Molybdenum Addition Enhancing the Corrosion Resistance of Ni16Cr Alloy in Aqueous Solution

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Abstract: The influences of Mo on the structures and the electronic properties of passive films on Ni16CrMo (γ=0wt.%, 2wt.%, 5wt.%, 8wt.%, 12wt.% and 16wt.%) alloys in pH 1.0 sulfuric acid solution, pH 8.5 borate buffer solution and pH 13 sodium hydroxide solution were investigated using X-ray photoelectron spectroscopy (XPS), potentiodynamic polarization curve, Electrochemical impedance spectroscopy (EIS) and Mott-Schottky plot. The results showed that the addition of Mo can evidently refine the microstructure of Ni16Cr alloy, and the grain size sharply decreased with increasing Mo. Ni16Cr alloy was passivated in pH1 sulfuric acid solution, pH8.5 borate buffer solution and pH13 sodium hydroxide solution, each passive current density decreased and each passive potential region enlarged with the increment of Mo. XPS results showed that the passive films on Ni16CrγMo alloys were mainly composed of the inner Cr2O3 layer and the outer NiO layer with a little amount of Cr2S3, NiS and NiSO4. The resistances and compactness of the passive films on Ni16Cr alloy in the three solutions increased with the increased Mo, which implied the enhanced protection of the passive film. Mott-Schottky plots revealed that the passive film on Ni16Cr alloy appeared the p-n heterojunction, the defect number of the outer film increased with the increment of Mo, while for the inner film, the defect number decreased with Mo, while the total protection of the passive films to the metal matrix was improved with increasing Mo.

1. Introduction
Nickel based alloys were widely used in the chemical industry, food industry and especially in nuclear industry or petrol industry for their superior anti-corrosion performance [1-5]. A compact, several nanometer thickness, and highly defective passive film can automatically form on the surface of the nickel based alloys in the existence of oxygen [6-12], the passive film existing between the substrate and the aggressive electrolyte can be deemed as the ions barrier to protect the substrate from further corrosion.

NiCr alloy, like other ternary or quaternary nickel based alloy, was easily passivated in the atmosphere containing oxygen, and the passive film formed on NiCr alloy endowed it to representing the gold based alloy in the dental clinical application [13, 14] or was manufactured as NiCr coating to improving anti-corrosion behavior of the substrate [15, 16]. While for the passive film on NiCr alloy, it was generally agreed that Cr2O3 was the major component of the inner passive layer, and there were some debates about the composition of the outer layer [17-19]. The reason maybe related to the different formation conditions of the passive films (including the different studied solutions and different NiCr substrates), the composition and structure of the passive film on NiCr alloy was not invariability, and it was decided by the formation environment and the substrate composition.
However, the dependence of the film composition on the substrate component provided a possible method to improving the anti-corrosion behavior by altering the substrate component. The alloy element Mo, was an important alloy element, which was widely used in metallurgy. The beneficial effect of Mo on the corrosion resistance had been attributed to several factors, such as the enrichment of Cr and Mo in the oxide layer [20-25], stabilization the passive film [26], thickening of the passive film [27], by synergistic interaction of Mo ions with other oxides of the passive film [28, 29], and by elimination of the active surface sites through formation of Mo oxides [30]. Despite numerous papers focused on the influence of Mo on the passivity of stainless steel or other alloys, however, systematic studies on the effect of Mo on the corrosion behaviors of NiCr alloy, especially on the electronic properties of the passive films on NiCr alloys were scarce.

Therefore, molybdenum was introduced into Ni16Cr alloy to manufacture the Ni16Cr7Mo (χ = 0, 2, 5, 8, 11 and 16) alloys. The objective of this work was to investigate the Mo effect on the electronic property of the passive film on Ni16Cr alloy in pH1 H2SO4 solution, in pH8.5 borate buffer solution and in pH13 sodium hydroxide solution using electrochemical impedance spectroscopy (EIS), Mott-Schottky plot and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1 Sample preparation

The samples were prepared by melting the mixture of pure Ni (99.99 wt. %), pure Cr (99.99 wt. %) and pure Mo (99.99 wt. %) in a vacuum electric furnace with high purity argon as the protecting gas. The molten temperature dropped to 1673K, after adequate stirring for 30 min. When the molten temperature dropped to 1673K, the molten alloy was poured into a cast iron mould in the electric furnace to form the blank rod (Φ200×300 mm), then the rod was homogenized by vacuum 120 min at 1473K, hot rolling into 5 mm thick plate. Finally, the thick plate was solution annealed at 1323K for 60 min, air cooling. The samples were prepared by manufacturing the thick plate into the size of Φ10×5 mm. The compositions of the samples were determined by chemical analysis, the result was listed in table 1. One end surface of the sample was abraded with 2000 grit SiC paper, polished with 0.5 μm Al2O3 powder and then cleaned using double-distilled water, while other surfaces were sealed with epoxy resin in the lower part of an L-shaped glass tube. The electrolytes were pH8.5 borate buffer solution, pH1 H2SO4 solution and pH13 sodium hydroxide solution, respectively.

Table 1 The chemical compositions of NiCrMo alloys (wt.%)

| Sample | Cr | Mo | Ni |
|--------|----|----|----|
| 1#     | 16 | 0  | 84 |
| 2#     | 16 | 2  | 82 |
| 3#     | 16 | 5  | 79 |
| 4#     | 16 | 8  | 76 |
| 5#     | 16 | 12 | 72 |
| 6#     | 16 | 16 | 68 |

2.2 Electrochemical measurements

A conventional three-electrode system was used, and the counter electrode was a Pt wire. All of the potentials were measured against a saturated calomel electrode (SCE). All of the experiments were performed on an EG&G Model 273A potentiostat/galvanostat with a M5210 lock-in amplifier. Prior to the electrochemical experiment, the working surface was reduced potentiostatically at −1.2 V (vs. OCP) for 10 min to remove any oxides.

Potentiodynamic curves were measured ranging from -0.25V_{OCP} to 1.2V_{SCE} with a scanning rate of 1 mV/s.

