Research Article

Passivity and Semiconducting Behavior of a High Nitrogen Stainless Steel in Acidic NaCl Solution

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Received 7 September 2016; Accepted 17 October 2016

Academic Editor: Paolo Ferro

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The passivity and semiconducting behaviors of a high nitrogen-containing nickel-free stainless steel (HNSS) in 0.05 mol/L H₂SO₄ + 0.5 mol/L NaCl have been investigated. Results indicated that HNSS offered excellent pitting corrosion resistance in corrosive environments. Three corrosion potential values were observed in potentiodynamic polarization response, indicating the existence of an unstable system. The current transient and Mott-Schottky plots demonstrated that the stability of passive films decreased with the increase of applied potentials. The angle resolved X-ray photoelectron spectrometric results revealed that the primary constituents of passive films formed in 0.05 mol/L H₂SO₄ + 0.5 mol/L NaCl solution were composed of iron oxides, manganese oxides, Cr₂O₃, and Cr(OH)₃. Meanwhile, it indicated that molybdenum oxides did not exist in the oxide layer, but chloride ions were present in the passive films.

1. Introduction

Since the first report about the use of nitrogen as an alloying element in 1938, research on the nitrogen-containing stainless steels has been widely carried out [1]. As a beneficial alloying element, the effect of nitrogen on mechanical properties and corrosion resistance of stainless steels have been deeply investigated since the 1990s. It has been reported that the addition of nitrogen could drastically increase both the yield strength and ultimate tensile strength without sacrificing the ductility and toughness [2–6]. Moreover, the addition of nitrogen could also improve the corrosion, corrosion fatigue, and stress corrosion cracking resistance of stainless steels [5, 7–13]. Therefore, nitrogen is a strong austenite stabilizing element and is expected to substitute for relatively expensive element of nickel to make HNSS a resource-saving materials.

With these increasing demands, it is necessary to investigate the passive behavior and properties of passive films of the HNSS. Generally, the passive films formed on stainless steels are mainly composed of metal oxides and/or hydroxides which envisaged semiconductors and ranged from 1 nm to 10 nm in thickness. The electrical properties of which are

expected to be crucially important for understanding the protective characters against corrosion. Passive films formed on surfaces of stainless steels have been described as a bilayer structure of (Cr(III) and Fe(III)) mixed inner layer enriched with Cr₂O₃ and Cr-hydroxide outer layer. Previous results revealed that the passive films on stainless steels were mainly composed of Cr₂O₃, Cr(OH)₃, MoO₂, MoO₃, Fe₂O₃, Fe₃O₄, FeOOH, and so forth, which was caused by either cation transport through interstitial diffusion or anion diffusion inwards the metal [8, 12, 14–18]. However, the composition of films are influenced by both the chemical composition [8] and pH value of the solution [12, 16, 19]. Moreover, the formed films could affect their semiconducting properties and protection ability [20]. In the investigation of passive films on HNSS, Fu et al. reported that the ratio between Cr-oxide and Cr-hydroxide increased with the nitrogen concentration [12]. Ningshen et al. found that the nitrogen content influenced the semiconducting nature of the passive film and the oxide layers in passive films could be modified by nitrogen additions [16]. Although some attempts were made to correlate the electronic nature of passive films with their protectiveness on stainless steels, it still lacks a systematical investigation about

FIGURE 1: Microstructure (a) and X-ray diffraction pattern (b) of the investigated HNSS.

the electronic properties of passive films of HNSS. In this work, the target is to investigate the passivity behavior and semiconducting properties of surface films formed on a high nitrogen-containing nickel-free stainless steel.

