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NOTICE

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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

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Abstract

Alloys 600 and X-750 have been shown to exhibit a maximum in primary water stress corrosion cracking (PWSCC) susceptibility, when testing is conducted over a range of aqueous hydrogen (H_2) levels. Contact electric resistance (CER) and corrosion coupon testing using nickel specimens has shown that the maximum in SCC susceptibility occurs in proximity to the nickel/nickel oxide (Ni/NiO) phase transition. The measured location of the Ni/NiO transition has been shown to vary with temperature, from 25 scc/kg H_2 at 360°C to 4 scc/kg H_2 at 288°C. New CER measurements show that the Ni/NiO transition is located at 2 scc/kg H_2 at 260°C. An updated correlation of the phase transition is provided. The present work also reports CER testing conducted using an Alloy 600 specimen at 316°C. A large change in resistance occurred between 5 and 10 scc/kg H_2 , similar to the results obtained at 316°C using a nickel specimen. This result adds confidence in applying the Ni/NiO transition measurements to Ni-Cr-Fe alloys. The understanding of the importance of the Ni/NiO transition to PWSCC has been used previously to quantify H_2 effects on SCC growth rate (SCCGR). Specifically, the difference in the electrochemical potential (EcP) of the specimen or component from the Ni/NiO transition (*i.e.*, $EcP_{Ni/NiO} - EcP$) has been used as a correlating parameter. In the present work, these SCCGR- H_2 correlations, which were based on SCCGR data obtained at relatively high test temperatures (338 and 360°C), are evaluated *via* SCCGR tests at a reduced temperature (316°C). The 316°C data are in good agreement with the predictions, implying that the SCCGR- H_2 correlations extrapolate well to reduced temperatures. The SCCGR- H_2 correlations have been revised to reflect the updated Ni/NiO phase transition correlation. New data are presented for EN82H weld metal (also known as Alloy 82) at 338°C. Similar to other nickel alloys, SCC of EN82H is a function of the aqueous H_2 level, with the SCCGR exhibiting a maximum near the Ni/NiO transition. For example, the SCCGR at 8 scc/kg H_2 is $\sim 8.1\times$ higher than at 60 scc/kg H_2 . The 8 scc/kg H_2 condition is near the Ni/NiO transition (located at ~ 14 scc/kg H_2 at 338°C), while 60 scc/kg H_2 is well into the nickel metal regime. A hydrogen-SCCGR correlation is provided for EN82H. The data and understanding obtained from the present work show that SCC can be mitigated by adjusting the aqueous H_2 level. For example, SCCGR is typically minimized at relatively high aqueous H_2 levels, that are well into the nickel metal regime (*i.e.*, far from the Ni/NiO transition).

Introduction

Testing of nickel-based alloys at various aqueous H_2 levels and temperatures has shown that a maximum in PWSCC susceptibility exists in proximity to the Ni/NiO equilibrium.¹⁻¹² The theory that the stability of NiO influences PWSCC is supported by microscopy studies in which the crack tip oxide often exhibits a NiO crystal structure (*i.e.*, $Ni(Cr,Fe)O$) as opposed to the spinel structure oxides (*i.e.*, $Ni_xFe_{1-x}Cr_yFe_{2-y}O_4$) typically found on the external metal surface.¹³ Spinel structure oxides have also been observed at the crack tip in some cases.¹⁴ Changing the aqueous H_2 level can stabilize or destabilize NiO, due to the reaction between NiO and H_2 (*i.e.*, $NiO + H_2 = Ni + H_2O$). CER measurements of the Ni/NiO phase transition¹⁵ have been used to quantify H_2 effects on SCCGR, based on the understanding that the H_2 dependency can be fundamentally described by the extent that the EcP of the alloy deviates from the potential of the Ni/NiO transition (*i.e.*, $EcP_{Ni/NiO} - EcP$). This potential difference (ΔEcP) likely represents the relative stability of oxides that can influence SCC. SCCGR- H_2 correlations were developed for Alloys 600, X-750 HTH and X-750 AH in terms of the parameter ΔEcP .⁴ Knowledge of the location of the Ni/NiO phase transition as a function of temperature allows these correlations to be extrapolated to lower temperatures *via* the assumption that the magnitude of the dissolved H_2 effect is temperature independent (*i.e.*, it is assumed that the only effect of temperature is to change the location of the Ni/NiO phase transition). Using these correlations, SCCGR effects can be predicted at a given aqueous H_2 level and temperature, for each material tested.

Experimental Procedure

Environment: Testing was conducted in deaerated water at a high temperature pH of ~ 7 . The desired H_2 levels were obtained by varying the feed tank H_2 overpressure according to Henry's law. The room temperature H_2

calculations were conducted using a Henry's law coefficient¹⁶ of 0.85 psia/(scc/kg). Mixed gas of 4 or 14.7% hydrogen with the balance being argon was used to obtain coolant hydrogen levels less than 20 scc/kg H₂.

CER Measurements: The CER method¹⁷⁻¹⁹ can be used to analyze surface resistance in metal-environment systems. Figure 1 shows a schematic diagram of the CER instrument used in the present work. The test specimen was nickel (99.5 wt%) at 260°C and Alloy 600 at 316°C. Iridium was used as an oxide-free, inert specimen in both cases. Testing details have been provided previously.¹⁵ Pre-test specimen processing was conducted to minimize film formation. The specimen tips were polished using grinding paper prior to each test run. The specimens were then pushed together prior to admitting water to the system. A cathodic current (~ -100 μ A) was then applied until the specimen reached its intended pressure and temperature, at which time the CER test was started.