EIS measurements were performed at the open circuit potential or corrosion potential (E_{corr}), a sweeping frequency ranging from 10 KHz to 5 mHz with a potential amplitude of 10 mV was used, the experimental data were analyzed using the ZsimpWin software.
Mott-Schottky plot was performed within the potential region of -0.6\text{V}_{SSCE} to 1.4\text{V}_{SCE} with a 20mV/s scanning rate, and the measured frequency was 1\text{KHz}.

3. Results and Discussion

3.1 Microstructure of NiCr\textsubscript{x}Mo alloy

The microstructures of Ni16Cr\textsubscript{x}Mo alloys were depicted in Fig.1, it can be seen that the microstructure of Ni16Cr alloy was composed of equiaxed dendrites, but the grain size varied heavily. The dendrites were gradually refined as the addition of Mo (Figs.1b, c, d, e and f), the grain size sharply decreased when the Mo content was over 2wt.%. The change of the grain size can be more clearly seen by the solutionized microstructures shown in Fig.2b, the average grain size decreased from 0.18mm to 0.006mm with the increment of Mo content. The refined microstructure was attributed to the formation of the second phase of Ni\textsubscript{4}Mo existing in the grain boundaries (seen Fig.2), the dispersed second phase in the grain boundaries can restrict the growth of the NiCr solid solution. The XRD diffractograms of Ni16Cr2Mo alloy showed in Fig.2a revealed that the second phase dispersed in the grain boundaries was mainly composed of Ni\textsubscript{4}Mo.

Fig.1 Metallographic structures of Ni16Cr\textsubscript{x}Mo (\textit{x}=0, 2, 5, 8, 11and 16) alloys, a) Ni16Cr alloy; b) Ni16Cr2Mo alloy; c) Ni16Cr5Mo alloy; d) Ni16Cr8Mo alloy; e) Ni16Cr11Mo alloy and f) Ni16Cr16Mo alloy

Fig.2 XRD analysis of Ni16Cr16Mo alloy (a) and the variation of the average grain size with Mo (b)
3.2 Passive response of Ni16Cr4Mo alloy

The Potentiodynamic polarization curves of Ni16Cr4Mo (χ=0, 2, 5, 8, 12 and 16) alloys in pH1 H2SO4 solution, pH8.5 borate buffer solution and pH13 sodium hydroxide solution at ambient temperature, were represented in Fig.3. It was evident that all the tested samples were spontaneously passivated in three solutions, as indicated by no observed active/passive transient peaks in all curves. Fig.3a showed that Ni16Cr4 alloy was in the steady passive state in the potential region from 0.18V_{SCE} to 0.75V_{SCE} in pH1 H2SO4 solution, the corresponded steady passive current density was 4.304E-5 A·cm². With the increment of Mo, the steady passive potential region enlarged, and the steady passive current density decreased, which implying the enhanced anti-corrosion behaviors of Ni16Cr4 with Mo. Ni16Cr4 alloy also exhibited the passivated behaviors in pH8.5 borate buffer solution and pH13 sodium hydroxide solution, respectively. The steady passive potential originated approximately from -0.134 V_{SCE} to 0.403 V_{SCE} with the corresponded passive current density of 3.77E-5 A·cm² in the case of pH8.5 borate buffer solution. While for pH13 sodium hydroxide solution, the steady passive potential originated approximately from -0.509 V_{SCE} to 0 V_{SCE}, and the corresponded passive current density was 2.584E-5 A·cm². Significantly, the steady passive current density obtained in pH1 H2SO4 solution reached to the maximum value, and i_{pass} acquired the minimum value in pH13 sodium hydroxide solution. Additionally, the initial passive potential of Ni16Cr4 alloy shifted to negative position by increasing the pH value of the studied solution, the above conclusions indicating the passive capability of Ni16Cr4 alloy in the above aqueous solutions obeying the following order: pH13 sodium hydroxide solution > pH8.5 borate buffer solution > pH1 H2SO4 solution.

The values of the related electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), passive current density (i_{pass}) and anodic (β_a) and cathodic (β_c) Tafel slopes were determined from the potentiodynamic polarization curves and were summarized in table2. It can be seen that the cathodic (β_c) Tafel slope was very close, ranging from -208.87 to -250.55 mV·decade⁻¹, ranging from -79.77 to 95.52 mV·decade⁻¹ and ranging from -95.46 to 140.18 mV·decade⁻¹ in pH1, pH8.5 and pH13 solutions, respectively. While the anodic (β_a) Tafel slope increased, the corrosion potential (E_{corr}) moved to positive direction, and both the corrosion current density (i_{corr}) and passive current density (i_{pass}) decreased with increasing Mo, suggesting the addition of Mo had a positive effect on the anti-corrosion performance of Ni16Cr4 alloy in the studied aqueous solutions.

![Fig.3 Potentiodynamic polarization curves of Ni16Cr4Mo (χ=0, 2, 5, 8, 12 and 16) alloys in pH1 H2SO4 solution, pH8.5 borate buffer solution and pH13 sodium hydroxide solution, respectively. a) pH1 H2SO4 solution, b) pH8.5 borate buffer solution and c) pH13 sodium hydroxide solution](image)

| Parameters | pH1 H2SO4 solution | pH8.5 borate buffer solution |
|------------|-------------------|----------------------------|
| E_{corr} / V | Ni16Cr4 | Ni16Cr2Fe | Ni16Cr5Fe | Ni16Cr8Fe | Ni16Cr12Fe | Ni16Cr16Fe |
| i_{corr} / A·cm² | -208.87 | -199.42 | -224.75 | -222.14 | -206.06 | -250.55 |
| i_{pass} / A·cm² | 85.41 | 88.59 | 105.41 | 118.4 | 121.7 | 111.66 |
| β_a / mV·decade⁻¹ | 1.07e-4 | 9.527e-6 | 5.736e-6 | 3.293e-6 | 2.976e-6 | 2.41e-6 |
| β_c / mV·decade⁻¹ | 4.304e-5 | 3.948e-5 | 5.564e-5 | 3.175e-5 | 2.963e-5 | 2.809e-5 |

Table 2 Electrochemical parameters extracted from potentiodynamic polarization curves of investigated samples in the studied solutions
3.3 Electrochemical impedance spectra of the passive films on Ni16CrγMo alloys

