

Article

Effect of Nitrogen on the Corrosion Resistance of 6Mo Super Austenitic Stainless Steel

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Abstract: 6Mo super austenitic stainless steel (SASS) with nitrogen contents of 0.2 and 0.4 (wt.%) was melted, and solution treatments at 1100, 1180, and 1250 °C for 30 min were performed. The effects of nitrogen on the microstructure and pitting resistance of the two steels that signed as 0.2N and 0.4N samples were investigated. At a heat-treatment temperature of 1180 °C, the alloy demonstrates the highest corrosion resistance, attributed to the combined effects of grain size and precipitates. The structure of the passivation film changes with increasing nitrogen content, with the Cr/Fe ratio is significantly higher in the 0.4N sample compared to the 0.2N sample. Moreover, the increase in nitrogen content results in thicker Cr and Mo oxide layers and higher levels of NH_3 and NH_4^+ , thereby improving the corrosion resistance of the stainless steel.

Keywords: super austenitic stainless steel; nitrogen; corrosion resistance; passive film



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1. Introduction

The 6Mo super austenitic stainless steel (SASS) is rich in a large amount of chromium, molybdenum and nickel. These elements facilitate the spontaneous formation of a continuous dense passive film on the surface, which significantly enhances the corrosion resistance and mechanical properties of stainless steel [1–3]. Currently, 6Mo SASS is widely used in aggressive environments such as the petrochemical industry, flue gas desulfurization, seawater desalination systems, and pulp mill bleaching systems. The research on the performance of 6Mo SASS has also attracted more and more researchers' interest. For instance, Sandra et al. [4] found that 6Mo high-nitrogen grade UNS S31266 showed excellent corrosion resistance in acidic media containing chloride. Behrens et al. [5] found that the combination of high nickel content and nitrogen in 6Mo super austenitic stainless steel resulted in favorable low sigma solvent temperatures, and high chromium and molybdenum content resulted in resistance to common forms of corrosion and localized corrosion in chlorine-containing media. Ren et al. [6] studied the effect of boron addition on the oxide skin of S31254 super austenitic stainless steel in high-temperature air, and the results showed that the addition of B could inhibit the diffusion of Mo to the surface and promote the diffusion of Cr to the surface to form a dense Cr_2O_3 film. Yang et al. [7] found that the grain boundary segregation of B and Ce had a significant inhibitory effect on precipitates, and the addition of B and Ce could greatly improve the corrosion resistance of S31254 SASS. Dou et al. [8] investigated the passivation performance of S31254 SASS in simulated condensate after flue gas desulfurization at different temperatures. The results revealed that acidic condensation accelerated the preferential dissolution and subsequent precipitation of Fe and the oxidation of Mo, resulting in the formation of a mixed Cr-Fe-Mo oxide/hydroxide surface layer. Chen et al. [9] studied the effect of Cl^- on the corrosion and passivation behavior of the same steel in blast furnace gas (BFG) electrolyte. The results indicated that the passivation ability of S31254 SASS was greater under low-chloride ion concentrations compared to high concentrations. In addition, Liu et al. [10] reported that the pH value significantly influenced the passivation behavior of S31254 SASS in NaCl

solution. In weakly acidic and strongly acidic solutions, the main components of the passive film outer layer were iron oxide and $\text{Cr}(\text{OH})_3$, respectively. Li et al. [11] demonstrated that the corrosion resistance of 6Mo SASS initially improved but later weakened with increasing copper content.

The influence of nitrogen on the properties of stainless steel has drawn significant attention from researchers. Nitrogen not only enhances the re-passivation ability of stainless steel but also plays a crucial role in improving the passive film [12,13]. For example, Aamani et al. [14] observed that nitrogen addition leads to grain refinement and an increased proportion of low-energy boundaries, thereby enhancing corrosion resistance. Loable et al. [15] reported a synergistic effect between nitrogen and molybdenum on the pitting potential. Moreover, Dai et al. [16] demonstrated that nitrogen significantly enhances the corrosion resistance of 316 L stainless steel in a thiosulfate-chlorine solution by promoting the formation of chromium oxide and iron oxide in the passive film. Gao et al. [17] reported a higher proportion of stable oxides, such as chromium oxide, in the passivation film of high-nitrogen stainless steel. The results also revealed that the content of ammonium ions is higher in high-nitrogen stainless steel, effectively inhibiting passive film breakdown and pitting. Furthermore, Zhang et al. [18] investigated the impact of nitrogen on precipitation behavior, intergranular corrosion resistance, and mechanical properties of S32654 SASS. The results indicated that S32654 with medium nitrogen content exhibits the smallest total amount of precipitates after aging treatment and the best intergranular corrosion resistance. Nevertheless, the influence of nitrogen content on the corrosion resistance and passive film structure of 6Mo SASS remains unclear.

In this study, 6Mo SASS with nitrogen contents of 0.2 and 0.4 (wt.%) was melted and solid solution treatments at 1100, 1180, and 1250 °C for 30 min were performed. The effects of nitrogen on the microstructure and pitting resistance of the two steels with different solution treatments were investigated. The impact of nitrogen on the structure of passive film was studied using X-ray photoelectron spectroscopy (XPS) analysis.

2. Experimental Procedure

2.1. Material Preparation

Super austenitic stainless steels with nitrogen contents of 0.2 and 0.4 wt.% were prepared for this study. The steels were melted in a 25 kg vacuum induction furnace and deoxidized using nickel magnesium. The steels were cast into ingots and subsequently rolled into plates through forging. The chemical composition of the steel was quantitatively analyzed using the inductance method, and the results are presented in Table 1.

Table 1. Chemical composition of test steel/wt.%.

NO.	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	B	N	Fe
0.2N	0.019	0.59	1.55	0.009	0.005	19.88	18.69	6.14	1.02	0.004	0.20	Bal.
0.4N	0.013	0.54	1.56	0.007	0.004	20.34	18.89	6.14	0.98	0.004	0.38	Bal.

The hot-rolled plates were then cut into blocks with dimensions of 15 mm × 15 mm × 2 mm using a wire-cutting machine. After solution treatment at temperatures of 1100 °C, 1180 °C, and 1250 °C for 30 min, the samples were rapidly quenched in water. The samples after solution treatment were denoted as 0.2N-ST and 0.4N-ST.

2.2. Microstructure Characterization

All samples were polished with SiC papers up to 3000 grit and cleaned with ethanol and distilled water in an ultrasonic bath. Then, the samples were etched with aqua regia for microstructure observation. The microstructure was observed using a Leica DM 6 M optical microscopy (OM) (Leica, Solms, Germany), an EVO18 scanning electron microscope (SEM) (JEOL, Tokyo, Japan), and a Rigaku Smatlab (Malvern Panalytical, Malvern, UK)

X-ray diffraction (XRD). The number and size of grains and precipitates were quantified using Image Pro Plus 6.0 software.

