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Corrosion Behaviors of 316L Stainless Steel with Various Grain Sizes in a Simulated Cathodic Environment of a PEMFC

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The corrosion behaviors of 316L stainless steel with various grain sizes in 0.05 M H₂SO₄ solution with 1×10^{-6} M F⁻ (simulating the cathodic environment of a PEMFC) are studied in this work using potentiodynamic curves, electrochemical impedance spectroscopy (EIS), Mott-Schottky plots and auger electron spectroscopy (AES). The results show that 316L stainless steel is in the passive state in the studied solution but is vulnerable to pit corrosion when passivated at 0.6 V_{SCE} (which is equal to the working potential of the cathodic bipolar plate) due to the passive potential of $0.6 V_{SCE}$ falling into the metastable pit growth region. The strength of 316L stainless steel increases and the elongation decreases with decreasing grain size. The compactness and resistance of the passive film at 0.6 V_{SCE} increase with decreasing grain size, thereby implying increased corrosion protection of the passive film. The passive film is mainly composed of an inner Cr₂O₃ film and an outer Fe₂O₃ film, where the inner Cr₂O₃ film exhibits p-type semiconductive characteristics and the outer Fe₂O₃ film exhibits n-type semiconductive properties. The acceptor density of the inner Cr₂O₃ film and the donor density of the outer Fe₂O₃ film decrease with increasing grain size, thereby indicating enhanced homogeneity of the passive film. The flat band potential of the passive film moves in a positive direction with decreasing grain size, which demonstrates that the density of the absorbed F⁻ ions on the film surface decreases, which may lead to a decreased tendency for pit corrosion by F⁻ ions and, therefore, improved pitting corrosion resistance of the passive film. AES shows that the content of the inner Cr₂O₃ film increases with decreasing grain size due to the decrease in carbide accumulation in the grain boundary regions.

Keywords: PEMFC; Cathodic environment; 316L SS; Grain size; Passive Films

1. INTRODUCTION

With the development of the economy, people's demand for energy is increasing. However, the reserves of traditional fossil energy are limited, and the large-scale use of fossil energy causes obvious environmental pollution. Therefore, people have to seek new energy to replace traditional fossil energy

or decrease the demand for fossil energy. Proton-exchange membrane fuel cells (PEMFCs) are widely studied by an increasing number of researchers due to their low emission, high efficiency, easy manufacture and stable performance [1-5]. In the operation of a PEMFC, the cathodic environment is acidic and of high temperature and contains fluorine ions. In this environment, the cathodic bipolar plate is vulnerable to corrosion, thereby leading to a reduced service life of the battery. Therefore, in recent years, extensive research has focused on the corrosion behavior of cathodic bipolar plates, but most of these studies have focused mainly on the surface coating of stainless steel and new plate materials [6-10], and only a few papers have discussed the manufacturing process effect on the corrosion behavior of 316L stainless steel in the cathodic environment of a PEMFC [11-15]. A good candidate material for bipolar plates for PEMFCs is 316L stainless steel because a passive film can be formed on the surface during the operation of the PEMFC and this passive film can act as an ion barrier to effectively protect the substrate from further corrosion. The corrosion protection of the passive film is dependent on its electronic properties, and many factors can affect these properties, such as pH value, temperature, aggressive ions, and passive potential, among others [16-18]. These factors can be deemed external factors, and current research is mainly focused on the influence of external factors on the corrosion behavior of 316L stainless steel in the cathodic environment of PEMFCs. Compared with the external factors, the internal factors, including the chemical composition, grain size, gas content, plastic deformation and deformation rate, and heat treatment, play a decisive role in the electronic properties of the passive film and have a direct effect on the corrosion behavior of the substrate. However, only a few articles have researched the influence of the manufacturing process on the corrosion resistance of 316L stainless steel in the cathodic environment of PEMFCs [19]. Unsatisfactorily, to date, no paper has focused on the effect of grain size on the corrosion behavior of 316L stainless steel in the cathodic environment of PEMFCs. This article aims to study this issue using potentiodynamic curves, electrochemical impedance spectroscopy (EIS), Mott-Schottky plots and Auger electron spectroscopy (AES).