Hydrogen fugacity measurements: Testing was performed at 260°C in the CER facility using a silver-palladium tube, as a spot-check to ensure that the H₂ levels in the test facility were properly controlled. Testing was conducted at an autoclave pressure of 1800 psi. Details of the experimental apparatus and test method have been provided.²⁰

Electrochemical measurements: EcPs were measured on electrically isolated specimens vs. a platinum (Pt) electrode as well as (in some cases) a yttria-stabilized zirconia-iron/iron oxide (YSZ-Fe/Fe₃O₄) electrode. Prior work has shown that the YSZ-Fe/Fe₃O₄ probe is an effective reference electrode in simulated primary water.²⁰

Materials for SCCGR Tests: This study investigated EN82H weld metal, mill-annealed Alloy 600, and Alloy X-750 in the AH heat treatment. Alloys 600 and X-750 AH were tested at 316°C and at initial K_I levels of 65.9 MPa $\sqrt{m}$ (Alloy 600) and 39.5 MPa $\sqrt{m}$ (X-750 AH). Additional test details for Alloys 600 and X-750 AH are provided in Reference 4. The composition of the EN82H material is listed in Table 1. The yield strength of the as-deposited weld metal is 397 MPa. EN82H material was deposited *via* the gas tungsten arc welding process, using 100% argon as a shield gas. Weld metal was deposited into a 'weld pad' geometry (*i.e.*, using a baseplate but no sidewall materials). The EN82H weld pad was fabricated into standard 25.4 mm thick compact tension (CT) specimens with 10% side grooves. Specimen orientation was such that crack growth occurred from the root to the crown of the weld, with the loading axis perpendicular to the direction of welding. In ASTM notation, this orientation is referred to as T-S, as described previously.²¹ Specimens were air fatigue precracked to an initial a/W of 0.5, using the fatigue precracking procedure from ASTM E399 Annex 2. A 10 minute, 10% daily unload was performed. EN82H tests were conducted at 338°C, an autoclave pressure of 2500 psi, at an initial K_I level of 38.5 MPa $\sqrt{m}$, and at hydrogen levels ranging from ~ 0.1 to 120 scc/kg H₂.

SCCGR Tests: Tests were conducted in active load servoelectric machines with digital control electronics monitored through a computerized data acquisition system. A description of the recirculating high flow rate autoclave system has previously been provided.²² EN82H specimens were preconditioned with no applied load at 260°C for 1 week at the test hydrogen concentration. Crack lengths were monitored *in-situ* using electrical potential drop according to ASTM E647, Annex 3, and using front-face linear variable displacement transformers (LVDTs). However, neither type of instrumentation was successful in detecting the onset of crack growth, which is not unusual for the irregular crack fronts associated with weld metal SCC. SCCGRs were based on post-test destructive examination (DE) data. Upon completion of testing, all specimens were heat-tinted in air at 454°C for 8 hours to facilitate fractographic inspections. The Alloy 600 and EN82H specimens were fatigued apart to minimize deformation of the SCC surface, and were then pulled apart in tension. The higher strength X-750 specimens were simply pulled apart in tension. The amount of SCC in each specimen was measured by optical examination using the procedure in ASTM E813. Due to the typically irregular nature of SCC cracks in weld metal, 30 measurement locations were used across the crack front. Crack growth rates were determined by dividing the average SCC extension by the test duration.

Results and Discussion

CER Testing using a Nickel Specimen

In this test, which was conducted at 260°C, the initial H₂ level was 60 scc/kg H₂, which is well into the nickel metal stability regime based on prior data at 288°C. As shown in Figure 2, a very low resistance (~ 0.001 Ω) was observed, consistent with previously measured Ni regime values.¹⁵ From this point, the H₂ level was decreased incrementally, to determine the H₂ level at which an increase in resistance (corresponding to oxidation) occurred. Very low resistances were measured at 60, 30, 5, and 2 scc/kg H₂. Data were lost due to an interruption in power between 767 and 797 hours. Although an apparent minor increase in resistance was observed when the power was restored, this increase is not real. As explained previously,¹⁵ this apparent increase is due to the drifting apart of the

specimens, as confirmed by readjusting the 'home' position (*i.e.*, re-setting the gap) of the specimens at 863 hours. Reducing the H₂ level from 2 to 1 scc/kg at 984 hours led to a steady increase in resistance for ~ 18 days, at which time the H₂ level was increased to 3 scc/kg. This change in the H₂ level caused a clear decrease in resistance, within 0.5 hours after the feedtank H₂ pressure was increased. Summary data are provided in Table 2.

It is evident that at 260°C, 1 scc/kg H₂ resides in the nickel oxide stability regime and that 60, 20, and 3 scc/kg H₂ are located in the nickel stability regime. It is not as straightforward to assess the condition of 2 scc/kg H₂. Figure 2 shows that no evident film formation occurred at this condition for 146 hours. Since oxide formation could have occurred at longer times, however, it is difficult to classify 2 scc/kg H₂ as residing within either the nickel or nickel oxide stability regime. Since 1 scc/kg H₂ is known to be in the nickel oxide regime and 3 scc/kg H₂ is known to be in the nickel stability regime, it seems reasonable to define the transition hydrogen level at 260°C as 2 ± 1 scc/kg H₂.