2.3. Electrochemical Experiment

The open circuit potential (OCP) of solution-heat treated samples was tested in a 3.5% NaCl solution with a pH of 1 for 60 min to ensure the stability of the open potential before conducting the potential polarization test. In the potentiodynamic polarization test, the scanning rate was set to 1.667 mV/s, with a scanning range between -0.5 V and 1.5 V, and scanning stopped when the current density reached 10^{-2} mA. For the potentiostatic polarization test, a potential of 0.4 V was applied for 10 min, as this potential falls within the passivation range of a 3.5% NaCl solution with a pH of 1. Electrochemical impedance spectroscopy (EIS) was performed under a 10 mV sinusoidal AC disturbance with a frequency of 100 kHz to 0.01 Hz to study the corrosion resistance of passive films. The experimental data were fitted and analyzed using Zview software (3.0a Scribner Associates, Inc., Southern Pines, NC, USA). Each experiment was repeated at least three times to ensure repeatability. Mott–Schottky curves were generated by setting the frequency to 1000 Hz, the amplitude to 10 mV, and the potential step size to 10 mV within the range of 0 to 1.2 V. Each experiment was repeated at least three times to ensure repeatability.

2.4. XPS Analysis

To elucidate the relationship between the passive film composition of 0.2N-ST and 0.4N-ST stainless steel with depth, the passive film composition of samples heat-treated at 1180 °C was characterized using XPS. The passive film of the sample was polarized at 0.4 V in 3.5% NaCl solution with a pH of 1. The sputtering rate was calibrated with silica and was about 3 nm/min. The photoelectron peak binding energy of other elements was corrected using the position of the hydrocarbon C 1s peak of 284.8 eV. XPS peak 41 software was utilized to fit the spectrum, and a Shirley-type correction method was applied for background subtraction.

3. Results and Discussion

3.1. Microstructure Characterization

Figures 1 and S1 are OM images of 6Mo super austenitic stainless steel after hot rolling and solution treatment at different temperatures, respectively. It can be seen from Figure S1 that the grain size of the two alloys without solution treatment is relatively small. However, there are a lot of precipitated phases in both samples, which will seriously reduce the corrosion resistance of the hot-rolled steel. Figure 2 shows the SEM image after solution treatment. No precipitates are observed in the samples heat-treated at 1180 °C and 1250 °C. Meanwhile, an undissolved second phase is presented in the samples treated at 1100 °C due to a lower heat treatment temperature. The change in particle size with solution temperature is illustrated in Figure 3. The results indicate that the average grain size of both samples increases with the increase in solution temperature. Furthermore, under all conditions, the grain size of the 0.4N-ST sample is smaller than that of the 0.2N-ST sample, suggesting that the increase in nitrogen content has a positive effect on grain refinement.

Figure 4 shows the XRD diffractograms of the two alloys after solution treatment at 1180 °C. All peaks belong to the austenitic phase of the face-centered cubic structure, mainly including γ (111), γ (200), and γ (220). It can be seen from Figure 4b that the γ (111) diffraction peak of the 0.4N sample slightly shifts to a lower angle than that of 0.2N sample. The change in the peak position of the austenite diffraction peaks is related to the change in the lattice parameters of the austenite phase, and the increase of nitrogen atoms may cause lattice distortion [19,20].

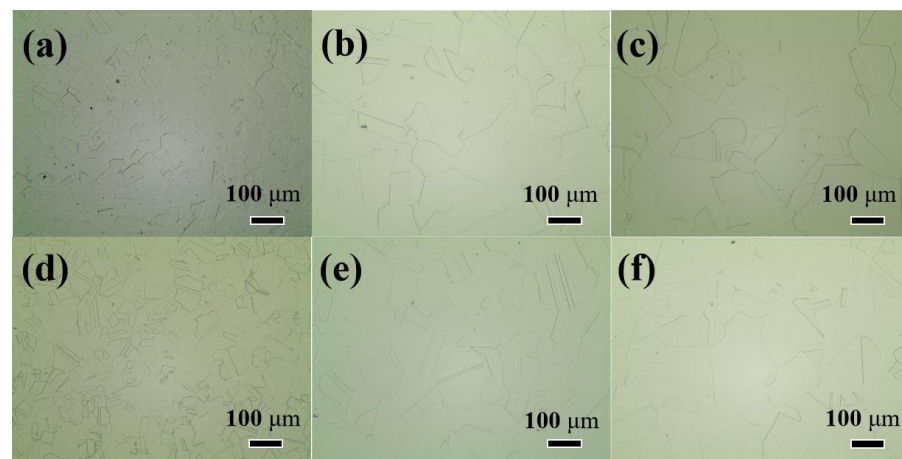


Figure 1. The OM observation of 0.2N-ST (a–c), 0.4N-ST (d–f) alloy solution at 1100 °C (a,d), 1180 °C (b,e), and 1250 °C (c,f) for 30 min.

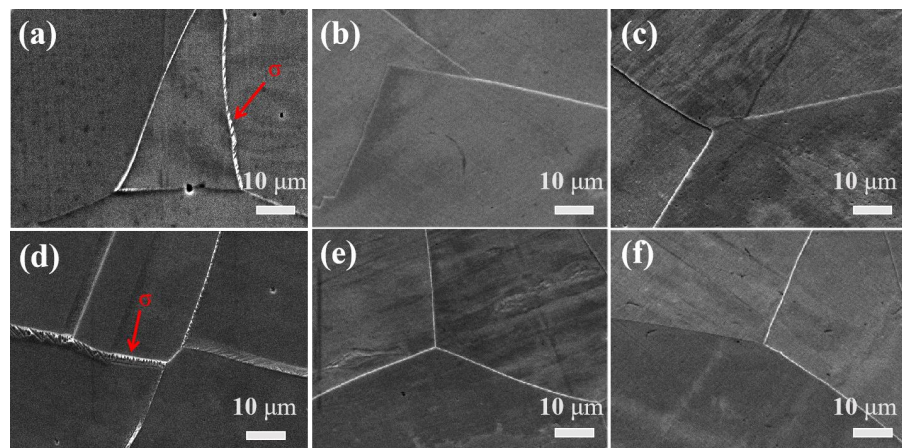


Figure 2. The SEM observation of 0.2N-ST (a–c), 0.4N-ST (d–f) alloy solution at 1100 °C (a,d), 1180 °C (b,e), and 1250 °C (c,f) for 30 min.

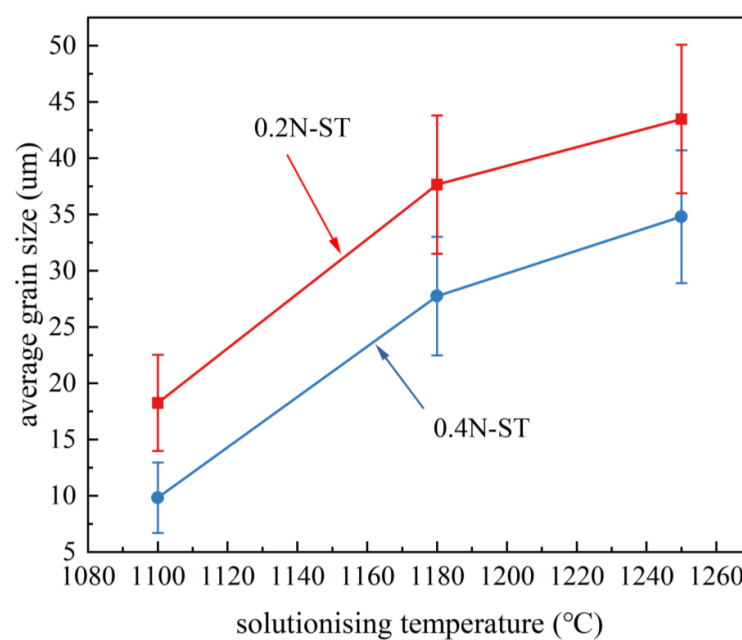


Figure 3. Average grain size as a function of solution temperature.

