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

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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.

Keywords: Ni-based alloy; stress corrosion cracking; hydrogen; electron microscopy; spectroscopy; electrochemical analysis.

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 to 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. 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 x 1 x 0.22 m³). 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 x 10 x 3 mm³ 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%) 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/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.

2.3 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

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 degrees 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).

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 background Raman spectrum of bare metal was subtracted from the spectra of the oxide films.

2.5 Photoelectrochemical characterization

Mott-Schottky analysis

The capacitance of Alloy 182 coupons was measured ex situ at room temperature. A buffered solution composed of 0.05M H_3BO_3 + 0.075M $\text{Na}_2\text{B}_4\text{O}_7$ (pH 9.4) was used as electrolyte for the room temperature measurements. It is assumed that a film formed in high-temperature water does not dissolve substantially in the low temperature mildly alkaline buffer solution and will not change during the measurement, as explained in [26]. A conventional 3-electrode glass cell was used. The reference electrode was Ag/AgCl (3 M KCl) and the counter electrode was a Pt wire. Before the measurements, the electrolyte was deaerated with nitrogen gas for 60 min. According to [26], the oxide film capacitance did not significantly change in the higher frequency range, $f > 500$ Hz. Hence, the capacitance at the conventional frequency value of 1 kHz in a potential range from -1 V to +1 V was used in the Mott-Schottky analysis. The polarization was applied in successive steps of +50 mV. The M-S measurements were performed using a Gamry[®] potentiostat system.

Photoelectrochemical analysis

The photoelectrochemical characterization was carried out with a setup consisting of a 150 W Xe arc lamp (LOT-Oriel Instruments) as the irradiation source and a Cornerstone motorized 1/8 m monochromator. Photocurrent spectra were acquired with the same solution as the Mott-Schottky analysis at a potential of 200 mV (vs. Ag/AgCl). Photocurrent spectra were

measured in a three-electrode configuration, consisting of $\sim 0.79 \text{ cm}^2$ oxidized Alloy 182 corrosion coupon specimen as photoanode area, platinum wire as a counter electrode and an Ag/AgCl (3 M KCl) electrode as a reference by a JAISSE IMP 83 PCT-BC Potentiostat-Galvanostat. The wavelength of the incident light was varied from 700 to 300 nm in step of 10 nm, with 10 s radiation and 20 s dark time for each measurement cycle.

3. Results and discussion

SEM and TEM results

Typical features of the surface oxides which formed on the Alloy 182 coupons at different DH levels (10, 253, 600 and 2200 ppb) are shown in Figure 1. Figure 1 (a) and (b) show the oxide films formed in the DH range of 10 and 253 ppb. The surface contains large discrete crystals in the μm -range, which homogeneously distributed over the surface, as well as needle-like oxides covering the whole surface. The oxide film morphology at 10 ppb DH does not exhibit significant difference to that formed at 253 ppb DH. The morphologies of the needle-like oxides are similar at 10 ppb DH, while the coverage density by needle-like oxides is higher. Typical SEM images of the surface oxides formed in higher DH level environments (600 and 2200 ppb) in the Ni stability region are shown in Figure 1 (c) and (d), where the large crystallites do not appear. At 600 ppb DH, the morphologies of the needle-like oxides are the same as in case of the low DH environments but with a much lower coverage density. At the highest DH level of 2200 ppb, the oxide film morphology changed significantly from the previous DH conditions. New type of small oxide crystallites appeared with a round and plate-shaped form, which indicates a transition boundary of a certain oxide between 600 and 2200 ppb DH. This feature will be discussed later.

A cross-sectional TEM picture of the oxide film formed in the environment with 253 ppb DH is shown in Figure 2. There is a Pt deposit layer on top of the picture to protect the oxide film from the contaminations during FIB milling. Two oxide crystallites (indicated as A and B) and a thin layer (indicated as C) of $\sim 20 \text{ nm}$ between the crystallites and the substrate can be identified. EDX analysis was conducted at these indicated positions as well as from the underlying substrate. The atomic percentage of the main alloying elements and O are summarized in Table 3. The higher Ni and O content suggest that the oxide crystallite A might be NiO. The crystallite B with relatively high Cr, Fe and O content may be 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. [27], who examined these oxides using EDX in a TEM and proposed a composition of $\text{Ni}(\text{Cr}_{0.5}\text{Fe}_{0.5})_2\text{O}_4$. The chemical composition of the thin layer indicates a highly Cr enriched oxide layer under the other oxide crystallites. Some authors reported the existence of a thin Cr_2O_3 layer beneath the spinel oxide layer due to a selective oxidation process, because Cr has a higher affinity to oxygen than other alloy constituents [19]. Most of the literature indicating the presence of Cr_2O_3 on Alloy 600 are based on XPS data, which do not give a reliable indication of the oxide structure. However, both X-ray and electron diffraction measurements do not show this Cr-rich inner oxide layer [20] and no Cr_2O_3 layer was observed at the oxide metal interface [27]. This suggests that the chromium rich oxide is amorphous or consists of too small crystals to obtain diffraction peaks. Due to the limited resolution of the TEM used in this study, it is not clear whether this high-Cr oxide layer has exactly the composition of Cr_2O_3 . 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. The composition of the bulk material obtained using TEM/EDX is in reasonable agreement with the results obtained using ICP-OES.

