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Measurement of the Nickel/Nickel Oxide Phase Transition in High Temperature Hydrogenated Water Using the Contact Electric Resistance (CER) Technique

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Abstract

Prior studies of Alloy 600 and Alloy X-750 have shown the existence of a maximum in stress corrosion cracking (SCC) susceptibility in high temperature water (*e.g.*, at 360°C), when testing is conducted over a range of dissolved (*i.e.*, aqueous) hydrogen (H_2) concentrations. It has also been shown that this maximum in SCC susceptibility tends to occur in proximity to the nickel/nickel oxide (Ni/NiO) phase transition, suggesting that oxide phase stability may affect primary water SCC (PWSCC) resistance. Previous studies have estimated the Ni/NiO transition using thermodynamic calculations based on free energies of formation for NiO and H_2O . The present study reports experimental measurements of the Ni/NiO transition performed using a contact electric resistance (CER) instrument. The CER is capable of measuring the surface resistance of a metal to determine whether it is oxide-covered or oxide-free at a given condition. The transition aqueous hydrogen (H_2) concentration corresponding to the Ni/NiO equilibrium was measured at 288, 316, 338 and 360°C using high purity Ni specimens. The results showed an appreciable deviation (*i.e.*, 7 to 58 scc H_2 /kg H_2O) between the measured Ni/NiO transition and the theoretical Ni/NiO transition previously calculated using free energy data from the Journal of Solution Chemistry. The CER-measured position of the Ni/NiO transition is in good agreement with the maxima in PWSCC susceptibility at 338 and 360°C. The measured Ni/NiO transition provides a reasonable basis for estimating the aqueous H_2 level at which the maximum in SCC susceptibility is likely to be observed at temperatures lower than 338 to 360°C, at which SCC tests are time-consuming to perform. Limited SCC data are presented which are consistent with the observation that SCC susceptibility is maximized near the Ni/NiO transition at 288°C.

Introduction

Extensive testing conducted at various aqueous H_2 levels and temperatures (*e.g.*, 338, 360 and 399°C) has shown that a maximum in PWSCC susceptibility exists for nickel-based alloys in proximity to the Ni/NiO equilibrium.¹⁻⁵ The theory that the stability of NiO influences PWSCC is supported by analytical electron microscopy (AEM) 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.⁶ Spinel structure oxides have also been observed at the crack tip in some cases.⁷

Thermodynamic properties have been used in prior work to predict the stability domains of Ni and NiO at different aqueous H_2 levels.^{1,3,8} Changing the aqueous H_2 level can stabilize or destabilize NiO, consistent with LeChatelier's Principle. This effect is due to the reaction between NiO and H_2 (*i.e.*, $NiO + H_2 = Ni + H_2O$). Calculations indicate that the amount of H_2 required to reduce NiO to Ni increases as the temperature is increased. Since the accuracy of theoretical predictions is limited by uncertainties in thermodynamic properties such as free energies of formation, there is a benefit to experimentally evaluating film stability regimes using an instrument such as the CER.

Experimental Procedure

The CER method was first utilized by Marichev⁹, and has been used extensively by Saario and co-workers⁹⁻¹¹ to analyze surface resistance in several metal-environment systems. The CER setup used in the present study employed 2 cylindrical specimens (diameter ~ 2 mm) aligned end-to-end (Figure 1), in an autoclave capable of operating up to 360°C. Nickel (99.5 wt%) was used as a test specimen and Iridium (Ir) was used as an oxide-free inert specimen. The specimens were held apart with a user-adjustable gap (approximately 2.5 μm) and were attached to a mechanism that periodically pressed the specimens into contact and then retracted them to restore the gap. The specimens were contacted every 10 minutes, for a duration of 5 seconds. A shunt resistor (R_2) was placed in parallel with the specimens (Figure 1), and an ohmmeter was used to perform two resistance measurements: (i) specimens out-of-contact, and (ii) specimens in-contact. The difference in measured resistance between the two

Figure 1. Schematic of the CER setup.

