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Characterization of microstructure of A508III/309L/308L weld and oxide films formed in deaerated high-temperature water

Qi Xiong [a, b, c], Hongjuan Li [a, b, c], Zhanpeng Lu [a, b, c, *], Junjie Chen [a, b], Qian Xiao [a, b], Jiarong Ma [a, b], Xiangkun Ru [a, b]

[a] *Institute of Materials, School of Materials Science and Engineering, Shanghai University, 149 Yanchang Road, P.O.Box 269, Shanghai, 200072, China*
[b] *State Key Laboratory of Advanced Special Steels, Shanghai University, 149 Yanchang Road, Shanghai, 200072, China*
[c] *Shanghai Key Laboratory of Advanced Ferrometallurgy, Shanghai University, 149 Yanchang Road, Shanghai, 200072, China*

HIGHLIGHTS

- Surface films at LAS-309L/308L weld in deaerated high-temperature water at 290 °C.
- Less surface oxides on decarburization zone than on other zones in the LAS HAZ.
- More corrosion pits on 309L than on 308L due to the inclusion dissolution.
- Film on 309L with ~9% ferrite was thicker than that on 308L with ~12% ferrite.
- Cr content in the inner oxide layer on 308L was higher than that on 309L.

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ABSTRACT

The microstructure of A508III/309L/308L weld clad and the properties of the oxide films formed in simulated pressurized water reactor primary water at 290 °C were characterized. The A508III heat-affected zone (HAZ) consisted primarily of a decarburization zone with ferrite near the fusion line and a following pearlite structure with fine grains. A high hardness region in the HAZ could be the result of C-enrichment. $M_{23}C_6$ and M_7C_3 precipitates were observed in element transition zone. 308L stainless steel (SS) containing ~ 12% ferrites exhibited both ferritic-austenitic solidification mode (FA mode, $\delta \rightarrow \gamma$) and austenitic-ferritic solidification mode (AF mode, $\gamma \rightarrow \delta$), whereas 309L SS containing ~ 9% ferrites exhibited only FA mode. The A508III surface oxide film was mainly Fe_3O_4 in deaerated high-temperature water. The coarse grain zone covered with few oxide particles was different from other types of film on the other region of HAZ and the bulk zone. More pitting appears on 309L SS after immersion in deaerated high-temperature water due to the dissolution of inclusions. SS surface oxide films consisted primarily of spinels. The oxide film on SS was divided into two layers. Ni was concentrated mainly at the oxide/substrate interface. The oxide film formed on 309L was thicker than that on the 308L. The ferrite in the stainless steel could improve the oxidation resistance.

1. Introduction

In pressurized water reactor (PWR) nuclear power plants, low alloy steels (LASs) are widely used in reactor pressure vessels, pressurizer vessels, and other vessel components because of their high strength, good ductility and low price. Stainless steels are cladded on the inner wall of the LAS pipes or vessels due to their good corrosion resistance [1–4] to mitigate the corrosion of LAS by high-temperature water coolants. Since the stainless steel cladding is in direct contact with high temperature water in the PWR primary loop, LAS would be subject to corrosion by high temperature water once the cladding layer fails. Stress corrosion cracking is one of the potential degradation modes for stainless steel cladding, which is strongly affected by the alloy microstructure and the properties of oxide films. The corrosion resistance and integrity of the stainless steel cladding are critical for the safety and reliability

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* Corresponding author. Institute of Materials, School of Materials Science and Engineering, Shanghai University, 149 Yanchang Road, P.O.Box 269, Shanghai, 200072, China.
E-mail address: zplu@t.shu.edu.cn (Z. Lu).

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of LAS vessels and pipes. The reheat cracking in as-welded austenitic stainless steel components operating at high temperature in nuclear power plant have been reported [5]. Failures of dissimilar metal weld safe end nozzles due to stress corrosion cracking in PWR primary water have also been reported [6,7]. The material properties in the weld heat-affected zones and the weld metals in stainless steel welds and Ni-base alloy welds have been characterized [8–12] and were correlated to stress corrosion cracking behavior in high-temperature water environments. The microstructural and chemical properties in dissimilar welds would have significant effects on corrosion and stress corrosion cracking behavior in high-temperature water environments. One part of the dissimilar metal weld safe end is the stainless steel cladding on the inner wall of low alloy steel pipes. Ming et al. [13] studied the microstructural property of SA508-309L/308L-316L dissimilar metal welded safe-end joints, and found that the HAZ with a complex structure gradient appeared in LAS near the fusion boundary. The transition zone has a complex structure and carbon migration from the LAS to SS results in a hardness decrease in LAS and an increase in the carbon-rich zone [14]. Li et al. [15,16] studied the structure of low alloy steel to stainless steel transition weld and SCC behavior in simulated PWR primary water at 290 °C and found that the transition zone showed a higher susceptibility to SCC. Intergranular cracking mainly occurred in the austenitic layer, whereas transgranular cracking mainly occurred in low alloy steel.

