Stress corrosion cracking initiation and short crack growth behaviour in Alloy 182 weld metal under simulated boiling water reactor hydrogen water chemistry conditions

Juxing BAI¹, Stefan RITTER¹, Hans-Peter SEIFERT¹, Sannakaisa VIRTANEN²

¹*Paul Scherrer Institut, Nuclear Energy and Safety Research Division,
Lab. for Nuclear Materials, 5232 Villigen PSI, Switzerland, juxing.bai@psi.ch*

²*Friedrich-Alexander University Erlangen-Nürnberg, Germany*

Abstract

The effect of dissolved hydrogen on the stress corrosion cracking initiation and short crack growth behaviour of Alloy 182 weld metal was evaluated in 274 °C hydrogenated high-purity water using accelerated crack initiation and growth tests with sharply notched fracture mechanics specimens and in-situ crack initiation and growth monitoring. A maximum in initiation susceptibility and crack growth rates was observed at the Ni/NiO phase transition line. Grain boundary misorientations and mismatch in Schmid factor were measured by electron backscattered diffraction along intergranular stress corrosion cracks and at crack initiation sites. Low angle boundaries seem to be particularly resistant to cracking.

Key words: Stress corrosion cracking; Ni-base alloy; boiling water reactor; hydrogen; initiation;

List of abbreviations

ASTM E1681	Standard test method for determining a threshold stress intensity factor for environment-assisted cracking of metallic materials under constant load
ASTM E399	Standard method of test for plane strain fracture toughness of metallic materials
BWR	Boiling water reactor
C(T)	Compact tension fracture mechanics specimen
CSL	Coincidence site lattice

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DCPD	Direct current potential drop
DH	Dissolved hydrogen
EBS	Electron backscattered diffraction
ECP	Open circuit free electrochemical corrosion potential
EDX	Energy dispersive X-ray spectroscopy
EPRI	Electric power Research Institute
FEGSEM	Field Emission Gun Scanning Electron Microscope
HAB	High-angle grain boundary
HWC	Hydrogen water chemistry
IGSCC	Intergranular stress corrosion cracking
LAB	Low-angle grain boundary
NMCA	noble metal chemical application
OM	optical microscopy
ppb	Part per billion, $\mu\text{g/kg}$
PWR	Pressurized water reactor
SCC	Stress corrosion cracking
SEM	Scanning electron microscopy
UTS	Ultimate tensile strength
YS	Yield stress

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) and 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]. The possibility of SCC crack growth in Alloy 182 weld metals in high-purity BWR (neutral high-purity water, 274 to 288 °C, $\text{pH}_T = 5.6$) and PWR (slightly alkaline borated and lithiated water, 290 to 360 °C, $\text{pH}_T \sim 7$, 2 to 3 ppm dissolved hydrogen (DH)) environment has also been demonstrated by laboratory investigations. In PWR environment, SCC in Ni-based alloys is strongly influenced by the temperature (high Arrhenius activation energy for SCC of ~ 130 kJ/mol)) and the DH content of the high-temperature water. A peak in SCC initiation and crack growth susceptibility at the Ni/NiO phase transition line was observed at 320 to 360°C [11, 12]. This thermodynamic boundary is predicted to decrease from 2.3 ppm DH at 360°C to 0.25 ppm DH at 274°C (Table 1) [13, 14]. In BWRs with moderate hydrogen water chemistry (HWC, ~ 100 to 300 ppb H_2) or noble metal chemical application (NMCA)-HWC (~ 20 to 40 ppb H_2), the DH concentration is close to this DH concentration (Table 2). Andresen et al. [15] confirmed the existence of this maximum in SCC crack growth rate for Alloy 182 at the Ni/NiO phase transition line at lower temperatures of 300 °C in BWR environment also. Richey et al. [16, 17] measured the SCC initiation times as a function of DH for Alloy 600 at 360 °C and compared them with the reciprocal of crack growth rate data, and has shown that the DH effects on SCC initiation and crack growth rate were analogous. More recent results from the authors [18] indicate that the SCC initiation time is much longer in the NiO region than in the Ni region, so a lower DH level seems more effective to mitigate SCC initiation. The advantageous effect of low DH levels on SCC initiation is also confirmed in [19, 20], where three-point-bend specimens of weld metal Alloy 182 and Alloy 600 were exposed up to 4.5 years (32600 h) to simulated PWR primary water with DH levels varying from 0.45 to 2.23 ppm. During the exposure experiment, periodic visual inspections were performed to examine the ratio of cracked specimens. For the environment with the lowest DH content (0.45 ppm), the crack initiation time is about 50%

longer than in the other two environments (1.34 and 2.23 ppm), which suggests that the effect of hydrogen on the initiation of PWSCC is the same for Alloy 600 wrought and Alloy 182 weld metal. In a more recent work conducted by Molander et al. [21], SCC initiation of Alloy 600 was studied in simulated PWR environments with hydrogen contents from 0.45 up to 6.26 ppm. At the high hydrogen content of 6.26 ppm, the time to crack initiation was approximately doubled compared to the initiation time at 2.68 ppm, the resistance to SCC initiation increased significantly at low hydrogen levels. The minimum in initiation time and the maximum in crack growth rate were both located in proximity of the NiO/Ni phase transition line.

So far, the focus of the experimental investigations was placed to SCC crack growth with Alloy 600 under PWR conditions. The Alloy 182 weld metal has never been used for crack initiation tests under BWR conditions before, although it has been proved to be susceptible to IGSCC in crack growth rate tests [15]. Furthermore, the very limited existing data of tests with Alloy 182 conducted under PWR conditions did not reveal a clear trend with regard to DH effects on SCC initiation, because of the inherent large scatter and significant variations in test parameters in the individual experiments. Mechanistic studies of IGSCC in Ni-based alloys have increased in recent years and several mechanisms have been proposed such as slip-dissolution [22], selective internal oxidation [23], hydrogen assisted cracking/hydrogen embrittlement, and vacancy condensation [24], however, the SCC mechanism is still under very controversial discussion. A convincing mechanistic explanation for the effect of DH is still missing. Other studies focused to the effect of grain boundary structure on intergranular SCC and corrosion susceptibility in austenitic stainless steels and Ni-alloys revealed that twin boundaries are highly resistant to SCC cracking and represent a strong barrier for IGSCC [25-28]. Attempts were done to increase the IGSCC resistance by increasing the share of more resistant grain boundaries and to break-up the connectivity of susceptible grain boundaries with

resistant ones by specific thermo-mechanical treatments (“grain boundary engineering”) [29]. Some studies also showed that the twin boundary structure can be damaged by cold working induced during fabrication and installation of components [30-32] that increases the SCC susceptibility.

The aim of this study is to evaluate the unexplored effect of DH content on the SCC initiation and subsequent short crack growth behaviour in Alloy 182 weld metal under BWR/HWC conditions, and thus to identify optimal operation DH levels to mitigate SCC in BWRs. In BWR/HWC, the DH content at different locations in the reactor strongly varies depending on the H₂ injection rate in the feedwater, reactor design, downcomer γ dose rates, recirculation flow etc. In BWRs with moderate HWC, the DH concentration could be close to the peak SCC susceptibility region (Table 2).

In this work, accelerated SCC initiation and short crack growth tests under simulated BWR environments at different DH levels were performed with sharply notched fracture mechanics specimens. The crack initiation sites, crack path and fracture mode were characterized by optical and scanning electron microscopy (SEM). Grain boundary misorientations and mismatch in Schmid factor were measured by electron backscattered diffraction (EBSD) along intergranular stress corrosion cracks and at crack initiation sites. The present paper summarizes the most important results and conclusions of these investigations. In a related work, we are also investigating SCC initiation with smooth tapered tensile specimens in slow strain rate and constant load tests and the results will be published soon also.

2. Material and Experimental Procedure

2.1 Material and specimens

2.1.1 Alloy 182 weld

The Alloy 182 test weld was fabricated according to nuclear welding specifications by filling an U-shaped groove in a large quenched and tempered SA 508 Cl. 2 low-alloy steel plate (1 m x 1 m x 0.22 m). 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 grinded and post-weld heat treated at 620 °C for 9 h 15 min in air. The groove was then filled by multipass SMAW (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 butter layers. The chemical composition of the Alloy 182 weld metal was inspected by inductive coupled plasma optical emission spectroscopy and by combustion analysis by the hot gas extraction infrared absorption method (Table 3). The mechanical tensile test properties of small round tensile specimens (3 mm diameter, 18 mm gauge length) at 25 and 288 °C in air at a strain rate of 10^{-3} s^{-1} are summarized in Table 4.

