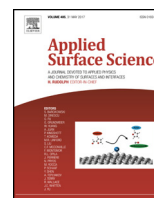




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Full Length Article

A pre-passive state observed for the passive film formed on Alloy 625 in a hydrochloric acid solution

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ABSTRACT

Investigation on oxide films of Inconel alloy 625 formed in 0.5 M HCl solution was performed, mainly by means of Electrochemical Impedance Spectroscopy (EIS) measurements, potentiostatic polarization and X-ray photoelectron spectra (XPS) analysis. The steady state current density at elevated temperatures in a low anodic range was found to be lower than that at 25 °C. Through the EIS measurements in the entire anodic range, two time constants were observed, while a semi-infinite spectrum associated with mass transport was found at only room temperature in the low anodic potential range. A new electrical equivalent circuit (EEC) was proposed for the spectrum in low potential range. The EEC indicated that there was a pre-passive process at room temperature before the passivity, and the film formed was incomplete. The increase of temperature promoted the pre-passive state into the passive state. XPS results confirmed that the film thickness was susceptible to temperature.

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1. Introduction

Reactive metals and alloys exhibit excellent stabilities in oxidizing environments due to the formation of the passive film. This thin film (only a few nanometers thick), which forms as long as the metals and alloys react with oxygen or water, can effectively isolate the metal from the corrosive environment and prevent further deterioration [1–3].

The film composition and microstructure of Ni–Cr–Mo alloys have been studied by using of XPS, AES, SIMS, and STM. It was shown that the film generally comprises bilayered structures consisting of an outer hydroxide layer and a Cr₂O₃ rich inner barrier layer – that grows directly into the metal [2,4–6]. A stable and complete Cr₂O₃ film was always observed to rapidly form, meaning that it directly enters into the passive state [7,8]. However, our recent study of the passivity of Alloy 625 under potentiostatic polarization found that the steady state current density (I_{ss}) at 65 °C and 85 °C in a low anodic range was lower than that at 25 °C. This is an unusual phenomenon, because the I_{ss} should increase due to the decreasing of corrosion resistance with the rising temperature. The objective of this work is to investigate the pre-passive state under potentiostatic polarization, then to propose a new model for the

state according to the EIS spectrum, finally to describe the kinetic mechanism of the state.

2. Experimental

2.1. Materials and electrode preparation

The composition of the wrought alloy 625 are shown in Table 1 (supplied by Chongqing Material Research Institution, China). The sample was prepared in cylindrical specimens by cutting from plate materials with a diameter of 8 mm and a height of 3 mm. The surface of each specimen was ground with a series of SiC papers from 240 grit up to 1200 grit. Then a connecting rod was attached to the back of the sample for electrical connections to external circuit. Each specimen and connecting rod was insulated with PTFE, allowing only the bottom circular face (area size of 0.50 cm²) to be exposed to the electrolyte. The specimens were again mirror polished with 5.00, 0.25, and 0.05 μm alumina powder suspensions, and then cleaned with distilled water prior to testing. The solution in the cell was deaerated with ultra-high purity nitrogen for at least 0.5 h prior to measurements, and continuously applied during the experiment. Before every measurement, the working electrode was polarized at a cathode potential for 5 min to reduce air-formed oxides.

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Table 1
Chemical composition (wt.%) of Alloy 625.

Alloy	Ni	Cr	Mo	Fe	Mn	C	Others
Alloy 625	Bal.	23	9	5	0.5	0.1	Nb:3.2

2.2. Electrochemical test

Electrochemical tests were conducted in 0.5 M HCl solutions (pH ~ 0.3) in a 250 ml three-electrode cell, and the cell contained a pure platinum (99.95% purity) counter electrode (CE) and a silver/silver chloride (Ag/AgCl) reference electrode (RE) (0.199 V vs. SHE at 25 °C). All potentials (E) are quoted on this electrode. The operation temperature was maintained using a heating mantle and a temperature controller. The oxide films were formed at different potentials by potentiostatic polarization for 10 h. EIS tests were conducted on passive films with an amplitude of ± 10 mV over the range from 1×10^5 Hz to 0.5×10^{-3} Hz. To ensure that the steady-state was maintained over the duration of the measurement, Kramers–Kronig transformation of the experimental data was also performed to ensure their validity [9]. All the electrochemical measurements were performed by the electrochemical workstation (IM6eX ZAHNER, Germany) and all the EIS spectra were analyzed with Zview software.

2.3. Surface analyses

The XPS measurements were carried out on a Kratos Axis Ultra spectrometer using a monochromatic Al K α (1486.6 eV) source. The X-ray power was 150 W. The samples were prepared by the same procedure as for the electrochemical experiments. After 17 h of immersion, the alloy 625 sample was removed from the solution, rinsed with ethanol then dried in cool air and placed in a vacuum chamber. Angle-resolved measurements were made at a take-off angle = 90° (normal to the metal surface). High-resolution spectra were obtained using a 40 eV pass energy, whereas survey spectra were recorded using a 160 eV pass energy. The experimental resolution of the binding energy was 1 eV. The Shirley method was used for background subtraction and peak deconvolution was performed using CASA XPS software. Binding energies were corrected for possible charging effects by referencing to the C1s (284.8 eV) peak.

