

Stress Corrosion Cracking of Copper in Nitrite/Chloride Mixtures at Elevated Temperatures

NWMO TR-2007-04

November 2007

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ABSTRACT

Title: Stress Corrosion Cracking of Copper in Nitrite/Chloride Mixtures at Elevated Temperatures
Report No.: NWMO-TR-2007-04
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Abstract

In this study, stress corrosion cracking (SCC) tests were carried out on oxygen-free phosphorous-doped copper specimens in nitrite-only solutions and in various nitrite/chloride mixtures at elevated temperatures of 100°C and 130°C, under both freely corroding and galvanostatic conditions. The results were compared with the results of previous SCC tests at room temperature of 22°C.

All copper specimens showed more ductile behaviour at 100°C. The stress corrosion factor (SCCF1) and surface crack extension rate (SCER) both suggested ductile or mixed SCC/ductile behaviour, but not pure SCC. The SCCF1 and SCER parameters were not sufficiently discriminating to distinguish between degrees of SCC and ductile tearing. Visual examination of the specimens was required to qualitatively estimate the amount of SCC for a copper specimen.

The results of experiments performed in nitrite-only solutions with a $1 \mu\text{A}\cdot\text{cm}^{-2}$ applied current (to simulate natural oxidation of copper) show that increasing the testing temperature from room temperature to 100°C decreases the extent of SCC and the surface-crack velocity. SCC was not observed for an applied current of $0.01 \mu\text{A}\cdot\text{cm}^{-2}$ suggesting that SCC susceptibility decreases with corrosion current.

In chloride-containing nitrite mixtures at elevated temperatures, all copper specimens tested displayed ductile cracking and no SCC. All chloride concentrations and nitrite/chloride concentration ratios tested inhibited the formation of SCC.

The experimental results show that SCC in nitrite and nitrite/chloride environments is suppressed at elevated testing temperatures. Therefore, the general SCC behaviour of copper in nitrite-only and nitrite/chloride environments at elevated temperatures may be conservatively assessed by performing appropriate SCC tests at room temperature.

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1. INTRODUCTION

Oxygen-free phosphorous-doped (OFP) copper has been selected as the reference corrosion barrier material of used-fuel containers for a hypothetical deep geological repository (DGR) in crystalline rock of the Canadian Shield (Maak 1999). Since it is well known that copper and copper alloys can be susceptible to stress corrosion cracking (SCC), there is a need to assess whether SCC can be a potential container corrosion failure mechanism. The overall mechanism for SCC requires that a susceptible metal be exposed to sufficient tensile stress and an active SCC agent. A common feature for SCC of copper appears to be the formation of a thin oxide or tarnish film (Ikeda and King 2001). When this film does not form, SCC is not observed.

SCC of copper has been observed in nitrite, ammonia, and acetate containing environments. Although these species are not normally found in the natural groundwaters of the Canadian Shield, they could be introduced by mining activities, microbial activity, or gamma radiolysis. SCC in nitrite solutions is most likely during the initial warm and oxidizing period of the container lifetime. Other factors, e.g., chloride content and temperature, could act to mitigate the effect of nitrite and diminish the potential for SCC. In order to produce SCC, the oxidizing conditions must also be conducive to the formation of an appropriate surface oxide film. Electrochemical methods can be used to simulate natural oxidation and control the formation of the surface film. The application of a constant current to a specimen would simulate a constant rate of supply of oxidant to the container surface.

Previous work has shown that chloride inhibits SCC in nitrite solutions at room temperature (Ikeda and Litke 2000). The general observations and conclusions from Ikeda and Litke (2000) are summarized as follows:

- a) OFP copper is susceptible to SCC in oxidizing nitrite solutions at room temperature under adequate mechanical conditions.
- b) Increasing chloride concentration of the solution inhibits SCC at room temperature. However, if the concentration ratio of nitrite to chloride was sufficiently large to overcome the inhibitive effect of chloride, SCC was still observed.
- c) In the absence of SCC, the Constant Extension Rate Test (CERT) will force a slow crack to continue propagating at a minimum surface-crack velocity of approximately $2 \text{ nm}\cdot\text{s}^{-1}$; the value was estimated using the surface crack extension rate (SCER).
- d) An SCC factor (SCCF1) > 4 suggested that the copper specimen was subjected to only ductile crack growth (i.e., no SCC), which was driven by the experimental application of strain. An SCC factor < 4 indicated that the specimen was subject to some degree of SCC.
- e) Under these CERT test conditions, the stress intensity, K_{I} , was sufficient to initiate SCC, but can neither be used to predict crack growth rates, nor to distinguish between susceptible or non-susceptible SCC conditions.