To insight into the effect of Mo on the electronic property of the passive film on Ni16Cr alloy, Fig 4 displayed the Nyquist plots and the corresponded Bode diagrams of the passive films on Ni16CrγMo alloy at various passive potentials for 24h in three solutions, respectively. It was clear that all Nyquist plots showed the depressed semicircles, and the corresponding Bode diagrams appeared high symmetry with the phase angles approaching 90° in the low frequency range, it was the typical passive character observed on other metal or alloy [31-35]. Additionally, it was clearly seen that the diameters of the capacitive arcs enlarged and the constant maximum phase angle increased with increasing Mo at one fixed formation potential and in one fixed solution, suggesting Mo greatly improving the film protectiveness. The modified Randles equivalent circuit with a CPE (shown in Fig.5) was used to fit the EIS taking into account only one time constant, in which Rp represented the solution resistance. The polarization resistance, Rp, can be attributed to the contributions of the passive film resistance, the charge transfer resistances and the migration of point defects mediating the growth of the passive film, the resistive contributions of the metal/film and film/solution interfaces. The constant phase element (CPE) was employed to study the dispersion of the system. The impedance and admittance of the CPE can be obtained with the following relationship [36,37]:

\[
Z_{CPE} = \left[ Y_0(j\omega)^\alpha \right]^{-1}
\]

(1)

\[
Y_{CPE} = Y_0(j\omega)^\alpha
\]

(2)

Where j was the imaginary number, and \(\omega\) was the frequency of the alternative current. The exponent, \(\alpha\), was defined as the CPE power, which was adjusted between 0 and 1. For \(\alpha=1\), the CPE described an ideal capacitor with \(Y_0\) equal to the capacitance \(C\). For \(\alpha=0\), the CPE was an ideal resistor. When \(\alpha=0.5\), the CPE represented the Warburg impedance with diffusion character. The CPE had the properties of a capacitance when \(0.5<\alpha<1\). The CPE described the frequency dispersion of the time constants due to local inhomogeneity [38-41], porosity and roughness of the electrode surface [42,43].

Table 3 summarized the fit parameters for equivalent circuits corresponding to EIS measurements of the passive films on Ni16CrγMo alloy in three studied solutions, the chi-squared (\(\chi^2\)) values of the order of 10^3 showed satisfactory agreement between the experimental and theoretical values, suggesting that this equivalent circuit model reasonably reflected the electrochemical process occurring in the NiCrMo alloy/passive film/solution system. From table3, it was clear that the ohmic resistances \((R_F and R_S)\) were dependent on the formation potential and Mo content, which implying the Mo effect on the anti-corrosion behaviors of Ni16Cr alloy. In order to visually displayed the Mo effect on ohmic resistance of electrochemical process, Fig.6 showed the variations of polarization resistances and molybdenum content in different formation potentials and solutions, it can be seen that Rp rapidly increased with the increment of Mo in the case of one fixed passive potential and in one fixed studied solution, which indicating the increased corrosion resistance. However, the polarization resistance, Rp, obtained from EIS data was highly dependent on the solution, therefore, Rp was not suitable for evaluating the electrochemical process of the passive film. While the capacitance, C, was independent on the solution conditions and was, therefore, a much reliable means of determining the electrochemical properties and the thickness of the passive film [44]. Subsequently, the value of C of the passive film can be acquired by calculating the effective capacitance from the modified Randles equivalent circuit with a CPE [45]:

\[
C = Q^{1/\alpha} \left( R_S^{-1} + R_p^{-1} \right)^{(\alpha-1)/\alpha}
\]

(3)

The fitted results showed in table2 revealed that \(R_p>>R_s\), and then Eq.3 can be simplified to Eq.4.
\[ C = \frac{Q^\alpha}{R_p^{1-\alpha}} \]  

Substituting the fitted polarization resistance \( R_p \), the constant phase element \( Q \), and the CPE power \( \alpha \) into Eq.(4), the effective capacitance \( C \) of the passive film can be obtained. Consequently, Fig.7 exhibited the variations of film capacitance with Mo in three studied solutions, it was evident that the film capacitance decreased with increasing Mo at one fixed formation potential and in one fixed solution, indicating the enhanced protecting properties of the passive film. Since film capacitance and polarization resistance obtained from EIS data can only reflect the physical property of the passive film and not direct reply the corrosion rate, thereupon, the parameter of time constant of the relevant electrochemical process was employed to tackle this problem. According to Petrossians [46], the time constant \( \tau \) can be calculated as following relationship:

\[ \tau = C \times R_p \]  

where, the unit of \( C \) is equal to s/ohm-cm² and the unit of \( R_p \) was ohm-cm², the time constant \( \tau \) therefore had the unit of time (s). Based on the combination of Eqs. 4, 5 and the fitted results of the impedance (seen table 2), the variation in the time constant \( \tau \) and Mo was presented in Fig.8, \( \tau \) displayed an obvious increase as Mo increased in the case of every formation potential and every solution. As the time constant in the equivalent circuit (shown in Fig.5) was not only related to the electrochemical process occurring at the film/solution interface but also to the electrochemical process occurring at the substrate/film interface, the increased time constant maybe attributed to the increased film thickness [47], hence to restrain the charge transfer process in the film/solution interface and the ionic movement through the passive film.

Another important parameter for the passive film was the film thickness, \( L_{ss} \), which can be acquired using Eq. (6):

\[ L_{ss} = \frac{\varepsilon \varepsilon_0}{C} \]  