The properties of oxide film have proven to play an important role in SCC initiation and the growth of materials in high-temperature water environments [17–19]. Characterization of the oxide films formed on different parts of the LAS-SS cladding in simulated primary water is expected to provide mechanistic information on SCC susceptibility. Cunha Belo et al. [20] analyzed the oxide films that formed on 316L stainless steel in high-temperature water at 350 °C and found that the outer oxide film was mainly $Ni_{0.75}Fe_{2.25}O_4$ inverse spinel, whereas the inner oxide film was mixed chromium oxides. Chen et al. [8,9] found that the double-layered structure was composed of mixed iron-nickel and chromium oxides. With a decreasing the oxygen content in high-temperature water, the chromium content increased in the oxide film on stainless steel and hematite tended to diminish, whereas spinel appeared [21]. Das et al. [22] studied the oxidation behavior of Fe-Cr-Ni ternary alloys by means of quantum chemical molecular dynamics at 288 °C and found that iron and chromium migrated faster in the surface layer than nickel did. Higher chromium content led to the formation of more ferrite and of compact oxide film [23]. To reveal the properties of oxide films on LAS-SS cladding, the properties of oxide films formed on various locations of the LAS-SS weld cladding block in simulated PWR primary water are characterized and correlated to the material properties at these locations. Metallographic examination, scanning electron microscopy (SEM) measurement, Raman spectroscopy, focused ion beam (FIB) sampling and transmission electron microscopy (TEM) are used in the analysis.

2. Experimental

2.1. Material and specimen preparation

This work was conducted on LAS to SS cladding (A508III/309L/308L) that was obtained from a PWR pressure vessel nozzle and pipe weld joint mock up. Low alloy steel base metal was made from Mn-Ni-Mo forgings, and the main chemical compositions of each part are listed in Table 1. Considering the elements (Cr, Ni) dilution of dissimilar metal welding, the first 309L SS cladding layer of about 2.5-mm-thick on LAS was used as the isolation layer and proper heat treatment was conducted; then, a layer of 308L SS was used as the corrosion resistant layer, and proper post weld heat treatment was carried out. The heat treatment parameters are shown in Table 2.

The specimens with a size of 20 mm × 8 mm × 3 mm were cut from a plate sample. Fig. 1 displays the macroscopic sketch map of the plate, where the red box shown in Fig. 1(b) indicates the sampling location where the A508III/309L/308L welds were acquired as shown in Fig. 1(c). To reveal the microstructure, the samples were prepared by grinding and polishing. Before optical microscope observations, various parts of dissimilar metal joints were etched separately; the low alloy steel side was etched by 4% nital solution for approximately 10 s, and the stainless steel was electro-etched in 40% NaOH solution for 30 s with a DC of 5–6 V.

The microstructural features were then examined using a VHX-100 digital microscope and a field-emission scanning electron microscope equipped with an electron backscattered diffraction system operating at 20 kV. The fusion zone was studied using a JEM 2010F transmission electron microscope with selected area electron diffraction analyses (SAED) operating at 200 kV. To reveal the chemical composition, energy dispersive spectroscopy (EDS) equipped on an Apollo 300 SEM was used at 15 kV.

2.2. Immersion tests in high temperature water environment

Immersion tests in simulated pressurized primary water environments at 290 °C were conducted to study the characteristics of oxide film on the weld. The immersion samples were punched with a diameter Φ2 circular hole in the low alloy steel side to facilitate hanging in the autoclave. Then, the specimens were polished with metallographic sandpaper to 1500 grit before being cleaned with deionized water and alcohol. Immersion tests were carried out in deaerated PWR water. The solution for immersion tests was made by adding 2 ppm lithium (with $LiOH \cdot H_2O$) and 1200 ppm boron (with H_3BO_3) to deionized water. Deaerated water was achieved by purging N_2 gas for 2.5 h and slowly heating the water to 290 °C at ~7.2 MPa. For this work, the oxygen content and hydrogen content in the deaerated PWR water was expected to be below 10 ppb through bubbling with nitrogen gas into the autoclave for a period of time, which was significantly lower than that in oxygen-containing water. Deaerated high temperature water was used to simulate the local or abnormal conditions in the plants where dissolved hydrogen concentration can be low. Immersion tests were carried out for 168 h. Samples were cleaned with deionized water, rinsed in acetone and dried with cold air before using.

2.3. Characterization of oxide films formed in high temperature water

The surface oxide film morphology of specimens after immersion tests was observed by Apollo 300 thermal field emission SEM. The structure of surface oxide was detected using an INVIA Raman spectrometer with a laser wavelength of 514.5 nm. Cross sections of the oxide films were used for further study with TEM observation. To prepare the TEM specimens, FEI Helios Nanolab 600i dual-beam focused ion beams with Ga ion sputtering were used to obtain the oxide film cross section. SAED was conducted using a JEOL JEM-2100F TEM equipped with an EDS system operating at 200 kV. The chemical composition of oxide films formed on specimens was analyzed by EDS.

3. Results

3.1. Microstructure at various locations in the weld

The microhardness profiles of the LAS-SS weld are shown in Fig. 2. The highest hardness is detected near the fusion line. The