from 30.49 at% to 14.85 at% and the Cr content increases from 4.53 at% to 12.01 at%. As is known that Cr is necessary to form a stable passive film to protect steels against corrosion, and the corrosion resistance increases with increasing amount of Cr [48], therefore, Sn addition has improved the content of Cr compound in the passive film, thus enhancing the pitting resistance of 316LX stainless steel.

4 Conclusions

1. The electrochemical corrosion characteristics and the properties of passive films of 316LX austenitic stainless steel with different Sn contents are investigated by the potentiodynamic polarization, CPT, EIS, MS measurements and the XPS characterization. With increasing the Sn content, the CPT, *E*_{corr} and *E*_{pit} values increase, demonstrating the enhanced pitting resistance of 316LX austenitic stainless steel. The surface morphology shows that all the pits are round-shaped. The current-time transient measurements reflect that the initiation of metastable pitting can be significantly inhibited by increasing the addition of Sn.
2. The values of *R*_p for the 316L-0.062Sn and 316L-0.21Sn samples are higher than that for the 316L-0Sn sample, showing that Sn has a positive effect on the stability and corrosion resistance of passive films. The donor density in passive films

decreases, leading to a lower passive current density and the less disordered passive films. The calculated thickness of passive film increases with the increase in Sn content. The results are in accord with previous results related to ferritic stainless steels.

3. XPS spectra illustrates the existence of Sn^{2+} and Sn^{4+} in the passive film. The Sn-rich oxide layer plays an important role in reducing the dissolution of specimen. The 316L–0.21Sn sample also has a higher content of Cr in the passive film.
4. On the basis of the above results, the compact and uniform Sn-rich passive layer decreases the susceptibility of metastable pits and improves the pitting resistance. In the meantime, the addition of Sn promotes the Cr content in the passive film so as to improve the stability of passive film.

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