positions is ΔR ($\Delta R = |R_{out} - R_{in}|$). Using parallel resistor laws, it can be shown¹¹ that the resistance of the specimen (R_S) is:

$$R_S = \frac{R_2^2}{\Delta R} - R_2 \quad [1]$$

Tests were conducted by varying the H_2 level and measuring R_S vs. time. The CER is particularly effective in distinguishing between film-free and oxide-filmed states, due to the 2-6 order of magnitude difference¹⁰ in resistance between these conditions (it was found in the present work that a 10Ω shunt resistor provides acceptable data at both high and low resistance values). Note that the present study did not aim to measure

absolute film resistance, but rather focused on distinguishing the film-free and oxide-filmed states. This distinction is important, since a concern relative to resistance values measured using the CER is that the actual contact area is unknown due to surface roughness. Thus, absolute resistance values are subject to an error with a magnitude that is difficult to estimate; this error, however, does not affect the utility of the present measurements. Although the performance of the CER system was excellent in most respects, one persistent problem was that as a test progressed, the specimens slowly drifted apart for a reason which is unknown. This issue is relevant because it sometimes led to a slight apparent increase in resistance during a test. This artifact arises when the specimen gap increases and effective specimen contact is diminished. The decreasing contact area is registered as a minor apparent increase in resistance. Fortunately, this specimen drift was readily distinguishable from film growth, since the software permits manual readjustment of the 'home' position of the specimens to the initial gap dimension. Any slight increase in resistance which had occurred due to specimen drift was discernible upon readjusting the 'home' position since a clear decrease in resistance, which appeared as an offset in the resistance versus time data, was observed. The reason for the home position drift is unknown at present, though creep of the zirconium spring is a possible cause.

Testing was conducted in deaerated water buffered to a high temperature pH of ~ 7 . The desired H_2 concentrations 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 coefficient¹² of $0.85 \text{ psia}/(\text{scc}/\text{kg})$, the solubility of hydrogen in water at 25°C (note that an air conditioner was utilized to prevent appreciable changes in ambient temperature in the laboratory). Mixed gas of 4 or 14.7% hydrogen with the balance being argon was used to obtain coolant hydrogen levels less than $20 \text{ scc}/\text{kg } H_2$. Electrochemical corrosion potentials (ECPs) were measured vs. a platinum (Pt) electrode as well as an iron/iron oxide ($\text{Fe}/\text{Fe}_3\text{O}_4$) electrode. Niedrach¹³ has shown that if the pH of the environment is essentially constant and reasonably well known (as is the case for the buffered water used in the present study), the $\text{Fe}/\text{Fe}_3\text{O}_4$ electrode exhibits a unique (and calculable) potential on the standard hydrogen electrode (SHE) scale.

Results and Discussion

Resistance versus time data

The ability of the CER to detect the nucleation and growth of an oxide film is shown in Figure 2. The initial H_2 level in this test was $60 \text{ scc}/\text{kg}$, which was predicted by thermodynamic calculations³ to be in the Ni metal regime at 316°C . Indeed, a very low resistance ($< 0.002 \Omega$) was observed, consistent with values measured by Ehrnsten and Saario¹⁰ for Ni at $30 \text{ scc}/\text{kg}$ at 320°C . From this point, the aqueous H_2 level was decreased incrementally, to determine the H_2 level at which an appreciable increase in resistance (corresponding to oxide formation) occurred. Very low resistances were measured at 60, 20, 15, and $10 \text{ scc}/\text{kg}$ as shown in Figure 2. Although a very minor increase in resistance can be discerned at

Figure 2. Resistance vs. time data at 316°C .

10 scc/kg H_2 , it is strongly suspected that this increase is due to the drifting apart of the specimens, based on the fact that two subsequent tests at 316°C confirmed that no film formation occurred at 10 scc/kg H_2 . (In addition, it has been observed that during film growth, the rate of increase in resistance with time is far greater than that corresponding to the minor increase at 10 scc/kg H_2 in Figure 2.) Reducing the H_2 level from 10 to 5 scc/kg led to an increase in resistance of more than two orders of magnitude, initiating within ~ 5 hours after the reduction in H_2 level. The observation of a dramatic increase in resistance upon transitioning from a film-free to a film-covered state is consistent with prior work by Ehrnsten and Saario¹⁰. Although the maximum resistance values attained in Figure 2 (~ 0.1 to 0.2 Ω) are somewhat lower than the values of ~ 5 to 20 Ω previously observed¹⁰ for the film-covered condition, the resistance values in Figure 2 still appeared to be increasing when the test was terminated prematurely due to system problems. A subsequent test was conducted at 316°C, as shown in Figure 3, in which the film was permitted to grow to an essentially steady-state resistance of ~ 3 to 10 Ω . This test was conducted by sparging with nitrogen (N_2) rather than H_2 , which is the same condition at which Ehrnsten and Saario¹⁰ measured ~ 5 to 20 Ω .

Figure 3. Resistance vs. time data at 316°C.