XPS results

For the corrosion coupons exposed to high-temperature water with different DH contents, all XPS peaks were found at the same positions, however, with different peak intensities. The XPS O1s, $\text{Fe}2p_{3/2}$, $\text{Cr}2p_{3/2}$ and $\text{Ni}2p_{3/2}$ and $\text{Ni}2p_{1/2}$ spectra measured for the oxide film formed in high-temperature water with 10 ppb DH are exemplary presented in Figure 3. The O1s spectrum shows that the oxide films formed on Alloy 182 consist of both hydroxide and oxide. The $\text{Cr}2p$ spectrum indicates that Cr appears in a completely oxidized state as Cr^{3+} , since no metallic Cr peak can be found. The identification of iron chemical states is more complicated, because iron may exist in different valences as well as in mixed valences, with binding energy peaks close to each other. Furthermore, Ni as the major alloy element has a strong Auger peak in the vicinity of the $\text{Fe}2p_{3/2}$ peak, which could also interfere with the iron peaks. Peaks at 710.9, 713.3 and 723.9 eV were evident, which could be attributed to the binding energy of $\text{Fe}^{3+}2p_{3/2}$ and $\text{Fe}^{2+}2p_{3/2}$ and indicate the existence of Fe_3O_4 or NiFe_2O_4 [28]. Typically, the satellite peak of $\text{Fe}^{3+}2p_{3/2}$ is located 8 eV higher than the main $\text{Fe}2p_{3/2}$ peak and the $\text{Fe}^{2+}2p_{3/2}$ satellite peak is 6 eV higher than the main $\text{Fe}2p_{3/2}$ peak. However, the satellite peak is measured about 10 eV higher than the main $\text{Fe}2p_{3/2}$ peak, at 723.9 eV. This could be correlated to the data in [29], with the main Fe_3O_4 peak located at 724.07 eV without satellite

peak. It is important to notice, that the binding energies show a small mismatch to the reference data obtained from single crystals in the literature. The reason might be that between magnetite (Fe_3O_4) and nickelferrite (NiFe_2O_4) spinel, there exists a gapless solid-solution of the general form $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$. For Ni2p, peaks at approximately 855.7 and 857.5 ($\text{Ni}2p_{3/2}$), 861.5 and 863.9 eV ($\text{Ni}2p_{3/2}$ satellite peak), 873.5 and 875.9 eV ($\text{Ni}2p_{1/2}$) could be identified after peak fitting, indicating the presence of both Ni^{2+} hydroxide and Ni^{2+} oxide. By comparing these data with published data in [30], the observed chemical state of Ni corresponds to $\text{Ni}(\text{OH})_2$ and $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ ($x=0, 0.5, 1$ and 1.5).

Analysis of pure crystalline phases of $\text{Ni}(\text{OH})_2$ has revealed the existence of different structures which include a more stable β - $\text{Ni}(\text{OH})_2$ and a more hydrated unstable α - $\text{Ni}(\text{OH})_2$ [31]. Moreover, it is evident that the stable β - $\text{Ni}(\text{OH})_2$ is by now well characterized, but α - $\text{Ni}(\text{OH})_2$ still requires more work. Such characterization work is particularly difficult because of the multitudinous forms of α - $\text{Ni}(\text{OH})_2$, the tendency to incorporate variable amounts of water and/or impurities and its poor long-term stability. Based on the XPS results, it cannot be determined unambiguously whether the nickel hydroxide is in the α or β form. More information can be drawn from the Raman spectra due to their different lattice modes. The Ni-Cr-Fe-O spinels show very similar binding energies and thus are difficult to be identified explicitly. Beside the information about binding energies obtained by XPS, the sub-peak areas could also indicate the relative ratio of existence of metal in different compounds. Figure 4 shows the changes of Ni 2p_{3/2} spectra of the oxide films formed on Alloy 182 in high-temperature water with 10 ppb and 2200 ppb DH. It is very clear that with increasing DH content the Ni^{2+} oxide peak became dominant. The areas of Ni^{2+} oxide and hydroxide peaks were integrated using OriginLab® and plotted as function of ECP difference to the Ni/NiO phase transition line in Figure 5. In the NiO stability region, oxidized Ni existed in both $\text{Ni}(\text{OH})_2$ (~35%) and Ni oxide (as spinel, ~65%) and remained constant until the Ni/NiO phase transition line. In the Ni stability region, the amount of $\text{Ni}(\text{OH})_2$ dropped dramatically with increasing DH content. At 2200 ppb DH content, over 95% of the Ni exists as spinel. These observations are in good agreement with the predicted Ni/NiO phase transition line.