2. Experimental Procedures

2.1. Material. The HNSS used in this study was supplied by Northeastern University, Shenyang, China. The chemical compositions (in wt.%) of the alloy are C 0.058, Si 0.19, Cr 19.55, Mn 19.51, Mo 2.26, $P \leq 0.03$, S 0.003, Al 0.04, N 0.96, and Fe balance. A rolled sheet (220 mm $\times$ 120 mm $\times$ 5 mm) of HNSS was annealed at 1150°C for 1 h and followed by water quenching to room temperature. The HNSS sample was polished down to a diamond finish of 1.5 μ m and then electrolytically etched in 10% oxalic acid reagent at 12 V for 90 s for the microstructural observations. Figure 1 shows SEM observations of the typical microstructure of HNSS used in the present study. It can be seen that HNSS consisted of austenite grains and some twins. No precipitates exist inside austenite grains and at grain boundaries. XRD analysis shows that HNSS is mainly composed of austenite (γ) phase. The sheet was cut into coupons of 10 mm $\times$ 10 mm $\times$ 5 mm and the working surfaces of coupons exposed to test solutions was 10 mm². Moreover, all the unexposed area was coated with paraffin-resin mixture. Before the measurements, the surfaces of working electrode were polished with a series of silicon carbide abrasive paper to a finish grit of 800#. After that, samples were placed in an ultrasonic acetone bath for about five minutes and then air-dried.

2.2. Electrochemical Measurements. All electrochemical measurements were performed in a standard three-electrode system in a 1.5 L glass cell using a model Cortest CS350 potentiostat/galvanostat. A three-electrode cell setup consisting of a Pt counterelectrode, a saturated calomel electrode (SCE), and specimen as working electrode was employed.

The test electrolytes were 0.1 M NaCl, 0.5 M NaCl, and 0.05 M H₂SO₄ + 0.5 M NaCl. The purities of all chemicals

were the analytical grade. Experiments were carried out at room temperature in naturally aerated solution without stirring. Polarization curves were measured at a sweep rate of 0.333 mV/s. The anodic current transient curves were recorded at potentials ranging from -0.1 to $0.2 V_{SCE}$ to investigate the repassivation kinetic of tested samples. Mott-Schottky measurements were started from -1600 mV to 1600 mV with a sweep rate of 20 mV/s. Mott-Schottky analysis was carried out as follows. Each specimen was reduced potentiostatically at $-1.0 V_{SCE}$ for 120 s and then polarized at a desired potential for 60 min to form a steady passive film. The excitation voltage was sine wave modulated signal of 10 mV. Moreover, a step rate of 20 mV/s and a frequency of 1000 Hz were employed [21]. The measurement of capacitance-voltage profile for passive films formed at different potentials was carried out on the same sample. All the electrochemical measurements were repeated at least triple to ensure the good reproducibility.

Surface analyses of passive films were performed using an conventional angle resolved ESCALAB250 X-ray photoelectron spectrometric (ARXPS) with a monochromatic Al K α (1486.6 eV) radiation source. The photoelectron take-off angle being used is 0°. The binding energy scale was calibrated to give an Au 4f7/2 line position at 83.98 eV. Depth profile was measured using the argon ion bombardment with ion energy of 0.5 keV. The measured current of samples during the depth profile experiment was 0.5 mA, and the bombardment area was 2 mm $\times$ 2 mm. Peak identification was performed by reference to a database of XPS.

3. Results and Discussion

3.1. Potentiodynamic Responses. Figure 2 shows potentiodynamic polarization curves of HNSS measured in three solutions at room temperature. In this work, no pitting corrosion was detected for all conditions, indicating that HNSS has a relatively superior pitting corrosion resistance. Moreover, it can be seen that HNSS exhibited a transition from active to passivation in 0.1 mol/L and 0.5 mol/L NaCl solutions.

FIGURE 2: Potentiodynamic polarization curves for HNSS tested in different solutions. E_p : passivation potential; E_F : Flade potential; E_{tr} : transpassive potential.

The corrosion potentials (E_{corr}) of HNSS in 0.1 mol/L and 0.5 mol/L NaCl were -0.41 and -0.38 V_{SCE} , respectively. On the other hand, it clearly shows that the electrochemical corrosion behavior of HNSS is significantly affected by the concentration of Cl^- . Additionally, the polarization curves in anodic part can be divided into four regions, at which the current densities change suddenly. When the test started at E_{corr} and scanned towards the positive direction, an anodic current will increase almost linearly with the increased potentials, indicating the presence of a state of active dissolution. At characteristic potential E_p (passivation potential), the current density reached a maximum value. With the potential increasing, the current density decreased and reached a minimum value at passive potential (E_F). It has been reported that the absorbed iron hydroxide species into the passive oxide film could take place in this potential range [22]. The HNSS is in a state of passivation in the potential region ranging from E_F to E_{tr} (transpassive potential). In this region, the current density increases with the increasing of potential, indicating the stability degradation of passive film. When the potential is higher than E_{tr} , a new increase in the current will start. In this region, the passive film can be oxidized and accompanied with an increasing in corrosion rate or the start of oxygen evolution [23, 24].