Five separate tests conducted at 316°C demonstrate that a dramatic increase in resistance, attributed to the formation of an oxide film, was reproducibly obtained at the 5 scc/kg H_2 condition. Thus, it can be stated with confidence that this condition resides in the NiO stability regime. However, it is more difficult to assess the situation at 10, 15, and 20 scc/kg H_2 . Although no apparent film formation occurred at these conditions in the test shown in Figure 2, it is not clear whether an oxide film would have formed under these conditions if the test had been conducted for a longer duration at each condition. For this reason, two criteria were applied before rendering a judgement that a particular H_2 /temperature condition resides in the Ni stability regime: (i) when starting with a film-free surface, a very low resistance (< 0.002 Ω) must be measured at the condition of interest, implying that film formation had not occurred, and (ii) an existing or a growing oxide film must exhibit reduction at the condition of interest. This concept is illustrated in Figure 4 (a), which shows a test conducted at 316°C. A low resistance typical of a film-free state is obtained at 40 scc/kg H_2 . The hydrogen level was subsequently decreased to 5 scc/kg at 119 hours. This decrease is registered by the electrochemical potential data in Figure 4 (b), where the corrosion potential (E_{corr}) for both Pt and Ni increases with respect to the Fe/Fe₃O₄ electrode, consistent with expectations for a reduction in H_2 level.

At the 5 scc/kg H_2 condition, a very clear increase in resistance (~ 1 order of magnitude) is obtained, implying that oxide film growth is occurring. At 365 hours, shortly after an adjustment in the home position, the hydrogen level was increased to 15 scc/kg. This increase in aqueous H_2 level is registered by a decrease in E_{corr} for both Pt and Ni as shown in Figure 4 (b). An immediate and very clear decrease in resistance is obtained. These data imply that at 316°C, 15 scc/kg H_2 resides in the Ni regime.

Figure 4. Resistance (a) and ECP (b) data at 316°C.

Resistance data obtained in this study are shown in Table 1. As stated previously, film formation was observed at 5 scc/kg H_2 in five separate tests at 316°C (i.e., test # 4, 6, 7, 8 and 9), implying that this condition corresponds to the

NiO regime. However, film formation was not observed at 10 scc/kg in three separate tests at 316°C, and partial reduction of a growing film was also observed at 10 scc/kg at 316°C, as shown in Figure 5, implying that this condition corresponds to the Ni regime. It should be noted that for certain cases (as indicated in Table 1 and illustrated by Figure 5 (a)), a partial but not complete reduction of an existing or growing film was observed. In this case, a judgement was made that if a clear and immediate decrease in resistance was evident upon transitioning to a given H₂ level and if no film formation was observed at the same H₂ level, that this condition was judged to be in the Ni regime. One reassuring aspect of this judgement is that when film formation was noted, the increase in resistance was typically evident within several hours. In fact, the data in Figure 4 (a), in which ~ 50 to 100 hours elapsed between the change in aqueous H₂ level and the initial increase in resistance, represents by far the slowest film formation events observed in this study. In nearly every other test, less than 10 hours was needed between the change in aqueous H₂ level and the observation of the initial increase in resistance (see Figures 2, 3, 5 and 6). Thus, although the reduction of the growing oxide was not complete at 10 scc/kg H₂ at 316°C, it is judged that this condition corresponds to the Ni regime since no film formation was evident for three separate tests conducted for 92, 101 and 172 hours at this condition (Table 1). Thus, at 316°C, the Ni/NiO transition is estimated as 7.5 ± 2.5 scc/kg H₂.

Figure 5. Resistance (a) and ECP (b) data at 316°C.

Data at 338°C are shown in Figure 6 (a). Very low resistance values indicative of a film-free condition are evident at 40, 19 and 15 scc/kg H₂. A significant increase in resistance, indicative of film formation, was noted at 10 scc/kg H₂, with the increase initially occurring about 7 hours after the H₂ level was reduced from 15 to 10 scc/kg. At 283 hours, the H₂ level was increased to 15 scc/kg; note again that this increase was registered by the E_{corr} data as shown in Figure 6 (b). An immediate and very clear decrease in resistance was obtained. A subsequent increase in H₂ level to 19 scc/kg appeared to cause little if any additional film reduction. These data indicate that at 338°C, 10 scc/kg H₂ resides in the NiO regime while 15, 19 and 40 scc/kg reside in the Ni regime. It is noted in Figure 6 (a) that the final resistance value after film formation and reduction was slightly greater than the initial resistance value. However, the final resistance value was extremely low ($< 0.002 \Omega$) and this condition is thus judged to represent complete reduction. This phenomenon was commonly observed, though the reason is not known. It can be speculated that roughening of the surface by corrosion during oxide formation may have led to a decrease in the contact area and a subsequent apparent increase in resistance after the oxide formation and reduction process, though no data are available to confirm this hypothesis.

Figure 6. Resistance (a) and ECP (b) data at 338°C.

Table 1. Film formation and reduction data measured via CER testing.