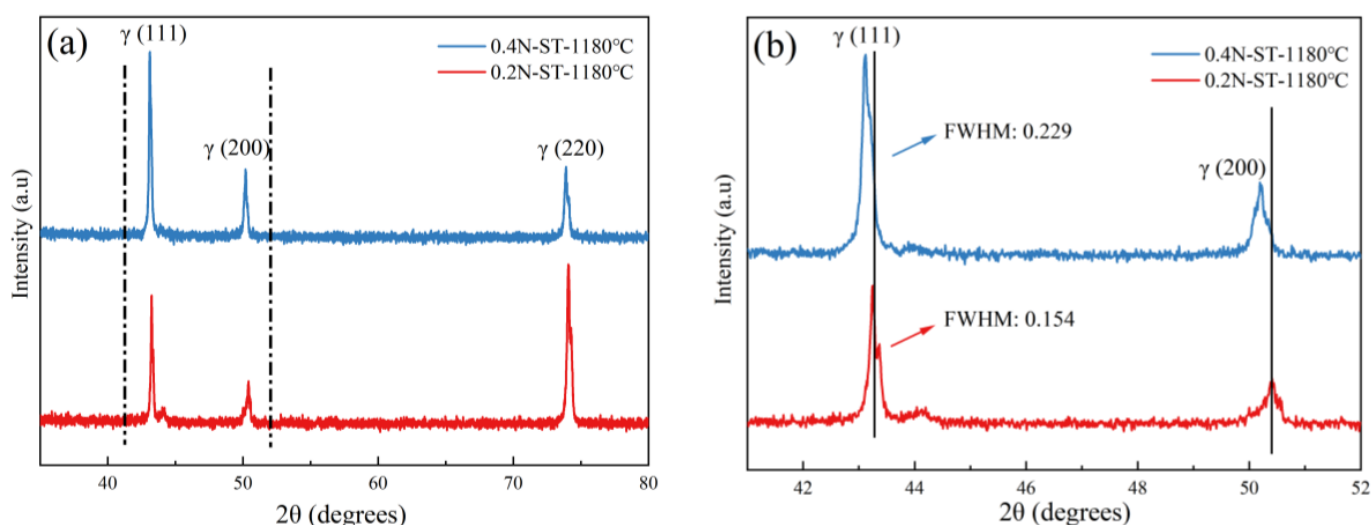


Figure 4. XRD diffractograms of the two alloys after solution treatments at 1180 °C. (a) XRD diffractograms; (b) high magnification in (a) at 2θ range from 42° to 52°.

3.2. Polarization Curve Measurements

Figure 5a shows the potentiodynamic polarization curve of 6Mo SASS in a 3.5% NaCl solution with pH = 1. Each curve exhibits a wide passive region with a passive potential value between −0.3 and 0.9 VSCE. During the process of spontaneous passivation, active/passive transient peaks are observed in each curve. Table 2 lists the electrochemical parameters derived from the polarization curve, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), and pitting potential (E_p). It can be seen that the change in nitrogen content and solution temperature has no effect on E_{corr} and E_p , but the corrosion current is different. The i_{corr} of both samples reaches its minimum under the solution heat-treatment condition of 1180 °C. However, under the same condition, the i_{corr} of 0.4N-ST samples is lower than that of 0.2N-ST samples, indicating that the corrosion resistance of passivated film is better [21,22]. Figure S2 shows the surface morphology of the 0.2N sample after solution treatment at 1180 °C following potentiodynamic polarization measurement. It can be seen that pitting pits appear on the surface of the material after potentiodynamic polarization measurement.

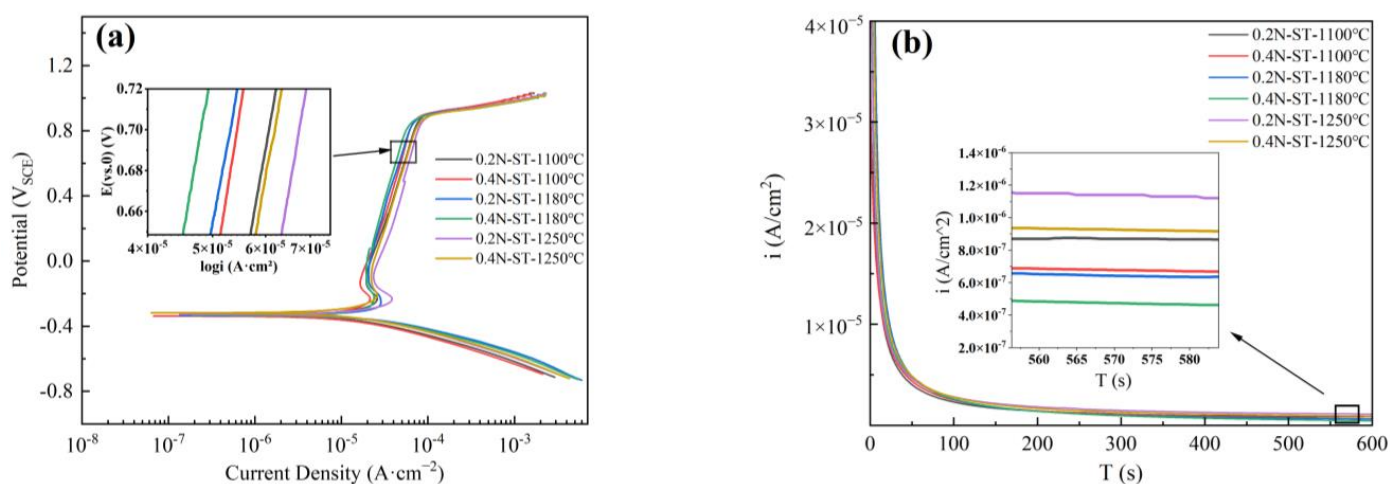


Figure 5. Potentiodynamic (a) and potentiostatic (b) polarization curve of 6Mo SASS sample in 3.5% NaCl with pH = 1.

Table 2. Electrochemical parameters derived from potentiodynamic polarization curves in Figure 5a.

NO.	Temperature/°C	$E_{\text{corr}}/V_{\text{SCE}}$	i_{corr}	E_p/V_{SCE}
0.2N-ST	1100	−0.338	2.231×10^{-5}	0.887
	1180	−0.339	1.338×10^{-5}	0.888
	1250	−0.333	2.611×10^{-5}	0.884
0.4N-ST	1100	−0.339	1.355×10^{-5}	0.889
	1180	−0.336	0.889×10^{-5}	0.889
	1250	−0.332	2.072×10^{-5}	0.886

The change in current density with passivation time is presented in Figure 5b. In the initial stage of potentiostatic polarization, the current density of all samples sharply decreases with time, indicating that the growth rate of the passive film exceeds the dissolution rate [23]. Subsequently, the current density gradually decreases and eventually stabilizes. Each curve exhibits a smooth shape, suggesting no breakdown in the passive film [10], and almost no metastable pitting process occurs during the entire measurement period. In addition, the current density first decreases and then increases with the increase in heat treatment temperature. The current density of both samples reaches its minimum when the heat-treatment temperature is 1180 °C. Notably, the current density of 0.4N-ST consistently remains lower than that of 0.2N-ST, indicating that passivation is more likely to occur at higher nitrogen contents.

