Applied Surface Science 360 (2016) 403–408

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Comparison of corrosion behavior between coarse grained and nano/ultrafine grained alloy 690

Lv Jinlong[a,b,*], Liang Tongxiang[a,b], Wang Chen[a,b], Guo Ting[a,b]

[a] Beijing Key Laboratory of Fine Ceramics, Institute of Nuclear and New Energy Technology, Tsinghua University, Zhongguancun Street, Haidian District, Beijing 100084, China
[b] State Key Lab of New Ceramic and Fine Processing, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form 31 October 2015
Accepted 3 November 2015
Available online 10 November 2015

Keywords:
EIS
Alloy 690
XRD
Passive films
X-ray photoelectron spectroscopy

ABSTRACT

The effect of grain refinement on corrosion resistance of alloy 690 was investigated. The electron work function value of coarse grained alloy 690 was higher than that of nano/ultrafine grained one. The grain refinement reduced the electron work function of alloy 690. The passive films formed on coarse grained and nano/ultrafine grained alloy 690 in borate buffer solution were studied by potentiodynamic curves and electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy. The results showed that the grain refinement improved corrosion resistance of alloy 690. This was attributed to the fact that grain refinement promoted the enrichment of Cr_2O_3 and inhibited $Cr(OH)_3$ in the passive film. More Cr_2O_3 in passive film could significantly improve the corrosion resistance of the nano/ultrafine grained alloy 690.

1. Introduction

The alloy 690 as the alternative material for austenitic stainless steel and the alloy 600, was widely used as stream generator tubing materials in pressurized-water reactor plants due to high strength and excellent corrosion resistance [1,2]. Moreover, the nickel based alloy 690 was proved to be beneficial to stress corrosion cracking resistance [3]. The corrosion resistance of the alloy 690 increased with the increasing of passivated potential in borate buffer solution with chloride ion [4]. The X-ray photoelectron spectroscopy (XPS) study revealed that the surface passive film formed on alloy 690 at the initial passivity potential contained $Cr(OH)_3$ in 0.5 M H_2SO_4 + 0.5 M NaCl solution, while the passive film formed at the higher anodic potential contained Cr_2O_3 [5]. Moreover, XPS analysis also revealed that the passive films formed on alloy 690 consisted of an outer hydroxide layer and an inner oxide layer in the borate buffer solution as well as the sulfuric acid solution [6]. The study showed the duplex layers passive films formed on alloy 690 in high temperature alkaline aqueous environments [7].

The effect of grain size on the corrosion response of metallic materials was widely studied. The corrosion rate decreased as grain size decreased for pure aluminium in 0.1 M NaCl solution and the Hall–Petch type relationship might exist between corrosion rate and grain size [8]. The linear polarization resistance value increased when grain size decreased for Mg–Y–RE magnesium alloy in 3.5 wt.% NaCl solution [9]. Balyanov et al. [10] found that ultrafine grained pure titanium produced by equal-channel angular pressing was more resistant to corrosion than coarse grained (CG) pure titanium in acid environment. This was believed to be attributed to rapid passivation of the ulturafine titanium. However, nanocrystalline titanium obtained by hydrostatic extrusion showed a slightly lower corrosion resistance than CG one in NaCl solution [11]. In addition, the grain orientation also could affect the corrosion resistance. For example, pure titanium with the highest atomic density planes parallel to the surface was found to offer the highest corrosion resistance, regardless of their grain size [12].

However, the effect of grain refinement on the corrosion resistance of alloy 690 has not been evaluated. The objective of this work was to evaluate the effect of nano/ultrafine grained (NUG) 690 alloy on corrosion resistance of passive films in borate buffer solution.

2. Experimental procedures

2.1. Sample preparation

The alloy 690 plate, with chemical composition (wt.%): 0.03 C, 0.28 Si, 0.25 Mn, 29.0 Cr, 0.02 Cu, 9.5 Fe, 0.002 S and balance Ni,

* Corresponding author at: Beijing Key Laboratory of Fine Ceramics, Institute of Nuclear and New Energy Technology, Tsinghua University, Zhongguancun Street, Haidian District, Beijing 100084, China. Tel.: +86 10 89796090; fax: +86 10 69771464.
E-mail addresses: ljltsinghua@126.com (L. Jinlong), txliang@mail.tsinghua.edu.cn (L. Tongxiang).

http://dx.doi.org/10.1016/j.apsusc.2015.11.031
0169-4332/

was cut to cuboid with a dimension of 10 mm × 10 mm × 2 mm for test. The samples were solution annealed at 1100 °C for 1 h in vacuum, then they were subsequently quenched into water. The NUG alloy 690 was obtained by 90% total thickness reduction in a laboratory rolling mill and annealed at 800 °C up to 500 s. All the samples were abraded with 1000, 2000 and 3000 grit silicon carbide paper and polished with 1.5 μm alumina powder. Then the polished samples were ultrasonically cleaned finally in acetone and ethanol. The X-ray diffraction (XRD) measurement was carried out by a Rigaku Ultima IV diffractometer using Cu K_α (0.154056 nm) and radiation at 40 kV and 40 mA. A JEM-2100F transmission electron microscopy (TEM) was used to examine the microstructures of NUG alloy 690. The samples for TEM observation were prepared using a twin-jet electropolishing at a voltage of 20 V at temperature of −25 °C. The electrolyte contained 10 vol.% of perchloric acid and 90 vol.% of alcohol.