Figure 1 shows a cut-out section of the multipass shielded metal arc welding with the main orientation of the plate, welding direction and location of the tensile and fracture mechanics specimens. The typical multipass SMAW weld microstructure on the T-S and L-S surface is shown in Figure 2. The microstructure with a fibre-like texture consists of large

columnar grains of several mm in length that may stretch over several weld passes and are parallel to the solidification and heat-flux direction during the solidification process (see Section 3.3.1 for more details).

2.1.3 Specimens

12.5 mm thick 0.5T compact tension (C(T)) fracture mechanics specimens with a sharp notch (notch radius ρ of 0.1 mm and notch depth a_0 to ligament width W ratio a/W of 0.3) were fabricated in T-S direction according to ASTM E399 [33] as shown in Figure 3. The notch/crack-tip and plane are located in the bulk weld metal and the orientation of the crack plane is parallel to columnar grains and main dendrite growth and solidification direction, which results in the highest SCC crack growth and initiation susceptibility [15]. The gauge length of the tensile specimens for the material characterization was in T orientation and parallel to the main loading direction of the fracture mechanics specimens.

The $K_{I\text{-validity}}$ limits according to ASTM E399 (plane strain and linear-elastic) and E1681 (linear-elastic) [34] with the flow stress $\sigma_y = (YS+UTS)/2$ of 510 MPa and specimen thickness B of 12.5 mm and un-cracked ligament width $W-a_0$ of 17.5 mm are $\sim 36 \text{ MPa}\cdot\text{m}^{1/2}$ and $60 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. For the given specimen configuration, the radius of plastic zone under plane strain conditions is 20 times smaller than the specimen thickness up to a K_I -value of $55 \text{ MPa}\cdot\text{m}^{1/2}$. It thus can be assumed that plane strain and linear elastic conditions should still prevail up to the highest tested K_I -level of $45 \text{ MPa}\cdot\text{m}^{1/2}$.

2.2 Experimental procedure

SCC and coupon exposure tests were performed in stainless steel autoclaves with integrated electromechanical loading systems, which were attached to sophisticated refreshing high-temperature water loops. During the experiments all important mechanical (load, pull rod stroke) and environmental parameters at inlet and outlet (DH, conductivity, temperature, pressure, flow) were recorded continuously. The C(T) specimens were electrically isolated from the autoclave using zirconia sleeves and Teflon spacers. The open circuit free electrochemical corrosion potential (ECP) of the specimens and the redox potential (platinum probe) were continuously monitored with Cu/Cu₂O ZrO₂-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.

2.2.1 Coupon exposure tests

To verify the position of the Ni/NiO phase transition line of the Alloy 182 weld metal (~ 69 % Ni, 16 % Cr, 5 % Fe) under BWR conditions at 274 °C, flat coupon specimens were exposed for 200 h in simulated BWR water at 274 °C with DH levels ranging from 50 to 600 ppb. In Figure 4, the Ni/NiO phase transition line (taken from [13]) as a function of DH concentration and temperature is shown as a red line. The exposure tests in relation to the Ni/NiO phase transition line are illustrated in Figure 4 as circles.

2.2.2 SCC initiation and short crack growth tests

Environmental conditions: The accelerated SCC initiation and short crack growth tests were performed in high-purity (inlet conductivity of $0.055 \mu\text{S/cm}$) high-temperature water under low-flow condition (6 autoclave exchanges per hour) at 274°C with 50, 253 and 600 ppb DH, respectively. The chosen DH concentrations represent the Ni stability (600 ppb), Ni/NiO phase transition line (253 ppb) and NiO stability region (50 ppb). The position of the used DH levels is illustrated in Figure 4 as triangles with the Ni/NiO phase transition line as reference. The corresponding redox potentials of the environment were $-496 \text{ mV}_{\text{SHE}}$ (50 ppb DH), $-534 \text{ mV}_{\text{SHE}}$ (253 ppb DH) and $-555 \text{ mV}_{\text{SHE}}$ (600 ppb DH).

After SCC initiation and some stable SCC crack growth, on-the-fly changes of DH (e.g., 253 ppb $\rightarrow$ 600 ppb $\rightarrow$ 253 ppb) were applied in selected tests to study their effect on SCC crack growth and compare it with the ordinary test results at constant DH.

Mechanical loading and notch conditions: Before application of loading sequences, the specimens were pre-oxidized in the test environment at a low constant pre-load of 0.5 kN for 7 days to stabilize the environmental conditions and to establish a homogenous surface oxide film. After the pre-oxidation phase, the load was increased from 0.5 kN to 3.5 kN ($10 \text{ MPa} \cdot \text{m}^{1/2}$) with 1 kN/min followed by a very slow rising load phase from 3.5 kN ($10 \text{ MPa} \cdot \text{m}^{1/2}$) to 15.8 kN ($45 \text{ MPa} \cdot \text{m}^{1/2}$) with 0.5 N/min ($\sim 400 \text{ h}$). Thereafter the load was kept constant at 15.8 kN ($45 \text{ MPa} \cdot \text{m}^{1/2}$) for ~ 500 -1600 h.

The main advantage of the selected specimen-loading configuration with respect to smooth specimens is that the location of crack initiation is fixed to the notch root and both crack initiation and subsequent short crack growth can be in-situ monitored by DCPD. Along the specimen thickness there is still a sufficiently large and statistically relevant number of

grain boundaries intersected by the notch root to study their influence on IGSCC initiation. The slow rising load phase is resulting in a continuous slow plastic straining of the notch ground in combination with a tri-axial stress state and thus aggressive mechanical conditions reducing the necessary time for crack initiation. The very slow loading rate of 400 h between 3.5 and 15.8 kN results in a very slow notch strain rate in the range of 2 to $3 \cdot 10^{-8} \text{ s}^{-1}$. After initiation and some small crack advance from the notch root ($\Delta a > \sim 1$ to $2 \cdot \rho$), the SCC crack growth can be followed under small scale yielding conditions in the same test. Furthermore, this configuration is not very different from component locations with geometric notches (e.g., weld root defects). It is stressed that, on the other hand, the accelerated test method with a strong mechanical driving force could oversee more corrosion-dominated slow initiation mechanisms and their precursors (e.g., oxidation of specific grain boundaries) in these short-term tests and thus eventually also underestimate the real SCC susceptibility in the field.

In the C(T) specimens with the deep ($a_0 = 7.5 \text{ mm}$, $a_0/W \sim 0.3$) and sharp notch (v-notch with $\rho = 0.1 \text{ mm}$) there is a multiaxial stress state (plane, biaxial stress at surface of the notch-root, plane strain in the region of the peak stress) with a high stress concentration $K_t = \sigma_{\max}/S_n$ and stress gradient $d\sigma/dr$ in the notch-root region. The plasticity is limited and confined to the direct vicinity of the notch-root. The elastic stress gradient is very similar to that of a sharp crack with same crack depth. For this configuration, the elastic peak stress $\sigma_{\max}$ at the notch-root of the C(T) specimen was estimated from the stress intensity factor K_I and the notch radius ρ according to equations (1) and (2) by linear elastic fracture mechanics (LEFM) [35, 36] with very high accuracy. Together with the nominal stress S_n in the notched C(T) specimen (equation (3)), a theoretical elastic notch stress concentration factor K_t can be derived according to equation (4).

$$\sigma_{\max} = \frac{1}{\sqrt{\pi}} \frac{K}{\sqrt{\rho}} \quad (1)$$

$$K_t = \frac{P f(a_0/W)}{B\sqrt{W}} \quad \text{with } f(a_0/W) \text{ according to ASTM E399} \quad (2)$$