Grain size significantly influences the corrosion resistance of stainless steel, generally improving as grain size decreases. A study reported that an increase in grain boundary density promotes Cr diffusion to the surface, facilitating the rapid formation of a uniform passivation film rich in Cr, thus enhancing corrosion resistance [24]. Although the sample after the solid solution at 1100 °C has a small grain size, the corrosion resistance is decreased due to incomplete dissolution of the second phase. Therefore, considering the combined effects of grain size and precipitates, the sample heat-treated at 1180 °C exhibits the best corrosion resistance.

3.3. Electrochemical Impedance Spectroscopy Measurements

The EIS are presented in Figure 6. It can be seen that compared with the sample of 0.2N-ST, the impedance mode and phase angle of the sample of 0.4N-ST in the low-frequency region are reduced, indicating that the corrosion resistance is improved [25,26]. Figure 6a indicates that the Nyquist diagram of each sample exhibits an arc feature, with larger arc radii indicating greater charge transfer resistance and thus better corrosion resistance. The arc radius of both samples is the largest for solution heat treatment at 1180 °C. At the same condition, the arc radius of the 0.4N-ST sample is larger than that of the 0.2N-ST sample, indicating superior corrosion resistance.

The EIS results were fitted using the equivalent circuit diagram shown in Figure 6a, and the fitting results are presented in Table 3. Here, R_s represents the resistance of the electrolyte solution, while R and CPE represent the resistance and capacitance of the passive film, respectively. The total impedance value of the circuit is expressed by

$$Z = R_s + \frac{1}{R + (j\omega)^n Q} \quad (1)$$

where Q is the CPE constant, ω is the angular frequency, j is the imaginary unit, and n is the CPE adjustment parameter. CPE behaves as an ideal capacitor when n is equal to 1 [27]. The χ^2 sum of each fitting value is small, indicating a small fitting error; thus, the EIS data after fitting has high reliability. With the increase in solution temperature, the R -value initially increases and then decreases. The R -value increases with the increase in nitrogen content, indicating a decrease in the charge transfer rate [28] and an improvement in the corrosion resistance of the steel.

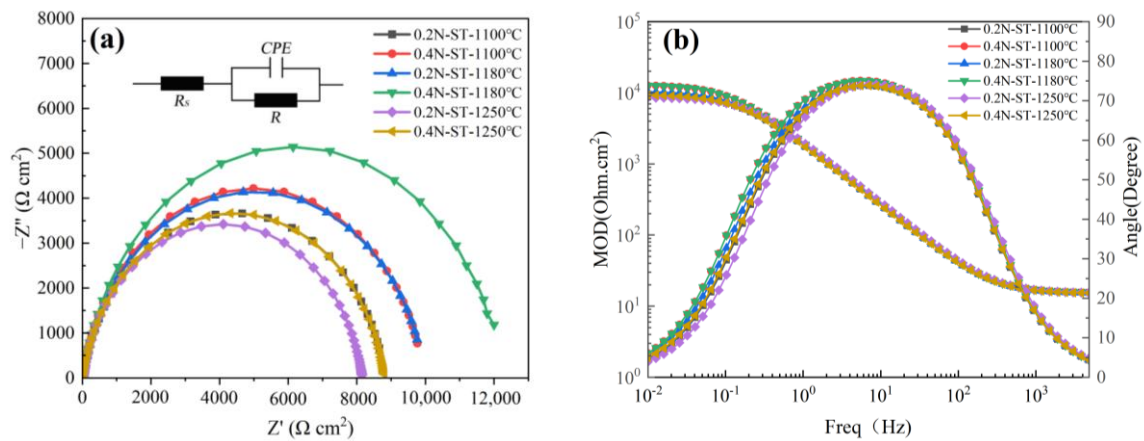


Figure 6. EIS of a 6Mo SASS sample in 3.5% NaCl with pH = 1. (a) Nyquist. (b) Byrd.

Table 3. Impedance spectrum fitting parameters of 6Mo SASS samples in 3.5% NaCl with pH = 1.

NO.	Temperature/°C	R_s/Ω	$Q/\times 10^{-5} \text{ F}$	N	R/Ω	$\sum \chi^2/\times 10^{-3}$
0.2N-ST	1100	18.17	10.308	0.8840	8813	1.601
	1180	18.03	10.459	0.8825	9985	1.604
	1250	18.17	9.207	0.8896	8143	1.692
0.4N-ST	1100	17.95	9.716	0.8958	9944	1.659
	1180	18.03	9.732	0.8884	12,264	1.609
	1250	18.57	10.593	0.8847	8795	1.806

3.4. Mott–Schottky Analysis

Mott–Schottky theory was employed to study the semiconductor properties of the stainless-steel surface passive film. The relationship between the space charge capacitance of the passive film and the applied potential is shown as follows:

$$\frac{1}{C^2} = \pm \frac{2}{\epsilon \epsilon_0 e N} \left(E - E_{fb} - \frac{KT}{e} \right) \quad (2)$$

where the positive sign and the negative sign represent n-type semiconductor and p-type semiconductor, respectively, ϵ is the dielectric constant, ϵ_0 is the vacuum dielectric constant ($8.854 \times 10^{-14} \text{ F cm}^{-2}$), e is the electron charge ($1.6 \times 10^{-19} \text{ C}$), N is the donor concentration (N_D) or acceptor concentration (N_A), T is the absolute temperature, K is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), E is the external electrode potential (VSCE), and E_{fb} is the flat band potential. Figure 7 illustrates the Mott–Schottky diagram of the 6Mo SASS samples under a 3.5% NaCl solution with pH = 1. All samples exhibit n-type semiconductor characteristics in the range of 0.1 to 0.75 VSCE, attributed to the outer layer's richness in Cr-Fe oxide and hydroxide. At higher potentials, the passive dissolution of the passive film leads to the accumulation of cation vacancies, resulting in all samples exhibiting p-type semiconductor characteristics above 0.75 VSCE [29].

The conductivity of the passive film is a critical parameter dictating the electrochemical corrosion resistance. The values of N_D and N_A determine the conductivity of the passive film. Figure 8 illustrates N_D and N_A values calculated from the slope of the Mott–Schottky curve according to Equation (2). The N_D and N_A values of the samples with different nitrogen contents reach their minimum under the solution heat-treatment condition of 1180 °C. However, in comparison with the sample of 0.2N-ST under the same condition, 0.4N-ST exhibits lower N_A and N_D values, indicating that the passive film defects formed by the 0.4N-ST sample are fewer than those of the 0.2N-ST sample. This suggests that the passive film of 0.4N-ST is more effective in preventing charge transfer, thereby reducing the possibility of passive film breakdown and pitting.