2. EXPERIMENTAL

2.1 Sample preparation

An electrolytic nickel sheet (99.9%), an electrolytic chromium block (99.9%), pure silicon (99.9%), a molybdenum sheet (99.9%), pure iron (99.9%) and carbon (99.9%) were put in a 25 kg vacuum electric furnace for melting, and the vacuum degree during the melting process was kept at 5 Pa below. The molten temperature was gradually increased to 1923 K, and the temperature was maintained for 30 min with adequate stirring. After stirring, the temperature of the melting liquid was dropped to 1723 K, and then the molten liquid was poured into a cast iron mold to form a cast sample of size $\emptyset150\times300$ mm. Then, the cast sample (sample 1) was heated to 1473 K and maintained at this temperature for 90 min, and finally, the cast sample was forged into rods with diameters of $\emptyset90$ mm (sample 2), $\emptyset60$ mm (sample 3) $\emptyset40$ mm (sample 4) and $\emptyset20$ mm (sample 5). After the forging process, all rods were heated to 1323 K and held at this temperature for 1 h for solid solution heat treatment. Finally, all rods were manufactured into samples of the size that is specified in Fig. 1 to measure the

mechanical properties. A rod that was manufactured into a size of $\emptyset 10 \times 5$ mm was used to carry out the electrochemical experiments. One round face and the cylindrical side were sealed by epoxy inside a PVC tube, and the other exposed round face was gradually abraded by grit SiC paper to 5000#. Then, the samples were polished by 0.5 µm Al₂O₃ powder, and finally, they were cleaned using double-distilled water. The chemical composition of the 316L stainless steel was obtained using chemical analysis, and the results are displayed in Table 1.

 Table 1. The chemical compositions of 316L stainless steel (wt%)

Sample	С	S	Р	Si	Mn	Mo	Ni	Cr	Fe
316L SS	0.018	0.0015	0.0029	0.78	1.50	2.5	12.0	17.0	balance

2.2 Mechanical property measurement

The mechanical properties of the 316L stainless steel with various grain sizes were determined using a Quasar 10 universal material tester, which was made in Italy, and the geometric size of the tensile specimen is specified in Fig. 1.

The metallographic microstructure was determined using a Zeiss Vert.A1 metallographic microscope.



Figure 1. Geometric size of the tensile specimen

2.2 Electronic property of 316L stainless steel

All electrochemical experiments were conducted using Solartron 1286 and 1287 electrochemical workstations. A traditional three-electrode system was used, in which the exposed round face was the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and Pt wire acted as the counter electrode. Before each experiment, the exposed round face of the working electrode was polarized at $-1.2 V_{SCE}$ for 20 min to remove any oxides. To simulate the cathodic environment of the PEMFC, 0.05M H₂SO₄ solution with 1×10⁻⁶ M F⁻ was used, and the solution was bubbled with air throughout the whole experiment.

Potentiodynamic polarization curve is scanned using a scan rate of 1 mV/s within the potential region from -0.25 V_{OCP} to 0.9 V_{SCE} .

EIS was measured within the frequency region of 10 kHz to 5 mHz with a potential amplitude of 10 mV, and the applied potential was 0 V versus Ecorr.

A Mott-Schottky plot was constructed within the potential region from -0.6 V_{SCE} to 1.4 V_{SCE} using a 10 mV/s scanning rate.

XPS and AES analyses were carried out with a PHI 5700 ESCA system that was equipped with an Al source, and the X-ray source was operated at 15 kV and 400 W.

3. RESULTS AND DISCUSSION

3.1 Effect of grain size on the microstructure of 316L stainless steel



Figure 2. Metallographic microstructures of sample 1 (a), sample 2 (b), sample 3 (c), sample 4 (d) and sample 5 (e)

The effect of the grain size on the metallographic microstructure of 316L stainless steel is displayed in Fig. 2. The microstructure of the cast sample (Fig. 2a, sample 1) showed columnar crystals accompanied by carbides that accumulated at the grain boundary, and the mean grain size of sample 1 was estimated to be 110 μ m. The mean grain size decreased to 60 μ m when the cast 316L stainless steel was forged into a round sample with a diameter of 90 mm (Fig. 2b, sample 2). As shown in Fig. 2b, the austenite structure was obvious, but carbides still accumulated in the grain boundary regions. The grain size continuously decreased to 35 μ m (Fig. 2c, sample 3), 25 μ m (Fig. 2d, sample 4) and 20 μ m (Fig. 2e, sample 5) with increasing forging ratio. Simultaneously, the intensity of the accumulated carbides in the grain boundary regions decreased with decreasing grain size (or increasing forging ratio), and for sample 5, as shown in Fig. 2e, the grain size was the finest.