Test #	T (°C)	Test Phase	Dissolved H ₂ level (scg/kg)	ECP _{Ni} vs. Fe/Fe ₃ O ₄ (V)	ECP _{Ni} (V _{SHE}) ^[1]	ECP _{Fe} vs. Fe/Fe ₃ O ₄ (V)	ECP _{Fe} (V _{SHE}) ^[1]	Calculated H ₂ fugacity (atm) ^[3]	Time interval (hours)	Result
1	288	1.1	19	0.196	-0.720	N/A ^[2]	N/A ^[2]	0.20	0 to 19	No film formation
		1.2	10	0.211	-0.705	0.215	-0.701	0.11	19 to 92	No film formation
		1.3	5	0.227	-0.689	N/A ^[2]	N/A ^[2]	0.05	92 to 163	No film formation
		1.4	3	0.234	-0.682	0.236	-0.680	0.03	163 to 433	Film formation
		1.5	5	0.223	-0.693	0.224	-0.692	0.05	433 to 623	Film reduction ^[4]
		1.6	10	0.209	-0.707	0.210	-0.706	0.11	623 to 810	Film reduction
2	288	2.1	10	0.208	-0.708	0.208	-0.708	0.11	0 to 144	No film formation
		2.2	N ₂ sparge	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A	144 to 164	Film formation
		2.3	5	0.220	-0.696	0.219	-0.697	0.05	164 to 335	Film reduction
3	316	3.1	60	0.193	-0.756	0.197	-0.752	0.43	0 to 116	No film formation
		3.2	40	0.203	-0.746	0.206	-0.743	0.29	116 to 194	No film formation
		3.3	30	0.211	-0.738	0.212	-0.737	0.22	194 to 282	No film formation
		3.4	25	0.214	-0.735	0.216	-0.733	0.18	282 to 479	No film formation
4	316	4.1	60	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.43	0 to 137	No film formation
		4.2	20	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.14	137 to 497	No film formation
		4.3	15	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.11	497 to 643	No film formation
		4.4	10	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.07	643 to 815	No film formation
		4.5	5	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.04	815 to 1054	Film formation
5	316	5.1	40	0.200	-0.749	0.203	-0.746	0.29	0 to 169	No film formation
		5.2	20	0.216	-0.733	0.218	-0.731	0.14	169 to 239	No film formation
6	316	6.1	20	N/A	N/A	N/A	N/A	0.14	0 to 148	No film formation
		6.2	15	0.223	-0.726	0.225	-0.724	0.11	148 to 215	No film formation
		6.3	10	0.231	-0.718	0.234	-0.715	0.07	215 to 316	No film formation
		6.4	5	0.246	-0.703	N/A ^[2]	N/A ^[2]	0.04	316 to 364	Film formation
		6.5	20	0.215	-0.734	N/A ^[2]	N/A ^[2]	0.14	364 to 391	Film reduction
7	316	7.1	20	0.216	-0.733	0.218	-0.731	0.14	0 to 22	No film formation
		7.2	10	0.231	-0.718	0.234	-0.715	0.07	22 to 114	No film formation
		7.3	5	0.245	-0.704	0.249	-0.700	0.04	114 to 451	Film formation
		7.4	10	0.231	-0.718	0.236	-0.713	0.07	451 to 555	Film reduction ^[4]
8	316	8.1	40	0.203	-0.746	0.207	-0.742	0.29	0 to 119	No film formation
		8.2	5	0.246	-0.703	0.251	-0.698	0.04	119 to 365	Film formation
		8.3	15	0.222	-0.727	0.227	-0.722	0.11	365 to 600	Film reduction
9	316	9.1	15	0.222	-0.727	0.228	-0.721	0.11	0 to 141	No film formation
		9.2	5	0.247	-0.702	0.252	-0.697	0.04	141 to 241	Film formation
		9.3	10	0.233	-0.716	0.238	-0.711	0.07	241 to 358	Film reduction ^[4]
10	316	10.1	25	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.18	0 to 11	No film formation
		10.2	20	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.14	11 to 13	No film formation
		10.3	N ₂ sparge	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A	13 to 17	Film formation
		10.4	20	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.14	17 to 21	Film reduction ^[4]
		10.5	30	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.22	21 to 27	Film reduction
11	338	11.1	40	0.222	-0.768	0.224	-0.766	0.20	0 to 162	No film formation
		12.1	40	0.222	-0.768	0.223	-0.767	0.20	0 to 67	No film formation
12	338	12.2	19	0.238	-0.752	0.238	-0.752	0.10	67 to 114	No film formation
		12.3	15	0.246	-0.744	0.247	-0.743	0.08	114 to 234	No film formation
		12.4	10	0.255	-0.735	0.256	-0.734	0.05	234 to 283	Film formation
		12.5	15	0.245	-0.745	0.249	-0.741	0.08	283 to 453	Film reduction
		12.6	19	0.238	-0.752	N/A ^[2]	N/A ^[2]	0.10	453 to 479	Film reduction
13	360	13.1	90	0.219	-0.829	0.222	-0.826	0.31	0 to 161	No film formation
		13.2	30	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.10	161 to 209	No film formation
		13.3	20	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.07	209 to 235	Film formation
		13.4	30	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.10	235 to 353	Film reduction ^[4]
		13.5	35	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.12	353 to 423	Film reduction ^[4]
		13.6	40	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.14	423 to 495	Film reduction ^[4]
		13.7	60	N/A ^[2]	N/A ^[2]	N/A ^[2]	N/A ^[2]	0.21	495 to 530	Film reduction ^[4]

