Comparison Study on the Semiconductive and Dissolution Behaviour of 316L and Alloy 625 in Hydrochloric Acid Solution

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Received: 3 September 2019 / Revised: 23 September 2019 / Published online: 17 December 2019
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Abstract

The corrosion behaviour of 316L and Alloy 625 was investigated using cyclic polarization, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy, Auger electron spectroscopy and induced coupled plasma-optical emission spectrometer. The results indicated that Alloy 625 showed better corrosion resistance than 316L and the prolonging immersion time could enhance corrosion resistance of the two alloys. The passive film formed on the surface of 316L exhibited an electronic structure of p–p heterojunction, with Fe_3O_4 and Cr_2O_3 enriched in the outer and inner layers, respectively. However, Alloy 625 presented the electronic structure of n–p heterojunction dominated by the outer $\text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4$ and inner Cr_2O_3 . This resulted in the opposite semiconductive properties of the passive films formed on the two materials. In the acid solutions, Fe and Mo suffered from selective dissolution while Cr and Ni were relatively stable. The corrosion rates were mainly dominated by the dissolution of iron. Alloy 625 presented better corrosion resistance than 316L due to the obviously lower content of Fe and the higher content of Cr and Ni in the passive film. The continuously selective dissolution of iron resulted in the increase in Cr/Fe ratio in the passive film, which was responsible for the enhancement in corrosion resistance.

Keywords Stainless steel · Induced coupled plasma (ICP) · Polarization · X-ray photoelectron spectroscopy (XPS) · Passive films

1 Introduction

Austenitic alloys, for example, 316L stainless steel and Alloy 625, are widely used as structural materials in oil and gas, nuclear power, marine, aerospace, and chemical industry due to their good corrosion resistance and mechanical properties [1–4]. In general, 316L and Alloy 625 could be spontaneously passivated owing to the formation of a protective film on their surface. In recent years, passive films have been characterized by numerous techniques, including atomic force microscopy (AFM) [5], X-ray photoelectron spectroscopy (XPS) [6, 7], transmission electron microscopy (TEM)

[8], and secondary ion mass spectrometry (SIMS) [9–13]. Agreements have been reached that the passive films were dominated by Cr, Fe, Mo and Ni species. Besides, the passive film was considered to have a bilayer structure with Cr and Fe enriched in the inner and outer layers, respectively.

However, the character of a passive film could be affected by the composition of materials. Jang and Kwon [14] found that the oxides of Ni and Mo would not precipitate in the passive film until the concentrations of Ni and Mo in the metal exceed critical values. Abreu et al. [15] reported that the increase in Ni content was beneficial for the formation of thinner and denser passive films. Liu et al. [16] found that Mo could suppress the formation of precipitates and result in the enhancement in fatigue resistance. Alloy 625 contains higher contents of Cr, Mo and Ni than 316L, and thus the passive films may be different in composition and structure.

As is known to all, the protectiveness of a passive film largely depended on the concentration of chromium. The higher Cr content in Alloy 625 would commonly result in the better corrosion resistance than 316L. Nevertheless, Alloy 625 was much more expensive than 316L. Hence, in some acidic environments, 316L and Alloy 625 were used

Available online at <http://link.springer.com/journal/40195>

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s40195-019-00979-z>) contains supplementary material, which is available to authorized users.

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together to reduce cost [17]. Since the difference in chemical composition, 316L and Alloy 625 might exhibit different electrochemical behaviours.

In this study, the corrosion behaviours of 316L and Alloy 625 were compared and investigated by electrochemical methods, and the composition and structure of passive films were characterized by XPS and Auger electron spectroscopy (AES). The electrochemical behaviour and its correlation with the passive film composition were discussed. Meanwhile, the selective dissolution of cation elements was directly studied.

2 Experimental

2.1 Materials and Solutions

The chemical compositions of 316L stainless steel and Alloy 625 used in this study are listed in Table 1. All the specimens were cut to 10 mm × 10 mm × 3 mm in size. The electrochemical coupons were mounted by epoxy resin leaving a working area of 1 cm². Prior to the experiments, the specimens were successively polished with SiC paper up to 2000 grit in order to obtain a fine specimen surface and minimize the errors caused by surface roughness. After polishing, the specimens were cleaned with distilled water and ethanol, consequently dried under cool air.