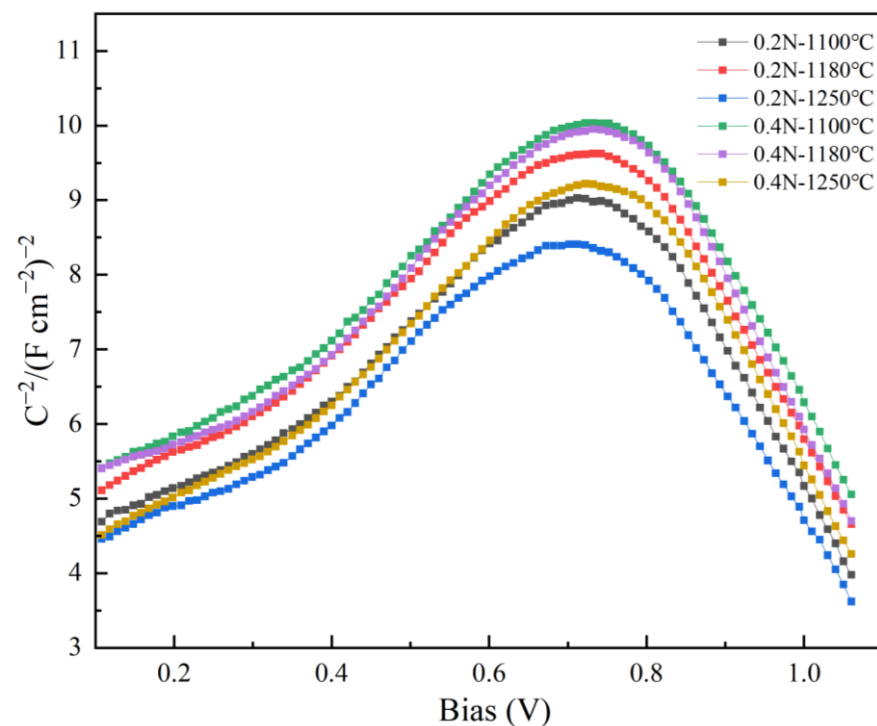


Figure 7. Mott-Schottky plots of a 6Mo SASS sample in 3.5% NaCl with pH = 1.

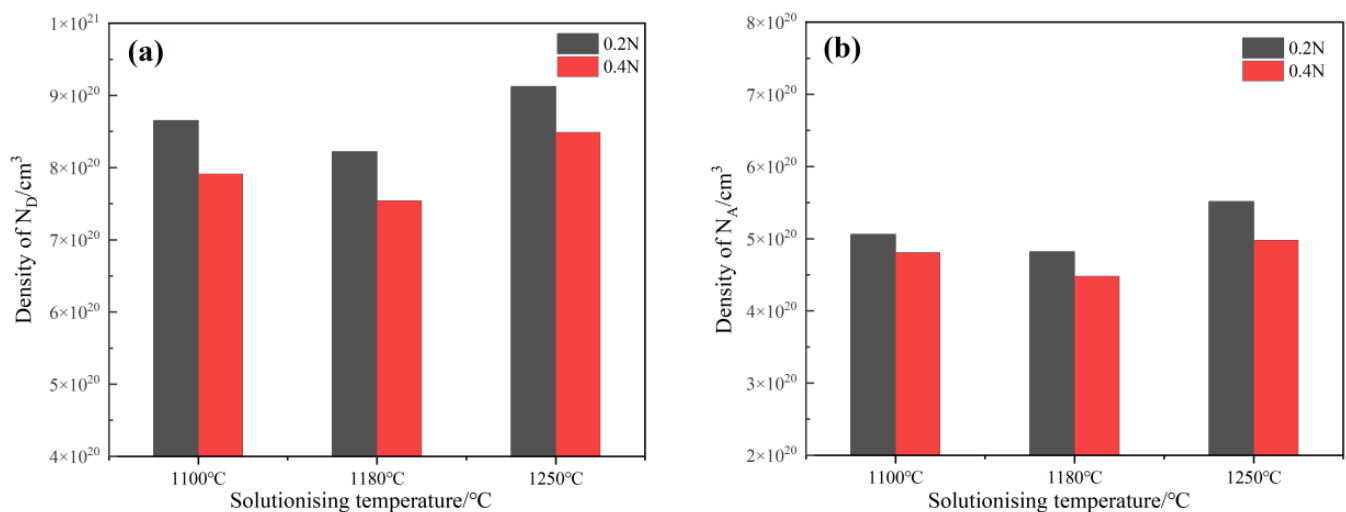


Figure 8. Density of N_D (a) and N_A (b) of 6Mo SASS sample in 3.5% NaCl with pH = 1.

3.5. XPS Analysis

Figure 9 illustrates the variation in element contents within the passive film over sputtering time after solution heat treatment at 1180 °C for the two samples. As sputtering time increases, the oxygen content consistently decreases, while the iron content progressively increases until stabilizing after 60 s. This phenomenon indicates the transformation of passive film to matrix. In the 0.2N-ST sample, the Fe content is consistently greater than that of Cr, whereas in the 0.4N-ST sample, Cr content exceeds Fe content in the initial sputtering stages (before 10 s) and is smaller between 10 s and 20 s. The Ni content shows significant depletion in the surface layer of the passive film, reaching its maximum at 30 s, indicating that Ni mainly exists in the inner layer of the passive film. No Ni was detected on the surface layer of the 0.2N-ST sample, suggesting that the increase in N content could partially inhibit Ni depletion on the film's surface.

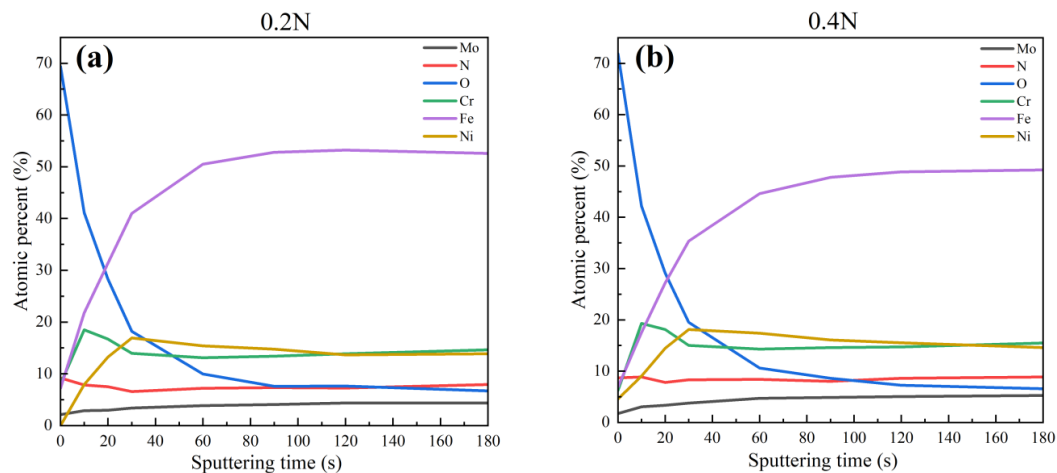
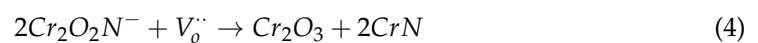


Figure 9. The change in passive film element concentration with sputtering time in 0.2N-ST (a) and 0.4N-ST (b) samples.