[1] ECP data were converted from the Fe/Fe₃O₄ scale to the SHE scale by subtracting 0.916, 0.949, 0.990 and 1.048 Volts at 288, 316, 338 and 360 °C, respectively. These values were calculated using the Nernst equation and thermodynamic data from Zienniak¹².

[2] Data not available (N/A) due to failure of the Fe/Fe₃O₄ reference electrode, or because a steady-state potential was not reached.

[3] Calculated using Henry's Law coefficients of 1.06×10^{-2} , 7.19×10^{-3} , 5.08×10^{-3} and 3.47×10^{-3} atm/(scg/kg) at 288, 316, 338 and 360 °C.¹²

[4] Film reduction definitely occurred, but the reduction was not complete (i.e., the final resistance was somewhat higher than prior to film formation), at least in the time allotted for that phase of the test.

Data at 288°C are shown in Table 1. No film formation was observed down to 5 scc/kg H₂. Film formation was evident at 3 scc/kg H₂, though the rate of increase in resistance was slower than that shown in Figures 2 to 6. Partial reduction occurred upon switching back to 5 scc/kg H₂ and complete reduction was observed at 10 scc/kg H₂. In the next test, a film was formed at a N₂ sparge condition and full reduction was observed at 5 scc/kg H₂. Thus, the Ni/NiO transition at 288°C resides at ~ 4 scc/kg H₂. Data at 360°C are shown in Table 1. Film formation was evident at 20 scc/kg H₂. Reduction occurred at 30 scc/kg H₂, though the reduction was not complete. The Ni/NiO transition is judged to reside at 25 scc/kg H₂ at 360°C. However, note that since this test has not been replicated, the Ni/NiO transition at 360°C is less definite than for the other temperatures at which more testing has been conducted.

Verification using corrosion coupons and x-ray diffraction

The results obtained from the CER were spot-checked using corrosion coupon exposure. A nickel coupon was exposed to 20 scc/kg H₂ at 338°C for 10 days. As shown in Figure 7, the coupon was essentially film-free after exposure to this autoclave environment, verifying that this condition does indeed reside on the Ni side of the Ni/NiO transition. A second nickel coupon was exposed in a different autoclave to the same nominal conditions (20 scc/kg H₂ at 338°C), for 10.7 days, for the purposes of replication. Again, the coupon was essentially film-free after exposure. It is noted that the corrosion coupon data and the CER data at this condition are complementary. Specifically, the coupon data verified the absence of oxide after autoclave exposure to 20 scc/kg H₂ at 338°C for ~ 10 days, but these data alone do not resolve the question of whether an oxide might form during a longer exposure time. However, the fact that the CER showed reduction of a growing oxide at 15 scc/kg H₂ provides additional strong evidence that 20 scc/kg H₂ is indeed located in the Ni regime at 338°C. An Alloy 600 coupon was placed in the autoclave for the test conducted at 20 scc/kg H₂ and 338°C for 10.7 days. This coupon, as shown in Figure 7, clearly exhibited film formation during the exposure. This data point proves that the autoclave exposure time (~ 10 days) is sufficiently long to cause film formation, at least on a Ni-Cr-Fe alloy (i.e., Alloy 600). Note, though, that the film on Alloy 600 is a spinel structure oxide (i.e., Ni₃Fe_{1-x}Cr₂Fe_{2-y}O₄) as opposed to nickel oxide.

Figure 7. Ni coupon (upper specimen) and Alloy 600 coupon (lower specimen) exposed to 338 °C at 20 scc/kg H₂ for 10 days.