The explanation of the chloride effect presented by Ikeda and Litke (2000) was that chloride enhanced the uniform corrosion rate of copper and hindered the formation of an oxide film at the crack tip. It was argued that increasing the temperature of a chloride containing solution would increase the uniform corrosion rate and diminish the susceptibility to SCC. Furthermore, the increase in temperature should decrease the strength of the matrix and lessen the maximum stress intensification possible at the crack tip. Alternately, an increase in temperature could accelerate the formation of the oxide layer. If chloride accelerates corrosion, but does not block

oxide film formation, then SCC could be possible. In this case, chloride would not inhibit SCC at elevated temperature, but could exacerbate SCC by promoting film growth. To distinguish between these possibilities, a series of elevated temperature SCC tests were performed and the results of these experiments are presented in this report.

In this study, the SCC susceptibility of the copper specimens at a temperature of 100°C was assessed by examination of the SCC factor (SCCF1) and surface crack velocity (SCER), and by visual examination. A recent examination of SCC in acetate environments has shown that visual examination of the specimen was required to identify the occurrence of SCC for SCCF1 values that do not clearly distinguish between SCC and ductile behaviour (Litke and Ikeda 2006).

2. EXPERIMENTAL

The Constant Extension Rate Test (CERT) involves the continuous loading of a compact tension (CT) specimen by increasing the distance between the loading holes at constant rate. These experiments were performed in the slow strain rigs described previously in Ikeda and Litke (2000). The rigs were modified to provide safe operation at temperatures $\geq 100^{\circ}\text{C}$. A registered, small-volume pressure vessel with a PTFE liner was used as the cell body and the vessel was wrapped with a removable electric heater. A proportional-control temperature controller was used to maintain constant temperature. Two independent controlled and high-temperature-trip thermocouples were located on the external surface of the vessel but under the heater. A third thermocouple passed through the pressure vessel head and was immersed in the test solution. This thermocouple was used to measure and monitor the solution temperature during the test.

The internal three electrode arrangement of the vessel was the same as reported previously for room temperature experiments (King et al. 1999) with the CT specimen as the working electrode. CONAX pressure fittings with PTFE inner-sealing ferrules were used to permit electrode connections to penetrate the pressure vessel head yet maintain both electrical isolation and the pressure boundary seal. Care was taken to ensure electrical isolation between the internal electrochemical cell and the external electric heater.

The experiments were performed under either freely corroding or galvanostatic (applied current of 0.01 or $1\ \mu\text{A}\cdot\text{cm}^{-2}$) conditions. Galvanostatic experiments were performed using a platinum mesh counter electrode, and a Thompson ministat for applying the constant current, as described previously (e.g., King et al. 1999a). For experiments CERT52 and CERT53, a commercially available room-temperature Ag/AgCl electrode ($3\ \text{mol}\cdot\text{L}^{-1}$ NaCl saturated with AgCl filling solution) was used to measure the corrosion potential (E_{cor}) of the copper specimen. The Vycor frit in this reference electrode proved to be unreliable. The potential measurements for these two experiments were discarded. For the remaining experiments, a commercially available high temperature Ag/AgCl reference electrode ($4\ \text{mol}\cdot\text{L}^{-1}$ KCl saturated with AgCl filling solution) was used. All potentials are reported against this reference electrode.

The load sustained by the CT specimen as a result of its extension was measured using a load cell attached to both the specimen and the load frame. The output from this cell was recorded and used to generate a load curve. The nominal extension was measured using a displacement gauge.

All electronic data were recorded at 60 s intervals, using an in-house data acquisition program powered by LABVIEW Version 5.2, running on a Compaq Deskpro Pentium computer with a Windows NT, Version 4.00.1381 operating system.