P : load, B : specimen thickness, W : specimen length

$$S_n = \frac{P}{B} \left[\frac{3(W + a_0)}{(W - a_0)^2} + \frac{1}{W - a_0} \right] \quad (3)$$

$$K_t = \frac{\sigma_{\max}}{S_n} \quad (4)$$

Additionally, the plastic notch-root strain ε was estimated numerically according to the concepts of Neuber [37] (equation (5)) and Glinka [38, 39] (equation (6)) with K_t and the experimentally-derived uniaxial stress-strain-curve of the material, which was modified for plane strain conditions by simple plasticity theory [39]. For the used notch configurations, the method of Glinka usually resulted in 20 to 40 % smaller notch strains (with growing difference with increasing strain) .

$$\text{Neuber: } K_t = \sqrt{(K_\sigma K_\varepsilon)} \quad (5)$$

$$\text{with } K_\sigma = \frac{\sigma}{S_n}, \quad K_\varepsilon = \frac{\varepsilon}{e_n} \quad \text{and} \quad e_n = \frac{S_n}{E}$$

σ, ε : notch stress and strain, S_n, e_n : nominal stress and strain, E : Young's modulus

$$\text{Glinka: } W_S = W_\sigma = \int S_{ij} d\varepsilon_{ji} = \int \sigma_{ij} d\varepsilon_{ij} \quad (6)$$

W_S : nominal strain energy density, W_σ : strain energy density at notch

The elastic notch stress concentration factor K_t was 21.2. The elastic stress amplitude σ_{max} ranged from ~ 600 to 2500 MPa at 3.5 kN and 15.8 kN, which corresponded to plastic notch strains ε of 0.28 to 2.9 % (Glinka) and 0.38 to 4.8 % (Neuber). The relation between the notch strain and related stress intensity factor K_I (for a sharp crack a_0) is shown in Figure 5.

For crack advances Δa from the notch root above the notch radius ρ , the resulting stress intensity factor K_I can be calculated with the actual crack length a with equation (2) of ASTM E399. The crack growth rate data are analysed in this way in the following. For very short crack advances $\Delta a \ll \rho$, the situation is dominated by the plastic zone at the notch root and an accurate estimation analysis would require an elastic-plastic finite element analysis. Furthermore, K_I is converging to 0 for very small crack advances ($K_I \rightarrow 0$ for $\Delta a \rightarrow 0$). A very rough K_I estimate for short crack advances $\Delta a \ll \rho$ can be made by the formula for an edge crack in a plate under uniform stress of the magnitude $K_t \cdot S_n$ with equation (7) [40].

$$K_I = 1.12 \cdot K_t \cdot S_n \cdot \sqrt{\pi \cdot \Delta a} \quad (7)$$

For an even crack advance Δa of 10 and 20 μm from the notch root and a load of 15.9 kN this would result in a K_I value of $16 \text{ MPa}\cdot\text{m}^{1/2}$ and $22 \text{ MPa}\cdot\text{m}^{1/2}$, which is a factor of 3 to 2 lower than the $45 \text{ MPa}\cdot\text{m}^{1/2}$ estimated with equation (2) for sharp cracks.

Crack initiation detection and crack length measurement: In all tests, crack initiation and growth were continuously monitored using the reversed direct current potential drop (DCPD) method. A direct current of 5 A with reversing polarity every 2 s was sent through specimen (U_{sp}) and through a cylindrical reference specimen (U_{ref}) of the same material. The latter is necessary to compensate the slow and small change of the specific resistance of the Ni-alloyed

weld metals with time at temperatures around 300 °C. The locations of potential and current probes and reference specimen are shown in Figure 6.

The crack length a from the load line was calculated by the Johnson equation [41] with the normalized potential drop U_{sp}/U_{ref} and the notch depth a_0 as initial crack length according to equation (8). The normalized potential drop $U_{sp,0}/U_{ref,0}$ at the crack initiation point was assigned to the initial notch depth a_0 . In contrast to notched tensile specimens [42] in slow strain rate tests or pre-cracked specimens in slow rising load tests [43, 44], the effect of the geometry change and blunting by plastic deformation and growth of plastic zone at the notch root on the DCPD potential drop in the sharply notched C(T) specimens under small scale yielding conditions in the rising load phase is very moderate. There is usually no or only a very small linear increase of U_{sp}/U_{ref} with the crack opening displacement at load line COD_{LL} or load before crack initiation. As soon as crack initiation and small crack growth occurs, U_{sp}/U_{ref} strongly increases. This point where the potential drop U_{sp}/U_{ref} starts to increase is assigned to SCC crack initiation and a_0 and $U_{sp,0}/U_{ref,0}$, respectively, as shown in Figure 7.

$$a = \frac{2 \cdot W}{\pi} \cdot \cos^{-1} \left(\frac{\cosh\left(\frac{\pi \cdot d}{2 \cdot W}\right)}{\cosh\left(\left(\frac{U_{sp}/U_{ref}}{U_{sp,0}/U_{ref,0}}\right) \cdot \cosh^{-1}\left(\frac{\cosh\left(\frac{\pi \cdot d}{2 \cdot W}\right)}{\cos\left(\frac{\pi \cdot a_0}{2 \cdot W}\right)}\right)\right)} \right) \quad (8)$$

In case of even crack growth from the notch root, the crack initiation derived by this procedure usually corresponds to a very small mean (average over the specimen thickness) crack growth increment from the notch root of about 5 to 10 μm as shown by corrosion fatigue tests with stainless steels in high-temperature water [45]. It is thus regarded as physical SCC

initiation. Unfortunately, SCC crack initiation is very localized and results in finger-like crack growth in the Alloy 182 weld metal, thus the uncertainty is somewhat higher.

The actual, small crack advances Δa were consistently underestimated by DCPD by a factor ranging from 6 to 10. In corresponding long-crack SCC growth investigations with Alloy 182, corresponding errors in the range of a factor of 1.5 to 3 are not unusual, whereas in corresponding wrought Ni-alloys or stainless steels this error is limited to a few % under optimal conditions. This underestimation is primarily due to the very localized finger-like crack growth (see section 3.2 for more details). Multiple SCC initiation sites at different locations and planes along the notch-root, the irregular shape and high roughness of the crack flanks or micro-branching and micro-crack coalescence are other factors that contribute to the large errors of measured crack length. Furthermore, the formation of Ni precipitates that act as electronic conduction paths between the crack flanks cannot be excluded in the crevice environment under some of the selected test conditions. Therefore, the reported crack advances and crack growth rates were linearly corrected by the measured real crack depths by post-test fractographical analysis in the OM and SEM. The average crack growth rates were calculated using average crack advance, which was obtained by dividing the total cracked area by the specimen thickness (notch width) B , and the maximal crack growth rates were calculated using the maximal depth of all cracks found.

2.3 Post-test characterization

After the high-temperature water exposure tests, the coupons were analyzed by a Zeiss ULTRA 55 field emission gun scanning electron microscope equipped with EDAX-EDX (energy dispersive X-ray spectroscopy) detector to analyze the oxide film formed under different water chemistry conditions. The C(T) specimens from the crack initiation/growth tests were broken open by fatigue in air for post-test fractographical analysis in the same SEM. The fracture surface and crack path and average and maximum local crack depths were analyzed by an optical microscope (OM) and SEM.

Selected C(T) specimens were first cut into two halves perpendicular to the notch root (along the T-S plane). One half was then broken open by fatigue for crack length measurement and the other half was grinded and electropolished for EBSD analysis. To determine the microstructure of the weld and along the SCC cracks by EBSD, the specimens were 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%) solution. The TEAM and TSL OIM software was used for EDX and EBSD data analysis for which a threshold of misorientation $\theta \geq 5^\circ$ between dendrite packets was selected to define a grain boundary. The grain boundaries were categorized into three groups according to the coincidence site lattice (CSL) approach using the Brandon's criterion [46] $\Delta\theta = 15^\circ \Sigma^{-1/2}$: (1) Low-angle grain boundaries (LAB, $\theta \leq 15^\circ$); (2) Random high-angle grain boundaries (HAB, $\theta > 15^\circ$); (3) CSL boundaries ($3 < \Sigma \leq 29$). The LABs are also termed $\Sigma 1$ boundaries, however, due to their different SCC susceptibility to other CSL boundaries ($3 < \Sigma \leq 29$), the LABs are considered in this study as an independent grain boundary type.