Raman analysis

The Raman spectra of the oxide films formed under various DH conditions are illustrated in Figure 6. For the oxide films formed at lower DH conditions, i.e. from 10 to 253 ppb, the Raman spectra showed similar peaks located between wavenumbers of 300-500 cm^{-1} and

$\sim 700\text{ cm}^{-1}$ wavenumbers. The peaks at $300\text{--}500\text{ cm}^{-1}$ indicate the existence of Ni(OH)_2 and Fe_2O_3 [32]. According to Hall et al. [33, 34], there are Raman-active lattice modes of $\alpha\text{-Ni(OH)}_2$ at 460 and 495 cm^{-1} , thus the Ni hydroxide could be identified as $\alpha\text{-Ni(OH)}_2$. Increasing the DH reduces the intensity of this peak and eventually could disappear completely above the Ni/NiO phase transition line. On the other hand, the peak at approximately 565 cm^{-1} began to emerge. This peak can be identified as the Cr_2O_3 peak [35]. The decrease of Ni(OH)_2 and increase of Cr_2O_3 peaks are in good agreement with the XPS measurements. As the DH content increased in the Ni stability region, Ni(OH)_2 is not expected to form in the outer oxide layer and the signal from the high Cr inner oxide layer began to appear. Reference measurements with pure NiO powder showed that the most intense peaks of NiO are located at 536 and 723 cm^{-1} . The weak shoulder peak at the right hand side of the 700 cm^{-1} main peak of oxide film formed in 10 ppb DH could indicate the existence of NiO. This shoulder peak became very weak under 253 ppb DH condition and disappeared in the Ni stability region (600 and 2200 ppb DH), which is very consistent with the proposed Ni/NiO phase transition line at 274°C .

The peak at $\sim 700\text{ cm}^{-1}$ can be attributed to NiFe_2O_4 [36] and with higher DH content, NiFe_2O_4 will be reduced as follows

Terachi et al. [20] calculated the $\text{NiFe}_2\text{O}_4/\text{Ni} + \text{Fe}_3\text{O}_4$ phase boundary as a function of DH and temperature. By extrapolating the data to 274°C , this phase boundary is located at $\sim 2\text{ ppm}$ DH. Figure 7 shows the exact positions of the NiFe_2O_4 peak under different DH conditions as function of relative distance in ECP to the Ni/NiO phase transition line. A shift to lower wavenumbers of the main peak occurred at 2200 ppb DH. The main peak of Fe_3O_4 in the Raman spectra is located $\sim 680\text{ cm}^{-1}$ (A_{1g} mode) [37]. Their calculation results are consistent with the observed peak shift in the Raman spectra. The change in the oxide morphology shows in Figure 1 (d) may also related to the phase transition of NiFe_2O_4 and the oxide crystallites with round- and plate-shaped form might indicate the formation of Fe_3O_4 .

Mott-Schottky analysis

The electrochemical behaviour of many oxide films formed on a metallic surface in an aqueous solution can be considered as an extrinsic semiconductor due to the imperfect

crystallography and donor or acceptor defects, and thus described using the Mott-Schottky model for semiconductors [26]:

$$\frac{1}{C^2} = \frac{2}{e\epsilon\epsilon_0 N_D} \cdot \left(E - E_{FB} - \frac{k_B T}{e} \right) \quad (1)$$

where C = film capacitance; e = electron charge (1.6×10^{-19} C), ϵ = dielectric constant of oxide, ϵ_0 = vacuum permissivity (8.85×10^{-14} F/cm⁻¹), N_D = doping species density (donors and acceptors), E_{FB} = flat band potential, k_B = Boltzmann constant ($1.38066 \cdot 10^{-23}$ J/K) and T = absolute temperature. For a p -type semiconductor, $1/C^2$ versus E is linear with a negative slope, which is inversely proportional to the acceptor density, and an n -type semiconductor yields a positive slope that is inversely proportional to the donor density. The capacitance was calculated by $C = (-Z''2\pi f)^{-1}$, where Z'' is the imaginary part of the impedance and f is the frequency. Often, the term $\frac{k_B T}{e}$ can be neglected, and the flat-band potential is determined from the intercept with the potential axis. If the dielectric constant is known, the donor and acceptor density can be calculated from the slope. Figure 8 shows the results of the capacitance measurements on the oxide films formed under different DH conditions, plotted as C^{-2} vs. potential. The Mott-Schottky behaviour of oxide films formed under 10-600 ppb DH is similar and the two linear regions can be related to the development of depleted layers by band bending. The flat band potential of these oxide films is approximately -0.5 V. When films are polarized at more positive potentials they behave as an n -type semiconductor (positive slope), and increasing the potential to more than 0.3 V, their behaviour is p -type like (negative slope). The Mott-Schottky behaviour of the oxide film formed under 2200 ppb DH condition is very different to the other oxide films. The flat band potential is ~0.5 V, thus the oxide film is expected to behave as an n -type semiconductor when polarized above 0.5 V and as a p -type below 0.5 V.

The positive and negative slope in the Mott-Schottky analysis were reported for austenitic stainless steels and nickel-based alloys in simulated PWR environments [26, 36, 38-40]. One possible explanation is related to the spinel structure of the oxides formed on these materials. A spinel has the general form of AB_2O_4 . The elementary cell consists of 32 oxygen atoms with cubic closest packing with 64 tetrahedral and 32 octahedral gaps. For a normal spinel the 8 bivalent A cations occupy the tetrahedral gaps and the 16 trivalent B cations occupy the octahedral gaps; for an inverse structure, the 8 bivalent A cations occupy the octahedral gaps and the 16 trivalent B cations divide in two groups, 8 B cations occupy the octahedral and 8

B cations the tetrahedral gaps. No interstitial anion is expected and the anion disorder can be neglected due to the closest packing. The possible structural disorder could be interstitial atoms and vacancies of A or B cations and/or O vacancy. Thus, electron transport through the spinel structure could be affected by these valences and different defect types could yield a variety of specific electron paths and the defects in the spinel oxides could cause a distribution of localized states in the band gap.