The experiments were performed in ~ 0.5 L of deaerated solution containing nitrite or nitrite and chloride mixtures. The solutions were prepared by dissolving the appropriate mass of nitrite salt in millipore purified deionised water, then adjusting the pH to 9.0 using dilute NaOH. The pH was measured using a commercial glass pH electrode. Solutions were prepared using reagent grade chemicals. The solution temperature was $\sim 100^{\circ}\text{C}$ although one experiment was performed at 130°C .

All experiments reported were performed at a constant cross-head speed of $8.5 \times 10^{-6} \text{ mm}\cdot\text{s}^{-1}$. Compact tension (CT) coupons were prepared from the SKB-4 OFP copper plate section B2, as described previously (Ikeda and Litke 2000). A summary of the experimental conditions is presented in Table 1.

The ratio of the CT specimen dimensions used to manufacturing the specimens conforms to the requirements of ASTM-E 399-90 (ASTM 1994), but the overall dimensions do not. The specimens are too small for an accurate plane-strain fracture mechanics analysis of a low ductility material such as copper. The stress intensity factor (K_Q) at the onset of cracking was estimated using the initial surface fatigue crack length and the 5% secant load (ASTM 1994). The calculated values for K_Q and crack velocity are used as qualitative indicators of crack growth for comparison purposes only. The measured surface crack velocity includes contributions from ductile tearing and measurement errors caused by the loss of surface planarity.

The specimens were manufactured with the crack oriented in a defined direction relative to the microstructure of the material (ASTM 1994). The designation of the crack orientation is based on the plane of the fracture surface (designated by the direction of the normal to the fracture surface), and the direction of the crack propagation, relative to the longitudinal (L, also the length of the plate), transverse (T, also the width), or short transverse (S, also the thickness) directions of the plate. All specimens tested were in the T-S orientation, that is, the fracture surface is in the transverse-longitudinal plane, perpendicular to the transverse direction, and the crack propagates in the short transverse direction (Figure 1).

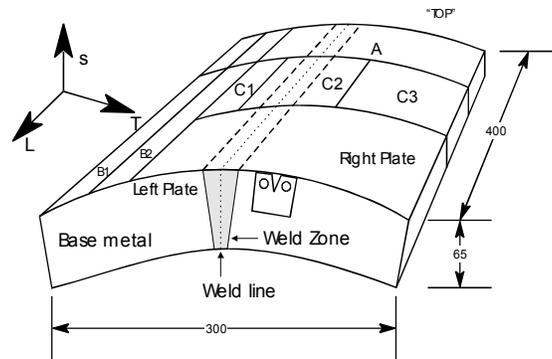


Figure 1: Schematic Diagram Showing Orientation and T-S Specimen Orientation Relative to Microstructure Designations Schematic of SKB4 Plate Material Showing the Location of Specimen Cuts

2.1 POST-TEST ANALYSES

Following the experiment, aliquots of the test solution were submitted for chemical analysis: by ion-coupled plasma spectroscopy to determine the total dissolved copper concentrations; and by ion chromatograph for chloride concentrations.

At the end of each experiment, a visual examination of the specimen was performed and features were noted. The specimen was then digitally imaged, and the images printed and stored for future reference. The degree and susceptibility of SCC were qualitatively estimated based on visual examination of the cracks on the specimen surface. The crack extension and crack-mouth opening values were measured from the overview sample image. The longest surface crack was measured using a grey-scale paper-image. The surface-crack velocity (or surface-crack extension rate, SCER) values were determined by dividing the measured maximum crack extension by the crack growth time. An SCC factor (SCCF1) was developed previously to overcome some of the difficulties associated with distinguishing between ductile rupture and crack propagation (Ikeda and Litke 2000). The width of the final “notch” and the length of the longest crack were determined from the calibrated image using the opened end of the specimen as a reference. These values were then corrected for the initial notch width, and for the initial notch and fatigue-crack lengths, and the SCCF1 factor calculated.

3. RESULTS

In the present study, SCC tests were carried out at temperatures of 100°C in a nitrite-only solution and various nitrite/chloride mixtures (with one test performed at 130°C). A summary of the data for all experiments performed in this study as well as comparable room temperature (22°C) experiments (Ikeda and Litke 2000) is presented in Table 1.