Test solutions contained 20 g L⁻¹ NaCl and 0.1 mol L⁻¹ HCl were prepared by using deionized water and analytical NaCl and HCl. All tests were conducted at ambient temperature (25 °C).

2.2 Electrochemical Measurements

All the electrochemical measurements were taken in a three-electrode cell. A platinum plate and a saturated calomel electrode (SCE) were utilized as the counter and reference electrodes, respectively. All the working electrodes were cathodically prepolarized at -0.6 V (SCE) for 5 min to remove the easily reducible surface films and then stabilized at the open-circuit potential (OCP) for 1 h.

The cyclic polarization curves were recorded from -0.2 V (vs. OCP) in the positive direction with a potential sweep rate of 0.5 mV s⁻¹. The scan reversed when the current density reached 5 mA cm⁻².

Electrochemical impedance spectroscopy (EIS) measurements were taken at OCP using an alternating current

voltage amplitude of 10 mV. The frequency varied from 100,000 to 0.01 Hz.

Mott–Schottky measurements were taken on the passive films from -0.3 to 0.7 V (vs. SCE) with a potential step of 50 mV. The high sweep rate was used to minimize the variation of defect density during the test [18]. The frequency was maintained at 1000 Hz, and an AC voltage amplitude of 10 mV was employed. It should be emphasized that Mott–Schottky measurements were taken on different specimens to avoid damage to the working electrodes during the polarization process. All the electrochemical tests were performed at least three times to ensure reproducibility.

2.3 Surface Characterization

In order to study the passive film evolution with time, samples were immersed in the above-mentioned solution for different periods. After carefully extracted from the immersion cell at various immersion time, the specimens were rinsed in deionized water, dried by highly purified nitrogen, and were ready for XPS and AES characterization. The composition of the passive films was analysed by XPS with an AXIS-Ultra-DLD instrument (monochromatic Al K α ($h\nu$ = 1486.6 eV)). Additionally, the C1s peak at 284.8 eV was used as a reference to adjust the shifted charge. An analysis of the peaks on the measured curves was conducted via the commercial software XPSpeak version 4.1.

In order to analyse the element distribution in the passive films, AES depth profiles were measured by a PHI-700 scanning Auger microprobe (ULVAC-PHI, Japan) with a coaxial electron gun and a cylindrical mirror analyser (CMA). The Auger spectra were taken at 5 keV with an energy resolution of 0.1%, and the electron incidence angle with respect to the normal average surface plane was 30°. The vacuum level of the analysis chamber during measurement was of the order of 3.9×10^{-9} Torr. The sputtering rate, as determined from thermal oxidation of SiO₂/Si standard, was approximately 4 nm min⁻¹.

2.4 Solution Analysis

The solutions were analysed by Agilent 5110 induced coupled plasma-optical emission spectrometer (ICP-OES) to detect metal release from the specimens during the immersion tests. After the samples were extracted, the solutions were thoroughly stirred to ensure homogeneity. The solutions to be analysed were stored in polypropylene tubes,

Table 1 Chemical compositions of the testing materials (wt%)

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	Nb	Fe
316L	0.022	0.47	1.2	0.02	0.003	16.7	2.35	10	–	Bal.
625	0.02	0.25	0.21	0.006	0.001	21.9	9	Bal.	3.51	5

which were carefully cleaned with ultrapure water to avoid contamination. The standard solutions were used to calibrate the instrument before analysis. All the ICP-OES results were repeated for twice.

3 Results

3.1 Polarization Behaviour

Figure 1 presents the cyclic polarization curves obtained for 316L stainless steel and Alloy 625 in the hydrochloric acid solution. It was seen that both 316L and Alloy 625 displayed typical passive behaviour under this condition. No active–passive transition region appeared on the curves, indicating that the materials could spontaneously passivate in their natural states. The passive region of 316L ranged from -0.32 to 0.20 V (SCE). At potentials higher than 0.2 V(SCE), 316L suffered from pitting corrosion, leading to the larger current densities during the reversing scan [19]. This conclusion was confirmed by corrosion pits observed on the samples after polarization tests. Alloy 625 showed better corrosion resistance than 316L. The passive region of Alloy 625, ranging from -0.11 to 0.85 V (SCE), was much broader than that of 316L. Besides, hysteresis loop was not found on the polarization curve of Alloy 625, which indicated that Alloy 625 was pitting resistant under the testing condition. In general, the high current densities at noble potentials in the absence of hysteresis loop could be ascribed to oxygen evolution reaction or the uniform dissolution of the passive film [20, 21]. In this case, the high current densities at potentials more positive than 0.85 V (SCE) were most probably due to the uniform dissolution of the passive film, since oxygen evolution reaction would not commonly occur in acid solutions, as also reported in the literature [22]. Moreover, the passive current density of Alloy 625