Figure 3 shows a summary plot of CER measurements performed from 260 to 360°C using nickel specimens, from the present work and reference 15. Data are also shown from corrosion coupon tests at 338°C (12.5 and 20 scc/kg H₂), which were used to spot-check the CER measurements. In addition to the data shown in Figure 3, half of the nickel coupon which formed an oxide during exposure at 12.5 scc/kg H₂ (338°C) was re-exposed at 20 scc/kg H₂ (338°C), and significant film reduction was observed.¹⁵ Figure 3 also contains a thermodynamic model of the phase transition, which was obtained *via* regression to the experimental data, as discussed below.

In-Autoclave Hydrogen Fugacity Measurements at 260°C

Testing was performed at 260°C in the CER facility at hydrogen levels of 1, 5, 30, and 60 scc/kg H₂. Steady-state pressures, as reported previously,²⁰ were very consistent with the expected values using a Henry's law coefficient from Reference 16. The present work utilizes an improved Henry's law correlation from Moshier and Witt.²³ Table 4 shows that the measured hydrogen fugacity values are very similar to the hydrogen fugacity values calculated using this updated Henry's law correlation. This good agreement between measured and expected hydrogen fugacity values demonstrates that there are no spurious at-temperature sources or sinks of hydrogen causing the autoclave hydrogen concentration to be significantly different than the feedtank concentration.

Updated Thermodynamic Model for the Nickel/Nickel Oxide Phase Transition

In Reference 4, CER and corrosion coupon data were used to develop a two-parameter thermodynamic model for the Ni/NiO transition. The model is updated herein to incorporate the new CER data at 260°C, plus an improved Henry's law correlation.²³ (Note that this Henry's law correlation was developed by Moshier and Witt²³ by performing hydrogen fugacity measurements at various temperatures and autoclave pressures, and then fitting the data to the Krichevsky-Kasarnovsky equation from Reference 24.) The model is developed using a thermodynamic equation for the phase transition reaction ($\text{Ni} + \text{H}_2\text{O} = \text{NiO} + \text{H}_2$). Specifically:

$$\Delta G = \Delta H_{298} - T \cdot \Delta S_{298} = -R \cdot T \cdot \ln(f_{\text{H}_2}) \quad [1]$$

where ΔG is the Gibbs free energy, ΔH_{298} and ΔS_{298} are the enthalpy and entropy of formation for the phase transition reaction, R is the universal gas constant (8.314 J/mol-K), T is the temperature in Kelvin, and f_{H_2} is the hydrogen fugacity in atmospheres (note that the activities of Ni, H₂O, and NiO are $\cong 1$). Rearranging [1] yields:

$$\ln f_{\text{H}_2} = -\frac{\Delta H_{298}}{R} \left(\frac{1}{T} \right) + \frac{\Delta S_{298}}{R} \quad [2]$$

Figure 4 shows an empirical fit of the measured Ni/NiO phase transition data to equation [2]. The hydrogen fugacity values corresponding to the measured Ni/NiO phase transition were determined from the data in Figure 3 (and listed in Table 5), plus the appropriate Henry's law coefficient²³ for each test condition (Table 5). The parameters ΔH_{298} and ΔS_{298} were determined *via* linear regression to be 38,400 J/mol and 43.5 J/mol-K, respectively. Note that these values are different than those reported in Reference 4, since the model has been updated to account for the new data at 260°C, and because different Henry's law coefficients were used. As compared to the Reference

4 values, the updated values of ΔH_{298} and ΔS_{298} are closer to the 'theoretical' NiO thermodynamic values of 46,100 J/mol and 68.0 J/mol-K obtained from thermodynamic tables.²⁴

Thus, on a hydrogen fugacity basis, the thermodynamic model is:

$$f_{H_2} = \exp(-4619.2 \cdot [1/T] + 5.2302) \quad [3]$$

where f_{H_2} is in atmospheres. The thermodynamic model can also be presented on a hydrogen concentration basis:

$$[H_2]_{Ni/NiO} = \frac{\exp(-4619.2 \cdot [1/T] + 5.2302)}{k_H} \quad [4]$$

where $[H_2]_{Ni/NiO}$ is the hydrogen concentration (in scc/kg) corresponding to the Ni/NiO phase transition, and k_H is the Henry's law coefficient at the temperature and pressure of interest in atm/(scc/kg H₂). Figure 3 and Table 5 show that the thermodynamic model provides a good approximation of the measured Ni/NiO transition over the range of 260 to 360°C.

CER Testing using an Alloy 600 Specimen

As described in reference 15, several prior CER tests have been conducted at 316°C using a nickel specimen. These tests consistently showed a large increase in resistance when the H₂ level was lowered from 10 to 5 scc/kg H₂, and a large decrease in resistance when the hydrogen level was raised back to 10 scc/kg H₂. Figure 5 shows that a similar pattern is evident for Alloy 600 in a test conducted at 316°C. If one first focuses on the portion of the test starting at 306 hours (after the data loss due to home position problems), it is observed that a steady-state resistance was established for ~ 24 hours (306 to 330 hours) at 10 scc/kg H₂. At 330 hours, the hydrogen level was lowered to 5 scc/kg H₂. An increase in the resistance was noted within approximately 2 hours, and the resistance eventually increased by nearly two orders of magnitude at this condition. The H₂ level was subsequently raised to 10 scc/kg H₂ at 478 hours. A nearly immediate decrease in resistance was observed, and this decrease continued for the next several days. Thus, there is a strong oxidation/reduction reaction (presumably related to nickel and its oxides) in the vicinity of 5 to 10 scc/kg H₂ at 316°C – this effect is noted whether the test specimen is pure nickel (as in reference 15) or Alloy 600 (as in the present work).