3.2 Effect of grain size on mechanical properties of 316L stainless steel

The metallographs revealed that the density of the carbides and the grain size changed with the forging ratio, which must have had a direct effect on the mechanical properties of the 316L stainless steel. Fig. 3a presents the stress–strain curves of the five samples. Sample 1 showed the minimum tensile strength and elongation. However, the tensile strength increased and the elongation decreased with decreasing grain size. Correspondingly, Fig. 3b quantitively lists the dependence of the tensile and yield strengths on the sample order, which clearly shows that either the tensile strength or the yield strength increased with decreasing grain size. However, the decrease in grain size was accompanied by increased grain boundaries, which could effectively prevent dislocation motion by the formation of dislocation piles [20-22]. Fig. 3c lists the variation in the yield strength with the mean grain diameter (D). The yield strength linearly increased with increasing $D^{-1/2}$, which agrees with the Hall–Petch relationship [21]. However, the increase in strength inevitably led to a decrease in ductility, and the inset of Fig. 3a shows that the elongation decreased with decreasing grain size, thereby indicating decreased ductility, which is also in agreement with the Hall–Petch relationship.



Figure 3. Stress verse strain curves of five samples (a), the variations of strength and sample orders (b) and the yield strength verse the reciprocal of the square root of the mean grain diameter $(D^{-1/2})$ plot of five samples

3.3 Effect of grain size on the passive characteristic of 316L stainless steel

The influence of grain size on the passivity of the stainless steel is depicted by the potentiodynamic curve in Fig. 4a, which reveals that the current density initially decreased and subsequently became constant with increasing potential when the applied potential exceeded ca. -0.1 V_{SCE}, the current density slightly increased with the increased potential when the potential exceeded ca. $0.5 V_{SCE}$, and finally, the current density increased when the applied potential exceeded ca. $0.8 V_{SCE}$. Thus, the potentiodynamic curve was divided into three regions according to the change in the current density with the potential: regions I (-0.1 V_{SCE}-0.5 V_{SCE}), II (0.5 V_{SCE}-0.8 V_{SCE}) and III (over 0.8 V_{SCE}). Region I corresponds to the generation of the stable passive film, region II is related to the metastable growth of pitting corrosion, and finally, region III corresponds to the stable growth of pitting corrosion [23]. Overall, 316L stainless steel was deemed in the passive state within the potential region from approximately -0.1 V_{SCE} to 0.8 V_{SCE}, and similar features of the potentiodynamic curve have been obtained for other stainless steels in other acid solutions [24]. Unfortunately, the passivity of 316L stainless steel could not be easily evaluated from the steady passive current density (ip) because no constant current density appeared in the passive potential region. To solve this problem, a method for obtaining the maximum and the minimum values of the passive current density (i_{p.max} and i_{p.min}) was utilized, which is provided by reference 25 [25], and the values of i_{p,max} and i_{p,min} were calculated according to this reference. The average of i_{p,max} and i_{p,min} was used to represent ip in this work (see Fig. 4b), which differed from the above reference. According to the calculation method of i_p, Table 2 lists the i_p values and other corrosion parameters that were extracted from Fig. 4a. Obviously, the corrosion potential (E_{corr}) increased and the corrosion current density (i_{corr}) and the passive current density (i_p) decreased with decreasing grain size, thereby indicating enhanced corrosion resistance of 316L stainless steel due to improved passivity in the studied solution. Additionally, the working potential of the cathodic polar plate was reported to be ca. 0.6V_{SCE} [26], and this working potential falls into region II, namely, a passive film was formed on 316L stainless steel during PEMFC operation, and the formed passive film was vulnerable to pitting corrosion within this potential region. The reason may have been related to the absorption of F⁻ ions on the film surface, and the pitting corrosion tendency will be examined in detail in Fig. 8. Meanwhile, the current density in region II decreased with decreasing grain size; hence, the resistance to pitting corrosion growth increased with decreasing grain size.



Figure 4. Potentiodynamic curves of five samples in 0.05M H_2SO_4 solution with 1×10^{-6} M F⁻ (a), the calculated method of i_{ss} in each potentiodynamic curve (b) and potentiodynamic curve of sample 1 within the weak polarization region

Sample order	i_{corr} / A·cm ⁻²	E_{corr} / V_{SCE}	i _{p,max} / A·cm ⁻²	$i_{p,min}$ / A·cm ⁻²	$i_p / A \cdot cm^{-2}$
Sample 1	9.09e-6	-0.211	2.121e-5	1.072e-5	1.596e-5
Sample 2	8.34e-6	-0.206	1.882e-5	0.984e-5	1.433e-5
Sample 3	8.164e-6	-0.204	1.854e-5	0.906e-5	1.378e-5
Sample 4	7.87e-6	-0.196	1.554e-5	0.879e-5	1.217e-5
Sample 5	6.53e-6	-0.193	1.5048e-5	0.852e-5	1.178e-5