Ni and N exhibit a synergistic effect in enhancing the corrosion resistance of nitrogenous stainless steel [30]. N significantly contributes to improving the alloy's corrosion resistance. However, it also reduces the protective effect of the passive film at a certain depth by reducing the fraction of chromium ions in the film. When there is a small amount of Ni present in the alloy, N further enhances the protective capability of the passive film by increasing the Cr fraction within the film. As a result, the impact of increased N content on the pitting potential level is more pronounced. The depletion of Ni in the surface layer may be one reason for the alloy's decreased corrosion resistance.



Figures S3–S5 show the spectral changes of Cr 2p_{3/2}, Fe 2p_{3/2}, and Ni 2p_{3/2} passive films with sputtering time, respectively. As sputtering time increases, the content of Cr(OH)₃ decreases, and the spectral intensity of metal Cr increases. This indicates that Cr(OH)₃ predominantly exists in the outer layer of the passive film. Cr(OH)₃ may undergo hydrolysis into Cr³⁺ (as shown in Equation (3)), resulting in a depletion of Cr in the passive film and a reduction in corrosion resistance [31]. Some N atoms existing in the form of Cr₂O₂N[−] can neutralize oxygen vacancies and form Cr₂O₃ and CrN (as shown in Equation (4)), thereby reducing donor density and enhancing the protective ability of passive film [32]. As sputtering time increases, the content of FeOOH decreases, indicating that FeOOH primarily appears in the outer layer of the passive film. According to the Fe²⁺ to Fe³⁺ ratio, the outer layer of the passive film consists mainly of Fe³⁺ (as shown in Equations (5) and (6)). As sputtering time further increases, the content of Fe²⁺ increases (as shown in Equation (7)). As we all know, Fe³⁺ is more stable than Fe²⁺; Fe³⁺ and Cr₂O₃ are the effective components of passive film, and their content ratio can determine the performance of the passive film [33]. At the same sputtering depth, the content of Cr₂O₃ in the 0.4N-ST sample is higher than that in the 0.2N-ST sample, and the Fe²⁺/Fe³⁺ ratio of

0.4N-ST sample is lower than that of the 0.2N-ST sample. Throughout the entire sputtering process, Ni mainly exists in the metallic state, indicating that Ni oxides and hydroxides are not the main components of the passive film. However, the presence of Ni reduces the conductivity of the passive film, promoting the formation of more resistive oxide films and thereby improving the film's protective effect [34].

Figure 10 illustrates the change in Mo 3d spectra of passive films for the two samples over sputtering time. Due to spin-orbit coupling, Mo $3d_{5/2}$ and Mo $3d_{3/2}$ exist in Mo elements, resulting in six component peaks in Mo 3d photoelectron spectra. These include metallic Mo at 227.7 ± 0.1 eV and 230.8 ± 0.1 eV, Mo⁴⁺ at 228.6 ± 0.1 eV and 231.7 ± 0.1 eV, and Mo⁶⁺ at 232.2 ± 0.1 eV and 235.3 ± 0.1 eV, respectively [11,35]. Notably, Mo⁶⁺ represents the predominant Mo oxide which effectively prevents the outward dissolution of certain cations, thereby favoring the passivation of stainless steel. At the initial stage of sputtering, the Mo⁶⁺ content is highest. However, as sputtering time increases, the Mo⁶⁺ content gradually decreases, and the content of Mo⁴⁺ gradually increases. The results show that Mo mainly exists in the form of Mo⁶⁺ and Mo⁴⁺ in the outer and inner layers of the passive film, respectively. After sputtering for 30 s, only metallic Mo and Mo⁴⁺ were detected in the 0.2N-ST sample, while a small amount of Mo⁶⁺ persists in the 0.4N-ST sample even after 30 s, and the content of Mo⁴⁺ was larger.

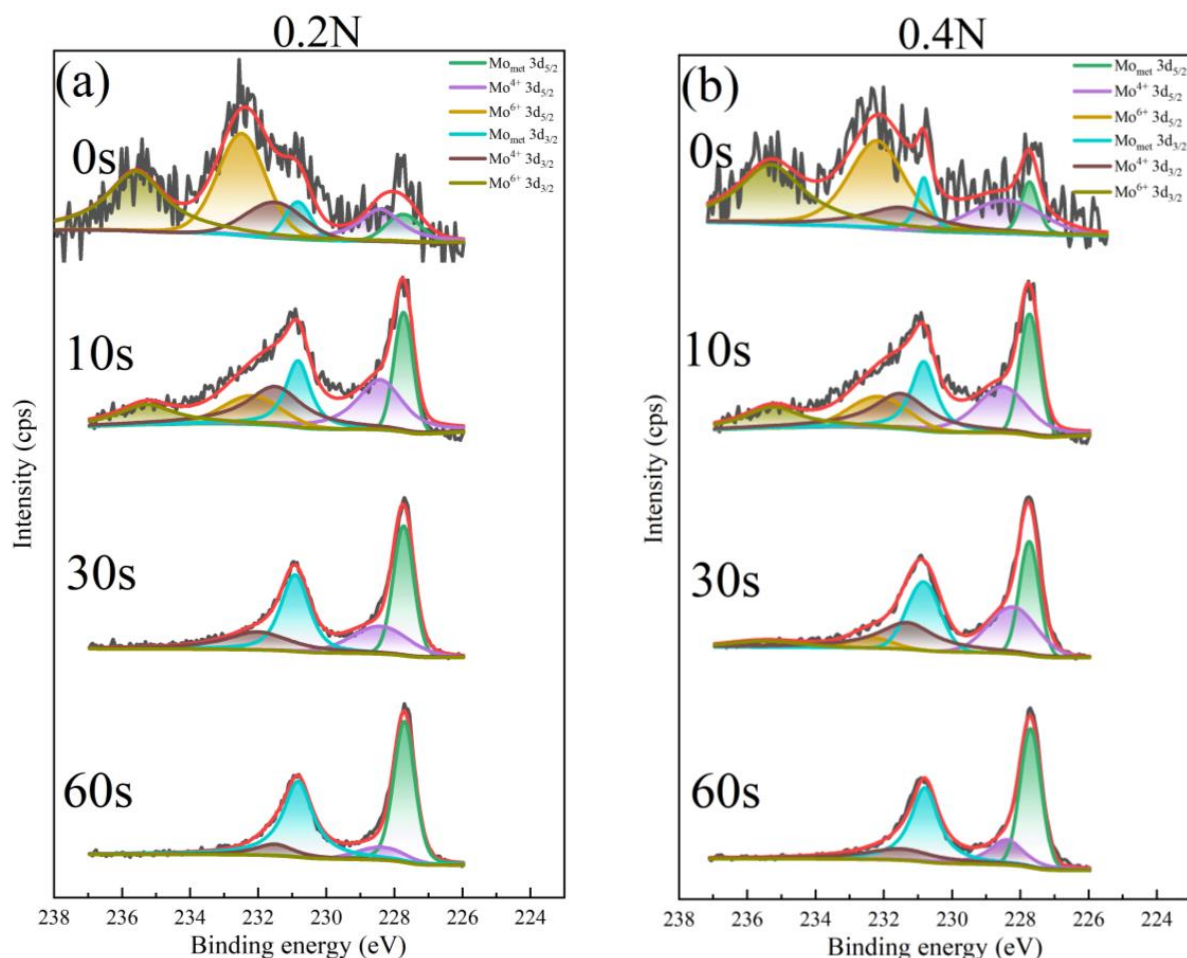


Figure 10. The change in Mo 3d spectra of 0.2N-ST (a) and 0.4N-ST (b) samples with sputtering time.