Table 4 shows the slopes of the Mott-Schottky plots and the donor and acceptor densities calculated with dielectric oxide constant assumed to be 15.6 from [41]. The donor and acceptor densities are plotted vs. ΔE_{CP} against the corrosion potential of the Ni/NiO transition in Figure 9. The donor densities in the oxide films show a maximum in the vicinity of the Ni/NiO transition line, while the acceptor densities do not show a clear trend.

Photoelectrochemical analysis

The photoelectrochemical behaviour of the oxide films was investigated by determining the photocurrent, generated under illumination as a function of the incident light energy. Figure 10 exemplarily shows the typical photocurrent transient of the oxide film formed under different DH conditions. The oxide films formed under 10-600 ppb DH condition showed a positive photocurrent response while the oxide film formed under 2200 ppb DH condition showed a negative response, indicating that the first kind of oxide films are *n*-type and the later *p*-type semiconductors. The photocurrent responses are consistent with the Mott-Schottky analysis. It can also be noted, that the photocurrent density was very small, typically lower than 0.5 nA/cm^2 . The photocurrent should rise continuously with increasing potential above the flatband potential until the band bending is so large that all holes generated by the incident light can reach the electrode surface. Efforts were done to measure the photocurrent-wavelength curve at different polarization potentials. However, no photocurrent could be detected until the potential was increased to 0.2 V. The transient photocurrent was not constant during the illumination phase, which indicates that the generation of charge carriers was the rate determining step. Figure 11 presents the photocurrent spectra of oxide films formed under different DH conditions. It can be seen that the photocurrents were very low for 10 and 600 ppb DH conditions and that the onset of the photocurrent occurs at shorter wavelength.

In order to obtain the optical bandgap energy values, E_g , of the oxide films, the data were plotted according to Equation 2

$$\eta = \frac{I_{ph}}{\Phi_0} = eAw \frac{(h\nu - E_g)^m}{h\nu} \quad (2),$$

where η is the quantum efficiency, defined as the ratio between the photocurrent I_{ph} and the incident photon flux Φ_0 of energy $h\nu$. A is a constant, w the space charge layer thickness and m depends on the type of the transition between the valence band and the conduction band. According to Johnson [42] the value of $m=0.5$ is expected for a direct transition and $m=2$ for an indirect transition. Throughout the experiments a value of $m=2$ is the most appropriate value to represent the photoelectrochemical behaviour observed. Figure 12 shows the determination of the optical band gap for oxide films formed under different DH conditions. For the oxide films formed under 10-600 ppb DH the band gap energy is 2.2 eV (*n*-type), whereas for 2200 ppb DH the band gap is 2.7 eV (*p*-type).

The band gap energies of Ni, Cr and Fe oxides have been searched and collected from the literature. Within the possible oxides in the oxide films, α -Ni(OH)₂, Fe₂O₃ and NiFe₂O₄ are *n*-type semiconductors; NiO, β -Ni(OH)₂, FeCr₂O₄, NiCr₂O₄, Cr₂O₃ and Cr₂(OH)₃ are *p*-type semiconductors. It can be noted that all Cr-compounds show *p*-type semiconductive behaviour. Fe₂O₃ has a band gap energy of about 1.95 eV [43] and NiFe₂O₄ of ~2.2 eV [44]. The band gap energy of β -Ni(OH)₂ appears to lie in the range 3–3.5 eV [31]. α -Ni(OH)₂ was determined to be an *n*-type semiconductor [45], but the exact band gap energy could not be determined. Di Quarto et al. [46, 47] developed a semi-empirical correlation between the optical band gap of oxides and hydroxides and the electronegativity of their constituents and calculated the band gap energy of nickel hydroxide as 2.25 eV, which could be attributed to α -Ni(OH)₂. The nickel oxide NiO has a band gap of 3.8 eV assuming an indirect transition [48]. The band gap of Cr₂(OH)₃ has been measured at 2.4 and 2.75 eV by different authors [47, 49]. For bulk Cr₂O₃, the value of ~3.5 eV is generally reported [50]. Henry et al. reported a second contribution at 2.9 eV of Cr₂O₃ located in the inner part of the oxide scale. No band gap energy values were found for NiCr₂O₄ and FeCr₂O₄.

The band gap energy of 2.2 eV (*n*-type) could be attributed to the presence of nickel hydroxide. Nevertheless, this band gap energy could also be attributed to NiFe₂O₄. The presence of Ni(OH)₂ and NiFe₂O₄ are both consistent with XPS and Raman spectroscopy results. The band gap energy of 2.6 eV (*p*-type) can be attributed to Cr₂O₃/Cr₂(OH)₃. Belo et al. [36, 51] reported that the passive films on both Alloy 600 and stainless steel formed in alkaline solution at room temperature have the same band gap energy of 2.3 eV. This result

seems to emphasize the role of iron-related oxides on the semi-conductive behaviour of these oxide films.

