# Effect of thermal aging on the corrosion behaviors of ER316L stainless steel welds in simulated PWR environments

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#### 1. Introduction

In light water reactor (LWR) nuclear power plants (NPPs), stainless steels with duplex phases are applied as the important pressure boundary components of the primary coolant loop, such as the cast primary coolant circuit pipes, the safety-ends of the pressure vessels, and the cases of main pumps [1-4]. Nuclear grade welded austenitic stainless steels with a certain amount of ferrite are widely used in LWR NPPs and subjected to thermal aging during long-term service. The thermal aging results in degradation of the corrosion resistance of the austenitic stainless steels with a certain amount of ferrite, which leads to a potential concern to the structural integrity of the relevant LWR components. In the present work, the corrosion behaviors of as-welded and thermal aged 10,000 hours ER316L stainless steel welds in simulated PWR primary water environment were studied.

## 2. Methods and Results

#### 2.1 Materials

Blocks of welds were fabricated by building-up commercial grade welding wires of ER316L (Mocontaining low carbon grade) on 316L stainless steel plates by gas tungsten arc welding (GTAW) method. The compositions of weld wires with  $\delta$ -ferrite content of around 10 vol.% in the finished welds were used. The chemical composition of as-welded materials was analyzed using inductively coupled plasma (ICP) method and the results are given in Table 1. Phase fraction of  $\delta$ -ferrite content was determined by image analysis, and the results are also given in Table 1. Then the as-welded blocks were sectioned into small pieces and thermally aged at an accelerated aging condition of 400 °C in air environment for 10,000 h.

Table 1 Chemical composition and ferrite content of welding block

Fe	Cr	Ni	С	Si	
Bal.	18.4	11.0	0.008	0.4	
Mn	Мо	Ferrite content (vol.%)			
1.74	2.56	Schaeffle diagram	-	Phase fraction	
		11	12.	3 ± 1.3	

2.2 Oxidation test procedures in simulated PWR primary water

The size of the specimen for the exposure test was 10  $mm \times 5 mm \times 3 mm$ . They were mechanically polished to 1 µm and followed by 0.06 µm alumina suspension. All specimens were degreased with ethanol before exposure. The tests were conducted in a 316 SS autoclave equipped with water circulating loop system. To reduce the effect of autoclave body on the oxide formation on the specimens, the autoclave has been operated in the test solution for more than one week to stabilize the autoclave walls before the immersion tests. The testing solution was simulated PWR primary water (B: 1200 ppm (ppm in this paper refers to weight percentages) as H<sub>3</sub>BO<sub>3</sub>, Li: 2.2 ppm as LiOH, flow rate: ~3 L/h, Pressure ~ 13 MPa) at 325 °C. The normal PWR primary water chemistry with a DO level < 5 ppb and a DH level of 30 ml/kg water STP was achieved by H<sub>2</sub> purging in the make-up water tank and maintaining a certain H<sub>2</sub> overpressure.

#### 2.3 Oxides microstructure analysis methods

The surface morphologies of specimens after exposure tests were observed by Hitachi SU-5000 thermal field SEM. The cross-sections of the oxide films formed on the surface of specimens were examined via TEM. For analysis, thin foil specimens were prepared using an FEI Helios G4 UX dual-beam focused ion beam (DB-FIB) with Ga ion sputtering after a protective Pt strap was deposited on the oxide films. TEM and selected area electron diffraction analyses (SAED) were conducted using an FEI Talos F200X TEM equipped with an energy dispersive spectrometer (EDS) system operating at 200 kV. High-angle annular dark-field (HAADF) images were obtained.

# 2.4 Effect of thermal aging on the corrosion behaviors

As shown in Fig. 1, duplex oxide films were formed on the surface of as-welded ER316L specimen. The outer oxide particles on ferrite and austenite were spinel-type oxides enriched in Fe. The inner oxide films formed on ferrite were chromia with thickness around 10 nm. The inner oxide films formed on austenite were amorphous Fe- and Cr-rich spinel oxides. Ni enrichment in the matrix at matrix/inner oxide film was higher in ferrite than that in austenite.

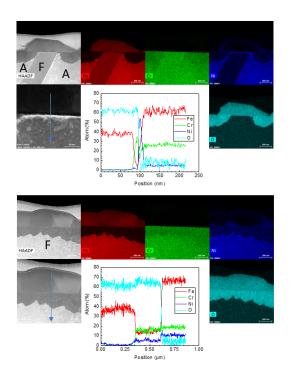


Fig. 1. TEM-EDS results of oxide films formed on as-welded ER316L specimens.

As shown in Fig. 2, duplex oxide films were formed on the surface of thermal-aged ER316L specimen. The outer oxide particles on ferrite and austenite were spinel-type oxides enriched in Fe. The inner oxide films formed on ferrite were chromia with thickness around 10 nm. The inner oxide films formed on austenite were amorphous Fe, Cr-rich spinel oxides. Ni enrichment in the matrix of ferrite at matrix/inner oxide film was similar than that in the matrix of austenite.

Comparing the TEM-EDS results between as-welded and thermal-aged ER316L specimens, the Ni enrichment in the matrix of ferrite at the matrix/inner oxide film was higher in as-welded specimens, and the Fe content in outer oxide particles on the austenite was slightly higher in thermal-aged specimens.

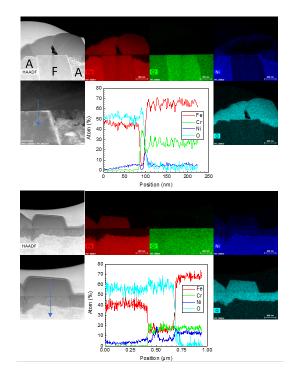


Fig. 2. TEM-EDS results of oxide films formed on thermal-aged ER316L specimens

## 3. Conclusions

For as-welded and thermal-aged 10,000 hours ER 316L welds in simulated PWR primary water environment, duplex oxide films were formed with spinel-type outer oxide particles and chromia- or spinel-type inner oxide films. The chromia-type inner oxide film formed on ferrite were thinner than the spinel-type inner films on austenite. Higher Ni enrichment in the matrix of ferrite at the matrix/inner oxide film was in as-welded specimens, and slightly higher Fe content in outer oxide particles on the austenite was in thermal-aged specimens.

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