In addition to the above observations, EBSD analysis could also provide information on the small misorientation (0° to 5°) within the sample. As dislocations form in the material, the residual strain is presented as local variations in lattice orientation. Thus, local misorientation maps give an indication of the residual strain distributions in the material [47]. A kernel is a set of points of defined size surrounding a scan point. For a hexagonal measurement grid (as used in this article), this is the average misorientation between the orientation of a certain scan point and the orientations of the six equidistant neighbors. The influence of grain boundary on local misorientation can be removed by only calculating points misoriented relative to the center point within a prescribed value. Beside local misorientation map, a Schmid factor map can also be constructed using OIM. The Schmid factor could predict the yield response of a grain relative to a given stress state. Grains with higher Schmid factors are oriented for relatively easy slip, while grains with lower Schmid factors may tend to be resistant to yielding. The boundaries separating grains with high degree of mismatch in Schmid factor may be more susceptible to intergranular damage and thus to SCC. The challenge of conducting the Schmid factor analysis is properly identifying the stress state in the notch tip area in a C(T) specimen. In this study, the stress is assumed to be uniaxial tension vertical to the crack propagation direction.

3. Results and Discussion

3.1 Coupon exposure tests in simulated BWR/HWC conditions

Typical features of the surface oxides, which formed on Alloy 182 coupons in lower DH level environments (50, 200 and 230 ppb) in the NiO stability region are shown in Figure 8. The surface contains large crystals in the μm -range (indicated as A) and smaller crystals (indicated as B), which are spread over the surface, as well as needle-like oxides covering the whole surface. Chemical compositions of different positions marked in Figure 8 obtained using SEM/EDX analysis are shown in Table 5. The A-type large crystallite has a significant Ni and O content. Besides Ni and O, the B-type crystallite additionally has a remarkable content of Fe. A high-resolution SEM image of the needle-like crystallites (C-type) is shown in Figure 9. The length of the needle-like crystallites are typically in the 100 nm range. The EDX-analysis thus also includes the excited X-Ray signal coming from the underlying base material, which explains the high Ni content (constituent element).

Typical SEM images of the surface oxides formed in higher DH level environments (300 and 600 ppb) in the Ni stability region are shown in Figure 10, where the coarse crystallites do not appear. The higher Ni and O contents suggest that the A-type oxide crystallites might be NiO. Individual NiO crystallite precipitates were also reported by Morton et al. [48], who examined oxide films formed on Alloy 600 on tensile specimens tested in hydrogenated water at 360 °C. The B-type crystallites might be spinel-like oxides in the form of $(\text{Ni}_x\text{Fe}_{1-x})\text{Fe}_2\text{O}_4$ [49] and their composition strongly depends on the surface condition of the base metal and the saturation of the adjacent aqueous environment in Fe and Ni cations. In our test conditions, these crystallites are present predominantly at low DH levels, and are completely absent at 600 ppb DH.

The needle-like oxides with relatively high Cr and O content may be Cr-rich spinel-like oxides in the form of $(\text{Fe,Ni})(\text{Fe,Cr})_2\text{O}_4$. This assumption is also consistent with the study of Morton et al. [48], who examined these oxides using EDX in transmission electron microscopy and proposed a composition of $\text{Ni}(\text{Cr}_{0.5}\text{Fe}_{0.5})_2\text{O}_4$. Some authors reported the existence of a thin Cr_2O_3 layer beneath the Cr-rich spinel oxide layer due to a selective oxidation process, because Cr has a higher affinity to oxygen than other alloy constituents [49]. However, no Cr_2O_3 layer was observed at the oxide metal interface despite of extensive efforts [48]. In the current tests conducted at relatively low temperature (as compared to PWR conditions) the oxide film is very thin, typically below 30 nm in thickness, thus the elemental analysis on cross sections was very poor and could not provide evidence supporting the existence of the Cr_2O_3 layer. Most available information on the structure of the oxide film formed on Ni-based alloys is focused on PWR conditions. The oxide species formed under BWR conditions might deviate from those under PWR conditions.

Although the exact nature and structure of the oxide films could not be revealed by the current analysis of the coupon specimens, a clear difference of the surface oxides below and above the Ni/NiO transition line could be revealed that confirmed the location of the Ni/NiO phase transition line as proposed by Morton, et al. [13]. Therefore, this phase transition line was chosen for the current study.

3.2 SCC crack initiation and short crack growth experiments

In Figure 11, an example of the corrected mean mean crack advance from the notch root (derived by DCPD and post-test fractography) and the corresponding K_I value (for a sharp crack with a_0) during the slow rising load and constant load phase in a test with a DH of 50

ppb. SCC crack initiation occurred during the slow rising load phase at a notch strain of 2 % and K_I -value of $37 \text{ MPa}\cdot\text{m}^{1/2}$. After initiation the cracks were growing with a fast and constant mean crack growth rate of $1.1 \cdot 10^{-10} \text{ m/s}$ under slow rising load. After switching to constant load, the growth rate of the cracks was continuously decaying with time. A few hours to a few ten hours later, the SCC cracks were growing with a much slower and constant rate of $5 \cdot 10^{-12} \text{ m/s}$. This behaviour was observed in all tests.

IGSCC initiation occurred at several locations along the notch root. The subsequent short crack growth of these initiated micro-cracks had a finger-like interdendritic appearance (Figure 12 and Figure 13). Furthermore, crack coalescence was sometimes observed for neighbouring micro-cracks. The localized and very directed crack growth is quite different from IGSCC in austenitic wrought materials (Ni alloys and stainless steels), where crack growth often spreads out in a fan-shaped manner from the initiation sites and results in semi-elliptical surface micro-cracks. This localized crack growth is the result of the special weld microstructure with elongated grains as well as of the significantly different susceptibilities of different grain boundary types. Certain boundaries seem to represent a significant barrier for SCC crack growth. Depending on the degree of SCC crack engagement along the notch root, the maximum local SCC crack growth can be a factor of 3 to 10 higher than the average crack growth rate over the specimen thickness. Testing with pre-cracked specimens and service experience (field cracks) clearly reveal that SCC crack growth engagement is usually increasing with increasing testing period and crack advance due to crack coalescence and (retarded) failure of un-cracked ligaments. The local maximum SCC crack growth rates are then only slightly higher than the mean rates for relatively even cracks.

Figure 15 and Figure 15 summarize the effect of DH on SCC initiation during the slow rising load phase for Alloy 182 in simulated BWR water at 274 °C. The mean notch strain at

SCC initiation from several specimens is plotted versus the DH content in Figure 14. The corresponding equivalent mean stress intensity factor $K_{I,i}$ (for a sharp crack with the crack depth a_0) at SCC initiation is shown as a function of the potential difference between the corrosion potential ECP of the specimen and the potential $ECP_{Ni/NiO}$ at the Ni/NiO phase transition line for Alloy 182 in simulated BWR water at 274 °C. Additionally, the results of the individual tests are shown in this figure. The mean results show a clear maximum in SCC initiation susceptibility (minimum in initiation notch strain and stress intensity factor $K_{I,i}$) at the Ni/NiO transition line for BWR conditions also. There is significant specimen to specimen scatter that is similar for all DH contents. This is not unusual for SCC initiation tests and further confirms the need of multiple specimen experiments.

Figure 16 and Figure 17 summarize the effect of DH on the local maximum and mean short SCC crack growth rates of Alloy 182 in BWR environments at 274 °C, respectively. Furthermore, the mean values of several specimens for the maximum and mean crack growth rates for given DH conditions are shown. Additionally, the resulting SCC crack growth rates are compared with the EPRI BWRVIP-59-A [50] SCC growth rates for Alloy 182 in BWR/HWC environment for the same loading conditions. Both local maximum and mean short SCC crack growth rates are higher than the disposition line, which indicates a high SCC susceptibility for Alloy 182 under HWC conditions. Nevertheless, the SCC susceptibility under HWC conditions is much lower than under NWC conditions. After some crack advance from the notch root ($\Delta a > 0.1$ mm), the resulting stress intensity factor K_I for the SCC cracks in all specimens is in the range of $\sim 45 \text{ MPa}\cdot\text{m}^{1/2}$. It is stressed that above $30 \text{ MPa}\cdot\text{m}^{1/2}$ the SCC growth rates are almost independent on the applied K_I . As for initiation, a clear maximum in the SCC crack growth rates is observed for the mean values at the transition line of Ni/NiO for Alloy 182 in BWR environments at 274 °C, respectively. The average maximum SCC crack

growth rate at the Ni/NiO phase transition line were a factor of 2.1 higher than at a ΔECP of +39 mV in the NiO region. This difference is expected to further increase for a higher ΔECP . Furthermore, the BWRVIP SCC curves were exceeded in this region by the local maximum SCC rates and are thus not conservative at the Ni/NiO transition line and for moderate HWC. The large specimen to specimen scatter for the mean SCC crack growth rates for a given DH may be due to selected combined initiation-crack growth test type, the localized crack growth and different SCC engagement along the notch root as well as to the low SCC crack growth rates at 274 °C. The scatter for the local maximum growth rates is significantly smaller and in the usual range for a weld metal and moderate SCC growth rates.