was slightly lower than that of 316L, which indicated that the film formed on Alloy 625 was more protective.

3.2 EIS Results

Figure 2 presents the impedance spectra of 316L and Alloy 625 measured at various immersion time in hydrochloric acid solutions. All the impedance results were validated by Kramers–Kronig transformation to confirm the constraints of liner system theory. It could be seen that all the plots presented typical capacitance characteristics. In Fig. 2a, b, each Nyquist plot was composed of one depressed capacitive semi-arc, which was related to the passive film [5, 21]. In general, the diameters of the impedance arcs increased and then stabilized with the prolonging time. In Fig. 2c, d, the impedance was around $4 \Omega \text{ cm}^2$ in the high-frequency region and then increased at the slope of approximately 1 with the decreasing of frequencies. This was a characteristic response of the passive film capacitive behaviour. In comparison, the impedance for Alloy 625 measured at 0.01 Hz was larger than that of 316L under the corresponding testing conditions. In Fig. 2e, f, all the phase angles were very close to zero degree at $10,000$ Hz, indicating that the impedance at this high frequency was dominated by the solution resistance between the working and reference electrodes. The phase angle then dropped towards the negative direction with decreasing frequencies and reached the peak values of approximately -80° . The phase angles tended towards -80° over a wider range of frequencies for Alloy 625, indicating the better protectiveness of the passive film [23].

The EIS data were fitted with the electrochemical equivalent circuits, which are shown in Fig. 3. In the circuits, R_s is the solution resistance; R_f is the resistance of passive film; W is the Warburg impedance; and Q_f represents the passive film capacitance. The presence of Warburg impedance in a passive system was commonly believed to be related to the vacancy migration under the electric field across the passive film [24], which has been widely reported in the investigations on austenitic stainless steels [24–27]. The presence of Warburg impedance indicated that the corrosion process of 316L was controlled not only by a charge transfer process but also by a diffusion control process. In the above circuits, Q is the constant phase element (CPE). CPE was commonly used in the case of uneven current distribution at the surface or in the case of increased surface roughness. The impedance of CPE was given by

$$Z_{\text{CPE}} = (1/Y_0)(j\omega)^{-n}, \quad (1)$$

where Y_0 is a proportionality constant; $j^2 = -1$; and n is an empirical exponent between 0 and 1. When $n = 1$, the CPE represents a pure capacitive element. When $n = 0$, the CPE

Fig. 1 Cyclic polarization curves obtained for 316L stainless steel and Alloy 625 in the hydrochloric acid solution

Fig. 2 Nyquist and Bode plots of testing materials in the hydrochloric acid solution: **a** Nyquist plots for 316L, **b** Nyquist plots for Alloy 625, **c** impedance magnitude versus frequency for 316L, **d** impedance magnitude versus frequency for Alloy 625, **e** phase angle versus frequency for 316L, **f** phase angle versus frequency for Alloy 625

represents a resistor, and when $n=0.5$, the CPE represents the Warburg impedance.

The values of the equivalent circuit elements calculated at various time are listed in Table 2. In general, R_f increased at the beginning and then got relatively stable for both 316L and Alloy 625. This suggested that the prolonging immersion time could induce the formation of more stable and protective passive films for both the two alloys. Additionally, the values of Y_0 decreased with time, which demonstrated

the thickening of passive films [28]. In detail, R_f of 316L increased from 53 k Ω at 1 h to 84 k Ω at 3 h. Thereafter, the film resistance fluctuated and stabilized at around 80 k Ω , showing a 50% increase in R_f . However, for Alloy 625, the film resistance significantly increased for 42 times from 106 k Ω at the beginning to 4504 k Ω at 50 h. This result implied that Alloy 625 was much more protective than 316L and its corrosion resistance was strongly enhanced during immersion. Besides, the values of n for 316L were slightly

Fig. 3 Equivalent circuits for simulating EIS results: **a** used for fitting the plots of 316L, **b** used for fitting the plots of Alloy 625

lower than those for Alloy 625, which indicated the higher heterogeneity of the film formed on Alloy 625.