Although the nickel and Alloy 600 specimens tested at 316°C exhibited a similar trend when the hydrogen level was changed from 10 to 5 scc/kg H₂ and then back to 10 scc/kg H₂, it is noted that the absolute values of the resistances measured were quite different. In prior tests using a nickel specimen, the obtained resistance at 60 scc/kg H₂ was very low (~ 0.001 to 0.002 Ω). In the present Alloy 600 testing, the initial resistance value was low (~ 0.004 Ω), presumably due to the efforts to minimize film formation prior to and during heatup (e.g., specimen polishing, pushing the specimen tips together to minimize water access, and application of a cathodic current). However, once the test temperature of 316°C was reached, the specimen gap was restored and the cathodic current was turned off. At this point, film growth occurred, as evidenced by the increasing resistance from 0 to ~ 20 test hours. After this point, the rate of change in resistance diminished. It is expected that a steady-state resistance value was reached sometime during the period of time where no data were available, given the fact that the resistance was extremely stable during the ~ 1 day period from 306 to 330 hours. It appears that an oxide film grew initially upon exposure of the Alloy 600 specimen to the 316°C water and then stabilized for at least 24 hours until the H₂ level was decreased at 330 hours. Note that the oxide formed on the Alloy 600 CER specimen was not analyzed, since such an analysis would be destructive in nature, and it was desirable to have the ability to perform future testing on the specimen.

Data from other investigators: CER data reported by Ehrnsten *et al.*¹⁸ at 320°C using Alloy 600 as a test specimen is broadly consistent with the present Alloy 600 CER data. In their work, a large increase in resistance was observed when the amount of hydrogen was lowered from an at-temperature hydrogen partial pressure of 0.25 bars (~ 30 scc/kg H₂) to a nitrogen (N₂)-deaerated condition. When the hydrogen level was subsequently raised from the N₂-deaerated condition to an at-temperature hydrogen partial pressure of 0.6 bars, (~ 72 scc/kg H₂), a large decrease in resistance was observed. Examination of Figure 3 shows that at 320°C, 30 and 72 scc/kg H₂ are on the 'reducing'

side of the Ni/NiO phase transition, while a N₂ sparge condition (which was estimated as ~ 0.1 scc/kg H₂ in a previous test in our laboratory⁴) is on the 'oxidizing' side of the transition.

In their work,¹⁸ it was presumed that a spinel structure oxide was formed on the Alloy 600 specimen in the nitrogen-deaerated condition. It was stated that the lower resistance values observed at the elevated hydrogen conditions may be due to stringers of metallic nickel in the oxide, which increase the electrical conductivity of the film. It was suggested that when the dissolved hydrogen level was reduced, the exposed part of these stringers may have been oxidized (e.g., to NiO), resulting in the observed increase in resistance. Ehrnsten *et al.*¹⁸ note that the presence of metallic Ni in the oxide film growing on Alloy 600 in water containing hydrogen has been experimentally verified by Airey.²⁵ While this explanation seems reasonable, it is noted that other investigators²⁶ have shown that at short times, the oxide film on Ni-Cr-Fe alloys can assume a nickel oxide structure with iron and chromium incorporated within the oxide. In this case, the NiO structure oxide is metastable, and eventually transforms to a spinel structure.

In summary, while the oxide character and the electrochemical reactions taking place on Alloy 600 CER specimens when the hydrogen level is adjusted are not known with certainty, it seems reasonable to believe that oxidation of nickel within the film is likely playing a role. Additionally, the present CER data support the view that a large change in the oxidation/reduction behavior of Alloy 600 is occurring in the vicinity of the measured Ni/NiO phase transition. This observation adds confidence in applying the Ni/NiO transition measurements to Ni-Cr-Fe alloys.

SCCGR Testing

Alloy 600 at 316°C: Prior work⁴ on Alloy 600 was conducted at 338°C at initial K_I values of 27.5 and 65.9 MPa√m (it was demonstrated that the H₂ functionality was not appreciably influenced by the stress intensity factor). As described in Reference 4, a correlation was developed for Alloy 600 SCCGR, using the parameter $E_{CP_{Ni/NiO}} - E_{CP}$. One important question is whether this correlation extrapolates correctly to lower temperatures. The extrapolation⁴ was based on the assumption that the magnitude of the dissolved hydrogen effect is temperature independent. That is, it was assumed that the only effect of temperature is to change the location of the Ni/NiO phase transition.