Experiment COM0301 was performed in deionized water at 100°C. The load curve and the data in Table 1 show that this experiment did not exhibit SCC. The load curve remained flat, and the specimen was oxidized to an orangey layer, a different colour than any specimen exposed to NO_2^- , regardless of the Cl^- concentration in solution. The SCCF1 value was 5.56 and the SCER was $2.08 \text{ nm}\cdot\text{s}^{-1}$, values that may be used as indicators of purely ductile behaviour at 100°C. The influence of nitrite and chloride on SCC of copper at 100°C can be compared with the results of experiment COM0301 to indicate an environmental effect on SCC.

3.1 GENERAL OBSERVATIONS

The loading curves of the SCC tests at elevated temperature are shown in Figure 2. The maximum load for the elevated-temperature tests was generally lower than that for the comparable room-temperature test, except for the experiments performed in nitrite alone (Table 1, Figure 2). The duration of the load near the maximum was longer at higher temperatures (Figure 3). Mechanically, a decrease in strength and an increase in ductility with an increase in temperature could explain a lower maximum load, and longer duration near maximum load. Experiment CERT52 was performed at the highest test temperature (130°C) and had the lowest maximum load, but also had an unusually long fatigue pre-crack which resulted in a smaller initial load-bearing area, and the lowest measured K_Q value. This maximum load value should not be compared directly with the other specimens. The lowest comparable maximum load (experiment CERT59) at 100°C was within 10% of the average load (2.2 kN) for all experiments reported. Despite the different test conditions, the shape of all the load curves at 100°C are similar and consistent with the observed cracking behaviour, as discussed below.

All measured values of K_Q are greater than the critical K_Q value reported for constant load OFE specimens at room temperature, and should be above the critical value for SCC (King et al. 1999). Based on the available room temperature data, the applied K_Q should have been sufficient to initiate SCC cracking for all specimens tested at elevated temperatures in this study.

Valid potential measurements were obtained for four of the 100°C experiments (Figure 4). The potential values were noisy, but stable.

The chloride concentration at the end of the nitrite-only experiments were high (Table 1), indicating leakage from the reference electrode. The shift in potential for experiment CERT56 may be an indication of the increasing chloride concentration during the experiment.

Visual examination of the specimens following the elevated-temperature experiments revealed significant surface oxidation of the boldly exposed surfaces. The dark surface layer observed in

Figure 5 appears to be a loosely adherent film that can be readily wiped off the surface. This may indicate a precipitated layer that may have formed as or after the experiment cooled to room temperature. The colouration of the surface layers in the images (e.g., Figure 5) may vary because of lighting and printing artefacts in Figure 5. The lightly coloured surfaces appeared to be thin, more tightly adherent films.

A visual examination of specimens tested at elevated temperatures showed mostly ductile tearing deformation in the region of the crack-tip (Figure 5). As shown in Figure 6, the crack-tip geometry can be used to qualitatively assess the amount of SCC component. The specimen from CERT 22 (tested at 22°C) showed substantial SCC. This specimen shows an angular crack-tip and a crack with straight sides extending from the notch to the crack tip. The specimen from CERT 59 shows no SCC component and it has a rounded crack-tip. The specimen from CERT 56 shows a smaller SCC component and it has an angular crack-tip. This examination is subjective, but the roundness of the crack tip is often clear.

The surface of each specimen was depressed in a hemispherical region around the crack indicating significant ductility. Following the experiments, the loading pins were more difficult to remove and a slight change in the shape of the loading pin-holes was observed. The observed ductile deformation of the specimens is consistent with the shape of the loading curves.

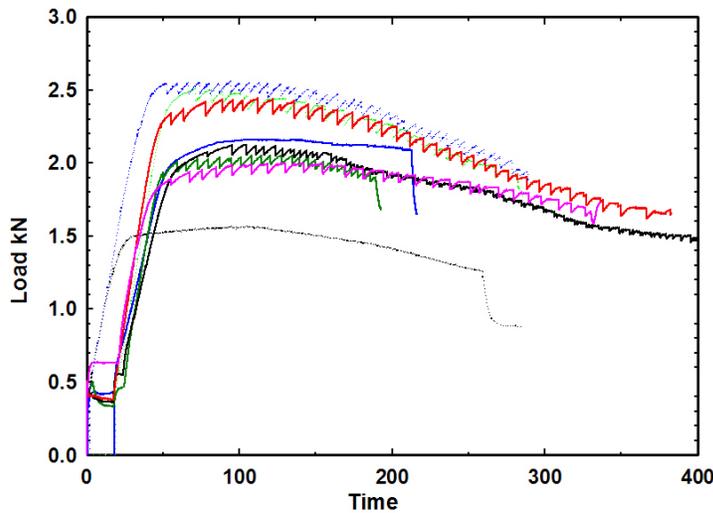


Figure 2: Load Curves for SKB-4 OFP Copper Compact Tension Specimens Exposed to pH 9 Nitrite and Nitrite/Chloride Solutions at 100°C