The slopes in Figure 12 were calculated and are presented in Figure 13, which indicates the trend of the photocurrent response of the oxide films formed under different DH conditions. The maximum of the photocurrent response is located in the vicinity of Ni/NiO phase transition line.

Summary of the oxide film characteristics in correlation with the DH content

According to the results obtained in the present investigation, the photoelectrochemical behaviour and capacitance for Alloy 182 in simulated BWR environments could be discussed using a hetero-junction model. The oxide film formed at lower DH consists of an *n*-type outer oxide layer with E_g of 2.2 eV and a *p*-type inner oxide layer with E_g of 2.6 eV. An electronic energy band model of a *p-n*-heterojunction can be proposed as roughly illustrated in Figure 14. The band model consists of 3 interfaces: metal/inner oxide layer, *p-n*-conjunction interface and the outer oxide layer/solution. At the outer oxide layer solution interface, a depletion layer would form because of the *n*-type semiconductive behaviour. At the interface between the two semiconductor layers, the space charge region inside the inner oxide film should bend downwards as the depleted state of a *p*-type semiconductor, because negative photocurrents were generated. The space charge region on the hydroxide/spinel side would also be in the depleted state, according to the classical *p-n*-conjunction theory [52]. The band structure at the interface of the metal/inner oxide layer is unknown. Under higher DH conditions (> 2 ppm DH), the band of the outer oxide layer of spinel and hydroxide does not exist and the band structure of the oxide film is the same as a *p*-type semiconductor in contact with solution.

The influence of DH on the oxide film morphology and electrochemical behaviour is summarized in Figure 15. Below the Ni/NiO phase transition line, large NiO crystallites, Ni hydroxide and spinels were found in the outer oxide film. Under medium DH conditions (<2 ppm), the oxide species in the outer layer were similar as formed under low DH condition, yet the large NiO crystallites disappeared. Under high DH condition (>2 ppm), no Ni (hydr)oxide and only small amount of spinel can be found, and Fe₃O₄ appeared in the outer oxide layer. Under all DH conditions, there exists a Cr-rich inner oxide layer beneath the outer oxide layer. The highest defect (doping) density and photocurrent were found at the Ni/NiO phase transition line, which correlates with the highest SCC susceptibility. According

to [53], the thickness of the oxide film formed on Alloy 600 strongly depends on the DH concentration and exhibits a maximum at a corrosion potential close to the Ni/NiO phase transition line. This behaviour is also expected for the weld metal Alloy 182 used in the current study.

Mechanistic considerations in the context of SCC

In the following, the observed phenomenology and possible correlation with SCC mechanisms is discussed based on the obtained surface oxide film characteristics and SCC results from another study [15] and literature. As pointed out in the introduction, no single mechanism could fully explain all the SCC parameter effects, metallographic and fractographic observations.

Among the proposed mechanisms, the selective internal oxidation is unlikely to be the mechanism explaining SCC in Alloy 182 in 274 °C hydrogenated water. Cross-sectional samples containing actively growing crack-tips were analysed carefully by high-resolution SEM, without evidence of oxidized grain boundaries ahead of the crack-tip [15]. This is not surprising because the reported activation energy for oxygen diffusion is much higher than the one for SCC in Ni-base alloys (~ 400 kJ/mol for oxygen diffusion vs. ~150 kJ/mol for SCC). The oxygen diffusion coefficient at 400 °C was stated to range from $3.5 \cdot 10^{-19}$ to $1.5 \cdot 10^{-18}$ m²/s by Capell and Was [54]. By estimating the diffusion coefficient at 274 °C using the activation energy from literature, the calculated crack growth rates would be several magnitudes lower than the measured crack growth rates in the current study. Nevertheless, selective internal oxidation could still be responsible for precursor processes for SCC initiation in Ni-based alloys at higher temperatures.

Concerning the hydrogen-assisted cracking mechanism, which is generally agreed to be responsible for low-temperature crack propagation in high-strength Ni-based alloys below 150 °C, a case of hydrogen-assisted cracking was reported up to 300 °C in Ni-based alloys [55]. However, it required specimens pre-charged with several tens of ppm hydrogen. In the current study, the DH content is too low to be absorbed in relevant amounts and to cause bulk embrittlement. Another important discrepancy for a hydrogen-assisted cracking mechanism is the temperature dependency. The activation energy of hydrogen uptake is ~14 kJ/mol and of diffusion is 42 kJ/mol [56] in Alloy 600, which are too low for the observed activation energy of PWSCC of Ni-based alloys. One possible explanation is that hydrogen affects some other processes, such as creep. Hall proposed a detailed SCC model based on hydrogen-assisted

