Electrochemical and spectroscopic characterization of oxide films formed on Alloy 182 in simulated boiling water reactor environment: Effect of dissolved hydrogen

Juxing Bai[a], Rik-Wouter Bosch[b], Stefan Ritter[a,*], Christof W. Schneider[a], Hans-Peter Seifert[a], Sannakaisa Virtanen[c]

[a] *Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland*
[b] *SCK•CEN, Mol, Belgium*
[c] *Friedrich-Alexander University of Erlangen-Nuremberg, Erlangen, Germany*

ARTICLE INFO

ABSTRACT

In boiling water reactor (BWR) environments, the content of dissolved hydrogen (DH) in the high-temperature water has an influence on the stress corrosion cracking (SCC) susceptibility of Ni-based alloys. In order to understand the possible role of different types of surface oxide films in the SCC initiation process, oxide films formed on Alloy 182 weld metal under simulated BWR conditions at 274 °C with varying contents of DH from 10 to 2200 ppb, were investigated by electrochemical and spectroscopic methods. The influence of the DH content on the nature of the oxide films is discussed in the context of SCC mechanisms.

1. Introduction

The Ni-based Alloy 182 is widely used in light water reactors as weld filler metal and attachment pad metal to join the low-alloy steel reactor pressure vessel to both, wrought Ni-based alloys (e.g., Alloy 600) or austenitic stainless steels (e.g., AISI 304L, 316L). In recent years, several intergranular stress corrosion cracking (IGSCC) incidents occurred in Alloy 182 dissimilar metal welds in both, boiling water (BWR) [1–4] and pressurized water reactors (PWR) [5–7], which affected the safe and economic operation of nuclear power plants. In case of BWRs, components such as different nozzle safe ends [4], bottom head penetration housings [8] and core shroud support welds [9] have suffered from SCC. The cracking was usually confined to the weld metal and none of the SCC cracks significantly penetrated the adjacent reactor pressure vessel base material, which is consistent with the very high SCC resistance of low alloy steel under light water reactor conditions [10]. SCC crack growth rates in Alloy 182 can be quite high and SCC initiation thus can cover a significant part of the component lifetime. So far, the focus of experimental investigations has been placed on PWR environments and SCC crack growth and to a much lesser extent on crack initiation.

In PWR environment, SCC initiation and crack growth in Ni-based alloys are strongly influenced by the dissolved hydrogen (DH) content of the environment. A strong effect of DH on SCC and peak in SCC susceptibility at the Ni/NiO phase boundary has been observed at 320–360 °C [11,12]. This Ni/NiO phase boundary is predicted to decrease from 2.3 ppm DH at 360 °C to 0.25 ppm DH at 274 °C [13,14]. A recent initiation and growth study with Alloy 182 in simulated BWR environments showed that the maximum in crack initiation and growth is located at the Ni/NiO phase transition line [15]. Mechanistic studies of IGSCC in Ni-based alloys have increased in recent years and several mechanisms have been proposed such as slip-dissolution [16], selective internal oxidation [17], hydrogen assisted cracking/hydrogen embrittlement, and vacancy condensation [18]. But none of the proposed mechanisms can explain all the observed parameter effects and metallographic and fractographic observations, and the exact mechanism is still under discussion. Some of the cracking mechanisms may be simultaneously active (e.g., slip dissolution and hydrogen assisted cracking (HAC)) and controlled by the same rate determining steps. Depending on the conditions, some mechanism can dominate over others. The mechanism can also gradually change with the precursor processes, initiation and subsequent crack growth.

Because SCC initiation is a surface phenomenon, the oxide film protecting the Ni-base alloys plays a key role in the SCC initiation. The structure and chemical properties of the oxide film may provide important information for a deeper understanding of the process of SCC initiation. Studies of oxide films on Ni-based alloys in PWR environments have been focused on the influence of DH on the oxide film.

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* Corresponding author.
E-mail address: stefan.ritter@psi.ch (S. Ritter).

Investigations have been carried out with advanced surface analysis techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) [19], secondary-ion mass spectrometry (SIMS) [19–22] and spectroscopic methods such as X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy [23]. In PWR primary water, the oxidation of Ni based alloys causes the formation of a multilayered oxide film. The external layer facing the aqueous environment consists of large Ni-rich crystallites, which are spread over the surface and are much lower in Cr content or even Cr-free. The inner compact Cr-rich oxide layer is assumed to be protective. The overall thickness of this oxide layer is larger than the passive layers formed at room temperature. Nevertheless, it is not fully understood whether only part of the inner oxide layer is truly protective. Because of the selective oxidation and the outward diffusion of Cr, there is a Cr-depleted layer beneath the inner oxide layer [19].

The corrosion of metals and alloys in high-temperature water environments is also an electrochemical process and studies of DH on the oxide films by electrochemical methods could provide complementary information and confirm the representativeness of the features obtained by local analysis, e.g., TEM. For this purpose, Mott-Schottky and photoelectrochemical analysis can be used in order to study the effect of DH on the nature of the oxide films in terms of semiconductor type, band gap energy as well as point and microstructural defects.