Meanwhile, in 0.05 mol/L H_2SO_4 + 0.5 mol/L NaCl solution, three corrosion potentials, at which the anodic current density is equal to the cathodic current density, existed in the active, active-passive, and passive regions, respectively. This finding is consistent with the results reported by Qiao et al. [9], Fu et al. [12], and Ye et al. [18]. It has been reported that the potentiodynamic polarization curves of stainless steels in acidic NaCl solution exhibited three corrosion potentials, which is mainly ascribed to the existence of an unstable system. Three corrosion potentials were determined to be

FIGURE 3: Schematic diagram of ideal polarization curves for HNSS tested in different solutions.

-0.57 , -0.36 , and 0.25 V_{SCE} , respectively. The current density remained constant in the potential region between -0.30 and 0.20 V_{SCE} , indicating that HNSS was in a state of passivation. Therefore, the potential range of -0.2 to 0.2 V_{SCE} was selected to investigate the passivity behavior and semiconducting properties of HNSS. Since no obvious pitting potentials were observed, HNSS could offer excellent pitting corrosion resistance in severe corrosive environments

Figure 3 illustrates the ideal schematic diagrams for the corrosion behavior of HNSS in tested solutions based on the mixed potential theory. In 0.1 mol/L and 0.5 mol/L NaCl solutions, the anodic and cathodic curves intersect at point A in active region. That is to say, there is only one corrosion potential (E_1) in the potentiodynamic polarization curve. The electrochemical state of HNSS in 0.05 mol/L H_2SO_4 + 0.5 mol/L NaCl solution is assumed to be decided by the anodic and cathodic curve at points B, C, and D in Figure 3, and the possible corrosion potentials are defined as E_2 , E_3 , and E_4 , respectively.

3.2. Current/Time Transient Measurements. The i - t transients of HNSS obtained at various potentials in 0.05 mol/L H_2SO_4 + 0.5 mol/L NaCl are shown in Figure 4. The value of transient current could be a sum of currents resulted from the film formation and dissolution of alloy into the solution. For all the applied potential values, at the initial stage, the current density decreased rapidly with the increased time. This may attributed to the nucleation and growth of passive films. During this stage, the rate of film formation was higher than the dissolution rate of metal. At an applied potential of -0.2 V_{SCE} , the current densities decreased continuously with time and subsequently achieved steady state. Such typical and smooth-shaped curve indicates that a stable passive film is formed on the surface with no breakdown occurrence during the entire measurement period. The current transient behavior of passive film is closely related to their protective ability. When passive film formed, the movement of cations

FIGURE 4: Current-time transients for HNSS in 0.05 M H_2SO_4 + 0.5 M NaCl solution.

and/or oxide anions through the passive film becomes the control step of the whole corrosion process [25]. In this case, the ion conductivity becomes a decisive factor to determine the passive current density. It indicates the formation of a compact passive film on the surface of specimen. At an applied potential ranging from -0.1 to $0.1 V_{\text{SCE}}$, the superimposed background current is the intermittent anodic current spikes that could be easily distinguished from the background current fluctuations. These current spikes are from either nucleation or metastable pitting events [26]. The steady-state current increased with the applied potentials. When the applied potential is $0.2 V_{\text{SCE}}$, the current density will firstly decrease to a minimum value which corresponds to the formation of passive film and then increase gradually which corresponds to pitting nucleation and growth. During this stage, the current is mainly attributed to the dissolution of the alloy and the film formation current with respect to steel dissolution current is relatively smaller. At an applied potential of $0.2 V_{\text{SCE}}$, the movement of the cations and/or oxide anions through passive film becomes easier. Thus, the higher passive current density will be obtained on passive films with higher conductivity, indicating their deterioration. Moreover, the penetration force for Cl^- through passive films increases with the applied potentials. Once Cl^- reached the metal/film interfaces, MCl_x compounds may form and induce the damage of passive films, finally resulting in the increase of current [4, 27].