3.3 Passive Film Composition

After the immersion tests, the chemical composition of the passive films was investigated by XPS measurements at the sputtering depth of approximately 1 nm. Figure S1 in Supporting Information shows the full XPS spectra diagram for the passive films formed on 316L and Alloy 625. It was observed that the main cation elements in the passive films were Fe, Cr, Mo, and Ni.

Figure 4 shows the high-resolution XPS spectra of Cr $2p_{3/2}$, Ni $2p_{3/2}$, Fe $2p_{3/2}$, and Mo $3d$ obtained on the 316L specimens after various immersion time. Two constituent peaks were identified in the Cr $2p_{3/2}$ signal, representing Cr⁰ in metallic state (573.67 eV), and Cr³⁺ in oxide (Cr₂O₃, 576.5 ± 0.1 eV), respectively. The relative content of Cr⁰ to Cr₂O₃ decreased with prolonging time, which demonstrated that the thickness of the passive films increased. The Ni $2p_{3/2}$ spectra were split into two constituent peaks, corresponding to the metallic state Ni⁰ (852.6 eV), and NiO (583.8 eV). The obviously higher peak intensities of Ni⁰ than NiO implied

that Ni mainly existed in the passive film in the form of Ni⁰. The Fe spectra were decomposed into two peaks corresponding to Fe⁰ (706.7 ± 0.1 eV), and Fe²⁺ (709.35 ± 0.1 eV). The Fe²⁺ peaks were thought to mainly correspond to Fe₃O₄, since FeO was not stable in the acid solutions [29]. The Mo spectra presented a doublet due to the spin-orbit coupling of Mo $3d_{5/2}$ and Mo $3d_{3/2}$. The spectra of Mo $3d$ could be split into three components, i.e. MoO₃ ($3d_{3/2}$ 235.6 eV and $3d_{5/2}$ 232.5 eV), MoO₂ ($3d_{3/2}$ 232.8 eV and $3d_{5/2}$ 230.3 eV) and Mo⁰ ($3d_{3/2}$ 231.1 eV and $3d_{5/2}$ 227.8 eV). The intensities of MoO₃ and MoO₂ were similar, demonstrating that the content of the two species was roughly equal. According to the above analysis, the compositions of the passive film formed on 316L were Cr₂O₃, Fe₃O₄, NiO, MoO₃, and MoO₂.

Figure 5 shows the high-resolution XPS spectra of Cr $2p_{3/2}$, Ni $2p_{3/2}$, Fe $2p_{3/2}$, and Mo $3d$, obtained on the Alloy 625 specimens after various immersion time. The Cr $2p_{3/2}$, Ni $2p_{3/2}$, and Mo $3d$ signal could be similarly identified as Cr⁰, Cr₂O₃, Ni⁰, NiO, MoO₃, MoO₂, Mo⁰, respectively. The peak corresponding to MoO₃ was not detected until the immersion time increased to 50 h. For both 316L and Alloy 625, all the dominating peaks of Ni $2p_{3/2}$ corresponded to metallic Ni. This phenomenon was widely reported in the literature [12, 30–34]. Ni was considered nobler than Fe and Cr in the passive film, and therefore Ni was less readily oxidized than Fe and Cr [35]. This resulted in the high proportion of Ni⁰ in the total nickel content. According to the intensity areas, the atomic ratios of Cr⁰ to Cr₂O₃ were calculated. The atomic ratios of Cr⁰ to Cr₂O₃ were approximately 0.3 for Alloy 625, and 0.05 for 316L. The higher content of the metallic Cr might indicate that the passive films formed on Alloy 625 were thinner than the films formed on 316L [36]. This conclusion would be further confirmed by the AES analysis. The Fe spectra were decomposed into two peaks corresponded to Fe⁰ and Fe³⁺ (711.5 eV). Iron tended to exist at a high valence state in the passive film formed on Alloy 625, which might be due to the fact that the open-circuit potentials (OCP) of Alloy 625 were more positive than those of 316L (Fig. S2 in Supporting Information). In general, Fe₂O₃ in the passive film formed on nickel-based alloys tended to incorporate with NiO to form spinel NiFe₂O₄ [37–39]. This conclusion was supported by