3. Results and discussion

The potentiodynamic curves of alloy 625 in 0.5 M HCl at three temperatures (25, 65 and 85 °C) were carried out, as shown in Fig. 1. It was suggested that, the passive range of alloy 625 was between 100 mV and 900 mV at 25 °C. With temperature rising, the passive current density, I_p increased from $0.2 \pm 0.05 \mu\text{A}/\text{cm}^2$ at 25 °C to $0.55 \pm 0.05 \mu\text{A}/\text{cm}^2$ at 85 °C. Meanwhile, the transpassive potential was also lowered with temperature. It was an indication that the film became less corrosion resistance with the temperature, which was ascribed to the increased vacancy density [10], the loss of Cr₂O₃ [11], or the accelerated interfacial reactions [12]. Meanwhile, we noted that there was an overlap of the anodic current in the lower potential region (between 0 mV and 150 mV), so the steady state current density (I_{ss}) versus time was studied at 100 mV with varying temperature. It was shown in Fig. 2 that the I_{ss} at 25 °C was the highest while the I_{ss} at 65 °C was the lowest. This behavior was very different from that of the oxide film in the passive range as we mentioned above, and was rarely reported before.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for investigating the mechanisms of electrochemical reactions, and for measuring the ionic and electronic properties of passive films [13]. Representative impedance spectra for Alloy 625 in deaerated

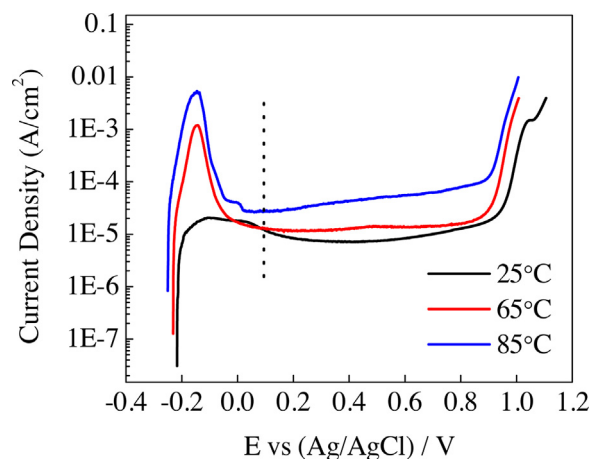


Fig. 1. Potentiodynamic curves of Alloy 625 in 0.5 M HCl solutions at temperature of 25 (black curve), 65 (red curve), and 85 °C (blue curve), respectively. The dotted line at 100 mV indicates that the anodic current increases with the temperature rising. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

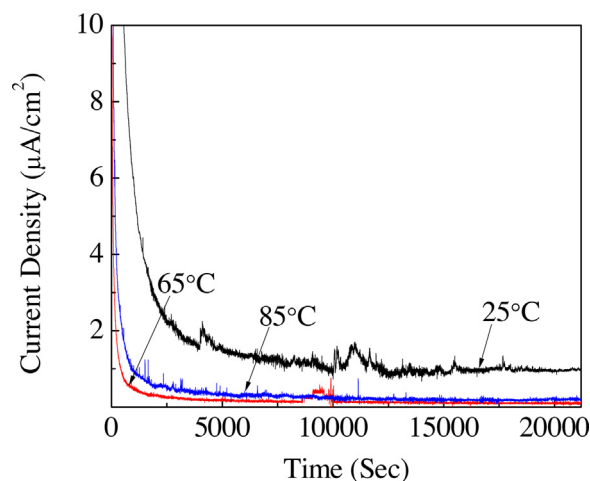


Fig. 2. Dependence of the I_{ss} for the film formed at 100 mV on temperature. The I_{ss} at 65 °C is the lowest, while the I_{ss} at 25 °C is the highest.

0.5 M HCl (25 °C) measured in the range from 100 mV to 900 mV were shown in the form of bode plot in Fig. 3. The effect of elevating temperatures on the film at 100 mV was also presented in Fig. 3a. Two time constants could be observed at each potential, but it was noted that for the film formed at 25 °C under 100 mV, as the frequency decreasing, the phase-angle approached 45°. This indicated a diffusion contribution to the low frequency impedance, and it disappeared with the increase of temperature or potential. Meanwhile, the impedance variation with temperature at 100 mV was in agreement with the results obtained in Fig. 2, that the film formed at 65 °C was the most resistant. Thus, it was speculated that there was a pre-passive process that could be observed at only room temperature.

Three time constants were usually used to model the impedance for the entire electrode/film/electrolyte system of such high corrosion resistance alloys in the passive range, as proposed by Macdonald et al. [14]:

$$Z_{\text{total}} = Z_{m/f} + Z_f + Z_{e/f} \quad (2)$$

where $Z_{m/f}$ ($R/C_{m/f}$) represents the metal/film interface impedance, Z_f (R/C_f) represents the film impedance, and $Z_{e/f}$ ($R/C_{e/f}$) represents the electrolyte/film interface impedance. However, not every time constant can be detected in all the cases, which may be

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