The testing performed in the present study was designed to evaluate the ability of the correlation to extrapolate to reduced temperatures. Figure 6 shows SCCGR data for Alloy 600 at a K_I value of 65.9 MPa√m, plotted using the parameter $E_{CP_{Ni/NiO}} - E_{CP}$ (details for constructing plots using the $E_{CP_{Ni/NiO}} - E_{CP}$ scale are provided later in this paper). The square symbols represent the prior data,⁴ which was generated at 338°C (640°F). The triangles are new data generated at 316°C (600°F), at hydrogen levels of 7, 40, and 120 scc/kg H₂. It is apparent that the 316°C data are in good agreement with the 338°C data. The magnitude of the hydrogen effect can be defined by the ratio between the maximum SCCGR and the minimum SCCGR at a specific temperature. At 316°C, the SCCGR at 7 scc/kg H₂ (0.151 mils/day) is ~ 2.7x greater than the SCCGR measured at 120 scc/kg H₂ (0.056 mils/day). Thus, the magnitude of the H₂ effect is similar to that reported at 338°C (~ 2.8x).⁴ The 316°C data are also consistent with the understanding that SCCGRs increase as the Ni/NiO phase transition is approached, given that the CER-measured phase transition is 7.5 ± 2.5 scc/kg H₂ at this temperature. Overall, Figure 7 supports the view that the correlation⁴ developed for Alloy 600 based on testing at 338°C is also appropriate for the 316°C data.

Comparison to Alloy 600 Data from Other Investigators: In a previous paper,¹⁵ the location of the measured Ni/NiO phase transition was compared to data compiled by Cassagne *et al.*¹ The present work compares the Ni/NiO and SCCGR data to the work of other investigators. One study of particular interest is that of Totsuka,¹⁰ since this work evaluated the SCC response of Alloy 600 as a function of aqueous hydrogen level at two different temperatures.⁽¹⁾ As shown in Figure 7, the SCC susceptibility exhibited a maximum at both temperatures, though the location of the susceptibility maximum changed from approximately 33 scc/kg H₂ at 360°C to approximately 11 scc/kg H₂ at 320°C. The fact that the maximum in SCC susceptibility appears to reside at a lower hydrogen concentration at the lower temperature is qualitatively consistent with the view that proximity to the Ni/NiO phase transition is a key

⁽¹⁾ The work of Totsuka *et al.*¹⁰ was performed using constant extension rate test (CERT) specimens, so the crack growth rates reported in these tests may be influenced by a finite crack incubation time. The specimens used by Totsuka *et al.*¹⁰ contain a significant amount of cold work due to cold pressing of the flat tensile specimens on a die.

factor in the hydrogen dependency of PWSCC. Quantitatively, the location of the measured phase transition at 360°C (25 scc/kg H₂) and at 320°C (~ 8 scc/kg H₂) is also in good agreement with the data of Totsuka *et al.*

Lee *et al.*²⁷ showed that Alloy 600 exhibits a maximum in SCC susceptibility at ~ 8 to 17 scc/kg H₂ at 330°C. Thus, the location of the SCC susceptibility maximum in their work is very similar to the location of the measured Ni/NiO phase transition, which is ~ 11 scc/kg H₂ at 330°C (Figure 3). In their work, the magnitude of the effect was slightly higher (~ 4.3x), as compared to ~ 2.8x reported in reference 4 for Alloy 600.

Alloy X-750 Condition AH at 316°C: Prior work⁴ on Alloy X-750 AH was conducted at 338°C at an initial K_I value of 27.5 MPa√m. As described in Reference 4, a correlation was developed for the SCCGR of Alloy X-750 AH, using the parameter $EcP_{Ni/NiO} - EcP$. Similar to the situation discussed above for Alloy 600, it is important to investigate whether this correlation extrapolates correctly to lower temperatures. Figure 8 shows SCCGR data for Alloy X-750 AH. The circular symbols represent the prior data⁴, which was generated at 338°C. The diamond symbols are new data generated at 316°C, at hydrogen levels of 2, 10, and 60 scc/kg H₂. In terms of the magnitude of the H₂ effect at 316°C, the SCCGR at 2 scc/kg H₂ (1.6 mils/day) is ~ 6.7x greater than the SCCGR measured at 60 scc/kg H₂ (0.24 mils/day). Thus, the magnitude of the H₂ effect is similar to that reported at 338°C (~ 7.2x).⁴ As was observed previously,⁴ the maximum in SCC susceptibility for Alloy X-750 AH resides slightly into the nickel oxide regime. It is speculated¹⁵ that this result may be due to the fact that the oxide near the crack tip in Alloy X-750 AH tends to be (Ni,Nb,Ti)O, in contrast to the cubic NiO structure (*i.e.*, (Ni,Cr,Fe)O) often found as the crack tip oxide in Alloys 600 and X-750 HTH. Overall, the data sets are in good agreement, and the correlation developed for X-750 AH based on testing at 338°C is also appropriate for the 316°C data.

EN82H Weld Metal at 338°C: It was shown previously²¹ using a limited data set that the hydrogen functionality of EN82H SCCGR is qualitatively consistent with the behavior observed for other nickel-based alloys. Specifically, for tests conducted at 338°C, faster SCCGRs were obtained at 20 scc/kg H₂ than at 40 scc/kg H₂ using the same heat of weld material. Since the measured Ni/NiO phase transition at 338°C is 13.8 scc/kg H₂, the data are consistent with the observation that SCCGRs tend to increase as the phase transition is approached. However, insufficient data were available in that study to quantitatively evaluate the effect of hydrogen on the SCCGR of EN82H.

In the present work, testing was conducted at 338°C, at an initial K_I value of 38.5 MPa√m. As shown in Figure 9, EN82H exhibits the typical maximum in PWSCC susceptibility at an intermediate hydrogen level. In this case, the maximum in SCCGR was measured at 8 scc/kg H₂. This value is in close proximity to the measured Ni/NiO phase transition at 338°C (*i.e.*, 13.8 scc/kg H₂). The magnitude of the H₂ effect is quite significant for EN82H. In fact, the SCCGR at 8 scc/kg H₂ is ~ 8.1x higher than at 60 scc/kg H₂, which is well into the nickel metal regime. Note that the data are normalized to the SCCGR at 60 scc/kg H₂ (0.21 mils/day) rather than to the SCCGR at 120 scc/kg H₂, since there is less confidence in the latter data point due to a lesser amount of SCC extension during the test.