Table 2 Obtained equivalent circuit parameters

Condition	1 h		3 h		6 h		15 h		24 h		50 h	
	316L	625	316L	625	316L	625	316L	625	316L	625	316L	625
R_s (Ω cm ²)	3.63	3.77	3.62	4.27	3.64	4.28	3.63	4.41	3.87	4.35	3.63	4.37
Y_o ($\times 10^{-5}$ Ω^{-1} cm ⁻² s ⁿ)	8.13	6.29	7.34	4.33	7.24	4.05	7.06	3.65	7.13	3.53	6.90	3.17
n	0.90	0.92	0.88	0.94	0.87	0.94	0.87	0.94	0.87	0.94	0.86	0.94
R_f (k Ω cm ²)	53.4	106.4	84.0	894.1	80.7	1602	76.3	3757	74.1	4062	77.9	4504
W ($\times 10^{-4}$ Ω cm ² s ^{-0.5})	2.38	–	1.33	–	1.20	–	1.03	–	0.93	–	0.77	–

Fig. 4 High-resolution XPS spectra of Cr 2p_{3/2}, Ni 2p_{3/2}, Fe 2p_{3/2}, and Mo 3d obtained on the 316L specimens after various immersion time

the similar distribution behaviour of iron and nickel, which would be presented in Sect. 3.4. In summary, the passive films formed on Alloy 625 were composed of Cr₂O₃, NiO, Fe₂O₃/NiFe₂O₄, MoO₃, and MoO₂.

According to the XPS results, the atomic fractions of metallic elements in different oxidation states in the passive films formed on the two materials are illustrated in Fig. 6.

Cr, with an atomic concentration of around 30%, was one of the main ingredients in the passive films for both 316L and Alloy 625. It mainly existed in the form of Cr₂O₃. The concentration of Cr increased with time, which indicated the good stability of Cr₂O₃ in acid solutions. For Alloy 625, the contents of chromium, molybdenum and nickel species in the passive films were higher than that for 316L, while the

Fig. 5 High-resolution XPS spectra of Cr 2p_{3/2}, Ni 2p_{3/2}, Fe 2p_{3/2}, and Mo 3d obtained on Alloy 625 specimens after various immersion time

concentrations of iron were lower. This was in accordance with the relative content of elements in the metal matrix. However, it was noticed that the atomic concentrations of Mo were relatively low in the passive films formed on both two materials, demonstrating the depletion of Mo in the passive films. This phenomenon was also reported in literature [11, 40, 41].

3.4 Distribution of Cation Elements in the Passive Films

Figure 7 shows the AES depth profiles of the passive films formed on 316L at various immersion time. The atomic percent of Fe firstly decreased with the sputtering depth and then increased to its background level (approximately 70%).

Fig. 6 Atomic fractions of metallic elements in different oxidation states in the passive films formed on 316L and Alloy 625

Conversely, the Cr content in the passive films increased from around 30% in the outmost layer and then decreased to its substrate level 17%. The conversion occurred when the sputtering time was 0.5 min, i.e. 2 nm vs. Si/SiO₂. The results indicated that Fe was enriched in the outer layer, while Cr was enriched in the inner layer. According to the XPS analysis, the outer layer mainly consisted of Fe₃O₄ and the inner layer was dominated by Cr₂O₃. Moreover, the contents of Cr and Fe in the passive film were more than 80%, which implied that the film was mainly composed of chromium and iron species. As the immersion time increased, the concentration of Cr increased while Fe concentration decreased. Since Cr could promote the formation of a protective surface oxide, the higher amount of Cr resulted in the enhanced corrosion resistance of 316L. Besides, atomic per cent of Ni slightly decreased as the sputtering depth increased, while Mo content increased with sputtering. In general, Fe and Mo were depleted in the passive films, while Cr and Ni were enriched. The thickness of the passive film was estimated according to the distribution of cations. The passive films were around 4 nm in thickness when the

immersion time was less than 15 h and then the film slightly thickened to 5 nm after immersion for 50 h.