Where \( \varepsilon \) was the dielectric constant of the passive film, \( \varepsilon_0 \) was the vacuum permittivity \((8.854 \times 10^{-14} \text{ F/cm})\), and \( C \) was the film capacitance \((\mu \text{F/cm}^2)\). The average field strength of the passive film, \( \bar{E} \), can be obtained from the slope of the \( E_{a0}-L_{ss} \) linear plot, and the variations of the field capacitance \( \varepsilon \) of the passive films and molybdenum content in different solutions was showed in Fig.9, it can be observed that the film field strength was in the order of \( 10^{6} \text{ V/cm} \), which was close to the field strength previously reported [48-51]. The film field strength, \( \varepsilon \), decreased with the increment of Mo in the case of one fixed solution, and \( \varepsilon \) decreased with increasing pH value in the case of one fixed Mo content.
Fig. 4 The Nyquist plots and the corresponded Bode in phase plots of the passive films on Ni16Cr7Mo alloys at different passive potentials in three solutions, a) Nyquist plots and b) Bode in phase plots of the passive films on Ni16Cr7Mo alloys at 0.3V in pH 1 H2SO4 solution; c) Nyquist plots and d) Bode in phase plots of the passive films on Ni16Cr7Mo alloys at 0.5V in pH 1 H2SO4 solution; e) Nyquist plots and f) Bode in phase plots of the passive films on Ni16Cr7Mo alloys at -0.1V in pH 8.5 borate buffer solution; g) Nyquist plots and h) Bode in phase plots of the passive films on Ni16Cr7Mo alloys at 0.2V in pH 8.5 borate buffer solution; i) Nyquist plots and j) Bode in phase plots of the passive films on Ni16Cr7Mo alloys at -0.5V in pH 13 sodium hydroxide solution; k) Nyquist plots and L) Bode in phase plots of the passive films on Ni16Cr7Mo alloys at -0.2V in pH 13 sodium hydroxide solution.

Fig. 5 Schematic representation of the metal/passive film/solution interfaces and an Equivalent electronic circuit used for fitting the impedance.
Table 3 Fit parameters for equivalent circuits corresponding to EIS measurements of the passive films on Ni16Cr7Mo alloy at 0.5V for 24h in pH1 sulfuric acid solution

| Solutions | Samples | $R_p$ / $\Omega \cdot \text{cm}^2$ | $10^{-2}Q$ / $\mu$C | $\alpha$ | $10^{-2}R_e$ / $\Omega \cdot \text{cm}^2$ | $10^{-2}Z_f$ | $\Sigma\chi$ |
|-----------|---------|---------------------------------|-------------------|--------|---------------------------------|----------------|--------|
| PH=1      | 1#      | 9.48                            | 1.241             | 0.948  | 0.9199                          | 4.95           | 4.127  |
|           | 2#      | 14.17                           | 1.955             | 0.9238 | 0.9528                          | 19.89          | 4.092  |
|           | 3#      | 11.21                           | 1.173             | 0.9063 | 0.9549                          | 26.87          | 1.744  |
|           | 4#      | 10.06                           | 0.928             | 0.9173 | 0.9311                          | 33.83          | 1.002  |
|           | 5#      | 13.77                           | 1.716             | 0.9462 | 0.9277                          | 40.26          | 1.494  |
|           | 6#      | 13.97                           | 1.755             | 0.9457 | 0.9337                          | 84.4           | 2.009  |
| PH=8.5    | 1#      | 19.12                           | 3.764             | 3.04   | 0.9386                          | 3.838          | 5.272  |
|           | 2#      | 17.56                           | 2.458             | 2.258  | 0.9406                          | 8.385          | 5.764  |
|           | 3#      | 13.63                           | 1.571             | 0.9378 | 0.9418                          | 25.15          | 1.592  |
|           | 4#      | 14.44                           | 1.623             | 0.9457 | 44.32                           | 1.956          |
|           | 5#      | 13.6                            | 0.936             | 94.52  | 1.71                            |
|           | 6#      | 14.27                           | 0.9192            | 0.9257 | 957                              | 519.5          | 1.762  |
| PH=13     | 1#      | 22.04                           | 4.121             | 1.219  | 0.8879                          | 1.059          | 1.264  |
|           | 2#      | 13.3                            | 3.058             | 2.708  | 0.9284                          | 1.182          | 1.264  |
|           | 3#      | 14.34                           | 2.537             | 0.8949 | 0.9147                          | 2.74           | 2.654  |
|           | 4#      | 11.08                           | 2.292             | 0.9384 | 0.9242                          | 3.706          | 1.256  |
|           | 5#      | 11.29                           | 2.155             | 0.9306 | 0.9342                          | 5.275          | 1.256  |
|           | 6#      | 25.93                           | 1.893             | 0.901  | 0.9336                          | 5.899          |

Fig.6 Variations of polarization resistances and molybdenum content in different solutions, a) pH1 H$_2$SO$_4$ solution, b) pH 8.5 borate buffer solution, c) pH 13

Fig.7 Variations of film capacitance and molybdenum content in different solutions, a) pH1 H$_2$SO$_4$ solution, b) pH 8.5 borate buffer solution, c) pH 13
Before discussing the influence of Mo on the Mott-Schottky plot of the passive film on Ni16Cr alloy, it was necessary to clarify which frequency was selected to measure Mott-Schottky plot. The fitted EIS results shown in table 4 proposed the constant phase element \( C_{\text{f}} \), which was an indication of the obvious dependence of the capacitance of the passive film on the measured frequency. In order to gain more information about the ionic property of the passive film, the film capacitance can be calculated as:

\[
C = \frac{1}{2\pi fZ_{\text{im}}}
\]

Fig. 9 presented the typical \( C-f \) plots for the steady-state films formed on Ni16Cr\( _{x} \)Mo alloys and measured at -0.5V\(_{\text{SCE}} \) for 24h in pH 13 sodium hydroxide solution. It was seen that the film capacitance, \( C \), decreased with increasing Mo, which implied higher dielectric and protectiveness of the passive film. The frequency-dependence behavior of the measured capacitance was different in two frequency regions. In the frequency region from 10Hz to 10KHz, the measured capacitance values were almost constant; whereas in the low frequency region (f<10Hz), all capacitance curves were shifted to higher values, which indicated that the capacitance dependence on the frequency in the low frequency region. Therefore, the frequency of 1 KHz was used as the applied frequency to eliminate the capacitance dependence on the frequency in this paper.
The semi-conductive parameters of the passive films on metals were often acquired using the Mott-Schottky analysis based on the measurement of the electrode capacitance as a function of the applied potential. The reciprocal of the square of the capacitance (C) and the applied potential (E) exhibited a linear relationship under the depletion conditions. The basic equations for Mott-Schottky analysis were list as following [52-56]:

For an n-type semiconductor:

\[ C^{-2} = \frac{2}{\varepsilon_0 \varepsilon A N_D} (E - E_{FB} - \frac{KT}{e}) \]  \( \text{(7)} \)