Another nickel coupon was exposed to 12.5 scc/kg H₂ at 338°C for 63 days. As shown in Figure 8, this coupon was covered with oxide, though it is noted that visually the oxide appeared to be lighter in color (and thus, likely thinner) than oxides typically observed after autoclave exposure. Thus, the 12.5 scc/kg H₂ condition at 338°C is judged to reside just slightly into the NiO regime, and the Ni/NiO transition at 338°C is estimated as 13.75 ± 1.25 scc/kg H₂. Note that no resistance versus time data are available for the 12.5 scc/kg H₂ condition at 338°C; the data in Figure 6 imply that 10 scc/kg H₂ is in the NiO regime and 15 scc/kg H₂ is in the Ni regime at 338°C but provide no information as to the expectation for the 12.5 scc/kg H₂ condition. The oxide observed on the coupon exposed to 12.5 scc/kg H₂ at 338°C was examined via x-ray diffraction and was found to consist of cubic nickel oxide (NiO).

Figure 8. Ni coupon exposed to 338 °C at 12.5 scc/kg H₂ for 63 days.

Subsequently, one piece of the Ni specimen referred to above (exposed to 12.5 scc/kg H₂ at 338°C for 63 days) was re-exposed at 20 scc/kg H₂ at 338°C for 10.7 days. As shown in Figure 9, a partial reduction of the oxide occurred, with the oxide becoming 'patchy' after the second exposure. Areas of

Figure 9. Ni coupons. Upper specimen is same as shown in Figure 8. Lower specimen is the other half of the upper specimen, which was re-exposed to 338 °C at 20 scc/kg H₂ for 10 days.

essentially bare metal were noted after the second exposure (Figure 9). This result suggests that the second exposure did not simply provide a uniform partial reduction (*i.e.*, uniform thinning) of the film; rather, it is expected that continued exposure would have fully reduced the oxide. This data point supports the notion that the 20 scc/kg H₂ condition at 338°C resides in the Ni regime. Additionally, the reduction of this oxide confirms that there is no bias in the results due to the fact that the exposure time for the coupon tested at 12.5 scc/kg H₂ (*i.e.*, 63 days) was greater than the exposure times for the two separate coupons tested at 20 scc/kg H₂ (*i.e.*, 10 and 10.7 days).

Summary of Ni/NiO data and comparison with theoretical predictions

Figure 10 summarizes CER data at 288, 316, 338 and 360°C. The experimentally measured Ni/NiO transition was evaluated as the midpoint between the least reducing condition in the Ni regime and the least oxidizing condition in the NiO regime. Data from Ehrnsten and Saario¹⁰ are also shown on the plot. These data are broadly consistent with the Ni/NiO transition determined experimentally in this work, though it is noted that the prior work was not conducted at H₂ levels near the apparent Ni/NiO transition. The prior investigators¹⁰ observed a resistance characteristic of the film-covered condition in a nitrogen sparge test at 320°C and also observed resistance values characteristic of the film-free condition at 25 and 30 scc/kg H₂ at both 288 and 320°C.

Figure 10. Summary plot of CER data, on an scc/kg H₂ basis.

A substantial deviation is evident between the experimentally measured Ni/NiO transition and the theoretical Ni/NiO transition calculated by some of the present authors³ using thermodynamic data from the Journal of Solution Chemistry^{12,14}. The coupon data obtained at 20 scc/kg H₂ at 338°C show that the CER-measured Ni/NiO line is a more accurate representation of this transition than the theoretically calculated line (note that in a separate paper¹⁵, the measured data are used to derive more accurate thermodynamic data (*i.e.*, ΔH , ΔS)) and an equation for the measured Ni/NiO transition is provided). A lesser deviation is evident between the experimentally measured Ni/NiO transition and the theoretical Ni/NiO transition cited by Cassagne *et al.*¹ As shown in Figure 10, the experimentally measured Ni/NiO transition at 360°C is at ~ 25 scc/kg H₂. This point is somewhat lower than the calculated Ni/NiO transition shown as a short vertical bar (and labeled as Ni/NiO) on the lower x-axis of Figure 11 (note that the units of ml STP kg⁻¹ H₂ shown on the upper x-axis of Figure 11 are equivalent to scc/kg H₂). It is noted, however, that only one test has been conducted at 360°C in the present study, so the confidence in the measured Ni/NiO transition at that temperature is not as great as at 316 and 338°C for which more extensive testing has been performed.

Figure 11. Alloy 600 CGR data at 360°C.¹¹ Dashed line shows measured Ni/NiO transition.

The cause of the discrepancy shown in Figure 10 between the theoretical Ni/NiO transition and the measured transition has not yet been identified. Possible sources of the discrepancy are: (i) errors in the free energy of formation of NiO (or, less likely, H₂O) at 288 to 360°C, (ii) the free energy of formation of a surface oxide (*e.g.*, an NiO film) is different from that of a bulk oxide, (iii) errors in the elevated temperature Henry's law coefficient which converts theoretically calculated hydrogen fugacities to units of concentration (*i.e.*, scc/kg), or (iv) changes in the density/compressibility of water are not adequately accounted for. Further study is needed to resolve this issue.

