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Investigation of passive films formed on the surface of alloy 690 in borate buffer solution

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The passive film formed on the surface of the alloy 690 in borate buffer solution was studied by potentiodynamic curves and electrochemical impedance spectroscopy. With the increasing of the passivation potential, the corrosion resistance of the alloy 690 reduced. Moreover, the corrosion resistance of the passive film was the lowest in the vicinity of 0.6 V_{SCE}. These results were supported by XPS and Mott–Schottky analyses. The corrosion resistance of the alloy 690 increased with the increasing of passivated potential in borate buffer solution with chloride ion. The chloride ion decreased corrosion resistance of the alloy 690 according to point defect model.

1. Introduction

Nickel based alloy 690 was candidate materials for the storage of high level waste generated from reprocessing of spent nuclear fuel [1]. Moreover, the alloy 690 also was currently as an alternative to traditional austenitic stainless steel due to its high strength, lower nickel concentration and excellent corrosion resistance [2]. For example, the alloy 690 showed a better corrosion resistance than alloy 800 in simulated primary water [3], therefore, the alloy 690 was suitable to be used in aggressive environment. Due to high stress corrosion cracking and pit corrosion resistance in high temperature pressurized water reactor (PWR), the alloy 690 as the alternative material for the alloy 600, was widely used as stream generator tubing materials in PWR plants [4,5]. Electrochemical properties and growth mechanism of passive films on alloy 690 in high-temperature alkaline environments were investigated widely [6–8].

Moreover, the study showed that alloy 690 dissolved preferentially along the direction which had lower surface free energy in a solution of 0.1 M H_2SO_4 and 0.1 M NaCl at room temperature [9]. The passive film was formed rapidly and its growth decreased its the corrosion rate [10]. The passive films played an important role in preventing corrosion. Therefore, it was very important to deeply understand the form processes of passive films for estimating the structural integrity [11]. The passivation characteristics and corrosion resistance of the passive films formed on the alloy 690 in borate buffer solution without and with chloride ion were investigated in the present study.

2. Experimental procedures

Specimens from alloy 690 plate, with chemical composition (wt.%): 0.03C, 0.28 Si, 0.25 Mn, 29.0 Cr, 0.02 Cu, 9.5 Fe, 0.002 S and balance Ni, were cut to cuboid with a dimension of 10 mm × 10 mm × 2 mm for test. The specimens were solution annealed at 1100 °C for 1 h in vacuum, then the sheets were subsequently quenched into water.

The copper wires were welded to each specimen for electrical connection through the spot welding. All edges and surfaces of the test specimens were coated with epoxy resin prior to electrochemical test, leaving an active surface area of 10 mm × 10 mm exposed to the solution. Before the electrochemical test, all the specimens were abraded with 1000, 2000 and 3000 grit silicon carbide paper and polished with 1.5 μm alumina slurry. The polished specimens were ultrasonically cleaned finally in acetone and ethanol. A conventional three-electrode electrochemical cell was

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used. A platinum counter electrode and a saturated calomel reference electrode (SCE) were connected to a CHI 660E electrochemical station (Chenhua instrument Co. Shanghai, China) controlled by a computer and software. To ensure good reproducibility, a minimum of three sets of measurements of each specimen were taken and an average value was considered in borate buffer solution (0.05 M H_3BO_3 + 0.075 M $Na_2B_4O_7 \cdot 10H_2O$) solution without and with chloride ion. The electrochemical impedance spectroscopy (EIS) measurements were carried out using a frequency range of 100 kHz to 10 mHz and with a 5 mV amplitude of the ac signal.

The surface compositions of alloy 690 were measured by X-ray photoelectron spectroscopy (XPS) measurement. The XPS experiments were performed using PHI Quantera SXM (ULVAC-PHI, INC). Photoelectron emission was excited by monochromatic Al Kα radiation. The vacuum of the specimen chamber was 6.7×10^{-8} Pa. The C 1 s peak from adventitious carbon at 284.8 eV was used as a reference to correct the charging shifts. XPSPeak4.1 software was used to fit the XPS experiment data.

3. Results and discussion

XRD result of the solution annealed alloy 690 is shown in Fig. 1a. From the XRD spectra, the austenitic phase is found in solution annealed specimen with random grain orientation. The average grain size of the solid solution specimen is 28 μm in Fig. 1b and very few twins are produced due to annealing process.

The anodic polarization curve of the solid solution alloy 690 in borate buffer solution is shown in Fig. 2. In the anodic polarization curve, current density increases with applied potential and two obvious peak currents are observed at 0.6 V_{SCE} and 0.8 V_{SCE}, respectively. The current increases dramatically when the potential is higher than the transpassive potential. The previous study showed that the compacting and thickness of the passive film were important factors in determining the corrosion current density [12].