For a p-type semiconductor:

\[ C^{-2} = \frac{2}{\varepsilon_0 \varepsilon A N_A} (E - E_{FB} + \frac{KT}{e}) \]  \( \text{(8)} \)

Where \( e \) was the electron charge (1.602×10^{-19} \text{ C} ), \( N_D \) was the donor density, \( N_A \) was the acceptor density, \( \varepsilon \) was the dielectric constant of the passive film, taken as 30 [57], \( \varepsilon_0 \) was the vacuum permittivity (8.854×10^{-14} \text{ F/cm} ), \( K \) was the Boltzmann constant (1.38×10^{-23} \text{ J/k} ), \( T \) was the absolute temperature and \( E_{FB} \) was the flat band potential. The KT/e term can be neglected because it was only approximately 25 mV at room temperature. From Eqs. (7) and (8), \( N_D \) and \( N_A \) can be determined from the slope of the plot of the experimental \( C^{-2} \) as a function of \( E \), and \( E_{FB} \) can be obtained from extrapolation of the linear portion to \( C^{-2} = 0 \).

Fig. 11 showed the typical \( C^{-2} \) vs. potential plots for the passive films formed on Ni16Cr\(_2\)Mo alloys at different passive potentials for 24h in pH1 H\(_2\)SO\(_4\) solution, pH8.5 borate buffer solution, as well as pH13 sodium hydroxide solution, respectively. It can be seen that all \( C^{-2} \sim E \) plots can be divided into four regions based on the slopes, the slopes appeared positive in the potential regions of -0.85V\(_{SCE}\) and -0.6V\(_{SCE}\), implying the n-type semi-conductive character. The slopes became negative when the sweeping potential falling into potential region II (0.6V\(_{SCE}\) ~ -0.4V\(_{SCE}\)), it indicating the p-type semi-conductive character. When the sweeping potential region was in the range of -0.4V\(_{SCE}\) to 0.45V\(_{SCE}\), the \( C^{-2} \sim E \) plots re-exhibited positive slopes, which showing the n-type semi-conductive property. Finally, the reciprocal of the square of the capacitance decreased with the potential moving to positive direction within the potential region IV(0.45V\(_{SCE}\) ~ 0.9V\(_{SCE}\)), the decreased \( C^{-2} \) with potential implied the negative slope of \( C^{-2} \sim E \) plot, and it was corresponded to the p-type semi-conductive property. The variations of the slopes of the \( C^{-2} \sim E \) plots with the sweeping potential were often attributed to the compositions and structures of the passive films. According to PD M [58], the n-type semi-conductive characters of the passive films indicated the dominant defect in the passive films over...
the potential regions I and III was oxygen vacancies or metal interstitials, cation vacancies may be the dominant defects in the passive films over potential regions II and IV. Similar phenomena were observed on the passive films formed on stainless steels and nickel-based alloy [59-62]. Additionally, it was clearly seen from Fig.11 that the slopes of –2 versus E plots within regions I and II decreased with increasing Mo, while the slopes sharply increased with the increment of Mo within regions II and IV, which demonstrating the increased defect number in regions I and II with Mo, and the decreased defect number in regions II and IV. The slope dependence on the potential can be attributed to the variation of the composition and structure of the passive film. Fig.12 depicted the depth profile of elements in the passive films on Ni16Cr7Mo alloys at 0.4V_sce for 24h in pH1 H_2SO_4 solution, it showed that the passive films were mainly composed of Ni, Cr and O elements with a little amount of S, connecting with the Cr, Ni, Mo and S narrow spectra measured after sputtering for 0nm depth, it can be found that S appeared in the outer film in the features of NiS and NiSO_4, respectively. While for the passive film on Ni16Cr16Mo alloy, S existed in the outer film in the forms of CrS_2, NiS and NiSO_4, respectively. Significantly, the appearance of S in the outer film may change the structure of the initial outer film, and hence to affect the semi-conductive character of the passive film. According to PDM [58], ZnO, TiO_2, V_2O_5 and MoO_3 are n-type semiconductors characterized by the main defect of oxygen vacancy or metal interstitial. Conversely, Cu_2O, NiO and Cr_2O_3 are the representatives of the p-type semiconductors as the predominant defect is metal vacancy. The appearance of NiSO_4 in the outer film can lead to the increased oxygen vacancy in NiO lattice, and the non-stoichiometry NiO_1-x will be formed. Therefore, the semi-conductive properties of NiO can be transferred from p-type to n-type. Finally, the slope dependence on the potential can be explained by the following discussion: during the anodic polarization process between -0.85V_sce and -0.6V_sce, n-type oxide film MoO_3 is responsible for the Mott-Schottky response. Cr_2O_3 and NiO oxides controlled the Mott-Schottky response in potential region II (-0.6V_sce ~ -0.4V_sce). While in potential region III (-0.4V_sce ~ 0.45V_sce), the non-stoichiometry NiO_1-x will be formed, which appeared the n-type semi-conductive character. With the potential increasingly moving to positive direction, the dissolution of passive films occurred, the Mott-Schottky response was controlled by the un-dissolved Cr_2O_3 and NiO in the passive film.

As illustrated above, the passive films on nickel based alloys appeared the duplex structure, in which Cr_2O_3 was the major component of the inner film, nickel oxides were the dominant components of the outer film. Herein, the energy band of the inner film bend down in the inner film /outer film interface, and the energy band may bend up in the outer film/solution interface owing to the differences of the Fermi levels of the inner/outer films and the solution. Fig.15 showed the schematic of the bending of the energy band in inner film/outer film interface and outer film/solution interface, the bending of the energy band lead to the appearance of three space charge layers, which were named SCL_{p-n}, SCL_{p-n} and SCL_{n}, respectively. The total space charge capacitance can be expressed as following:

$$\frac{1}{C} = \frac{1}{C_{p-n}} + \frac{1}{C_{p-n}} + \frac{1}{C_{n}}$$  \hspace{1cm} (9)