Table 2. The parameters extracted from the potentiodynamic curves of five samples showed in Fig.4a

3.4 EIS and Mott-Schottky analysis

The potentiodynamic curve reveals that a passive film formed on 316L stainless steel within the potential region from -0.1 VSCE to 0.8 V_{SCE}; however, the working potential of the cathodic bipolar plate during PEMFC operation (0.6 V_{SCE}) was in the potential region of metastable pit growth (see Fig. 4a). Therefore, the cathodic bipolar plate that was manufactured from 316L stainless steel was vulnerable to damage caused by pitting corrosion during PEMFC operation, and the corrosion resistance of 316L stainless steel was mostly determined by the corrosion protection of the passive film. The corrosion protection of the passive film was evaluated using EIS and Mott-Schottky plots, and Fig. 5a shows the EIS results of passive films that formed on five samples at 0.6 V_{SCE} for 6 h in the studied solution. Significantly, the Nyquist plot in the whole frequency region from approximately 100 Hz to approximately 0.01 Hz consists of a depressed semicircle, thereby indicating the capacitive characteristic of the passive film. The semicircle enlarges with decreasing grain size, thereby suggesting an improvement in the film protection via the increased film impedance [27]. Meanwhile, the Bode phase plot displays a typical passivity characteristic, namely, the phase angle is almost a constant within a large frequency region (from approximately 100 Hz to approximately 0.1 Hz) [28], and the constant phase angle increased with decreasing grain size, which also demonstrated increased film protection. The Bode modulus plot shows that the modulus remained almost constant in the frequency region from 10^5 to 10^3 Hz (see Fig. 5c) for all samples, and the modulus at relatively high frequencies is generally associated with the solution resistance [29]; thus, it was concluded that the solution resistance changed slightly with the grain size. In the middle and low frequencies (from 103 to 10^{-2} Hz), the log of the modulus increased with decreasing log of the frequency, which was associated with the passive film. Additionally, Fig. 5c shows that the log of the modulus slightly increased with decreasing grain size for each frequency, thereby indicating the enhanced corrosion protection of the passive film due to the increased impedance, phase angle and log of the modulus [30]; therefore, it was concluded that the corrosion resistance of 316L stainless steel in the studied solution improved with decreasing grain size due to the increasing corrosion protection of the passive film.

Considering the compactness of the passive film on stainless steel, the equivalent electronic circuit, which is shown in Fig. 6, was used to acquire quantitative information from the measured EIS. In this model, R_s , R_{ct} and R_f are the solution resistance, charge transfer resistance and passive film resistance, respectively. Q_{cdl} (constant phase element, CPE) and Q_f are the capacitances of the electric double layer and passive film, respectively. The origin of a CPE was attributed to the inhomogeneity of

the electrode surface, and the impedance and admittance of the CPE were obtained with the following relationships [31, 32]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n}$$
(1)

$$Y_{CPE} = (j\omega)^n$$
(2)

Where j is the imaginary number, w is the frequency of the alternative current, and n is the CPE power, which ranges between 0 and 1. When n=1, the CPE describes an ideal capacitor with Y_0 equal to the capacitance C. When n=0, the CPE is an ideal resistor. When n=0.5, the CPE represents the Warburg impedance with a diffusion characteristic. The CPE has the properties of a capacitance when 0.5<n<1.



Figure 5. EIS of passive films formed on 316L SS with different forging ratio at $0.6V_{SCE}$ for 6h in 0.05M H₂SO₄ solution with 1×10^{-6} M F⁻, a) Nyquist plots, b) bode in phase plots, c) bode in modulus plots



Figure 6. The equivalent electronic circuit used to fit the EIS showed in Figure 5

Sample	R_s /	Q_{cdl}/Ω^{-}	n _{cdl}	R _{ct} /	$\mathrm{Q_f}/\Omega^{\scriptscriptstyle -}$	n _f	$R_{\rm f}$ /
order	$\Omega \cdot cm^2$	$^{1} \cdot s^{n} \cdot cm^{-2}$		$\Omega \cdot cm^2$	$^{1} \cdot s^{n} \cdot cm^{-2}$		$\Omega \cdot cm^2$
Sample 1	1.562	3.268e-5	0.9248	12.06	8.405e-7	0.9098	9.307e5
Sample 2	4.557	3.064e-5	0.9435	13.68	3.699e-7	0.9587	1.424e6
Sample 3	3.28	2.977e-5	0.9432	15.64	2.978e-7	0.857	2.497e6
Sample 4	5.964	2.903e-5	0.9455	14.45	2.622e-7	0.8892	2.846e6
Sample 5	9.28	2.585e-5	0.9365	17.23	2.244e-7	0.9425	4.488e6