Figure 8 presents the AES depth profiles of the passive films formed on Alloy 625 at various immersion time. It could be observed that Fe and Ni were enriched in the outer layer, while Cr was enriched in the inner layer. This result indicated that the passive films formed on Alloy 625 also presented the bilayer structure, where the inner layer was dominated by Cr₂O₃ and the outer layer was mainly composed of Fe and Ni species. Since for nickel-based alloys, NiO and Fe₂O₃ could incorporate to form NiFe₂O₄ [39], the enrichment of Ni in the outer layer was more evident for Alloy 625 than for 316L. Besides, the concentrations of Mo increased with sputtering depth, showing a similar variation trend with 316L. The peaks for Cr were located at the position where the sputtering depth was 1 nm, while for 316L, the depth was 2 nm. This result indicated that the outer layer of Alloy 625 was thinner than that of 316L. This phenomenon was related to the enhanced selective dissolution of iron, which would be further discussed in Sect. 4.2. However, the thickness of the inner layer did not significantly change. Therefore, the passive films formed on Alloy 625 were slightly thinner than on 316L. This conclusion was consistent with the result of Abreu et al. [15].

4 Discussion

4.1 Comparison of the Semiconductive Behaviour and Electronic Structure of Passive Films Formed on 316L and Alloy 625

Mott–Schottky measurements are often used to study the semiconductive behaviour of passive films. Through this method, the relationship between the passive film composition and its protectiveness can be established. The Mott–Schottky relation is given as [23, 42, 43]

Fig. 7 AES depth profiles of the passive films formed on 316L at various immersion time: **a** 1 h, **b** 15 h, **c** 50 h

Fig. 8 AES depth profiles of the passive films formed on Alloy 625 at various immersion time: **a** 1 h, **b** 15 h, **c** 50 h

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

where C is the capacitance of the space charge, ϵ is the dielectric constant of the oxide film ($\epsilon = 15.6$ was used in this study [44, 45]), ϵ_0 is the vacuum permittivity ($8.854 \times 10^{-14} \text{ F cm}^{-1}$), e is the electron charge ($1.602 \times 10^{-19} \text{ C}$), N is the donor or acceptor density (electron donor concentration for n-type semiconductors or hole acceptor concentration for p-type semiconductors), T is the absolute temperature, k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), E is the applied potential, and E_{fb} is the flat-band potential.

Figure 9a shows the Mott–Schottky plots for the passive films formed on 316L. The plots contained one negative slope and one positive slope at the potential regions A and B, respectively. This result indicated that the passive films formed in region A mainly presented p-type semiconductive behaviour. The inversion from p-type to n-type property occurred at 0.1 V(SCE), while in region B, the passive films presented n-type behaviour. Figure 9b shows the Mott–Schottky plots for the passive films formed on Alloy 625. The film exhibited n-type semiconductive behaviour at

lower potentials (region C) and reflected p-type semiconductive behaviour at higher potentials (region D). The above results indicated that the semiconductive behaviour of materials was highly related to the applied potential.

According to the PDM, the electron donors are mainly oxygen vacancies and metal interstitials, whereas the dominating acceptor species are cation vacancies [46, 47]. At different potential regions, the passive film presented either n-type or p-type behaviour, depending on the main defects existing in the film. Actually, oxides in the passive film were nonstoichiometric. Cation or oxygen vacancies would exist in order to preserve overall electrical neutrality in the crystal. The oxides presented p-type behaviour when cation vacancies were the main defects, and conversely the film would exhibit n-type behaviour. In general, species, such as MoO_3 , Fe_2O_3 , FeOOH , $\text{Fe}(\text{OH})_3$ and NiFe_2O_4 , commonly presented n-type semiconductive behaviour, while NiO , Cr_2O_3 , MoO_2 , FeCr_2O_4 and Fe_3O_4 mainly presented as p-type semiconductor [48].