3.3. Semiconducting Nature of the Passive Film. Generally, the passive films formed on most metals and alloys exhibit semiconducting behavior, which can be described by Mott-Schottky analysis [28]. Mott-Schottky analysis has been employed to determine the semiconductor type and doping

density of passive films. The Mott-Schottky equation is given by [19, 24, 29–31]

$$\frac{1}{C_{\text{SC}}^2} = \frac{2}{\epsilon \epsilon_0 q N_d} \left(E - E_{\text{fb}} - \frac{kT}{e} \right), \quad (1)$$

where C_{SC} is the space charge capacitance, N_d is the donor/acceptor density in the passive film, ϵ is the dielectric constant of the oxide (usually taken as 15.6 for the passive film on stainless steel [19, 29]), ϵ_0 denotes the vacuum permittivity ($8.85 \times 10^{-14} \text{ F}\cdot\text{cm}^{-1}$), q is the electron charge, and k , T , and E_{fb} are the Boltzmann constant, absolute temperature, and flat band potential, respectively. The flat band potential can be determined from the extrapolation of the linear portion to $C^{-2} = 0$. For a p-type semiconductor, C^{-2} versus E should be linear with a negative slope that is inversely proportional to the acceptor density. On the other hand, an n-type semiconductor yields a positive slope, which is inversely proportional to the donor density.

The Mott-Schottky curves of the HNSS in 0.05 M H_2SO_4 + 0.5 M NaCl at various formation potentials were shown in Figure 5. Although there are slight differences between five curves (may be due to the difference of the samples), they possess the same semiconductor properties and turning potentials of -0.2 , 0 , 0.2 , and $0.65 V_{\text{SCE}}$. The Mott-Schottky of HNSS is slightly different from the obtained curves of stainless steels [7, 17, 29, 32]. From the Mott-Schottky curves, it is clear that the electrode has an equivalent flat band potential and possesses p-type and n-type semiconductivity in the same potential ranges. In Figure 5, a positive slope exists due to the oxide film formed on HNSS in the range from -0.3 to $0 V_{\text{SCE}}$, indicating the electrochemical behavior of the n-type semiconductor. At the potential ranging from 0 to $0.2 V_{\text{SCE}}$, the plots also show a linear tendency. The

FIGURE 5: Mott-Schottky plots of HNSS in 0.05 M H_2SO_4 + 0.5 M NaCl at various potentials.

FIGURE 6: Donor density of the passive films formed on HNSS surfaces at various potentials for 90 min in 0.05 mol/L H_2SO_4 + 0.5 mol/L NaCl solution.

passive film possesses p-type semiconductor property due to the negative slope. Such variation of n-type to p-type repeatedly appears at the wide potentials ranging from 0.2 to $0.6 \text{ V}_{\text{SCE}}$ and from 0.7 to $1.2 \text{ V}_{\text{SCE}}$. This phenomenon is probably related to the composition and structure of passive films. The p-type semiconducting behavior is related to the presence of Cr_2O_3 in the inner part of passive films [32–34]. Virtanen et al. [35] found that chromium vacancies or excess oxygen can be correlated to this p-type semiconductor behavior of chromium oxide in passive films. The n-type semiconducting behavior is related to the presence of Fe_2O_3 in the outer part of the passive film. According to Hakiki et al. [15], the first and second slopes are attributed to Fe^{2+} located, respectively, in the tetrahedral and octahedral sites of a spinel type structure.

It is generally accepted that the stability of the passive film is affected by the concentration of the donor density and the

diffusion coefficient. The higher acceptor or donor density will lead to the higher conductivity of the passive film. Figure 6 shows the change in donor concentration with different applied potentials. In the applied potential ranging from -0.2 to $0.1 \text{ V}_{\text{SCE}}$, the donor density increases with the increased applying potentials, but the effect of applied potentials on the donor concentration is not obvious. It also shows that HNSS has a stable passive value at applied potential ranging from -0.2 to $0.1 \text{ V}_{\text{SCE}}$, indicating the degradation of passive films.