2.2. Electrochemical tests

The samples were successively ground with SiC paper up to a grit of #2000, polished with alumina slurry down to 0.3 μm. Electrochemical tests were performed with a CHI 660E electrochemical station (Chenhua instrument Co. Shanghai, China) controlled by a computer and software in three-electrode cell. The electrochemical measurements were conducted using a thin platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the experiments were carried out in pH 8.4 borate buffer solution (0.075 M $Na_2B_4O_7$ + 0.3 M H_3BO_3). Before electrochemical experiment the sample was cathodically polarized at −1.2 V_{SCE} for 300 s. The samples were firstly passivated at 0.4 V_{SCE} and 0.6 V_{SCE} for 1 h, then 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 at passivated potential.

The corrosion resistance of passive film was correlated with its semiconducting properties which could be measured by the Mott–Schottky analysis in high frequency domain [13]. Based on Mott–Schottky theory [14], the space charge capacitances of the *n*-type and *p*-type semiconductor are given by equation (1) and (2), respectively:

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

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

where C_H and C_{SC} are the Helmholtz capacitance and the space charge capacitance, respectively. ε_0 is the vacuum permittivity (8.854×10^{-12} F m^{-1}), ε_s is dielectric constant of the passive film, e is the electron charge (1.6×10^{-19} C), k is the Boltzmann constant (1.38×10^{-23} J K^{-1}), N_D and N_A are the donor and acceptor concentrations, respectively, T is the absolute temperature and E_{fb} is the flat-band potential. The capacitance value are calculated by equation (3)

$$C = (-Z_{im} 2\pi f)^{-1} \quad (3)$$

where Z_{im} is the imaginary part of the impedance and f is the frequency. The f is 1000 Hz in this study. From the slope of linear zone in Mott–Schottky plots, the donor and acceptor concentrations in passive film can be determined.

2.3. X-ray photoelectron spectroscopy (XPS) measurement

The surface compositions of the passive films formed on CG and NUG alloy 690 were measured by XPS. 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 1s peak from adventitious carbon at 284.8 eV was used as a reference to correct the charging shifts. Sputter depth profiles were measured and analyzed. XPSPeak4.1 software was used to fit the XPS experiment data.

3. Results and discussion

After the homogenization treatment, the average grain size of solution annealed CG alloy 690 is about 30 μm in Fig. 1a. After cold rolling and annealing, austenitic alloy 690 with the average size of 280 nm is obtained in Fig. 1b. It shows that the microstructure is mainly nano/ultrafine grain and most of the grain boundaries are high angle grain boundaries. The sharp diffraction spots in inset also indicate that many high angle grain boundaries are formed. The present obtained nano/ultrafine grained alloy 690 almost has no precipitation phase due to the high temperature and short time annealing. The statistical distributions for grain size in nano/ultrafine grained alloy 690 are shown in Fig. 1c.

The results of X-ray diffraction for CG and NUG alloy 690 are shown in Fig. 2. It is worthwhile to note that the grain orientation of CG alloy 690 is random. While NUG alloy 690 has a preferred (2 2 0)γ orientation. The significant texture changes may affect the corrosion resistance of NUG sample and the problem will be discussed in the following sections.

Fig. 3a and b illustrates the change trend of electron work function (EWF) value in CG and NUG alloy 690, respectively. The EWF fluctuates significantly in the grain boundary in Fig. 3a. Obviously, the EWF decreases due to grain refinement in Fig. 3b. Some studies showed the EWF could change due to grain orientation [15] and strain [16]. Our previous studies have shown that the EWF in CG 304 stainless steel is higher than that in NUG one [17]. This indicates that surface activity of nano/ultrafine structure is higher, which promotes formation of the thicker passive film. The thicker passive films can improve the surface corrosion resistance of NUG alloy 690.

The potentiodynamic polarization curves of CG and NUG alloy 690 in borate buffer solution are shown in Fig. 4a. Two samples show active–passive–transpassive behaviors in the solution. The NUG alloy 690 has higher corrosion potential and lower passivation current than CG alloy 690 in the borate buffer solution. This indicates that the former has higher corrosion resistance than the latter in borate buffer solution. Fig. 4b shows the OCP of CG and NUG alloy 690 in borate buffer solution. The NUG alloy 690 has higher OCP than CG alloy 690 in the borate buffer solution. This indicates that the corrosion resistance of alloy 690 increases due to grain refinement.

The EIS test was carried out to further investigate the corrosion resistance. The Nyquist plots of CG and NUG alloy 690 after being passivated at 0.4 V_{SCE} and 0.6 V_{SCE} for 1 h are shown in Fig. 5a and b, respectively. It can be seen that the depressed capacitive semicircles cover almost all frequency regions. The diameter of capacitive semicircle was associated with charge-transfer resistance of the passive film [18]. An increase in the semicircle radius indicates an improved corrosion resistance of the passive film formed on the surface of alloy 690 [19]. Higher passivated potential decreases corrosion resistance of alloy 690 in the borate buffer solution, especially for CG sample. At 0.6 V, the polarization curves showed a distinct peak current. This implies that the passive film significantly dissolves, especially for chromium element [20]. Therefore, the corrosion resistance of the passive films on alloy 690 decreases. The experimental results above show that the grain refinement can improve the corrosion resistance of 690 alloy in borate buffer solution. The Nyquist plots of CG and NUG alloy 690 after being