As can be seen in Fig. S2 in Supporting Information, the corrosion potentials for 316L and Alloy 625 during the immersion were always within the potential regions A and C, respectively. This indicated that the films formed on 316L

Fig. 9 Mott–Schottky plots for the testing materials at various immersion time: **a** 316L, **b** Alloy 625

and Alloy 625 presented opposite semiconductive properties, i.e. 316L exhibited p-type behaviour, while Alloy 625 showed n-type behaviour. According to the XPS analysis, the passive film formed on 316L mainly consisted of Cr_2O_3 , Fe_3O_4 , NiO , MoO_3 , and MoO_2 . Since Fe_3O_4 and Cr_2O_3 were, respectively, enriched in the outer and inner layers, the passive film exhibited an electronic structure of p–p heterojunction, which reasonably resulted in the p-type behaviour of 316L at potential region A. Moreover, the conversion for the semiconductive behaviour occurring at around 0.1 V(SCE) was most probably attributed to the oxidation reaction of Cr^{3+} to Cr^{6+} [14], which also resulted in the local breakdown of the passive film (316L showed metastable pitting at this potential, Fig. 1). For Alloy 625, the concentrations of p-type semiconductor forming elements, Cr and Ni, in the metal matrix were much higher than those for 316L. Hence, the p-type semiconductive behaviour was expected to be enhanced. However, Alloy 625 showed n-type behaviour under the testing conditions. Actually, the passive film formed on pure nickel always exhibited p-type semiconductor due to the existence of p-type products, NiO and Ni(OH)_2 [49, 50]. Nevertheless, the addition of Fe and Cr in pure Ni would lead to the reversed semiconductive behaviour. Numerous studies [22, 51–54] on the Ni–Cr–Fe nickel-based alloys have confirmed the n-type semiconductive behaviour in acid solutions. In this study, the passive films formed on Alloy 625 were composed of Cr_2O_3 , NiO , $\text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4$, MoO_3 , and MoO_2 . Moreover, iron and nickel species were enriched in the outer layer, whereas chromium oxides were enriched in the inner layer. Fe_2O_3 belongs to n-type semiconductor, and it could also incorporate with p-type NiO to form the n-type product, spinel NiFe_2O_4 [37, 38], which might further enhance the n-type property of the film. The enrichment of NiFe_2O_4 in the outer layer of the film formed on nickel-based alloys has been verified by literature [39]. Hence, Alloy 625 presented the electronic structure of n–p heterojunction composed of outer $\text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4$ and inner

Cr_2O_3 . Therefore, Alloy 625 exhibited the n-type semiconducting behaviour at OCP and then presented p-type semiconducting behaviour at higher potentials.

4.2 Selective Dissolution of the Cation Elements for 316L and Alloy 625

The solutions were analysed during the immersion tests at various time. Figure 10 presents the concentrations of Fe, Cr, Mo and Ni released into the solution as a function of immersion time. It was pointed out here that the solution before immersion tests was also analysed, and the release of the concerned elements, i.e. Fe, Cr, Mo and Ni, was not found. It could be observed that the concentration of Fe ion was obviously higher than those of Cr, Mo and Ni for both 316L and Alloy 625, indicating that the corrosion rates were mainly dominated by the dissolution of iron. Besides, the total cation concentrations of 316L were always larger than Alloy 625, which demonstrated that 316L was less corrosion resistant than those of Alloy 625. This conclusion was consistent with the electrochemical results. Moreover, the concentrations of Fe, Cr, Mo and Ni dramatically increased from 0 to 1 h, and then the metal release rates slowed down. This result indicated that the passive films became more protective with time.

A selective coefficient S_{Me} was employed to characterize the tendency of cations to dissolve into the solution [55]. The coefficient was defined as

$$S_{\text{Me}} = \frac{\text{Me in solution, wt\%}}{\text{Me in alloy, wt\%}}, \quad (3)$$

where S_{Me} is the selective coefficient for a metal element (Me). Me% is the weight percentage of Me to all the concerned cation elements. Me suffers from selective dissolution, if $S_{\text{Me}} > 1$. Me is relatively stable in the oxides when $S_{\text{Me}} < 1$.