Table 3. The fitted results of EIS

According to the equivalent electronic circuit, Table 3 lists the fitted results, which clearly show that the order of R_f reached $10^6 \Omega \cdot cm^2$, which is far higher than that of Rct. Similarly, the order of Q_f reached to $10^{-7} \Omega^{-1} \cdot s^n \cdot cm^{-2}$, which is far lower than that of Q_{cdl} . The higher Rf and lower Q_f (compared

with the corresponding R_{ct} and Q_{ct}) indicated the compactness of the passive film, and the accuracy of the equivalent electronic circuit was verified. Meanwhile, the R_f value obviously increased and the value of Q_f decreased with decreasing grain size, and a higher value of R_f and a lower value of Q_f essentially signified greater improvements in the compactness and resistance of the passive film, which led to improved film protection due to the restriction of electron and ion migration within the passive film and across the interfaces [17, 33].

As illustrated in the potentiodynamic curve, the cathodic bipolar plate was exposed to pitting corrosion during PEMFC operation, and pitting corrosion may have reduced the corrosion protection of the passive film. Therefore, the stability and homogeneity of the passive film were vital to the corrosion protection of the passive film, and the reaction of the vacancies within the passive film with F^- or CI^- ions was the main reason for pitting corrosion. Generally, the passive film exhibited semiconductive characteristics, and the film capacitance (C) was dependent on the sweeping potential within the space charge layer according to the Mott-Schottky equation [34, 35]:

$$C^{-2} = \frac{2}{\varepsilon \varepsilon_0 e N_D} (E - E_{FB} - \frac{KT}{e})$$
(3)
$$C^{-2} = -\frac{2}{\varepsilon \varepsilon_0 e N_A} (E - E_{FB} + \frac{KT}{e})$$
(4)

where Eq. (3) was used to represent the electronic property of the passive film with the n-type semiconductive characteristic and Eq. (4) is applicable to p-type semiconductive passive films. N_D and N_A represent the donor density and the acceptor density, respectively, and e is the electron charge (1.60 $\times 10^{-19}$ C). ε is the film dielectric constant, which was taken as 15.6 in this work [36], and ε_0 and K are constants, which were taken as 8.85 $\times 10^{-14}$ F/cm and 1.38 $\times 10^{-23}$ J/K, respectively. T is the absolute temperature, and E_{FB} is the flat band potential.

Fig. 7a shows the Mott-Schottky plots of the passive films on five samples at 0.6 V_{SCE} for 6 h. Significantly, the Mott-Schottky plots could be divided into three regions according to the slope of the straight line, namely, regions I, II and III. C⁻² linearly decreased with increasing sweeping potential in region I, thereby indicating the p-type semiconductive characteristic of the passive film. In region II, C-² changed slightly with the applied potential, and it has been reported that N_D and N_A are in equilibrium and E_{FB} often falls into this region [37]. C⁻² linearly increased with increasing potential when the potential exceeded 0.1 V_{SCE}, thereby implying the n-type semiconductive characteristic of the passive film in region III. The appearance of the positive and negative slopes was attributed to the double-layer structure of the passive film, in which the capacitance response in region I reflects the semiconductive characteristic of the inner Cr₂O₃ film and region III manifests the capacitance response of the outer iron oxides [38]. Meanwhile, C⁻² exhibited an increasing trend either in region I or in region III with decreasing grain size, and simultaneously, the flat band potential, E_{FB}, shifted to the positive direction with decreasing grain size. Based on Equations (3) and (4), Fig. 7b shows the variations in N_A and N_D with the sample order. N_A and N_D were of order of magnitude 10^{21} cm³, thereby indicating the high defect characteristic of the passive film [39], and similar orders of magnitude of N_A and N_D have also been reported for passive films on other types of stainless steels [37]. Moreover, N_A exceeded N_D for each sample, NA and ND decreased from sample 1 to sample 5, thereby indicating increased homogeneity of the passive film with decreasing grain size, whereas the reverse trend was reported by Pradhan [37].



