Applied Surface Science 431 (2018) 197–201

Contents lists available at ScienceDirect

Applied Surface Science

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

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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ARTICLE INFO

Article history:
Received 4 February 2017
Received in revised form 18 June 2017
Accepted 22 June 2017
Available online 23 June 2017

Keywords:
Passive films
Inconel alloy 625
EIS
Pre-passive process

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.

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 Cr_2O_3 rich inner barrier layer – that grows directly into the metal [2,4–6]. A stable and complete Cr_2O_3 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 increases 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 cm^2) 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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http://dx.doi.org/10.1016/j.apsusc.2017.06.234
0169-4332/