creep fracture [57]. However, experimental support for the hydrogen-assisted creep fracture mechanism is very limited. The hydrogen-enhanced decohesion mechanism with absorption of hydrogen at the grain boundaries appears as the most plausible mechanism for IGSCC in austenitic Ni-alloys, but also the localization of plastic deformation by hydrogen enhanced localized plasticity and interaction of deformation bands with grain boundaries could promote IG cracking. The limited hydrogen availability, low trapping efficiency and fast diffusion/permeation and release rates under light water reactor conditions at 274 to 350 °C impede the necessary significant hydrogen accumulation for hydrogen embrittlement and hydrogen-assisted SCC in austenitic SS and Ni-alloys. Furthermore, the trapping efficiency of dislocations at these temperatures is too low for hydrogen-enhanced localized plasticity, and only stronger traps like grain boundaries, oxide and MnS inclusions, carbides/carbonitrides like TiC or vacancies and vacancy clusters can still keep some hydrogen. Thus very high hydrogen contents are necessary for significant hydrogen effects under typical stationary light water reactor operation conditions that are one to three orders of magnitude higher than what can realistically be achieved in high-temperature water. Furthermore, many fundamental observations are hardly consistent with most hydrogen embrittlement mechanisms: E.g., an increase in hydrogen content and decrease in ECP or catalytic surfaces (noble metal chemical addition) usually result in a significant decrease in SCC crack growth rates in solution-annealed stainless steel and Ni-alloys [58]. The low-temperature crack propagation and embrittlement of high-strength Ni-alloys in hydrogenated high-temperature water at temperatures below 100 °C with very high DH contents, on the other hand, are believed to be due to hydrogen-assisted SCC and embrittlement, but the effects usually completely disappear above temperatures of 100 to 150 °C.

Apart from the peak in SCC in hydrogenated water at low ECP close to the Ni/NiO boundary, IGSCC in austenitic Ni-alloys and stainless steels in high-temperature water can be fairly well be described by the slip-dissolution model over a very wide range of system conditions, including the effect of ECP, chloride/sulphate, sensitization, strength, etc. Moreover, the potential transients in electrochemical noise signals under less reducing conditions (≤ 50 ppb DH) are probably related to oxide film rupture and repassivation events, which is also consistent with the slip-dissolution mechanism. The activation energy for IGSCC in stainless steel in oxygenated water at 250 to 300 °C, where the slip-dissolution mechanism is believed to be active, varied between 40 to 116 kJ/mol, the higher values being close to the range of activation energies of Ni-alloys in hydrogenated water at higher temperatures of 300 to

360 °C. Repassivation measurements with Ni-alloys suggest that the initial bare metal dissolution rates are decreasing with increasing DH, but that the repassivation is increasingly retarded by increasing DH [59], although the latter might be mainly related to the hydrogen oxidation at high DH. The peak in SCC cracking is probably related to a competition between initial anodic bare metal dissolution rate after a film rupture and subsequent repassivation rate and their dependence on DH with respect to the Ni/NiO boundary:

Ziemniak et al. [60] studied the solubility of Ni in hydrogenated high-temperature water with ammonia and sodium from 175 to 315 °C and formulated the oxidative dissolution reaction of metallic Ni:

This reaction is enhanced by the subsequent Ni^{2+} hydrolysis reactions:

where a can be 1 and 2. The hydrolysis product is consistent with the XPS and Raman results. Decreasing the DH content shifts the equilibrium towards the Ni^{2+} side, i.e., enhances Ni dissolution. Based on their calculations, the solubility of Ni^{2+} at the DH contents used in this study at 274 °C is roughly estimated to be 0.72 (2200 ppb DH), 2.64 (600 ppb DH), 6.26 (253 ppb DH), 15.84 (100 ppb DH) and 158.4 (10 ppb DH) nmol/kg. Decreasing the DH content from 2200 to 253 ppb results in an increase of the Ni^{2+} solubility by a factor of ~9. Although in the NiO stability region, Ni hydroxides are believed to form by dissolution and precipitation processes. Decreasing the DH content in the Ni-stability region leads to higher Ni^{2+} solubility, indicating a higher instability of Ni, the basis element of the alloy. In terms of the slip-dissolution mechanism, decreasing the DH content can promote Ni dissolution. It is reasonable to conclude that decreasing DH can increase the SCC susceptibility in the Ni stability region. If the DH content is further decreased to the NiO stability region, Ni will exist as Ni hydroxide/oxide in the oxide film due to the lower NiO solubility compared to Ni^{2+} ion solubility [61]. It should be noted that solubility of NiO is independent of hydrogen concentration according to the calculations in [60]. This phenomenon is also consistent with the XPS results shown in Figure 5, that the decrease of the DH content across the Ni/NiO phase transition line leads to a high plateau of the Ni^{2+} (hyd) peak. In terms of the slip-dissolution model, the increase in dissolution rate in the NiO stability region could yield higher crack growth rates. Xu et al. [23] observed an increase of the film resistance by

contact electric resistance and electrochemical impedance spectrum analysis when the DH content was decreased from the Ni to NiO stability region. Nevertheless, Cr_2O_3 can form under all DH conditions and act as diffusion barrier and protect the bulk material against further dissolution. A lower DH (higher ECP) corresponds to the faster formation of a protective passive oxide film and reduces the ion diffusion. Thus, decreasing the DH could lead to a thicker Cr-enriched inner oxide film, which can slow down ion diffusion and better protect the substrate against further dissolution. Furthermore, repassivation would start to dominate the effect of dissolution. These phenomena may explain why the SCC susceptibility decreases in the NiO region.