In Figure 10, the SCCGR data are correlated using the electrochemical potential of each data point relative to the EcP of the nickel/nickel oxide phase transition. Note that the data point for the nitrogen-deaerated condition (~ 0.1 scc/kg H₂) was normalized using an EcP value obtained from the yttria-stabilized zirconia/iron-iron oxide electrode. The correlation reasonably describes the data, and the maximum is located slightly (~ 10 mV) into the nickel oxide regime. The EN82H SCCGR-H₂ correlation is provided in Table 5. This correlation, in combination with the updated thermodynamic model for the Ni/NiO phase transition described earlier, can be used to extrapolate the EN82H SCCGR-H₂ effects over a relatively wide range of temperatures (*e.g.*, 260 to 360°C).

Construction of plots using the $EcP_{Ni/NiO} - EcP$ Scale: Details for how to calculate the potential difference used in the x-axis of Figure 7 are provided in Reference 20. Briefly, the Nernst equation can be used to demonstrate that:

$$EcP_{Ni / NiO} - EcP = 1000 \cdot \frac{RT}{2F} \cdot \ln \left(\frac{[H_2]_{test}}{[H_2]_{Ni / NiO}} \right) - (EcP_{Ni-alloy} - EcP_{Pt}) \quad [5]$$

where R and T have been defined previously, F is Faraday's constant (96,500 C/eq), $[H_2]_{test}$ is the test hydrogen concentration, and $[H_2]_{Ni/NiO}$ is the hydrogen concentration of the Ni/NiO phase transition (see Figure 3). In equation [5], ΔEcP was improved by subtracting the measured specimen-to-Pt EcP measurement (*i.e.*, $EcP_{Ni-alloy} - EcP_{Pt}$).

This modification corrects the specimen EcP for deviations from that of a true hydrogen electrode. This correction can become appreciable at hydrogen concentrations less than ~ 5 scc/kg,^{3,4,20} as shown in Figure 11, which summarizes EcP – EcP_{Pt} data for nickel and nickel-based alloys at several temperatures. This plot²⁰ has been updated to include EcP data for EN82H at 338°C, Alloys 600 and X-750 AH at 316°C, and nickel at 260°C. In general, all of these materials exhibit hydrogen electrode behavior above ~ 5 scc/kg H₂. Below this value, the nickel alloys tend to exhibit reducing potentials relative to platinum. At high hydrogen levels, the dominant anodic reaction on both platinum and nickel alloys is hydrogen oxidation, and thus all of the metals exhibit hydrogen electrode behavior. It is believed that at relatively low hydrogen levels, the corrosion reaction on the nickel alloys becomes significant, and a mixed potential develops. This issue is discussed in detail elsewhere.²⁰

The practical consequence of this result is that for $[H_2] > 5$ scc/kg, the Nernst equation for a hydrogen electrode is an excellent approximation of the EcP of a nickel alloy. However, below this point, the EcP of the material of interest should be measured relative to platinum if at all possible. In cases where one wishes to calculate ΔEcP using equation [5] but EcP – EcP_{Pt} data are unavailable, the empirical fit in Figure 11 can be used to estimate the deviation of the nickel alloys from hydrogen electrode behavior. Regression to the nickel alloy data yielded the following:

$$EcP_{Ni-alloy} - EcP_{Pt} \text{ (mV)} = 21.1 \cdot \ln[H_2] - 37.4 \quad [H_2] < 5 \text{ scc / kg} \quad [6a]$$

$$EcP_{Ni-alloy} - EcP_{Pt} \text{ (mV)} = -3.5 \text{ mV} \quad [H_2] \geq 5 \text{ scc / kg} \quad [6b]$$

One interesting observation, as made previously²⁰, is that for nickel, hydrogen electrode behavior seems to persist to lower H₂ levels than for the nickel alloys. It is not unreasonable to expect some differences in EcP behavior given the different elemental composition, corrosion behavior and oxides formed on nickel compared to the nickel alloys. Specifically, this result may be attributable to the absence of elements more electrochemically active than Ni (e.g., Fe, Cr) in the pure nickel specimens, since the standard potential for Ni is very close to that of a hydrogen electrode.

Updated SCCGR-Hydrogen Correlations

As was performed in Reference 4, a set of phenomenological correlations for the SCCGR-H₂ functionality were developed using the fundamental independent parameter ΔEcP and a symmetric exponential function:

$$\frac{SCCGR}{SCCGR_{min}} = \left(\frac{SCCGR_{max}}{SCCGR_{min}} \right) \cdot \exp \left(-0.5 \cdot \left[\frac{\Delta EcP + \Delta EcP_o}{\lambda} \right]^2 \right) \quad [6]$$

where $SCCGR_{max}/SCCGR_{min}$ is the ratio of the observed maximum to minimum crack growth rate for a given material. This ratio describes the magnitude of the SCCGR-H₂ effect for a specific material (e.g., $\sim 8.1\times$ for EN82H, as shown in Figure 10). ΔEcP is the distance of the condition of interest from the Ni/NiO phase transition, calculated via equation [5]. ΔEcP_o is a fitted parameter which describes the extent to which the maximum crack growth rate is offset from $\Delta EcP = 0$ (i.e., the location of the Ni/NiO phase transition). λ is another fitting parameter, which describes the breadth of the SCCGR vs. ΔEcP peaks. Values for ΔEcP_o and λ were obtained by linear regression analysis of a linearized version of equation [6]. Resulting values of ΔEcP_o and λ are given in Table 6 for EN82H weld material, wrought Alloy 600, Alloy X-750 HTH, and Alloy X-750 AH. Note that the correlations provided in Reference 4 have been updated to reflect the new Ni/NiO correlation shown in Figures 3 and 4.