Fig. 10 Concentrations of Fe, Cr, Mo and Ni released into the solution as the function of immersion time: **a** 316L, **b** Alloy 625

The selective coefficients of Fe, Cr, Mo and Ni were calculated, and the results are shown in Fig. 11. In general, Fe and Mo selectively dissolved into the solution, implying the low stability of Fe and Mo species in the passive film. The selective coefficients of Ni and Cr were lower than 1, which indicated that Ni and Cr species were relatively stable in acid solutions. Due to the low stability of iron oxides, the selective dissolution of Fe was very commonly reported [6, 12, 21, 56]. Cr was the key element in the passive film. Chromium oxides were more stable than iron oxides. They acted as the most important barrier to corrosion and were normally enriched in the film, especially in the inner layer. Accordingly, less amount of Cr dissolved into the solutions for both 316L and Alloy 625. Mo was beneficial to the pitting resistance of stainless steels. It was well known that Mo could ameliorate the defect structure of chromium species and therefore the addition of Mo could increase the corrosion resistance of the materials [57]. According to the XPS results, molybdenum participated in the passive film, showing different states of oxides. However, Mo was depleted in the passive film. This indicated that Mo oxides were not stable enough in strong acid solutions, which was supported by the literature [35]. Nickel was an important austenite forming element for the two materials. It presented in the passive film mainly in the form of metallic state Ni^0 , indicating that Ni^0 was thermodynamically more stable than NiO under the testing conditions. This result was supported by some researchers, who found that NiO and Ni(OH)_2 were unstable at lower pH [12, 33]. Actually, nickel was always depleted in the passive film and enriched in the metal/film interface [58]. Abreu et al. [15] thought that the presence of Ni could promote the formation of thinner chromium layers, attributing to the hindering effect of Ni underneath the film on Cr diffusion. However, in this study, nickel was enriched in the passive film instead of metal/film interface, due to the enhanced stability of Ni^0 in acid solutions. The diffusion of Cr towards the inner layer was not strongly inhibited

and thus the thickness of the inner layer was similar for the two materials. According to the ICP-OES analysis, Fe was selectively dissolved. The consumption of Fe in the passive film on Alloy 625 might not be adequately compensated like on 316L due to the low iron content in the nickel-based alloy matrix. Consequently, the Fe enriched outer layer became thinner than that for 316L.

In summary, species of Fe and Mo were less stable than those of Cr and Ni in acid solutions. Alloy 625 presented better corrosion resistance than 316L due to the obviously higher content of Cr and Ni in the passive film. The continuously selective dissolution of iron resulted in the increase in Cr/Fe ratio in the passive film, which was responsible for the slowdown of corrosion rates.

5 Conclusions

In the present work, the passive behaviour of 316L and Alloy 625 in hydrochloric acid solution was investigated. The conclusions were drawn as follows:

- (1) Alloy 625 showed better corrosion resistance than 316L. For Alloy 625, the passive region was much broader and the passive current density was lower than that for 316L. The prolonging immersion time could enhance corrosion resistance of the two alloys.
- (2) The composition of the passive films formed on 316L was Cr_2O_3 , Fe_3O_4 , NiO , MoO_3 , and MoO_2 , while the passive films formed on Alloy 625 were composed of Cr_2O_3 , NiO , $\text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4$, MoO_3 , and MoO_2 . Iron tended to exist at a high valence state in the passive film formed on Alloy 625.
- (3) The passive films formed on 316L and Alloy 625 presented opposite semiconductive properties due to the difference in film composition. The passive film formed on 316L exhibited an electronic structure of p-p hetero-

Fig. 11 Selective coefficients of Fe, Cr, Mo and Ni as a function of time: **a** 316L, **b** Alloy 625

junction, with Fe_3O_4 and Cr_2O_3 enriched in the outer and inner layers, respectively. However, Alloy 625 presented the electronic structure of n–p heterojunction composed of outer $\text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4$ and inner Cr_2O_3 .

- (4) Fe and Mo suffered from selective dissolution while Cr and Ni were relatively stable in the passive films. Alloy 625 presented better corrosion resistance than 316L due to the obviously higher content of Cr and Ni in the passive film. The continuous dissolution of iron resulted in the increase in Cr/Fe ratio in the passive film, which was responsible for the slowdown of corrosion rates.

Acknowledgements This work was financially supported by the Fundamental Research Funds for the Central Universities (No. FRF-IC-18-007) and the China Postdoctoral Science Foundation (No. 2019M650487).

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