- no applied current: — COM0301 deionized water (108°C,);
- 0.01 $\mu\text{A}\cdot\text{cm}^{-2}$ applied current: — CERT57 0.1 mol·L⁻¹ NaNO₂;
- 1 $\mu\text{A}\cdot\text{cm}^{-2}$ applied current: — CERT59 0.1 mol·L⁻¹ NaNO₂;
- CERT56 0.1 mol·L⁻¹ NaNO₂ ;
- CERT55 0.1 mol·L⁻¹ NaNO₂/0.001 mol·L⁻¹ NaCl;
- CERT54 0.1 mol·L⁻¹ NaNO₂/0.01 mol·L⁻¹ NaCl;
- CERT53 0.02 mol·L⁻¹ NaNO₂/0.01 mol·L⁻¹ NaCl;
- CERT52 0.001 mol·L⁻¹ NaNO₂/0.01 mol·L⁻¹ NaCl.

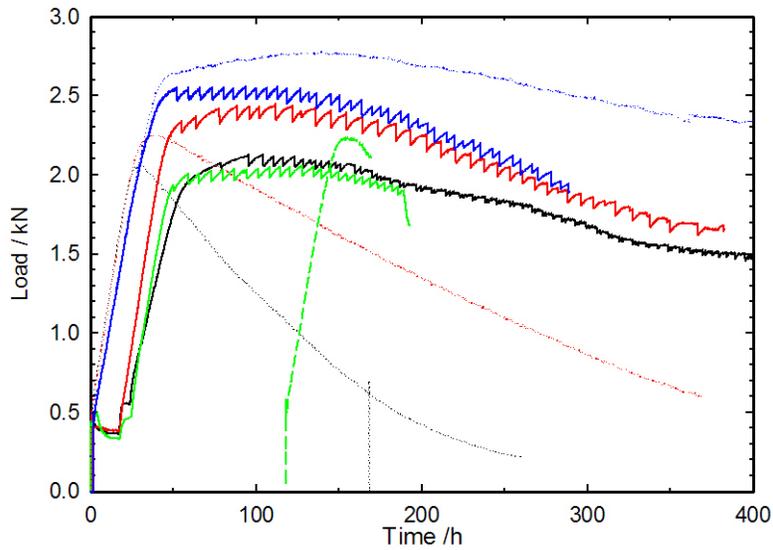


Figure 3: Comparison of Load Curves for SKB-4 OFP Copper Compact Tension Specimens Exposed to pH 9 Nitrite and Nitrite/Chloride Solutions at 22 and 100°C.

Solid lines experiments performed at 100°C, dashed lines experiments performed at 22°C.
 No applied current: -- CERT24 (Air) and -- COM0301 (Distilled water);
 -- CERT32 and -- CERT57 0.1 mol·l⁻¹ NaNO₂
 1 μA·cm⁻² Applied current -- CERT27 and -- CERT56 0.1 mol·L⁻¹ NaNO₂;
 -- CERT30 and -- CERT55 0.1 mol·l⁻¹ NaNO₂/0.001 mol·l⁻¹ NaCl.