In some selected tests, on-the-fly changes in DH were applied after some stable short SCC crack growth under constant load. Figure 18 shows a few examples of the SCC crack growth behaviour in tests with changing DH contents. The observed behaviour was reproducible and reversible. These tests again confirmed the maximum in SCC growth rates at the Ni/NiO phase transition line (253 ppb DH). The crack growth rates usually changed just a few hours after changing the hydrogen level, which is in line with crevice chemistry models and the fast hydrogen diffusion from the bulk water to the crack-tip and vice versa. In few isolated cases, the fast SCC growth rates could not be fully re-established after returning to the Ni/NiO line, eventually due to crack pinning in the previous phase.

The observed maximum in SCC initiation and crack growth susceptibility in BWR/HWC environment at 274 °C is thus in good qualitative agreement with similar investigations under PWR conditions at higher temperatures of 320 to 360 °C [12, 51] using pre-cracked specimens in BWR environment at 300 °C [15] as described in the Introduction Section 1. It is stressed that the type of loading (slow rising vs. constant load, load level) and specimens (sharply notched vs. smooth specimens, U-bends or pre-cracked) was quite different

and a direct quantitative comparison of initiation results is thus challenging. Based on the Arrhenius activation energy for SCC crack growth in Ni alloys of ~ 130 kJ/mol, the SCC crack growth rates at 274 °C should be a factor of ~ 11 lower than at 325 °C, if tested under the same ΔECP conditions [15]. In this light, the SCC growth rates in this study are thus in fairly good agreement with typical crack growth rates measured in simulated PWR water environments.

3.3 EBSD analysis of the SCC crack initiation sites and along the SCC propagation path

3.3.1 Grain structure of the weld material

The weld microstructure with grain orientation distributions (colour coded pole figures) on the T-S plane normal to the welding direction is shown in Figure 2 and Figure 19. Although the weld metal as a whole does not appear to be textured (see pole figure in Figure 19a), the presence of clusters of grains that have very similar orientations (pole figures in Figure 19 b-d) can be observed. In Figure 19 b-d, only the highlighted grains with certain orientations are shown in the corresponding pole figures. One can observe three clusters of neighbouring grains that share very similar orientations and have a fibre-like texture. This suggests that the grains are aligned through rotation around a specific $\langle 100 \rangle$ axis, and the deviation perpendicular to the axis is relatively small. The observed structure can be explained by the solidification process in this multi-pass weld and heat-flux direction in the weld configuration during welding.

The partially re-melted underlying weld layers act as heterogeneous nucleation structure for the solidification process. After nucleation the growth is epitaxial (same crystallographic orientation as the solid phase at the fusion boundary), which explains the continuity of grain boundaries in the weld metal. The grains that have a preferred growth direction ($\langle 100 \rangle$) parallel

to the temperature gradient and heat flux direction grow faster than the others, which finally leads to a weak $\langle 100 \rangle$ fibre texture. The general structure of an individual weld pass consists of elongated columnar dendrites at the edge of the melt pool, where heat transfer is highly directional, and more equiaxed cellular dendrites in the middle with slower cooling rates. The columnar grains are oriented parallel to the macroscopic heat flux direction, thus in thickness direction in the center of the weld and perpendicular to the fusion boundary and low-alloy steel base metal at the border of the weld. Furthermore, in multi-pass welds, each weld pass heats up the layers below and can cause recrystallization. Thus, the transition zone between two passes is tempered and recrystallized. This may lead to a different structure in this region with much smaller grains with random distributed orientations (indicated with circles in Figure 20).

During solidification, parallel bundles of columnar dendrites with nearly identical crystallographic orientation form and grow into the melt along the heat flux direction (e.g. towards the RPV steel at the border of the weld). The boundaries between these similarly oriented dendrites tend to have low angular mismatches, as well as low energy. Where different bundles of dendrites intersect or overlap, larger angular mismatches often occur between the columnar grains of the bundles. In this case, the resulting high-angle grain boundaries can be high energy random grain boundaries or coincident site lattice boundaries.

Figure 20 shows the grain boundary misorientation mapping of a large area of the weld metal including the transition region with the low-alloy steel, which is the black boundary on the left side and not visualized in the EBSD measurement. The grain boundary type distribution is summarized in Table 6 and Figure 21 a. The total CSL boundaries ($\Sigma 1$ -29) fraction in the bulk weld metal is 30% with a broad structure distribution. Within these CSL boundaries, the LABs ($\Sigma 1$, 20% of all GBs) are dominant. This is a significant difference to the corresponding Alloy 600 wrought metal, where the CSL boundaries are dominated by $\Sigma 3$ twin boundaries [25]. The

remaining 70 % of the boundaries are random, high-energy HABs without preferred misorientation.

3.3.2 Effect of grain boundary type on SCC initiation and propagation

To investigate the role of grain boundary type and misorientation on the SCC crack initiation and propagation behaviour, OIM scans were conducted on 25 cross sections (T-S plane) from different cracked positions along the notch root cut from a C(T) specimen (LS11 in Figure 18) tested in environment with on-the-fly changes of DH contents (600 ppb → 253 → 600 ppb). Figure 22 exemplarily shows such an OIM image example with the notch root. In this specific case, the SCC crack was initiating from a high angle grain boundary, but not from the LABs that were intersected by the notch root also.

The type and misorientation of all cracked boundaries both at crack initiation sites and along the propagation path are analyzed and summary statistics of grain boundary crystallographic parameters are presented in Table 6 and Figure 21 b and c. The frequency of different misorientation angles in the weld metal of all grain boundaries is very similar up to a high angle of 50° (Figure 21 a). The statistical distributions of all cracked grain boundaries along the crack path (Figure 21 b) and at crack initiation sites (Figure 21 c) are very different from the total grain boundary distribution in the weld metal. The distribution of misorientation angles of all cracked boundaries gets closer to a Gaussian normal distribution with a maximum at ~ 40 ° (along the crack path) and ~ 45 ° (at crack initiation sites). None of the LABs that roughly cover 20 % of the grain boundaries showed cracking, which confirms their exceptionally high SCC resistance. If LABs ($\Sigma 1$ boundaries) are excluded from the CSL boundaries population, the frequencies of cracked CSL boundaries are not significantly different from their occurrence

frequency in the original weld alloy (see Table 6). The non- $\Sigma 1$ CSL were thus susceptible to SCC. This is different from reference [52], where other CSL boundaries were also found to be resistant to SCC. The random high-energy high-angle boundaries showed a higher cracking frequency than their occurrence frequency in the weld metal, which thus suggests that these boundaries are particularly prone to SCC.

It is important to note that the CSL boundaries examined here have relative large deviations from ideal ones, although they are still within the Brandon's criterion. It is thus likely that these CSL boundaries are not low-energy boundaries even though they are close to a low Σ orientation. This is in very good agreement with [25], where other CSL boundaries also showed large angular deviations from real CSL boundaries and susceptibility to SCC cracking and only the twin ($\Sigma 3$) boundaries were found to be crack-resistant. However, the frequency of $\Sigma 3$ boundaries in the examined weld metal sample in this work was too low for a definite conclusion.

3.3.3 Local strain variations along crack propagation paths and at crack tips

The high level of residual plastic strain at crack initiation sites and around crack flanks and tips suggests that grain boundary deformation and grain boundary strain incompatibility are crucial factors for IGSCC. The grain boundary deformation (dislocation pile-ups, slip transfer to neighbouring grains, dislocation annihilation, grain boundary sliding, ...) depends on the grain boundary type/structure, misorientation, strength and precipitates as well as on the orientation of grains with respect to stress (Schmid factor), grain size and the intra-grain plastic deformation behaviour. Plastic deformation processes in the grain that lead to coarse planar slip particularly favour intergranular cracking.