Figure 11 illustrates the change in N 1s spectra of passive films for the two samples with sputtering time. N mainly exists in the form of CrN, NH₃, and NH₄⁺, with corresponding binding energies of 396.8 ± 0.1 eV, 399.2 ± 0.1 eV, and 400.3 ± 0.1 eV, respectively [16]. As sputtering time increases, the contents of NH₃ and NH₄⁺ gradually decrease. After

sputtering for 30 s and 60 s, only CrN is detected in the 0.2N-ST and 0.4N-ST samples, respectively, indicating that NH_3 and NH_4^+ are confined to the outer layer of the passive film. CrN effectively promotes the formation of Cr_2O_3 and enhances the protection of passive film [36]. Meanwhile, N improves the re-passivation ability of stainless steel by consuming H^+ in the pit cavity to inhibit acidification (as shown in Equations (8) and (9)), thereby preventing the development of metastable pits and inhibiting thiosulfate reduction [37,38]. The increase in N content, as confirmed by the CrN, NH_3 , and NH_4^+ content in Figure 11, enhances the corrosion resistance of the steel. The possible reactions involved are as follows.

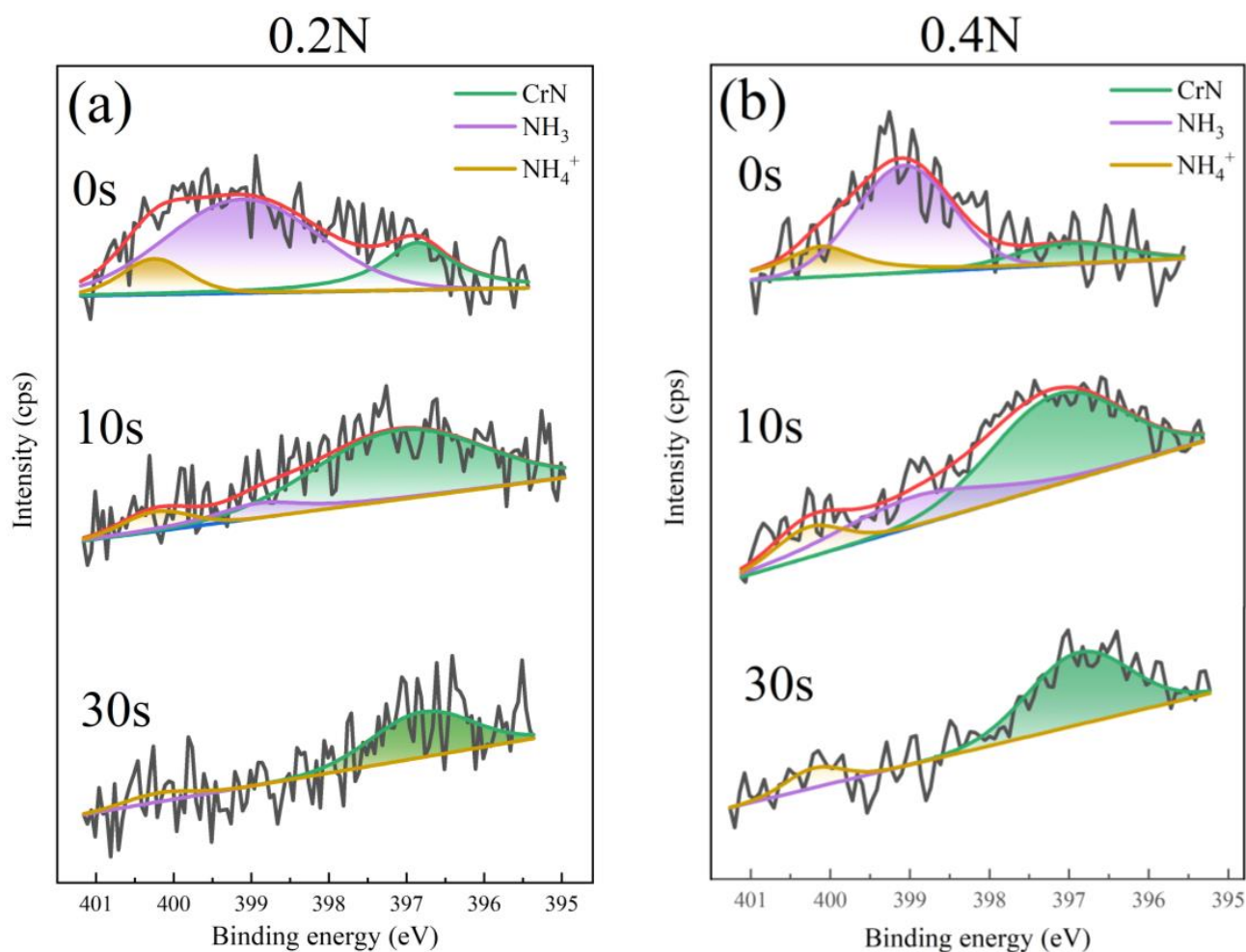


Figure 11. The change in N 1s spectra of 0.2N-ST (a) and 0.4N-ST (b) samples with sputtering time.

Figure 12 illustrates the composition of the passive films of the two samples after sputtering for 10 s. The Cr/Fe ratio of the 0.4N-ST sample is significantly higher than that of the 0.2N-ST sample. This indicates that the repair rate of the passive film increases relative to the dissolution rate with the increase in nitrogen content. Furthermore, the increase in nitrogen content promotes the formation of more Cr-rich oxides, thereby enhancing the stability of the passive film. Previous studies [15] have demonstrated that N and Mo synergistically improve the corrosion resistance of the alloy. Nitrogen effectively promotes the formation of metastable re-passivation, thereby inhibiting pit growth. In addition, nitrogen buffers the drop in pH and stabilizes molybdate, with molybdate also contributing to the formation of ammonium. Figure 12 indicates that the contents of NH_3 and NH_4^+ , as well as Mo^{6+} and Mo^{4+} , on the surface layer of the passive film increase with the increase in nitrogen content.