For Ni-base alloys in high-temperature water, a clear transition in the nature of the oxide film occurs around the Ni/NiO phase transition line with a maximum in defect density/photo current and film thickness at higher temperatures, and the repassivation behaviour could depend on the environmental condition. A sketch of the current behaviour in the slip-dissolution model is shown in Figure 16 (a) [62]. The passive current at the Ni/NiO phase transition line is higher than that in the Ni and NiO stability regions. The active initial bare metal dissolution current density caused by film rupture decreases with increasing DH content. After film rupture, the repassivation starts immediately and the current density decays exponentially with time: $i(t) \propto i_0^{-n} + i_p$. The total charge during the repassivation process $Q = \int i(t)dt$, indicates the amount of metal dissolution and SCC crack advance by dissolution. The repassivation exponent n is expected to show a minimum at Ni/NiO phase transition line due to the instability and defective structure of the oxide film, and thus leads to a longer repassivation time. The n value in NiO stability region is slightly higher than in Ni stability region because of higher driving force for oxidation (lower DH content). Thus, the total charge could exhibit an unsymmetrical behaviour with local maximum at the Ni/NiO phase transition line and would further increase for higher ECP levels (Figure 16 (b)). J. Wang et al. investigated repassivation measurements with Alloy 690 using oxide film scratching technique and found correlation of repassivation kinetics with SCC susceptibility in hydrogenated high-temperature water [63]. Figure 16 (c) shows PSI's SCC cracking results with Alloy 182 weld metal tapered specimens tested in high-temperature water containing different dissolved hydrogen contents from [64], and the trend of Q with ECP is consistent with that of the SCC initiation susceptibility with ECP.

Based on the Mott-Schottky results and the tailing effects (decrease of quantum efficiency with higher photon energy) of the oxide films formed close to the Ni/NiO phase transition line, the higher defect density and photocurrent response might be due to a higher density of states in the vicinity of the conduction band caused by higher doping concentrations [65]. It is well known that with amorphous semiconductors, where no periodic lattice structure is present, orbitals from the extended bands may be shifted into the gap region due to the distorted band geometry. This is actually the same case for Ni hydroxide and the spinel on the specimen surface, as they exist as individual crystallites and no long-range order is present. Gorse et al. [66] reported that due to irradiation with α -particles the photo response of the passive film on AISI 304 stainless steel increased. The main function of α -irradiation was structural distortion without change of chemical composition. This supports the argument that the increased photocurrent response of oxide films on the Alloy 182 specimens in vicinity of the Ni/NiO phase transition line is due to a more distorted structure of the passive film. Thus, it is logical to correlate that at the Ni/NiO phase transition line, the “defects” in the passive films could be considered as potential nucleation sites for SCC under applied stress. The formation of these “defects” in the passive film at the Ni/NiO phase transition line could be attributed to instability of the oxide film and Ni solubility. According to the slip-dissolution mechanism, it would correspond to an increase in crack growth rate. The results in terms of Mott-Schottky defect density and photocurrent response are also in agreement with the above discussion.

Therefore it may be concluded that probably a combination of different mechanistic models may describe the SCC behaviour of Alloy 182 in BWR/HWC environments. Combinations of different mechanisms may be simultaneously active during IGSCC in Ni-based alloys. At low temperature and high strength Ni-base alloys hydrogen-assisted cracking may dominate, in the intermediate temperature range (BWR/HWC) the slip-dissolution and at high-temperature in hydrogenated water selective internal oxidation may contribute to cracking.

4. Conclusions

The oxide films on Alloy 182, formed in simulated BWR environments with different DH contents were characterized using SEM/TEM/EDX, XPS, Raman spectroscopy, Mott-Schottky and photoelectrochemical analysis methods. The following conclusions can be drawn from the current study:

- 1) The oxide films formed under all DH conditions consist of an inner oxide layer with high Cr content and an outer oxide layer of hydroxide/spinel.
- 2) Ni exists in the form of Ni hydroxide and spinel in the outer oxide layer in the NiO stability region; in the Ni stability region, the amount of Ni hydroxide reduced dramatically and Ni is present predominantly as Ni spinel. Under the highest DH condition of 2200 ppb, NiFe_2O_4 was found to be reduced to Ni and Fe_3O_4 .
- 3) The electrochemical analysis results indicate that the oxide films formed on Alloy 182 in hydrogenated high-temperature water consists of an inner *p*-type semiconductive high Cr oxide layer with the band gap energy of 2.6 eV and a covering *n*-type semiconductive hydroxide/spinel layer with the band gap energy of 2.2 eV. This was consistent with results of the Mott-Schottky analysis.
- 4) A clear trend with DH contents was observed in the Mott-Schottky and photoelectrochemical analysis. A maximum in the defect concentration of the oxide films and highest photocurrent response were found at the Ni/NiO phase transition line, which corresponds to the maximum in SCC susceptibility in Alloy 182, as described in a related study [15, 64].
- 5) Mechanistic considerations could not come up with a single SCC mechanism being able to explain all experimental observations. The slip-dissolution model was considered to be the most plausible cracking mechanism that could explain the observed experimental results at 274 °C. The peak in SCC susceptibility at the Ni/NiO phase transition line (see [15, 64]) could be attributed to the competition between anodic dissolution and repassivation rates as function of DH, and a more defective and instable oxide film with poor protectiveness.