Implications for the effects of aqueous hydrogen level on PWSCC

Figure 12 shows SCCGR data^{3,5,15} for Alloy X-750 in the HTH heat treatment at 360°C. It is evident that the maximum in PWSCC susceptibility is in much closer agreement with the experimentally measured Ni/NiO transition than with the theoretical Ni/NiO transition reported previously³. The agreement is also very good for Alloy 600 (at 338°C), as shown in Reference 15. The agreement is reasonable though not as close for Alloy X-750 in the AH heat treatment (at 338°C).¹⁵ It is speculated that this result may be due to the fact that large portions of the oxide in the cracks in Alloy X-750 AH are (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 Alloy 600 and Alloy X-750 HTH.⁶ Figure 11 also shows that for a different set of data (reported by Cassagne *et al.*¹), the experimentally measured Ni/NiO transition is in close agreement with the peak in SCC susceptibility for Alloy 600, though it is acknowledged that the peak is quite broad in this figure.

This work has two major implications for understanding and predicting the effect of aqueous H₂ level on PWSCC. First, the fact that the maximum in PWSCC susceptibility is in close agreement with the experimentally measured Ni/NiO transition underscores a point made previously by other investigators¹⁶, namely that a corrosion process is likely involved in the mechanism of PWSCC, with the oxide perhaps being metastable in the vicinity of the Ni/NiO transition. Secondly, this work provides insight related to extrapolating the effects of aqueous H₂ to lower temperatures. In other words, extensive accelerated SCC testing has been conducted at 338, 360 and 399°C^{1-5,15} to determine the effect of aqueous H₂, but such tests are time-consuming to perform at lower temperatures. The present work provides the experimentally measured Ni/NiO transition at lower temperatures (down to 288°C, with the possibility of extrapolating to lower temperatures if needed). The Ni/NiO transition provides a reasonable basis for estimating the aqueous H₂ level at which the maximum in SCC susceptibility is likely to be observed, at a variety of temperatures.

Figure 12. SCCGR data for Alloy X-750 HTH at 360°C.¹⁵

Limited data acquired at 288°C are consistent with the notion that SCCGR of nickel-based alloys is heightened in the vicinity of the Ni/NiO transition at lower temperatures. The present SCCGR testing was conducted at 10 and 50 scc/kg H₂ on EN82H weld metal. The specimens were fabricated from a weld cradle made from a single heat of weld wire using a cold wire automatic gas tungsten arc welding process. The shield gas was 100% argon, and the specimens were tested in the as-welded condition. Specimens were 1T compact tension specimens, side grooved to a net thickness of 0.798" and air fatigue precracked to an initial crack depth-to-specimen width ratio (*a/W*) of ~ 0.5. Testing was conducted in the T-S orientation (*i.e.*, with the load applied perpendicular to the weld pass direction and with the crack growing from the root to the crown of the weld). Constant load was applied using an electric actuator, with an initial stress intensity factor (*K_I*) of 35 ksi√in. The pH of the water was similar to that described previously for the CER testing. The test conditions and SCCGR results are summarized in Table 2.

Table 2. SCCGR testing of EN82H weld metal at 288°C

Specimen Identification	Aqueous H ₂ level (scc/kg H ₂)	$\Delta a_{\text{SCC,max}}$ (μm)	Exposure time (days)	Estimated lower bound SCCGR _{max} (μm/hour)
ES4-05	50	180	172.7	0.043
ES4-06	50	240	84.9	0.12
ES4-03	10	1350	77.7	0.720

The crack front was highly non-uniform, as expected for weld metal¹⁷, with SCC occurring in several isolated pockets rather than continuously across the crack front. As a result, only a maximum crack extension ($\Delta a_{\text{SCC,max}}$), as opposed to an average crack extension, is reported. Additionally, the crack monitoring instrumentation (electric

potential drop monitoring, EPM) was ineffective at detecting the onset (*i.e.*, incubation) of SCC growth, since uniform SCC across the front of the fatigue precrack is needed for reliable *in-situ* monitoring. Thus, an estimated lower-bound SCCGR_{max} is reported, assuming an incubation time of zero. As shown in Table 2, significantly more crack extension occurred at 10 scc/kg H₂ as compared to 50 scc/kg H₂. Figure 13 demonstrates that these data points, while limited in number, are consistent with the view that SCC susceptibility increases as one approaches the Ni/NiO transition (which is located at ~ 4 scc/kg H₂ at 288°C according to the CER data). Thus, the SCCGR data suggest that the result previously demonstrated at 338, 360 and 399°C (*i.e.*, increased PWSCC susceptibility in the vicinity of the Ni/NiO transition) is also obtained at lower temperatures. Note that these data were collected using a single specimen at each H₂ level, and that the SCC extent was determined via destructive examination. EPM was used solely in an attempt to detect the onset (*i.e.*, incubation) of cracking, not to measure crack growth rates.