The Kernel average misorientation map in Figure 23a clearly shows that the residual plastic strain/deformation is confined around the crack initiation site and along the main crack's propagation path. The magnified picture of the marked area shows localized strain around crack micro-branches also. A high level of plastic strain was observed along both HABs and CSL boundaries and they showed no fundamental difference in plastic deformation behavior and SCC cracking behaviour. Alexandreanu and Was [53], on the other hand, observed dislocation annihilation at grain boundaries (as dominant process) is three times faster in HABs than in CSLs that were less prone to SCC cracking.

Figure 24 shows the distribution of mismatch in Schmid factor of adjacent grains in the original weldment material (a) and of every cracked grain boundary of 25 analyzed cross sections along the crack path (b) and at crack initiation sites (c). It is clearly shown that adjacent grain boundaries with a higher Schmid factor mismatch show a higher SCC cracking frequency. Thus, it is evident that a higher incompatibility in grain boundary strain promotes a higher susceptibility to SCC. Besides grain boundary misorientation, the strain incompatibility thus also plays a key role in crack initiation and propagation. However, in some cases, cracks did not initiate at susceptible HABs that appear to be favorably oriented for cracking, which indicates that other factors like grain boundary segregation (during solidification or heat treatment) and micro-chemistry or precipitates also play an important role in SCC crack initiation and propagation. These factors also depend on the grain boundary type/structure and may affect the electrochemical activity of the grain boundaries (e.g., Cr depletion and S enrichment) or the grain boundary deformation behavior (intra- & intergranular precipitates) [54, 55]. Thus, assessment of grain boundary susceptibility to SCC should not include only crystallography, but also microchemistry.

4. Summary and conclusions

The effect of dissolved hydrogen on the SCC initiation and subsequent short crack growth behaviour of Alloy 182 weld metal was evaluated in 274 °C hydrogenated high-purity water using accelerated crack initiation and growth tests with sharply notched fracture mechanics specimens and in-situ crack initiation and growth monitoring. These tests revealed the following important results:

1. Coupon exposure tests confirmed the position of the Ni/NiO phase transition line at 253 ppb DH in 274°C water as proposed in the literature [13].
2. Maxima in SCC initiation and crack growth susceptibility were observed in the proximity to the Ni/NiO phase transition line in BWR environment at a temperature of 274 °C. The observed effects of DH were very similar as those in PWR environment at higher temperatures. Conditions in moderate HWC are very close to this peak and SCC crack growth disposition lines might not be conservative here. Conditions in OLNC, on the other hand, are further away from this peak in the NiO stability region.
3. Only low angle boundaries ($\Sigma 1$) are highly resistant to IGSCC. The fraction of twin boundaries in the Alloy 182 weld metal is too low for solid conclusions. Crack initiation and propagation are much more likely to occur at HABs with the random high-energy HABs being most susceptible. The fraction of other cracked CSL boundaries and their frequency of occurrence in the original material are approximately the same, so the non- $\Sigma 1$ CSL boundaries cannot be considered to be resistant to SCC.
4. Higher level of residual strain/deformation has been found to be confined around the crack initiation site, along the main crack's propagation path and at the crack tip.
5. Higher number of Schmid factor mismatch between the adjacent grain at crack initiation

sites and along the SCC propagation path have been observed, indicating that strain/deformation incompatibility also plays a key role in crack initiation and propagation.

6. Besides crystallographic properties, other factors, e.g. grain boundary segregation and precipitation, could also have an impact on the resistance to SCC and should thus also be considered.

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6. References

- [1] O. Runevall, J. Lejon, M. Olsson, K. Tompuri, M. Bjurman, Water Chemistry Options for Internal Pump BWRs - the Nordic Operational Experience, in: 20th NPC International Conference, Brighton, UK, 2016.
- [2] H.P. Seifert, S. Ritter, H.J. Leber, S. Roychowdhury, Stress corrosion cracking behavior in the transition region of alloy 182/low-alloy reactor pressure vessel steel dissimilar metal weld joints in light water reactor environments, *Corrosion*, 71 (2015) 433-454.
- [3] H.P. Seifert, S. Ritter, T. Shoji, Q.J. Peng, Y. Takeda, Z.P. Lu, Environmentally-Assisted Cracking Behaviour in the Transition Region of an Alloy182/SA 508 Cl.2 Dissimilar Metal Weld Joint in Simulated Boiling Water Reactor Normal Water Chemistry Environment, *Journal of Nuclear Materials*, 378 (2008) 197 - 210.
- [4] R.M. Horn, P.L. Andresen, J. Hickling, BWR Alloy 182 stress corrosion cracking experience, in: 5th Int. Symposium on Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors (Fontevraud 5), Fontevraud, France, 2002, pp. 55-67.
- [5] H. Hänninen, P. Aaltonen, A. Brederholm, U. Ehrnstén, H. Gripenberg, A. Toivonen, I. Virkkunen, Dissimilar metal weld joints and their performance in nuclear power plant and oil

refinery conditions, in: VTT Research Notes, VTT, Technical Research Centre of Finland, Espoo, Finland, 2006.

[6] R. Pathania, A.R. McIlree, J. Hickling, Overview of primary water cracking of Alloys 182/82 in PWRs, in: 5th Int. Symposium on Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors (Fontevraud 5), Fontevraud, France, 2002, pp. 13-27.

[7] R. Gutti, G. Moffatt, A. McIlree, Metallurgical investigation of cracking in the reactor vessel alpha loop hot leg nozzle to pipe weld at the V.C. summer station, in: Fontevraud 5 International symposium, SFEN, Fontevraud, France, 2002, pp. 29-38.

[8] T. Matsunaga, K. Matsunaga, Stress corrosion cracking of CRD stub tube joint and repair at Hamaoka Unit 1, in: 11th Int. Conference on Nuclear Engineering, Shinjuku, Tokyo, Japan, 2003.

[9] A. Yamashita, K. Takeuchi, W. Sagawa, F. Manabe, The stress corrosion cracking at shroud support Tsuruga Unit 1 of CRD stub tube joint and repair at Hamaoka Unit 1, in: 9th Int. Conference on Nuclear Engineering, Nice, France, 2001.

[10] H.P. Seifert, S. Ritter, Stress Corrosion Cracking of Low-Alloy Reactor Pressure Vessel Steels under Boiling Water Reactor Conditions, J. Nucl. Mater., 372 (2008) 114-131.

[11] P.L. Andresen, J. Hickling, A. Ahluwalia, J. Wilson, Effects of Hydrogen on Stress Corrosion Crack Growth Rate of Nickel Alloys in High-Temperature Water, Corrosion, 64 (2008) 707-720.

[12] D.S. Morton, S.A. Attanasio, G.A. Young, P.L. Andresen, T.M. Angeliiu, The Influence of Dissolved hydrogen on Nickel Alloy SCC: A Window to Fundamental Insight, in: CORROSION 2001, Lockheed Martin Corporation, Schenectady, NY 12301 (US), Houston, TX, USA, 2001.

[13] S.A. Attanasio, D.S. Morton, Measurement of the Nickel/Nickel Oxide Transition in Ni-Cr-Fe Alloys and Updated Data and Correlations to Quantify the Effect of Aqueous Hydrogen on Primary Water SCC, in: 11th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Stevenson, WA, USA, 2003, pp. 143-155.

[14] S.A. Attanasio, D.A. Morton, M.A. Ando, Measurement and Calculation of Electrochemical Potentials in Hydrogenated High Temperature Water, including an Evaluation of the Yttria-Stabilized Zirconia/Iron-Iron Oxide (Fe/Fe₃O₄) Probe as a Reference Electrode, in: CORROSION 2002, Denver, CO, USA, 2002.

[15] P.L. Andresen, P. Chou, Effects of Hydrogen on SCC Growth Rate of NI Alloys in BWR Water, in: 15th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, John Wiley & Sons, Inc., Colorado Springs, CO, USA, 2011, pp. 2039-2059.

[16] E. Richey, D.S. Morton, R.A. Etien, SCC initiation testing of Nickel-based alloys in high temperature water, in: 13th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Whistler, B.C., Canada, 2007.