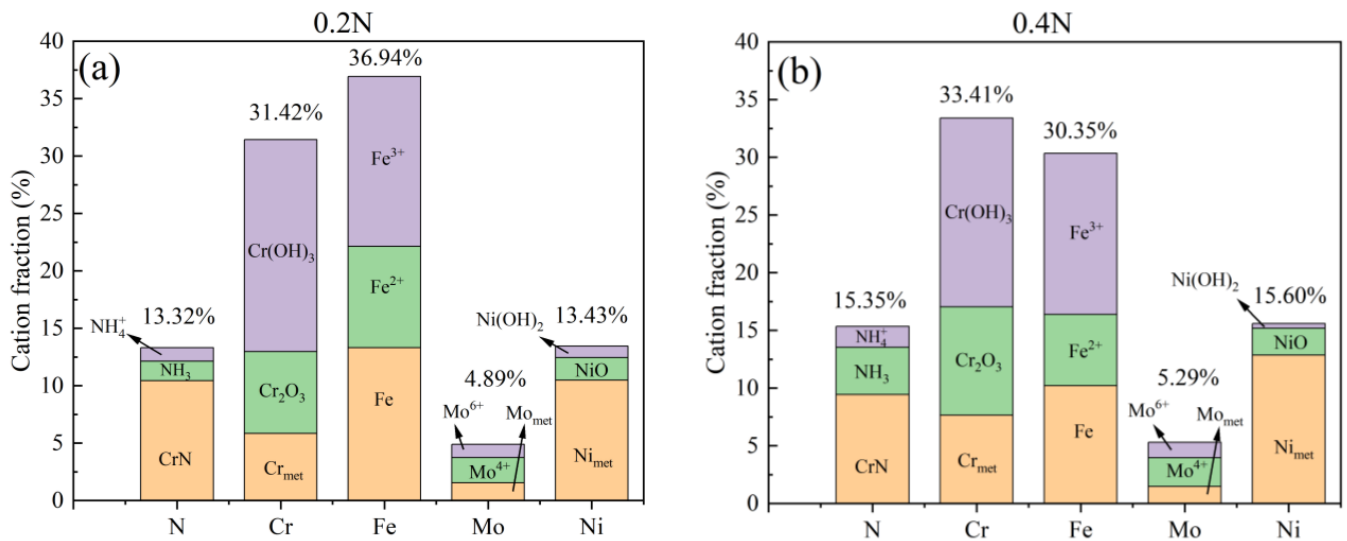


Figure 12. Surface passive film composition of 0.2N-ST (a) and 0.4N-ST (b) samples.

Based on the content of each element, the XPS fitting results and the model diagram of the mass fraction of the passive film with the sputtering depth were obtained. Figure 13 demonstrates the gradual transition from the surface layer of the passive film to the metal matrix. The outer layer of the passive film is rich in Cr, while the inner layer is rich in Fe. The hydroxides of Fe, Cr, and Ni mainly appear in the outer layer, while the inner layer mainly consists of oxides, with Cr oxide being the thickest. The Cr oxide of the 0.4N-ST sample is thicker than that of the 0.2N-ST sample. NH_3 and NH_4^+ mainly appear in the outer layer, while N in the inner layer mainly exists in the form of CrN. NH_3 and NH_4^+ , as well as Mo^{6+} and Mo^{4+} , in the 0.4N-ST sample are thicker than those in the 0.2N-ST sample.

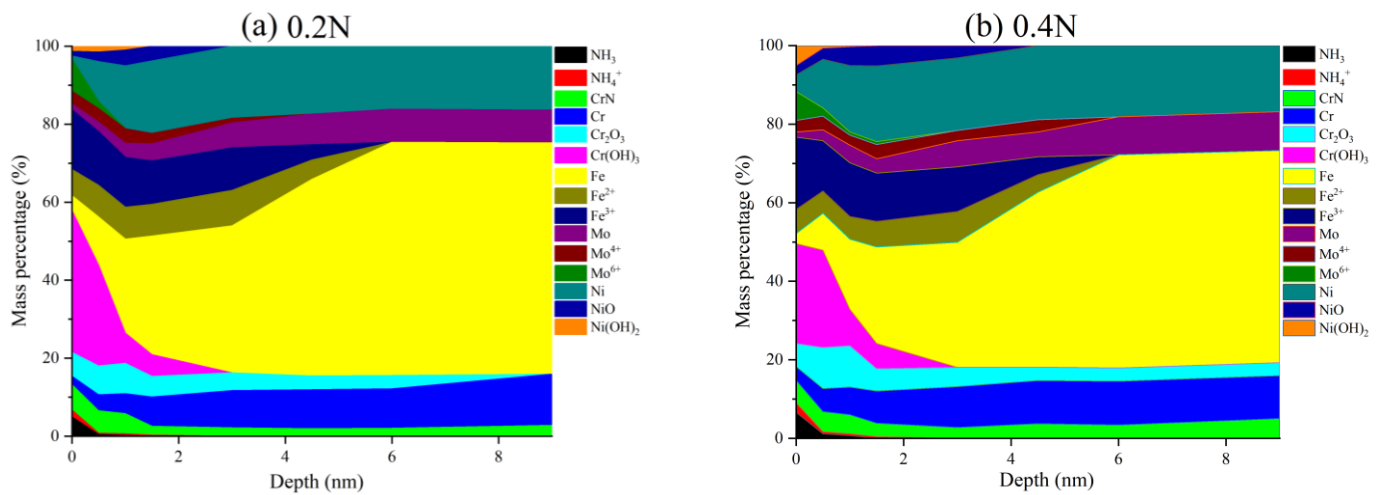


Figure 13. Mass fraction of passive films in 2N-ST (a) and 0.4N-ST (b) samples varies with sputtering depth.

4. Conclusions

The 6Mo SASS samples containing 0.2 and 0.4 wt.% nitrogen were prepared and subjected to solution treatment at temperatures of 1100, 1180, and 1250 °C for 30 min. Then, the influence of nitrogen on the microstructure, corrosion resistance, and passivation film structure of 6Mo SASS was studied. The findings are summarized as follows.

1. With increasing solution temperature, the grain size gradually increases, and alloys treated at 1100 °C exhibit incompletely dissolved second phases. The addi-

- tion of nitrogen effectively inhibits the grain growth of 6Mo SASS during solution heat treatment.
2. At a heat-treatment temperature of 1180 °C, the alloy demonstrates the highest corrosion resistance, attributed to the combined effects of grain size and precipitates. In 3.5% NaCl solution with pH = 1, the corrosion resistance and re-passivation ability of 6Mo SASS were improved when the nitrogen content was increased from 0.2% to 0.4% wt.%.
 3. Mott–Schottky and XPS analyses revealed that when the nitrogen content increased from 0.2% to 0.4%, the density of the donors and acceptors decreased and the structure of the passivation film changed, the Cr/Fe ratio at 0.4N being significantly higher than that at 0.2N. Moreover, the increase in nitrogen content results in thicker Cr and Mo oxide layers and higher levels of NH₃ and NH₄⁺, thereby improving the corrosion resistance of the stainless steel.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met14040391/s1>, Figure S1. The OM observation of 0.2 N (a) and 0.4 N (b) hot-rolled alloys. Figure S2. Corrosion morphology after potentiodynamic polarization test in 3.5% NaCl with pH = 1. Figure S3. The change of Cr 2p spectra of 0.2N-ST (a) and 0.4N-ST (b) samples with sputtering time. Figure S4. The change of Fe 2p spectra of 0.2N-ST (a) and 0.4N-ST (b) samples with sputtering time. Figure S5. The change of Ni 2p spectra of 0.2N-ST (a) and 0.4N-ST (b) samples with sputtering time.

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