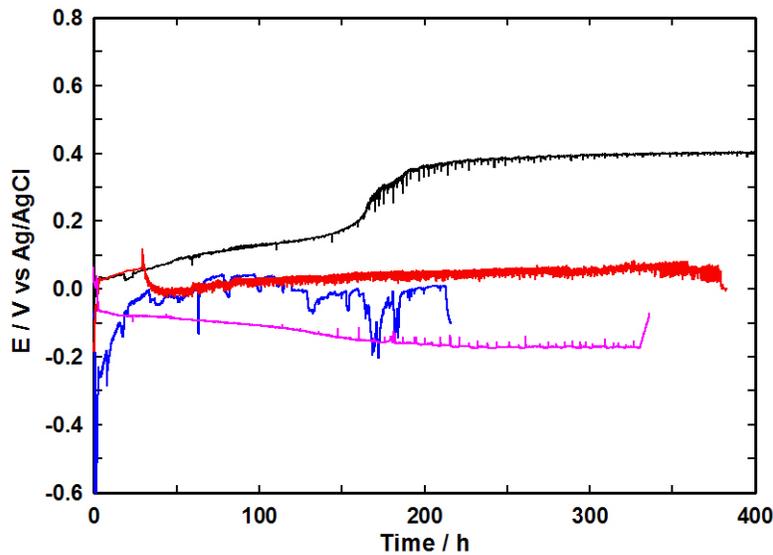


Figure 4: Potential Curves for SKB-4 OFP Copper Compact Tension Specimens Exposed to pH 9 Nitrite and Nitrite/Chloride Solutions at 100°C.

— CERT57 0.1 mol·L⁻¹ NaNO₂ free corrosion potential;
 — CERT56 0.1 mol·L⁻¹ NaNO₂ 1 μA·cm⁻²;
 — CERT59 0.1 mol·L⁻¹ NaNO₂ 0.01 μA·cm⁻²;
 — CERT54, 0.1 mol·L⁻¹ NaNO₂/0.01 mol·L⁻¹ NaCl 1 μA·cm⁻².

Table 1: Summary of Experiments Performed at Elevated Temperatures with a Comparison to Experiments Performed at Room Temperature¹

Test [*]	Sample	Current	[NaNO ₂] [†]	[NaCl]	[NaNO ₂]/ [NaCl] ratio	[Cu]	[Cl]	Aeration	Temperature	Max. Load	K ₀	SCER	SCCF1
No	No.	μA·cm ⁻²	mol·L ⁻¹	mol·L ⁻¹		mmol·L ⁻¹	mmol·L ⁻¹	Conditions	°C	(kN)	(MPa·m ^{1/2})	(nm·s ⁻¹)	
COM0301	SP12	OCP	0	0	n/a	n/a	n/a	Air	108	2.547	21.35	2.08	5.56
CERT27	SP7	1	0.1	0	n/a	0.0091	n/a	DA	22	2.057	23.40	7.27	1.66
CERT56	SP32	1	0.1	0	n/n	0.0025	9.31	DA	100	2.124	19.59	2.32	4.95
CERT32	SP13	OCP	0.1	0	n/a	0.0044	n/a	DA	22	2.251	20.77	3.47	2.97
CERT57	SP33	OCP	0.1	0	n/a	0.0049	9.59	DA	100	2.441	22.01	1.84	6.41
CERT58	SP65	0.01	0.1	0	n/a	0.0025	0.34	DA	22	1.907	21.06	3.83	3.10
CERT59	SP66	0.01	0.1	0	n/a	0.0039	3.16	DA	100	1.996	18.34	1.68	6.28
CERT34	SP17	1	0.001	0.01	0.1	<0.0003	n/a	DA	22	2.524	23.50	2.09	5.46
CERT52	SP2	1	0.001	0.01	0.1	0.0028	n/a	DA	130	1.564	17.31	1.43	7.10
CERT33	SP16	1	0.01	0.01	1	0.0019	n/a	DA	22	2.609	22.37	2.23	5.23
CERT53	SP25	1	0.02	0.01	2	0.0087	n/a	DA	100	2.508	24.36	2.33	5.00
CERT29	SP9	1	0.1	0.01	10	0.013	n/a	DA	22	2.731	26.32	4.40	2.70
CERT54	SP30	1	0.1	0.01	10	0.0074	n/a	DA	100	2.161	19.23	2.04	5.15
CERT30	SP10	1	0.1	0.001	100	0.0091	n/a	DA	22	2.233	21.46	7.66	1.37
CERT55	SP31	1	0.1	0.001	100	0.022	n/a	DA	100	2.051	21.63	2.02	5.60
CERT24	SP3	Air	n/a	n/a	n/a	n/a	n/a	Air	22	2.768	23.97	2.62	4.43