Fig. 3a and b shows the Nyquist plots and Bode plots of alloy 690 after passivation at the different potentials for 1 h. The diameter of semicircle in the Nyquist plot decreases firstly with the increasing of passivated potential in borate buffer solution. The smallest diameter of semicircle in the Nyquist plot is found at 0.6 V_{SCE}, then the diameter of semicircle in the Nyquist plot increases due to higher passivated potential. Bode plots are shown in Fig. 3b. One time constant is observed.

The equivalent circuit in Fig. 4 is proposed for fitting EIS data to quantify the electrochemical parameters [13]. In this equivalent circuit, Rs represents solution resistance; Q_1 is double charge layer capacitance; R_1 is the charge-transfer resistance. The electrochemical impedance parameters obtained from the fitting of

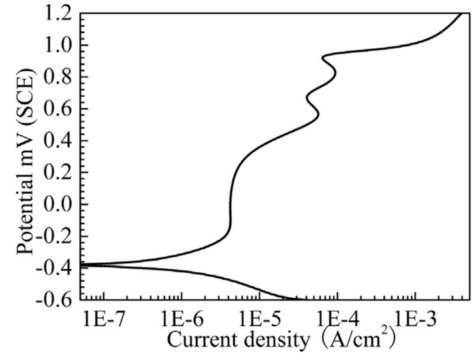

Fig. 2. The anodic polarization curves of the solution annealed alloy 690 in borate buffer solution.

electrochemical impedance spectroscopy (EIS) diagrams are shown in Table 1. The solution resistance changes from 32.49 to 34.17 Ω cm^2 for the alloy 690, indicating no obvious change of the solution during the form of the passive film. In addition, the charge transfer resistance of alloy 690 decreases from 1.67×10^6 Ω cm^2 to 3.49×10^4 Ω cm^2 with passivation potential increasing from 0 V_{SCE} to 0.6 V_{SCE}, then the charge transfer resistance increases up to 1.34×10^5 Ω cm^2 again at 0.8 V_{SCE}. The charge transfer resistance of the alloy 690 is smallest at 0.6 V_{SCE}, which indicates the changed composition and thickness of the passive film.

So, in the present study, the Mott–Schottky plots are used to explain the semiconductor properties of films on alloy 690. The linear region of the plots is attributed to the variation of the width of the space charge layer of the passive film on the specimen with the applied potential, according to

$$C^{-2} = C_H^{-2} + C_{SC}^{-2} = \frac{2}{\varepsilon_S \varepsilon_0 q N_D}\left(E - E_{fb} - \frac{kT}{e}\right) \quad (1)$$

$$C^{-2} = C_H^{-2} + C_{SC}^{-2} = \frac{-2}{\varepsilon_S \varepsilon_0 q N_A}\left(E - E_{fb} - \frac{kT}{e}\right) \quad (2)$$

where ε_0 is the vacuum permittivity ($8.854 \times 10^{-12} Fm^{-1}$), ε_s is the dielectric constant of the specimen, e is the electron charge (1.6×10^{-19}C), k is the Boltzmann constant ($1.38 \times 10^{-23} JK^{-1}$), N_D and N_A are the donor or acceptor density, respectively, T is the absolute temperature and E_{fb} is the flatband potential [14].

Fig. 5a shows the Mott–Schottky plots for alloy 690 after passivation at the different potentials for 1 h. The Mott–Schottky plots are measured by sweeping in negative direction. It can be seen that the passive film on the surface of alloy 690 possesses the same

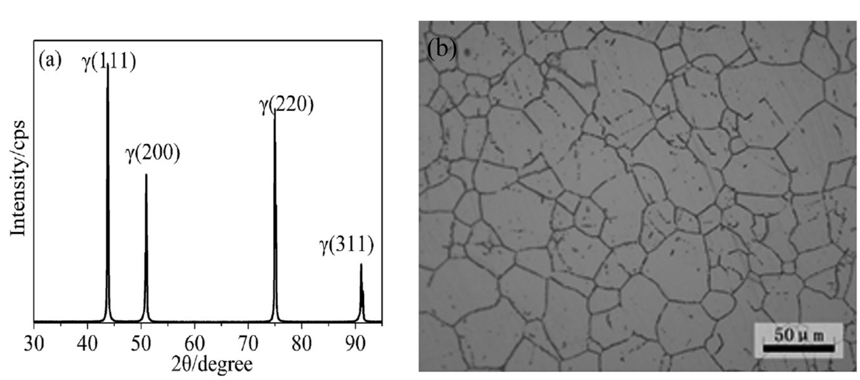

Fig. 1. (a) The X-ray diffraction patterns and (b) microstructures of the solution annealed alloy 690.