In order to quantitatively illustrate the Mo effect on the semi-conductive properties of the passive films on Ni16Cr alloys, the non-linear fitting method proposed by Chen [63] was used to calculated the defect numbers within three space charge layers. Fig.14 showed the decompositions of the space charge capacitances of the passive films on Ni16Cr alloy and Ni16Cr16Mo alloy at -0.2V for 24h in sodium hydroxide solution, the reciprocal of the square of the capacitance can be decomposed into the reciprocal of the square of the capacitance of the space charge layer in p-n heterojunction interface (C_{p-n}^{-2}) and the reciprocal of the square of the capacitance of the space charge layer in outer film/solution interface (C_{m}^{-2}), respectively. Subsequently, connecting the non-linear fitting method and Eqs.(7) and (8), the majority defect number of the innermost film (N_{p-n}), the majority defect number
of the outermost film ($N_{nd}$), the dominant defect number of the space charge layer (SCL$_{pn}$) in outer side ($N_{pn-d}$) and the dominant defect number of the space charge layer (SCL$_{na}$) in inner side ($N_{na}$), were calculated and depicted in tables 4, 5 and 6, respectively. The calculated results showed that the defect density reached the order of $10^{19} \sim 10^{21}$ cm$^{-3}$, which was in agreement with the data reported in the literature for passive films formed on Ni(15,30)Cr alloy in the borate buffer solution [64]. It can be seen from table 3, table 4 or table 5 that $N_{nd}$ and $N_{na}$ increased with increasing Mo, implying the increased defect density in the outer film with the increased Mo. $N_{pn-d}$ and $N_{pn-a}$, however, decreased with the increment of Mo, indicating the decrement of defect density within the inner film with the addition of Mo. The flat band potential ($E_{fb}$) is a critical parameter used to determine the positions of the semiconductor energy bands with respect to the redox potentials of electro active ions in the solution. The flat band potential provided useful information to understanding the localized corrosion resistance although the flat band potential was complicated by the presence of surface states and defects unavoidably connected with the nanometer size of the passive film [65-67]. Tables 3, 4 and 5 depicted that the flat band potential shifted to the positive direction with increasing Mo, suggesting the increment of the passive film stability [66].

The increased $N_{nd}$ and $N_{na}$ implied the defects density in the outer film increased, and the compactness of the outer film was destructed gradually as the increased in Mo. It was substantiated by the XPS results shown in Fig.12, S content increased in the outer film with the increased Mo, and lead to the increasing the defects’ concentration in the outermost layer. While the increments of $N_{pn-d}$ and $N_{pn-a}$ implied the enhanced compactness of the inner film with increasing Mo, whether the passive films on Ni16Cr$\chi$Mo alloys still had good protection or not, the answer can be yes by the following reason. The passive films on nickel based alloys mainly consisted of the inner Cr-rich oxide and the outer iron/nickel oxides, in which the inner Cr-oxide was the major contribution to the protection. Comparison the values of $N_{nd}$ / $N_{na}$ and the corresponding $N_{pn-d}$ and $N_{pn-a}$ values, it can be found that the value of $N_{pn-d}$ or $N_{pn-a}$ was lower than that of $N_{nd}$ or $N_{na}$, and $N_{pn-d}$ or $N_{pn-a}$ became more lower with increasing Mo, which indicated that the Mo effect on the compactness of the inner film was greater than that of the outer film, it demonstrated that the compactness of innermost layer was still enhanced with Mo, and the whole passive film still had the increased compactness to the Ni16Cr$\chi$Mo alloy with increasing Mo.
Fig. 11 The Mott-Schottky plots of the passive films on Ni16Cr7Mo alloys at different passive potentials in three solutions, a) 0.3V and b) 0.5V for 12h in pH 1 H2SO4 solution; c) -0.1V and d) 0.2V for 12h in pH 8.5 borate buffer solution; e) -0.2V and f) -0.5V for 12h in pH 13 sodium hydroxide solution.

Fig. 12 Depth profile of elements in the passive films on Ni16Cr7Mo alloys at 0.4V_{SCE} for 24h in pH1 H2SO4 solution, a) Ni16Cr alloy; b) Ni16Cr2Mo alloy; c) Ni16Cr5Mo alloy; d) Ni16Cr8Mo alloy; e) Ni16Cr12Mo alloy and f) Ni16Cr16Mo alloy.
Fig. 13 Cr, Ni, Mo and S narrow spectra of the passive film on Ni16Cr7Mo alloys at 0.4V_SCE for 12h in pH1 H2SO4 solution, a) Cr2p3/2 spectra after sputtering for 0nm depth for 1# sample; b) Ni2p3/2 spectra after sputtering for 0nm depth for 1# sample; c) Mo3d5/3 spectra after sputtering for 0nm depth for 1# sample; d) S2p3/2 spectra after sputtering for 0nm depth for 1# sample; e) Cr2p3/2 spectra after sputtering for 0nm depth for 6# sample; f) Ni2p3/2 spectra after sputtering for 0nm depth for 6# sample; g) Mo3d5/3 spectra after sputtering for 0nm depth for 6# sample; h) S2p3/2 spectra after sputtering for 0nm depth for 6# sample.
Table 4 Parameters of the Mott-Schottky plots for Ni16Cr16Mo alloys passivated at 0.3V and 0.5V for 24h in pH1 sulfuric acid solution

| Mo content | $10^{-21}N_{nd}/cm^3$ | $10^{-21}N_{nv}/cm^3$ | $10^{-21}N_{p,d}/cm^3$ | $10^{-21}N_{p,n}/cm^3$ | $E_{FB}/V_{SCE}$ |
|------------|------------------------|-----------------------|-------------------------|------------------------|-----------------|
| 0          | 1.062                  | 0.972                 | 1.147                   | 1.752                  | 0.3V            |
| 2          | 1.249                  | 1.099                 | 1.913                   | 2.505                  | 0.6V            |
| 5          | 1.632                  | 1.26                  | 2.013                   | 2.519                  | 0.95            |
| 8          | 1.858                  | 1.33                  | 2.446                   | 2.242                  | 1.25            |
| 12         | 2.087                  | 1.953                 | 2.642                   | 2.152                  | 1.55            |
| 16         | 2.213                  | 2.088                 | 3.036                   | 2.677                  | 1.85            |

