

In-situ oxide layer analysis of alloy 182 using electrochemical impedance spectroscopy in high dissolved hydrogen condition in PWR environment

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1. Introduction

Alloy 82/182 weld metals had been extensively used in joining the components of the PWR primary system. Unfortunately, the cracking caused by PWSCC usually occurs on Alloy 82/182 dissimilar metal welds (DMW). Previous studies indicated that the susceptibility of PWSCC is closely related to the oxide characteristics which are dependent on water chemistry condition, especially dissolved hydrogen (DH). Furthermore, in primary system of pressurized water reactor (PWR), crack initiation resulted from electrochemical instability of oxide film of Ni-base structural materials in various hydrogen concentrations. In this study, in-situ oxide analysis of Alloy 182 using electrochemical impedance spectroscopy (EIS) was performed in high dissolved hydrogen condition. Especially, to understand the effects of tensile loading on the oxide characteristics, we tried to characterize the oxides formed on the tensile loaded specimen using in-situ EIS analysis.

2. Experimental

2.1 Test material

Test material used in this study was manufactured from a weld deposit of Alloy 182 on a 316L plate with the dimension of T-direction (Transverse) 300mm, L-direction (Longitudinal) 500mm, and S-direction (Thickness) 55mm (Alloy 182 25mm + 316L SS 30mm). The chemical compositions of the test material are listed in Table I. For in-situ EIS analysis tensile-loaded and zirconia coated specimens as shown in Fig. 1 were used.

Table I: Chemical composition of Alloy 182

C	Si	Mn	P	S	Fe
0.03	0.34	7.35	0.009	0.001	2.81
Cu	Ni	Ti	Cr	Mo	Nb+Ta
0.01	73.0	0.02	14.2	0.63	1.57

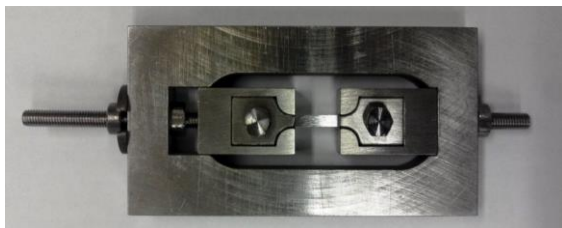


Fig. 1. Tensile-loaded and zirconia coated specimen for EIS test

2.2 Test system and conditions

The test environment was simulated PWR water containing dissolved boric acid and lithium hydroxide at 325 °C. The levels of DO, DH, conductivity and pH are monitored and controlled at room temperature. The DO was kept below 5 ppb, and dissolved hydrogen content was 50 cc/kg (high DH). The details of the test conditions are summarized in Table II.

Table II: Test environments

Environment		simulated PWR
Temperature		325 °C
Pressure		15.5 MPa
Water chemistry	DO	< 5 ppb
	DH	50 cc/kg
	Conductivity	~ 20~25 μ S/cm (1200 ppm H_3BO_3 + 2.2 ppm LiOH)
	pH	6~7

EIS tests were performed to evaluate in-situ oxide characteristics by measurement of impedance properties. Tensile-loaded and zirconia coated specimens of Alloy 182 was installed in the autoclave as shown in Fig. 2. The AUEN (Gold Electrode-Non PTFE) reference electrode and the Pt counter electrode were used. The impedance measurement were performed using a Gamry® potentiostat system (Reference 3000) at the open circuit potential using a frequency range from 100kHz to 1 mHz (10 points per decade) with perturbation amplitude of 10mV RMS.