Figure 13. SCCGR data for EN82H at 288 °C.

As illustrated in Figures 11, 12 and 13, operation in the Ni stability regime does not eliminate cracking. It is important to note that this observation does not preclude a role of corrosion in the SCC process, since Ni-Cr-Fe alloys still exhibit significant oxidation in the Ni regime. In fact, not only is the corrosion of Fe and Cr thermodynamically favored in the Ni stability regime, but the corrosion of Ni to form spinel oxides ($\text{Ni}_x\text{Fe}_{1-x}\text{Cr}_y\text{Fe}_{2-y}\text{O}_4$) can still occur on the Ni side of the Ni/NiO equilibrium. The film-covered Alloy 600 coupon shown in Figure 7 provides an example of corrosion of a Ni-Cr-Fe alloy in the Ni regime.

Relevance to Ni-Cr-Fe alloys

Although no CER testing has yet been performed on Ni-Cr-Fe alloys such as Alloy 600, Alloy X-750, or Alloy 718, it is important to recognize that CER tests using pure Ni are directly applicable to PWSCC of Ni-Cr-Fe alloys. As mentioned previously, the crack tip oxide for Ni-Cr-Fe alloys is often found to exhibit a NiO structure⁶, suggesting that NiO may be an SCC-controlling oxide. Also, the fact that the experimentally measured Ni/NiO transition is in good agreement with the maximum in PWSCC susceptibility for Ni-Cr-Fe alloys provides persuasive evidence that the data obtained on pure Ni are important to understanding the SCC performance of the Ni-Cr-Fe alloys. Note also that the presence of a spinel oxide may impede the ability to measure the Ni/NiO transition using Ni-Cr-Fe alloys.

Ni/NiO transition as a function of hydrogen fugacity

The CER facility is presently being equipped with a silver/palladium (Ag/Pd) cell, such that the Ni/NiO transition will also be able to be reported on a hydrogen fugacity basis. Figure 14 provides an estimate of the transition on a hydrogen fugacity basis, using Henry's law to calculate hydrogen fugacity values from the known aqueous H₂ level and temperature for each condition. The Henry's law coefficients used in this calculation¹² are 1.06×10^{-2} , 7.19×10^{-3} , 5.08×10^{-3} and 3.47×10^{-3} atm/(scc/kg H₂) at 288, 316, 338 and 360°C, respectively.

Figure 14. Summary plot on a fugacity basis.

Ni/NiO transition as a function of electrochemical potential

The iron/iron oxide ($\text{Fe}/\text{Fe}_3\text{O}_4$) electrode was used to measure E_{corr} values for Ni, and Figure 15 shows the transition corrosion potentials as a function of temperature. It is noted that changing the temperature affects the potential of the $\text{Fe}/\text{Fe}_3\text{O}_4$ electrode in addition to changing the Ni/NiO transition.

The potentials are plotted on the standard hydrogen electrode (SHE) scale in Figure 16. The conversions from the $\text{Fe}/\text{Fe}_3\text{O}_4$ scale to the SHE scale were conducted by subtracting 0.916, 0.949, 0.990, and 1.048 Volts (V) at 288, 316, 338 and 360°C, respectively. These values were calculated using the Nernst equation and thermodynamic data from Ziemniak¹².

Figure 15. Summary plot on an ECP basis.

Figure 16. Summary plot on an ECP vs. SHE basis.

Conclusions

1. The CER-measured transition H_2 level for the Ni/NiO equilibrium at 288 to 360°C was found to be lower than previously calculated by some of the present authors using thermodynamic data from the Journal of Solution Chemistry.
2. The CER data are consistent with corrosion coupon exposures at selected conditions.
3. The measured position of the Ni/NiO transition is in good agreement with the maximum in PWSCC susceptibility for Alloy 600 at 338 and 360°C and for Alloy X-750 in the HTH heat treatment at 360°C. The agreement is reasonable but not as close for Alloy X-750 in the AH heat treatment at 338°C.
4. The measured Ni/NiO transition provides a basis for estimating the aqueous H_2 level at which the maximum in SCC susceptibility is likely to be observed at lower temperatures for which SCC tests are time-consuming to perform. The limited PWSCC data presented are consistent with the idea that SCC susceptibility is maximized in the vicinity of the Ni/NiO transition at 288°C.

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