[17] E. Richey, D.S. Morton, M.K. Schurman, SCC Initiation Testing of Nickel-Based Alloys Using In-Situ Monitored Uniaxial Tensile Specimens, in: T.R. Allen, P.J. King, L. Nelson (Eds.) 12th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Snowbird, UT, USA, 2005, pp. 947-958.

- [18] R.A. Etien, E. Richey, D.S. Morton, J. Eager, SCC Initiation Testing of Alloy 600 in High Temperature Water, in: 15th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, John Wiley & Sons, Inc., Colorado Springs, CO, USA, 2011, pp. 2407-2417.
- [19] K. Dozaki, D. Akutagawa, N. Nagata, H. Takiguchi, K. Norring, Effects of Dissolved Hydrogen Content in PWR Primary Water on PWSCC Initiation Property, E-Journal of Advanced Maintenance, 12 (2010) 65-76.
- [20] D. Akutagawa, N. Nagata, K. Dozaki, H. Takiguchi, K. Norring, A. Jenssen, A. Molander, Environmental mitigation of PWSCC initiation-low DH chemistry for PWR primary system, in: 14th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Virginia Beach, USA, 2009, pp. 306-315.
- [21] A. Molander, K. Norring, Effects of water chemistry on PWSCC initiation and propagation in Alloy 600, in: EUROCORR 2011, EFC, Stockholm, Sweden, 2011.
- [22] F.P. Ford, Quantitative Prediction of Environmentally Assisted Cracking, Corrosion, 52 (1996) 375-395.
- [23] P. Scott, M. Le Calvar, Some possible mechanisms of intergranular stress corrosion cracking of alloy 600 in PWR primary water, in: 6th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, 1993, pp. 657-667.
- [24] K. Arioka, T. Miyamoto, T. Yamada, T. Terachi, Role of Cavity Formation on Crack Growth of Cold-Worked Carbon Steel, TT 690 and MA 600 in High Temperature Water, in: 15th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, John Wiley & Sons, Inc., Colorado Springs, CO, USA, 2011, pp. 55-69.
- [25] V.Y. Gertsman, S.M. Bruemmer, Study of grain boundary character along intergranular stress corrosion crack paths in austenitic alloys, Acta Mater., 49 (2001) 1589-1598.
- [26] E.M. Lehigh, A.M. Brennenstuhl, I. Thompson, On the relationship between grain boundary connectivity, coincident site lattice boundaries, and intergranular stress corrosion cracking, Corros. Sci., 46 (2004) 2383-2404.
- [27] Y. Pan, B.L. Adams, T. Olson, N. Panayotou, Grain-boundary structure effects on intergranular stress corrosion cracking of alloy X-750, Acta Mater., 44 (1996) 4685-4695.
- [28] A. Stratulat, J.A. Duff, T.J. Marrow, Grain boundary structure and intergranular stress corrosion crack initiation in high temperature water of a thermally sensitised austenitic stainless steel, observed in situ, Corrosion Science, 85 (2014) 428-435.
- [29] T. Watanabe, Grain boundary engineering: historical perspective and future prospects, Journal of Materials Science, 46 (2011) 4095-4115.
- [30] J. Hou, Q.J. Peng, Z.P. Lu, T. Shoji, J.Q. Wang, E.H. Han, W. Ke, Effects of cold working degrees on grain boundary characters and strain concentration at grain boundaries in Alloy 600, Corrosion Science, 53 (2011) 1137-1142.
- [31] J. Hou, T. Shoji, Z.P. Lu, Q.J. Peng, J.Q. Wang, E.H. Han, W. Ke, Residual strain measurement and grain boundary characterization in the heat-affected zone of a weld joint between Alloy 690TT and Alloy 52, Journal of Nuclear Materials, 397 (2010) 109-115.

- [32] S. Yamazaki, Z. Lu, Y. Ito, Y. Takeda, T. Shoji, The effect of prior deformation on stress corrosion cracking growth rates of Alloy 600 materials in a simulated pressurized water reactor primary water, *Corrosion Science*, 50 (2008) 835-846.
- [33] A. Standard, E399, Standard Method of Test for Plane Strain Fracture Toughness of Metallic Materials, (1971).
- [34] E. ASTM, 1681-95, Standard test method for determining a threshold stress intensity factor for environment-assisted cracking of metallic materials under constant load.
- [35] N.E. Dowling, W.K. Wilson, Results of elastic analysis of bluntly notched compact specimens, *Engineering Fracture Mechanics*, 20 (1984) 569-572.
- [36] W.K. Wilson, Elastic-Plastic Analysis of Blunt Notched CT Specimens and Applications, *Journal of Pressure Vessel Technology*, 96 (1974) 293-298.
- [37] H. Neuber, Theory of Stress Concentration for Shear-Strained Prismatical Bodies With Arbitrary Nonlinear Stress-Strain Law, *Journal of Applied Mechanics*, 28 (1961) 544-550.
- [38] G. Glinka, Calculation of inelastic notch-tip strain-stress histories under cyclic loading, *Engineering Fracture Mechanics*, 22 (1985) 839-854.
- [39] G. Glinka, Energy density approach to calculation of inelastic strain-stress near notches and cracks, *Engineering Fracture Mechanics*, 22 (1985) 485-508.
- [40] G.C. Sih, Handbook of stress-intensity factors, Lehigh University, Institute of Fracture and Solid Mechanics, 1973.
- [41] H. Johnson, Calibrating the electric potential method for studying slow crack growth(Calibration of electric potential technique to study slow or steady crack growth in high strength materials), *Materials Research and Standards*, 5 (1965) 442-445.
- [42] S. Ritter, H.P. Seifert, Detection of Stress Corrosion Cracking in a Simulated BWR Environment by Combined Electrochemical Noise and Direct Current Potential Drop Measurements, *Energy Materials*, 3 (2009) 72-80.
- [43] S. Roychowdhury, H.P. Seifert, P. Spätig, Z. Que, Effect of high-temperature water and hydrogen on the fracture behavior of a low-alloy reactor pressure vessel steel, *J. Nucl. Mater.*, 478 (2016) 343-364.
- [44] H.P. Seifert, S. Ritter, Strain-Induced Corrosion Cracking Behaviour of Low-Alloy Steels under Boiling Water Reactor Conditions, *J. Nucl. Mater.*, 378 (2008) 312-326.
- [45] H.P. Seifert, S. Ritter, H.J. Leber, Corrosion fatigue initiation and short crack growth behaviour of austenitic stainless steels under light water reactor conditions, *Corros. Sci.*, 59 (2012) 20-34.
- [46] D.G. Brandon, The structure of high-angle grain boundaries, *Acta Metallurgica*, 14 (1966) 1479-1484.
- [47] S.I. Wright, M.M. Nowell, D.P. Field, A review of strain analysis using electron backscatter diffraction, *Microscopy and microanalysis*, 17 (2011) 316-329.
- [48] D. Morton, N. Lewis, M. Hanson, S. Rice, P. Sander, Nickel Alloy primary water bulk surface and SCC corrosion film analytical characterization and SCC mechanistic implications, in: 13th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Whistler, B.C., Canada, 2007.

- [49] P. Combrade, P. Scott, M. Foucault, E. Andrieu, P. Marcus, Oxidation of Ni base alloys in PWR water: oxide layers and associated damage to the base metal, in: T.R. Allen, P.J. King, L. Nelson (Eds.) 12th Int. Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Snowbird, UT, USA, 2005, pp. 883-890.
- [50] BWRVIP-59-A: BWR Vessel and Internals Project, Evaluation of Crack Growth in BWR Nickel Base Austenitic Alloys in RPV Internals, in, Electric Power Research Institute, 2007.
- [51] D.S. Morton, S.A. Attanasio, J.S. Fish, M.K. Schurman, Influence of dissolved hydrogen on nickel alloy SCC in high temperature water, in: CORROSION 1999, NACE, San Antonio, TX, USA, 1999.
- [52] B. Alexandreanu, O.K. Chopra, W.J. Shack, The effect of grain orientation on the cracking behavior of Alloy 182 in PWR environment, in: T.R. Allen, P.J. King, L. Nelson (Eds.) The 12th International Conference on Environmental Degradation of Materials in Nuclear Power System, 2005.
- [53] B. Alexandreanu, G.S. Was, Grain Boundary Deformation-Induced Intergranular Stress Corrosion Cracking of Ni-16Cr-9Fe in 360°C Water, Corrosion, 59 (2003) 705-720.
- [54] W. Kuang, G.S. Was, The effects of grain boundary carbide density and strain rate on the stress corrosion cracking behavior of cold rolled Alloy 690, Corrosion Science, 97 (2015) 107-114.
- [55] Y.S. Lim, J.S. Kim, H.P. Kim, H.D. Cho, The effect of grain boundary misorientation on the intergranular M₂₃C₆ carbide precipitation in thermally treated Alloy 690, Journal of Nuclear Materials, 335 (2004) 108-114.