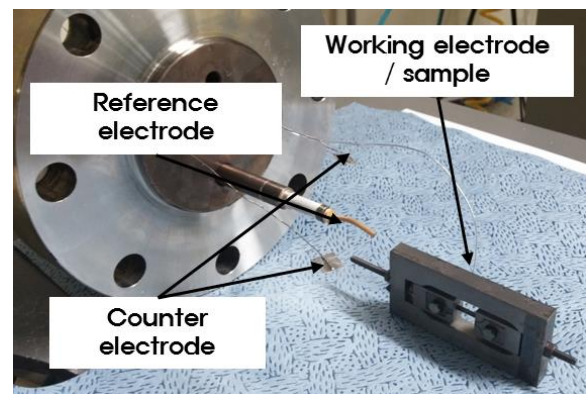


Fig. 2. Setup of the specimens installed in the autoclave for EIS test

3. Results and Discussion

3.1 The Nyquist plot and Bode plot

The in-situ EIS analysis was performed on the Alloy 182 exposed to high DH condition (50cc/kg) up to 500 hr and the results are shown as Nyquist plot and Bode plot. In Fig. 3, large semicircles in Nyquist plot indicating charge transfer phenomena consisted of a charge transfer resistance, R_{ct} , in parallel to an electric double layer capacitance, C_{dl} . It means that electron transfer reaction passing through interface between electrode and electrolyte. As shown in Fig. 4, increase in impedance was observed with the increase of exposure time on Bode-impedance plot as well as Nyquist plot, which implied an increase of surface film thickness. Also, the shapes of semicircles in Nyquist plot are somewhat depressed, probably due to the existence of defects and non-homogeneous part in the oxide film. Further quantitative analysis is needed for detailed oxide characterization. Currently, EIS analyses for the specimen exposed to different DH levels are underway and the effects of different DH levels will be analyzed.

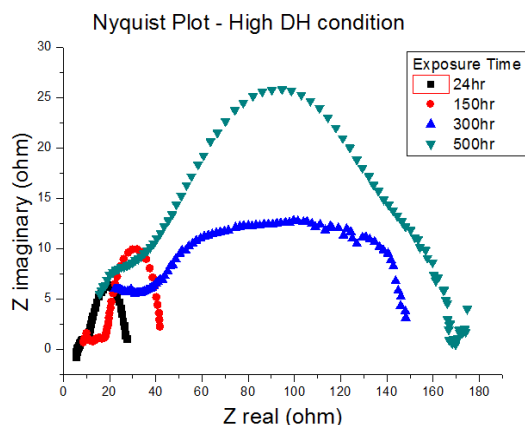


Fig. 3. Nyquist plot at high DH condition

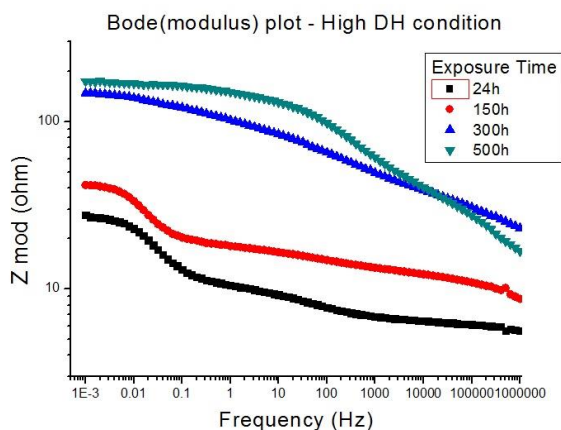


Fig. 4. Bode(modulus) plot at high DH condition

3.2 The equivalent circuit model

As an attempt to analysis the multi-layer structure of oxides, EIS data were fitted into an equivalent circuit model shown in Fig. 5. From this model, it is assumed that oxide layers consisted of 2 or 3 layers. Combrade et.al reported that the oxide structures divided into Cr-rich inner layer, Cr free external oxide layer [1]. To verify this assumption, SEM, TEM and EDS analyses for cross section of oxide structure are underway. Meanwhile, the equivalent circuit model can be changed as exposure time increased. It suggests that the oxide structure will be changed as time increased. In this regard, the film structure transition in accordance with exposure time will be analysed.

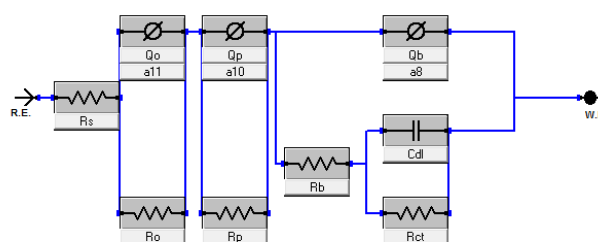


Fig. 5. An equivalent circuit model based on EIS data for 150 hr

4. Conclusions

The EIS analysis of oxide on Alloy 182 was performed. The increase of oxide film thickness was observed with the increase of exposure time. To analysis the multi-layer structure of oxides, an equivalent model was obtained by fitting EIS data. It is assumed that overall oxide structures were composed of 3 layers approximately. The analyses on cross section of oxide structures are underway to clarify appropriateness of the equivalent circuit model.

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