The correlations generated in the present study can be extended to a three-dimensional basis (SCCGR-H₂-T) through the use of appropriate thermal activation energy (Q_{SCCGR}) values. Figure 12 shows a 3-D plot of the EN82H correlation in temperature-hydrogen-SCCGR space. This plot was constructed using a Q_{SCCGR} value of 130 kJ/mole, which has been shown to be a reasonable value for Alloy 600 weld metal.^{21,28,29} Henry's law coefficients from Table 4 were used to construct this plot, and an additional temperature (349°C) was added to make the plot more readable.

Mitigation

The present study shows that SCC can be mitigated by adjusting the aqueous hydrogen level and temperature such that the condition of interest resides far from the Ni/NiO phase transition. In a single-temperature situation, this condition can be achieved by adjusting the aqueous hydrogen level such that it is either significantly higher or significantly lower than $[H_2]_{Ni/NiO}$ at the temperature of interest. In a multi-temperature system, it is important that the hydrogen level to mitigate SCC be selected such that it does not minimize SCC for one temperature but accelerate it at another. Reducing hydrogen to relatively low levels (*i.e.*, $[H_2] \ll [H_2]_{Ni/NiO}$) may be a viable approach in some cases, though there are some issues to consider. For example, the SCC benefit must be balanced with the need to maintain a reducing condition to minimize overall corrosion of plant materials. In a case such as that of EN82H, the mitigation range appears to be much more narrow at low hydrogen concentrations than at high hydrogen concentrations. Also, as observed in Figure 11, due to the nature of the temperature-dependence of the Ni/NiO phase transition, there is a much wider hydrogen space available on the nickel metal side of the phase transition than on the nickel oxide side of the transition as the temperature of interest decreases. Thus, while adjusting to low hydrogen levels may be beneficial in some cases, the authors believe that there are more advantages to adjusting the hydrogen level to higher levels.

An Illustration of the Benefits of Modifying the H_2 Level: Figure 12 can be used to quantitatively demonstrate the benefit of higher hydrogen levels for SCC mitigation. Specifically, if one postulates an initial condition of 25 scc/kg H_2 at 325°C (point A in Figure 11), the calculated SCCGR for EN82H is 0.39 mils/day. If one were to isothermally adjust the hydrogen level to 50 scc/kg H_2 (point B), the calculated SCCGR is 0.11 mils/day, which represents a decrease of $\sim 3.5\times$. This benefit is significant, as can be seen by comparing the temperature reduction that would be needed to produce a similar benefit. Using a thermal activation energy of 130 kJ/mole,^{21,28,29} the temperature would have to be reduced from 325°C to 297°C (point C) to decrease the SCCGR by a factor of 3.5x. This example illustrates the concept that adjusting the hydrogen level has the possibility of reducing SCC similar to that of a significant reduction in temperature. Adjusting H_2 may be more practical in many cases than reducing temperature.

Note that while all of the data discussed herein refer to crack growth, a similar H_2 functionality has been shown for the CERT specimens of Totsuka *et al.*,¹⁰ which include both initiation and growth. Thus, on the basis of Figure 7, it is expected that adjusting the H_2 level to mitigate crack growth would not have an adverse effect on SCC initiation.

Fundamental Understanding

The understanding of aqueous hydrogen effects has been greatly advanced by the recognition of the role of the Ni/NiO phase transition, and by the quantification of the location of the phase transition. It is well-known in SCC of many metal-environment systems that cracking propensity can be high in the region near an oxide phase transition, presumably due to the metastability of oxides. However, important questions remain. The specific changes in the oxide composition or in the corrosion tendency of the material as the phase transition is approached are not known with certainty. It is reasonable to believe that as one moves further into the nickel metal regime, oxides may become more chromium-rich and hence more protective. It is not as clear why SCC susceptibility decreases at very low hydrogen levels.

Also, it is not evident why each material exhibits an apparently different magnitude of the aqueous hydrogen effect. The magnitude of the hydrogen effect does not appear to correlate with overall SCC susceptibility, yield strength, chromium concentration, grain size, or many other typical material parameters. One aspect of these materials that might play a role is the differing grain boundary carbides experienced in different nickel-based alloys. Specifically, Alloy X-750 HTH tends to contain $Cr_{23}C_6$ carbides, Alloy X-750 AH contains (Nb,Ti)C carbides, Alloy 600 contains Cr_7C_3 carbides, and EN82H tends to contain both $Cr_{23}C_6$ and NbC carbides. It is possible that grain boundary carbide type influences the oxides formed, localized corrosion, and/or hydrogen recombination within SCC cracks. Further study is needed to resolve the issue of what phenomena give rise to the differing magnitudes of the SCCGR- H_2 effect for the various nickel-based alloys.

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Table 1. EN82H Material Composition (in weight percent).