Table 5 Parameters of the Mott-Schottky plots for Ni16Cr16Mo alloys passivated at -0.1V and 0.2V for 24h in pH8.5 borate buffer solution

| Mo content | $10^{-21}N_{nd}/cm^3$ | $10^{-21}N_{nv}/cm^3$ | $10^{-21}N_{p,d}/cm^3$ | $10^{-21}N_{p,n}/cm^3$ | $E_{FB}/V_{SCE}$ |
|------------|------------------------|-----------------------|-------------------------|------------------------|-----------------|
| 0          | -1.89                  | 1.115                 | 2.185                   | 2.126                  | -0.25           |
| 2          | 2.082                  | 1.189                 | 2.553                   | 2.378                  | -0.55           |
| 5          | 2.214                  | 1.223                 | 2.74                    | 2.523                  | -0.85           |
| 8          | 2.553                  | 1.375                 | 3.371                   | 3.092                  | -1.15           |
| 12         | 3.211                  | 2.271                 | 3.815                   | 3.516                  | -1.45           |
| 16         | 5.715                  | 3.00                  | 6.628                   | 5.54                   | -1.75           |

Table 6 Parameters of the Mott-Schottky plots for Ni16Cr16Mo alloys passivated at -0.5V and -0.2V for 24h in pH13 sodium hydroxide solution

| Mo content | $10^{-21}N_{nd}/cm^3$ | $10^{-21}N_{nv}/cm^3$ | $10^{-21}N_{p,d}/cm^3$ | $10^{-21}N_{p,n}/cm^3$ | $E_{FB}/V_{SCE}$ |
|------------|------------------------|-----------------------|-------------------------|------------------------|-----------------|
| 0          | 0.229                  | -0.2V                 | -0.2V                   | -0.2V                  | -0.25           |
| 2          | 0.394                  | 2.341                 | 0.628                   | 3.637                  | -0.55           |
| 5          | 0.443                  | 3.561                 | 1.005                   | 16.267                 | -0.85           |
| 8          | 0.857                  | 4.866                 | 2.002                   | 19.168                 | -1.15           |
4. Conclusion
The element Mo was added into Ni16Cr alloy to fabricate the Ni16Cr\textsubscript{\chi}Mo (\chi=0wt.\%, 2wt.\%, 5wt.\%, 8wt.\%, 12wt.\% and 16wt.\%) alloys. The structure and the electronic property of the passive films on Ni16Cr\textsubscript{\chi}Mo alloys in pH1 H\textsubscript{2}SO\textsubscript{4} solution, pH8.5 borate buffer solution and pH13 sodium hydroxide solution were explored using potentiodynamic polarization curve, electrochemical impedance spectra (EIS), Mott-Schottky plot and X-ray photoelectron spectroscopy (XPS). The following conclusions can be drawn as following:

1) Ni16Cr alloy was in the passive state in pH1 H\textsubscript{2}SO\textsubscript{4} solution, pH8.5 borate buffer solution and pH13 sodium hydroxide solution, the passive current density decreased and the passive potential region enlarged with the increased Mo;

2) Mo can enhance the protectiveness of the passive films on Ni16Cr alloy by improving the compactness of the passive film and by increasing the charge resistances between the film/solution and substrate/film interfaces;

3) The passive films on Ni16Cr\textsubscript{\chi}Mo alloys appeared the p-n heterojunction structure, the passive films were consisted of the inner Cr\textsubscript{2}O\textsubscript{3} layer and the outer NiO layer with a little amount of S compounds. The defect density was in the order of the magnitude of 10\textsuperscript{19} \sim 10\textsuperscript{21} cm\textsuperscript{-3}, the defect density of the outer film increased and the defect density of the inner film decreased with the increased Mo, the flat band potential moved to the positive direction with Mo.

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Reference
[1] M. Bojinov, A. Galtayries, P. Kinnuncen, A. Machet, P. Marcus, Electrochim. Acta, 52(2007)7475.
[2] B. Peng, B.T. Lu, J.L. Luo, Y.C. Lu, H.Y. Ma, J. Nuclear Materials, 378(2008)333.
[3] T. Chen, H. John, J. Xu, Q.H. Lu, J. Hawk, X.B. Liu, Corros. Sci., 77(2013)230.
[4] J.J. Gray, J.R. Hayes, G.E. Gdowski, B.E. Viani, C.A. Orme, J. Electrochem. Soc., 153(2006)B61.
[5] J.J. Gray, J.R. Hayes, G.E. Gdowski, C.A. Orme, J. Electrochem. Soc., 153(2006)B156.
[6] M.A. Rodriguez, R.M. Carranza, R.B. Rebak, Passivation and Depassivation of Alloy 22 in Acidic
Chloride Solutions, J. Electrochem. Soc., 157(2010)C1.

[7] A.M.P. Simões, M.G.S. Ferreira, B. Rondot, M. Da Cunha Belo, Study of Passive Films Formed on AISI 304 Stainless Steel by Impedance Measurements and Photoelectrochemistry, J. Electrochem. Soc., 137(1990)82.

[8] C. Sunseri, S. Piazza, F. Di Quarto, Photocurrent Spectroscopic Investigations of Passive Films on Chromium, J. Electrochem. Soc., 137(1990)2411-2417.

[9] S. Haupt and H.-H. Strehlow, Corros. Sci., 37(1995)43.

[10] P. Marcus and J. M. Grimal, Corros. Sci., 33(1992)805.

[11] C. Marconnet, Y. Wouters, F. Miserque, C. Dagbert, J.-P. Petit, A. Galerie, D. Féron, Electrochim. Acta, 54(2008)123.

[12] L.A.S. Ries, M. Da. Cunha Belo, M.G.S. Ferreira, I.L. Muller, Corros. Sci., 50(2008)676.

[13] J. Pan, J. G. Gerstorfer, D. Thierry, C. Leygraf, J. Electrochem. Soc., 142(1995)1454.

[14] G. AHL, S. Joiret, D. Abourazzouk, Electrochim. Acta, 43(1998)53.

[15] Sukhpal Singh Chatha, Hazoor S. Sidhu, Buta S. Sidhu, Surface and Coatings Technology, 206(2012)3839.

[16] Sukhpal Singh Chatha, Hazoor S. Sidhu, Buta S. Sidhu, Surface and Coatings Technology, 206(2012)4212.