Figure 1: Orientation of the compact tension and tensile specimens fabricated from the Alloy 182 weld.

Figure 2: Crystallographic orientation image showing the weld microstructure, T-S plane (left) and L-S plane (right).

(a)

(b)

Figure 3: Geometry of 0.5 T C(T) specimen (a) and position of welded wires for DCPD measurement, all units in mm.

Figure 4: DH concentrations for coupon exposure tests and SCC initiation and growth tests compared to the Ni/NiO phase transition line proposed by [13].

Figure 5: Relation between the notch strain and related stress intensity factor K_I for a sharp crack a_0 .

Figure 6: Experimental setup for in-situ crack initiation and growth measurements by DCPD.

Figure 7: Example of the DCPD potential drops of the compact tension specimen and reference specimen during slow rising load/constant load tests.

Figure 8: Typical appearance of the surface oxide layer formed in environments with lower DH concentrations (50, 200 and 230 ppb) in the NiO stability region, .

Figure 9: High resolution SEM image of the needle-like crystallites taken from the whole area of specimens tested in environments with lower DH concentrations (50, 200 and 230 ppb) in the NiO stability region.

Figure 10: Typical appearances of the surface oxide formed in environments with higher DH concentrations (300, 600 ppb) in the Ni stability region under (a) 10 k and (b) 100 k times magnification. The position of the higher magnification area is marked in the lower magnification micrograph.

Figure 11: Typical crack advance curve obtained by DCPD technique from a test performed with 50 ppb DH; the K_I value during the test is also plotted.

Figure 12: Multiple IGSCC initiation sites along the notch root in the Alloy 182 weld metal tested in 274 °C high-temperature water with 253 ppb DH. (a) The local SCC crack growth along notch root fracture surface with (b) typical interdentritic morphology confirmed by SEM.

Figure 13: Multiple SCC initiation along the notch root (a), EBSD picture of cross section (dashed line in (a)) of a selected SCC indication site (b).

Figure 14: Notch strain (according to Glinka) at SCC initiation as a function of $ECP-ECP_{Ni/NiO}$ of Alloy 182 in simulated BWR water at 274 °C.

Figure 15: Maximum in SCC initiation susceptibility (SCC initiation stress intensity factor $K_{I,i}$) at the Ni/NiO transition line of Alloy 182 in simulated BWR water at 274 °C.

Figure 16: Maximum in local maximum SCC crack growth rate at the Ni/NiO phase transition line and comparison with EPRI SCC disposition line [50].

Figure 17: Maximum in mean SCC crack growth rate at the Ni/NiO phase transition line and comparison with EPRI SCC disposition line [50].

Figure 18: SCC growth rate of alloy 182 under constant loading conditions in 274 °C pure water with various on-the-fly changes of DH.

Figure 19: Crystallographic orientation images of the original weld on the T-S plane and the corresponding 001 and 111 pole figures. Picture a shows the crystallographic orientation image of a large area, the corresponding pole figures do not show clear texture in total; pictures b-d illustrate 3 clusters of neighboring grains that have a fibre-like texture.

Figure 20: Grain boundary mapping of the original weld on T-S plane (■ Misorientation $> 15^\circ$ - random boundary, ■ Misorientation $< 15^\circ$ - low angle grain boundary, ■ Misorientation $> 15^\circ$ - CSL boundary).

Figure 21: Grain boundary misorientation angle distributions of (a) all grain boundaries, (b) all cracked grain boundaries, (c) cracked grain boundaries at crack initiation sites.

Figure 22: Image quality map (insertion) and the corresponding inverse pole figure map showing the SCC region ahead of the notch, (■ Misorientation $>15^\circ$ - random boundary, ■ Misorientation $< 15^\circ$ - low angle grain boundary).

Figure 23: OIM maps of SCC region at the notch root. (a) Kernel average misorientation map; (b) colour code inverse pole figure map, cracked boundaries are indicated by arrows.

Figure 24: Schmid factor mismatch distribution of all grain boundaries in the original weld, cracked grain boundaries and at crack initiation sites.

Table 1: DH concentration and ECP (for high-purity water) at Ni/NiO transition line.

Parameter	220 °C	274 °C	288 °C	360 °C
H ₂ Ni/NiO [ppb]	~50	253	362	2300
ECP Ni/NiO [mV _{SHE}]	-456	-535	-556	-645

Table 2: Different BWR water chemistries with corresponding hydrogen levels and the corresponding ECP and Ni oxidation stability regions (NWC: normal water chemistry, M-HWC: moderate hydrogen water chemistry, OLNC: on-line noble chem).

Water chemistry	Feed water H ₂ 220 °C [ppb]	Reactor water H ₂ 274 °C [ppb]	ECP [mV _{SHE}]	ECP- ECP _{Ni/NiO} [mV _{SHE}]	Stability region
NWC	0	5 to 40	+200	+750	NiO
M-HWC	1000 to 2000	100 to 300	-525	-5 to +20	Ni/NiO
OLNC	150 to 400	20 to 40	-480	+40 to +60	NiO

Table 3: Chemical composition of the Alloy 182 weld metal in wt.%.

C	Si	Mn	Cr	Mo	Ni	Nb	Al	Co	Fe	N	Ti
0.02 7	0.58 0	6.1 9	15. 9	0.17 2	69. 1	2.3 6	0.030 2	0.017 2	5.4 6	0.02 4	0.092 4

Table 4: Mechanical properties obtained from SSRT at room temperature and 274 °C in air.

Test temperature	Yield stress [MPa]	Ultimate tensile Strength, UTS [MPa]	Uniform strain [%]	Strain to failure [%]
25 °C	433	657	27.7	30.8
274 °C	408	614	26.2	29.2

Table 5: Chemical compositions of different positions marked in Figure 8 obtained using SEM/EDX analysis.

Position	Element	Atomic %	Position	Element	Atomic %	Position	Element	Atomic %
A	O	39.4	B	O	41.4	C	O	33
	Cr	4.6		Cr	13.2		Cr	23.3
	Fe	2.5		Fe	14.3		Fe	2.6
	Ni	45.5		Ni	31.7		Ni	28.6

Table 6: Grain boundary type distribution in [%]. The numbers of totally examined grain boundaries are in brackets.

Grain boundary type	HAB	LAB ($\Sigma 1$)	Total ($\Sigma 3-29$)	$\Sigma 3$	$\Sigma 5$	$\Sigma 7$	$\Sigma 9$	$\Sigma 11$	$\Sigma 13a$	$\Sigma 13b$	$\Sigma 15$	$\Sigma 17a$
All GBs (1215)	70.5	20.0	9.5	0.8	2.7	0.3	0.3	0.2	1.2	0.5	0.5	0.6
All cracked GBs (218)	91.3	-	8.7	-	0.9	2.3	0.0	1.4	0.9	-	-	-
Crack initiation sites (28)	100.0	-	-	-	-	-	-	-	-	-	-	-
Grain boundary type	$\Sigma 17b$	$\Sigma 19a$	$\Sigma 19b$	$\Sigma 21a$	$\Sigma 21b$	$\Sigma 23$	$\Sigma 25a$	$\Sigma 25b$	$\Sigma 27a$	$\Sigma 27b$	$\Sigma 29a$	$\Sigma 29b$
All GBs (1215)	0.1	0.2	0.1	0.3	0.1	0.2	0.7	0.1	0.1	0.4	0.2	0.0
All cracked GBs (218)	-	-	0.5	-	-	0.9	0.5	0.5	-	-	0.5	0.5
Crack initiation sites (28)	-	-	-	-	-	-	-	-	-	-	-	-