Figure 7. Mott-Schottky plots of passive films formed on 316L SS (a) and the variations of donor density (N_D) and acceptor density (N_A) with sample order (b)

To further investigate the effect of grain size on the corrosion behavior of 316L stainless steel, the current density during the film formation process was recorded, as presented in Fig. 8. All current densities sharply decreased with increasing time in the initial stage, and this stage was ascribed to the nucleation and growth of the passive film at a higher rate than that of film dissolution. Then, the current density reached a relatively stable value with increasing time, thereby implying that the passive film reached a balance between growth and dissolution [40]. The current density fluctuated with time even in the stable stage, and the fluctuation was attributed to the metastable pitting corrosion of the passive film [41], which was also supported by the formation potential of 0.6 V_{SCE} falling into the metastable pitting corrosion potential range. Fig. 8 also shows that the current density in the stable stage decreased with decreasing grain size (see the inset), thereby implying enhanced pitting corrosion resistance.

The above experimental results show that decreased grain size corresponded to improved corrosion resistance of 316L stainless steel in the studied solution, which is the reverse of the result that was reported by reference 37. The reason is believed to be that the carbides that accumulated at the grain boundaries affected the generation of the passive film. As shown in Fig. 1, carbides clearly accumulated at the grain boundaries in the coarse-grained (sample 1 and sample 2) microstructure. These accumulated carbides increased the grain boundary energy, and the grain boundaries with increased energy easily generated a higher density of point defects [42]. Finally, the passive film on 316L stainless steel with the coarse-grained microstructure had higher values of N_A and N_D . However, the carbides that appeared in the form of $Cr_{23}C_6$ decreased the chromium content within the grains [43], thereby resulting in the decreased chromium content reacting with oxygen to form a Cr_2O_3 passive film and, finally, reducing the corrosion protection of the passive film on 316L stainless steel due to the main corrosion contribution of the Cr_2O_3 film.





3.5 AES analysis of the passive film

The influence of grain size on the structure of the passive film was detected by AES, as shown in Fig. 9. The atomic concentration of O decreased and the atomic concentrations of Cr, Ni and Mo increased with increasing sputtering thickness.



Figure 9. AES of the passive films on five samples at 0.6V for 6h 0.1M H₂SO₄ solution with 1×10^{-6} M F⁻, a) sample 1, b) sample 2, c) sample 3, d) sample 4, e sample 5, and f) Cr atomic concentration verse sputtering thickness plot in the case five samples

The atomic concentration of Fe initially decreased and subsequently increased with increasing sputtering thickness; it was concluded that the passive film had a double-layer structure, which was composed of a major inner Cr_2O_3 passive film and major outer NiO and Fe₂O₃ passive films, and Mo

oxide was dispersed within the inner and outer passive films. According to a film thickness calculation method [44], the thickness of the passive film was estimated to be approximately 4 nm; the variation in the Cr atomic concentration with the sputtering thickness is displayed in Fig. 9f. It shows that the atomic concentration of Cr increased for each sputtering thickness within 4 nm with decreasing grain size, which indicates that the Cr_2O_3 content increased with decreasing grain size at each sputtering thickness. Considering the major contribution of the inner Cr_2O_3 film to the corrosion protection of the total passive film, the increased Cr_2O_3 content and the decreased donor density of the Cr_2O_3 film (see Fig. 7b) indicate that the corrosion protection of the passive film improved with decreasing grain size, which is consistent with the EIS, Mott-Schottky and potentiodynamic curve results.

4. CONCLUSIONS

The corrosion behaviors of 316L stainless steel with various grain sizes in 0.05 M H_2SO_4 solution with 1×10^{-6} M F⁻ were investigated using potentiodynamic curves, EIS, Mott-Schottky plots, and AES in this paper. According to the results, the following conclusions were drawn:

- 1) The tensile and yield strengths of 316L stainless steel increase and the elongation decreases with decreasing grain size.
- 2) 316L SS is in the passive state in the studied solution, and the passive film is easily eroded by pit corrosion due to the operation potential of the cathodic plate falling into the potential region of metastable pit growth. The resistance to pitting corrosion increases with decreasing grain size due to decreased absorbed density of F⁻ ions on the film surface.
- 3) The homogeneity of the passive film increases with decreasing grain size due to the decreased donor and acceptor densities.
- 4) The passive film that forms on 316L stainless steel has a double-layer structure, namely, it is composed of an inner Cr₂O₃ film and outer iron oxides, and the Cr₂O₃ content increases with decreasing grain size.

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