5. Acknowledgements

The results described in this paper were generated within the SAFE-I and -II research projects. The financial support of the project by the Swiss Federal Nuclear Safety Inspectorate (ENSI) is gratefully acknowledged. Parts of the measurements were funded by the Euratom 7th Framework Programme FP7/2007-2013 under grant agreement no. 604965. Special thanks are expressed to Marc Vankeerberghen (SCK•CEN) and Martin Weiser (University of Erlangen-Nuremberg) for their support and discussion with the Mott-Schottky analysis and Robert Hahn (University of Erlangen-Nuremberg) for his support with the photocurrent measurements.

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Figure 1: SEM images of coupon surfaces exposed to high-temperature water containing (a) 10 ppb, (b) 253 ppb, (c) 600 ppb and (d) 2200 ppb DH.

Figure 2: TEM cross-section of the oxide film formed on Alloy 182 in simulated BWR environment with 253 ppb DH. The chemical compositions of the positions A, B and C are given in Table 3.

Figure 3: XPS (a) $O1s$, (b) $Cr2p_{3/2}$, (c) $Fe2p_{3/2}$ and (d) $Ni2p_{3/2}$ spectra measured for the oxide film formed on Alloy 182 coupon exposed to high-temperature water with 10 ppb DH.

Figure 4: XPS $Ni2p_{3/2}$ spectra of the oxide films formed on Alloy 182 in simulated BWR environment with (a) 10 ppb and (b) 2200 ppb DH.

Figure 5: Ratio of peak areas of both Ni^{2+} (hyd) and Ni^{2+} (ox) of $Ni\ 2p_{3/2}$ peaks as function of ΔECP .

Figure 6: Raman spectra of the oxide films formed on Alloy 182 in simulated BWR environments with different DH contents (a) 10 ppb, (b) 253 ppb, (c) 600 ppb and (d) 2200 ppb.

Figure 7: Peak shift to lower wavenumbers of the $\sim 700 \text{ cm}^{-1}$ Raman peak indicating the reduction of NiFe_2O_4 at very high DH condition. The Ni/NiO phase transition line is taken from [13] and the $\text{NiFe}_2\text{O}_4/\text{Ni} + \text{Fe}_3\text{O}_4$ phase transition line is obtained by extrapolating the thermal dynamical calculation to 274°C from [20].

Figure 8: Mott-Schottky plots of the oxide films formed on Alloy 182 in simulated BWR environments with different DH contents (a) 10-600 ppb, (b) 2200 ppb.

Figure 9: Doping species density as function of ΔECP relative to ECP of Ni/NiO phase transition.

Figure 10: Typical examples of photocurrent transient obtained for the oxide films formed on Alloy 182 in simulated BWR environments with different DH contents (a) 100 ppb, (b) 2200 ppb.

Figure 11: Photocurrent spectra for the oxide films formed on Alloy 182 in simulated BWR environments with different DH contents (a) 10-600 ppb, (b) 2200 ppb.

Figure 12: Plots for an indirect transition for the oxide films formed on Alloy 182 in simulated BWR environments with different DH contents.

Figure 13: Comparison of the photocurrent response between the oxide films formed on Alloy 182 in simulated BWR environments with different DH contents.

Figure 14: A band structure model for oxide films formed on Alloy 182 in simulated BWR environments. At very high DH condition, the band model of outer oxide layer does not exist; the oxide film behaves like p-type semiconductor.

Figure 15: Schematic diagram of the DH effect on the oxide films formed on Alloy 182 in simulated BWR environments, the DH dependence of oxide film thickness is taken from [53].

Figure 16: Schematic illustration of the (a) repassivation current model and (b) the change of corresponding parameter as function of ECP. t is the time elapsed since the oxide film was ruptured, i_0 is the instantaneous bare metal dissolution current density at the moment of film rupture and i_p is the passive current, n is a constant describing the repassivation kinetics, and $Q = \int i(t)dt$ indicates the total amount of metal dissolution. (c) SCC cracking results of tapered specimens tested in high-temperature water containing different dissolved hydrogen contents with the crack length density and crack number density vs. $\text{ECP}-\text{ECP}_{\text{Ni/NiO}}$ [64].

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

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

Table 3: Chemical compositions of different positions marked in Figure 2 obtained using TEM/EDX analysis.

Position	Element	Atomic %	Position	Element	Atomic %
A	O	50.4	B	O	51.4
	Cr	4.3		Cr	12.1
	Fe	2.4		Fe	14.9
	Ni	37.9		Ni	11.7
C	O	53	Bulk material	Cr	19.1
	Cr	24.3		Ni	65.8
	Fe	2.8		Fe	6.9
	Ni	16.3		Mn	6.9

Table 4: Slope and doping species density of the oxide films formed under different DH conditions.

DH [ppb]	ECP [mV]	Δ ECP [mV]	n -slope [$F^{-2}cm^4V^{-1}$]	Donor density [$cm^{-3}10^{20}$]	p -slope [$F^{-2}cm^4V^{-1}$]	Acceptor density [$cm^{-3}10^{20}$]
50	-496	39	1172.3	0.077	-7172.4	0.013
200	-529	6	869.5	0.104	-5373.8	0.017
230	-532	3	906.3	0.100	-4087.0	0.022
300	-539	-4	1621.0	0.080	-5627.2	0.020
600	-555	-20	1319.5	0.069	-1140.1	0.028