The present study investigates the effect of DH on the oxide films formed on Alloy 182 in 274 °C high-temperature water. The aim is to find a relationship between the SCC susceptibility and the oxide film characteristics. Therefore, both surface analytical and electrochemical measurements were performed, including SEM, TEM, XPS, Raman spectroscopy, Mott-Schottky and photoelectrochemical analysis.

2. Experimental

2.1. Material

The Alloy 182 test weld was fabricated according to nuclear welding specifications by filling an U-shaped groove in a large quenched and tempered 22 NiMoCr 37 (=SA 508 Cl. 2) low-alloy steel plate $(1 \times 1 \times 0.22 \text{ m}^3)$. This plate is from the forged lower cylindrical shell of the Biblis C PWR reactor pressure vessel which was never commissioned. In a first step, a weld butter layer (double layer at the groove root, single layer on the groove flanks) was produced by shielded metal arc welding (110–115 A and 22 V, pre-heating temperature 125–140 °C), which was then ground and post-weld heat treated at 620 °C for 9 h 15 min in air. The buffer layers are thus "sensitized". The groove was then filled by multipass shielded metal arc welding (115–140 A and 22–24 V, interpass temperature 47–130 °C) without subsequent post-weld heat treatment. The bulk weld metal is thus in the as-welded "solution-annealed" condition, in contrast to the buffer layers. The chemical composition of the Alloy 182 weld metal was inspected by inductive coupled plasma-optical emission spectroscopy (ICP-OES) and by combustion analysis by hot gas extraction infrared absorption method (Table 1).

2.2. Coupon exposure experiments

Coupons of $10 \times 10 \times 3 \text{ mm}^3$ were cut from the bulk weld metal and first mechanically abraded to P2500, polished to 3 μm surface finish and then electropolished for 10 s at 45 V in a solution of 10% (volume fraction) perchloric acid in methanol (80%)/water (10%)

Table 2
DH contents for coupon exposure experiments and the corresponding ECP and stability regions.

DH [ppb]	10 (NiO)	100 (NiO)	253 (Ni/NiO)	600 (Ni)	2200 (Ni)
ECP [mV]	−458	−513	−535	−555	−599

solution. The coupon exposure tests were performed in stainless steel autoclaves, which were attached to sophisticated refreshing high-temperature water loops. During the experiments all important environmental parameters at inlet and outlet (DH, conductivity, temperature, pressure, flow) were recorded continuously. Experiments with exposure times of ≥200 h and different DH contents (10, 50, 253, 600 and 2200 ppb) were conducted. The DH contents and the corresponding electrochemical corrosion potentials (ECPs; also referred to as open circuit potential) and stability regions are shown in Table 2. The ECP of the specimens and the redox potential (Pt probe) were continuously monitored with Cu/Cu$_2$O ZrO$_2$-membrane reference electrodes. Ionic impurities of the water (inlet and outlet) were analysed by inductive coupled plasma-atomic emission spectroscopy and Ion Chromatography once during each test.

2.3. SEM and TEM analysis

After the high-temperature water exposure tests, the coupons were investigated by a Zeiss SEM equipped with energy dispersive X-ray spectroscopy (EDX) detector to analyse the oxide film formed under the different water chemistry conditions. Cross-sectional lamellas containing the surface oxide film were made using focused ion beam (FIB) and analysed by a JEOL-2010 TEM (200 kV) with EDX detector.

2.4. Spectroscopic characterization

2.4.1. X-ray photoelectron spectroscopy

The XPS measurements were conducted using a high-resolution PHI 5600 (USA) X-Ray photoelectron spectrometer, and monochromatic Al K_α radiation (1486.6 eV, 300 W) excitation source. The take-off angle of the emitted photoelectrons was adjusted to 45° with respect to the surface normal. A survey spectrum with 0.8 eV step size was first measured for each specimen, and then high-resolution measurements were taken for the relevant energy areas for different elements. The binding energies of the target elements (Ni 2p, Fe 2p, Cr 2p and O 1s) were determined at a pass energy of 23.5 eV, with a resolution of 0.2 eV. The background was subtracted using the Shirley method in all spectra. To obtain the molar fractions of each species, the peak areas of the measured XPS spectra were corrected with the photoionization cross sections of Scofield [24] σ and the asymmetry parameter β (orbital geometry) [25], which are contained in the sensitivity factors of the acquisition software (MultiPak V6.1A, 99 June 16, Copyright © Physical Electronics Inc., 1994–1999).

2.4.2. Raman spectroscopy

Raman spectra were measured using a LabRAM series Raman microscope (Horiba Jobin Yvon) with a He-Ne excitation laser λ: 632.8 nm, output power: ~10 mW, which was focused to a spot of diameter ~1 μm, and at least 3 points were analysed for each specimen. Reference measurements of bare metal before exposure to high-temperature water and on pure NiO powder were conducted. The

Table 1
Chemical composition of the Alloy 182 weld metal in wt.%.

C	Si	Mn	Cr	Mo	Ni	Nb	Al	Co	Fe	N	Ti
0.027	0.580	6.19	15.9	0.172	69.1	2.36	0.0302	0.0172	5.46	0.024	0.0924