Ni+Co	Co	Cr	Fe	C	Mn	S	Si	Cu	Pb	Ti	Nb+Ta	Ta	P
71.0	N/A	21.8	0.64	0.04	3.05	0.003	0.10	0.04	0.003	0.49	2.5	0.07	0.002

Table 2. Film formation and reduction data measured via CER testing using a nickel specimen at 260 °C.

Test #	Temperature	Autoclave Pressure (psig)	Test Phase	Dissolved H ₂ level (scc/kg)	EcP vs. Pt (V)	Time interval (hours)	Result
Ni-260	260°C	1000	Ni-260.1	60	-0.003	0 to 47	No film formation
			Ni-260.2	30	-0.001	47 to 384	No film formation
			Ni-260.3	5	+0.001	384 to 838	No film formation
			Ni-260.4	2	+0.001	838 to 984	No film formation
			Ni-260.5	1	+0.001	984 to 1462	Film formation
			Ni-260.6	3	N/A	1462 to 1516	Film reduction

Table 3. Nickel oxidation and reduction data measured via CER testing using an Alloy 600 specimen at 316 °C.

Test #	Temperature	Autoclave Pressure (psig)	Test Phase	Dissolved H ₂ level (scc/kg)	Time interval (hours)	Results
A600-1	316°C	3000	A600-1.1	60	0 to 90	Initial oxide growth
			A600-1.2	20	90 to 165	
			A600-1.3	10	165 to 330	Steady-state resistance established
			A600-1.4	5	330 to 478	Significant oxidation
			A600-1.5	10	478 to 666	Significant reduction

Table 4. Hydrogen Fugacity Data at 260 °C (1800 psi autoclave pressure) using a Silver-Palladium Tube.

Target H ₂ concentration	Henry's law coefficient ²³	Calculated H ₂ Pressure	Measured H ₂ Pressure ²⁸	Error
60 scc/kg	0.016 atm./(scc/kg)	0.960 atm.	0.932 atm.	3.0 %
30 scc/kg	0.016 atm./(scc/kg)	0.480 atm.	0.459 atm.	4.6 %
5 scc/kg	0.016 atm./(scc/kg)	0.080 atm.	0.078 atm.	2.6 %
1 scc/kg	0.016 atm./(scc/kg)	0.016 atm.	0.017 atm.	5.9 %

Table 5. Summary data for the measured Ni/NiO phase transition, plus the predictions using the thermodynamic model.

Autoclave Conditions		Henry's law coefficient ²³ (atm./(scc/kg))	Measured Phase Transition		Predicted Phase Transition using Thermodynamic Model	
T (°C)	P (psi)		H ₂ Concentration Basis (scc/kg)	H ₂ Fugacity Basis (atm.)	H ₂ Concentration Basis (scc/kg)	H ₂ Fugacity Basis (atm.)
260	1000	0.0160	2	0.0320	2.0	0.0324
288	1500	0.0122	4	0.0488	4.1	0.0497
316	3000	0.0101	7.5	0.0758	7.3	0.0733
338	3000	0.0072	13.8	0.0994	13.5	0.0975
360	3200	0.0049	25	0.1225	25.9	0.1271

Table 6. SCCGR-H₂ Correlations

Test Material and Condition	$\frac{SCCGR_{max}}{SCCGR_{min}}$	ΔEcP_e	λ	Range of Applicability [†]
EN82H, 338°C	8.09	10.5	20.2	- 52 mV < ΔEcP < 31 mV
Alloy 600, 338°C	2.81	-10.2	35.6	- 41 mV < ΔEcP < 61 mV
Alloy X-750 HTH, 360°C	4.89	4.2	20.4	- 41 mV < ΔEcP < 32 mV
Alloy X-750 AH, 338°C	7.19	30.8	40.0	- 110 mV < ΔEcP < 49 mV

[†] The SCCGR effect of dissolved H₂ seems to have an appreciable influence in a narrow range of EcP near the Ni/NiO phase transition.

Figure 5. CER data using an Alloy 600 specimen at 316°C.

Figure 3. Summary of CER and corrosion coupon data. $[H_2]_{trans}$ is the phase transition in scc/kg. T_K is the temperature in Kelvin and k_H is the Henry's law coefficient in atm/(scc/kg).

Figure 1. Schematic illustration of CER setup. The upper specimen is Ir, and the lower specimen is Ni or Alloy 600.

Figure 6. SCCGRs for Alloy 600 at 338°C (■) and 316°C (▲).

Figure 4. Thermodynamic model of the Ni/NiO transition.

Figure 2. CER data using a nickel specimen at 260°C.

Figure 7. Alloy 600 CERT data from Totsuka et al.¹⁰

Figure 8. SCCGRs for Alloy X-750 AH at 338 °C (●) and 316 °C (▲). The minimum SCCGR values are 0.64 mils/day and 0.24 mils/day.

Figure 9. SCCGRs for EN82H at 338 °C. The measured Ni/NiO transition at 338 °C is 13.8 scc/kg H_2 .

Figure 10. Normalized data for EN82H on a ΔEcP basis. SCCGRs are normalized to a minimum value of 0.21 mils/day (at 60 scc/kg). The value for 120 scc/kg is not used due to uncertainty.

Figure 11. EcPs of Ni and Ni-alloys relative to platinum.

Figure 12. 3-D plot of EN82H SCCGR correlation and data. Contours are shown at 260, 288, 316, 338, 349, and 360 °C.