3.4. XPS Results. XPS analysis was undertaken to provide more information about the properties of passive films formed on HNSS surfaces. Spectra of the primary compounds of passive film-chromium, iron, manganese, chloride, and oxygen are prepared based on their binding energies (EB). Figure 7 shows the identified elemental spectra in passive films after sputtering for 10 s. The oxide and metallic

FIGURE 7: ARXPS component analyses of HNSS surface after passivation at 0 V (SCE) for 90 min in 0.05 M H₂SO₄ + 0.5 M NaCl after sputtering time for 10 s.

states of the alloying elements Fe, Cr, and Mn were detected. The peak signals of Mo were relatively weak.

In the passivated film obtained in the tested solution, the signals corresponding to the Cr 2p_{3/2} spectra show that there exist three constituent peaks representing metallic state of (Cr⁰), Cr(OH)₃/CrOOH, and Cr₂O₃ [8, 14, 36–38]. Similar structures of (Cr(OH)₃ + Cr₂O₃) can be observed in the films formed on stainless steel in the strong (pH 0.8) and weak (pH 5) acid solutions [17]. According to the results reported by Singh and Ray [7], the chromium rich oxide-hydroxide film can be formed on the surface of stainless steels when exposed to acidic environments, which proceeds by solid-state mechanisms as

The presence of Cr⁰ indicated that most passive film was bombarded out and the exposed surface was near to bare alloy. The Fe 2p_{3/2} spectra were made up of three constituent peaks representing the metallic state (Fe⁰), bivalent (Fe(II)), and trivalent (Fe(III)) species. The peak indicates that Fe(III) is the primary iron oxidized species in passive films. The passive film is mainly comprised of Fe₃O₄, Fe₂O₃, and FeOOH.

The O 1s spectra can also be split into O²⁻ and OH⁻. It can be seen that the peak of OH⁻ corresponds to the formation of Cr(OH)₃/CrOOH and FeOOH. The peak of O²⁻ corresponds to the formation of Cr₂O₃, Fe₃O₄, Fe₂O₃, MnO, and Mn₂O₃. ARXPS results reveal that chlorides were found in passive film. The detected peak in ARXPS spectrum is due to the absorbed Cl⁻ in passive films. The presence of adsorbed Cl⁻ on passive films is known to create a concentration gradient that facilitates the diffusion of these ions into films [10, 39]. The transport of Cl⁻ into films will undergo hydrolysis and reduce the local pH, causing the film dissolution [39, 40].

ARXPS depth profiles are examined and the results are shown in Figure 8. It can be seen that the concentration of Cr is higher than that of Fe in the passive films during the initial stage of sputtering period. In addition, it indicates that the highest concentration of Cr is observed after sputtering period for 10 s. The Cr enrichment is due to the preferential dissolution of iron and manganese into the solution and low mobility of chromium in the surface films. Meanwhile, it was also observed that the Fe content increased during the initial stage of the sputtering period in the passive films. After sputtering for 30 s, the concentrations of Fe, Cr, and Mn become constant and attain to the alloying proportion, indicating the existence of film/metal interfaces.

FIGURE 8: ARXPS sputtering depth profiles of alloying elements in passive films of HNSS passivation for 90 min at 0 V_{SCE} in the 0.05 M H₂SO₄ + 0.5 M NaCl solution.

4. Conclusions

- (1) No obvious pitting corrosion observed even in acidic NaCl solution, demonstrating that HNSS offered excellent pitting corrosion resistance in corrosive environments. Potentiodynamic polarization in 0.05 mol/L H₂SO₄ + 0.5 mol/L NaCl has three corrosion potentials.
- (2) The Mott-Schottky plot indicated that the surface films of HNSS have both p-type and n-type electronic characteristics. Moreover, the protective ability of passive films decreased with the increase of formation potentials.
- (3) APXPS analyses revealed that the primary constituents of passive films formed in 0.05 mol/L H₂SO₄ + 0.5 mol/L NaCl solution were composed of iron oxides, manganese oxides, Cr₂O₃, and Cr(OH)₃.
- (4) After passivation, no molybdenum oxides were detected in passive films by ARXPS because of their dissolution in the electrolyte, whereas Cl⁻ was incorporated in the formed films.

Competing Interests

The authors declare no competing interests.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (nos. 51401092, 51304041, 51434004, and U1435205) and Fundamental Research Funds for the Central Universities (Grant no. N150204007).

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