[17] M. Bojinov, G. Fabricius, P. Kinnunen, T. L. Mäkelä, T. Saario, G. Sundholm, J. Electroanal. Chem., 504(2001)29.

[18] T. Jabs, P. Borthen, H.H. Strenblow, J. Electrochem. Soc., 144(1997)1231.

[19] A.S. Lim, A. Atrens, Appl. Phys. A., 54(1992)343.

[20] M.W. Tan, E. Akiyama, A. Kawashima, K. Asami, K. Hashimoto, Corros. Sci., 37(1995)1289.

[21] H. Habazaki, A. Kawashima, K. Asami, K. Hashimoto, Corros. Sci., 33(1992)225.

[22] C.M. Abreu, M.J. Cristóbal, R. Losada, X.R. Nóvoa, G. Pena, M.C. Pérez, Electrochim. Acta, 49(2004)3049.

[23] M.F. Montemor, A. Simões, M.G.S. Ferreira, M. Da Cunha Belo, Corros. Sci., 41(1999)17.

[24] Y.C. Lu, C.R. Clayton, Corros. Sci., 29(1989)927.

[25] V. Vignal, J.M. Olive, D. Desjardins, Corros. Sci., 41(1999)869.

[26] I. Olefjord, B. Brox, and U. Jelvestam, J. Electrochem. Soc., 132(1985)2584.

[27] J.W. Schultze, M.M. Lohrenegel, D. Ross, Electrochim. Acta, 28(1993)973.

[28] K. Sugimura, Y. Sawada, Corros. Sci., 17(1977)425.

[29] E. Akiyama, A. Kawashima, K. Asami, K. Hashimoto, Corros. Sci., 38(1996)1281.

[30] K. Hashimoto, K. Asami, K. Teramoto, Corros. Sci., 19(1979)3.

[31] A. Sun, J. Franc, D.D. Macdonald, J. Electrochem. Soc., 153(2006)B260.

[32] R.M. Fernández-Domene, E. Blasco-Tamarit, D.M. García-Garía, J. García-Antón, Electrochim. Acta, 95(2013)1.

[33] C. Valero Vidal, A. Lgual-Muñoz, Electrochim. Acta, 55(2010)8445.

[34] S.L.D. Assis, S. Wolynec, I. Costa, Electrochim. Acta, 51(2006)1815.

[35] J. Pan, D. Thierry, C. Leygraf, Electrochim. Acta, 41(1996)1143.

[36] K. Jutterm, Electrochim Acta, 35(1990)1501.

[37] V.A. Alves, M.A. Brett Christopher, Electrochim. Acta, 47(2002)2081.

[38] Z. Lukacs, J. Electroanal. Chem., 432(1997)79.

[39] Z. Lukacs, J. Electroanal. Chem., 464(1999)68.

[40] L. Young, Anodic Oxide Films, Academic Press, New York, 1961.

[41] C.A. Schiller and W. Strunz, Electrochim. Acta, 46(2001)3619.

[42] R. Jurczakowski, C. Hitz, and A. Lasia, J.Electroanal. Chem., 572(2004)355.

[43] T. Pajkossy, Solid State Ionics, 176(2005)1997.

[44] R.K. Potucek, R.G. Rateick, Jr., V.I. Birss, J. Electrochem. Soc., 153(2006)B304.

[45] S. P. Harrington and T. M. Devine, J. Electrochem. Soc., 155(2008)C381.

[46] A. Petrossians, J.J. Whalen III, J.D. Weiland and F. Mansfeld, J. Electrochem. Soc., 158(2011)D269.
[47] C. Boissy, C. Alemany-Dumont, B. Normand, Electrochemistry Communications, 26(2013)10.
[48] D.S. Kong, W.H. Lu, Y.Y. Feng, Z.Y. Yu, J.X. Wu, W.J. Fan and H.Y. Liu, J. Electrochem. Soc., 156(2009)C39.
[49] Z. Szkolarska-Smialowska, W. Kozlowski, in:M. Froment (Ed.), Passivity of Metals and Semiconductors, Elsevier, Netherlands, 1983.
[50] S. Haupt, C. Carinski, U. Collisi, H. W. Hoppe, H. H. Strebbolw, Surf. Interf. Anal. 9(1986)357.
[51] G. Vázquez and I. González, J. Electrochem. Soc. 154(2007)C702.
[52] R. De Gryse, W. P. Gomes, F. Cardon and J. Vennik, J. Electrochem. Soc., 122(1975)711.
[53] N.E. Hakiki, M. Da. Cunha Belo, A. M. P. Simões and M. G. S. Ferreira, J. Electrochem. Soc., 145(1998)3821.
[54] H. O. Finklea, J. Electrochem. Soc., 129(1982)2003.
[55] N. E. Hakiki, M. Da Cunha Belo, J. Electrochem. Soc., 143(1996)3088.
[56] G. Nogami, J. Electrochem. Soc., 129(1982)2219.
[57] M.A. Rodríguez and R. M. Carranza, J. Electrochem. Soc., 158(2011)C221.
[58] D.D. Macdonald, J. Electrochem. Soc., 139(1992)3434.
[59] N.E. Hakiki, S. Boudin, B. Rondot, M. Da. Cunha Belo, Corros. Sci., 37(1995)1809.
[60] A. Di Paola, D. Shukla, U. Stimming, Electrochim. Acta, 36(1991)345.
[61] L.A.S. Ries, M. Da Cunha Belo, M.G.S. Ferreira, I.L. Muller, Corrs. Sci., 50(2008)968.
[62] M. Da Cunha Belo, N.E. Hakiki, M.G.S. Ferreira, Electrochim. Acta, 44(1999)2473.
[63] R. Jiang, C.F. Chen and S.Q. Zheng, Electrochim. Acta, 55(2010)2498.
[64] H.J. Jang and H.S. Kwon, J. Electrochem. Soc., 3(2007)1.
[65] S.P. Harrington, T.M. Devine, J. Electrochem. Soc., 156(2009)C154.
[66] A.M. Schmidt, D.S. Azambuja, E.M.A. Martini, Corros. Sci., 48(2006)2901.
[67] E. Sikora, J. Sikora, D.D. Macdonald, Electrochim. Acta, 41(1996)783.