* All experiments performed at a cross-head speed of $8.46 \times 10^{-6} \text{ mm} \cdot \text{s}^{-1}$ with compact tension specimens cut from plate SKB4-B2 in a TS orientation

† Electrolyte solutions adjusted to pH 9 using NaOH

¹ Room temperature data taken from Ikeda and Litke 2000

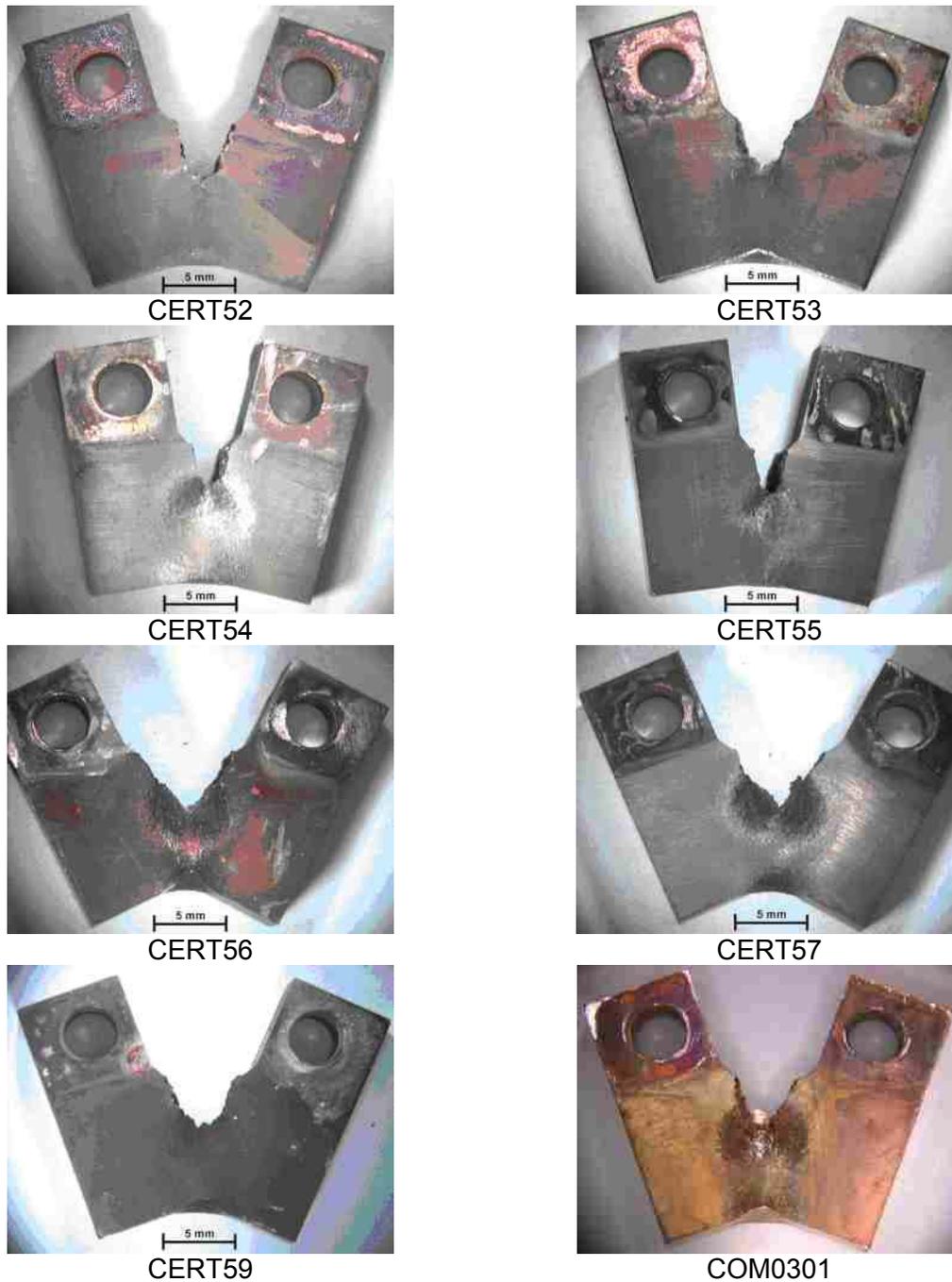


Figure 5: Overview of CT Specimens Following Exposure to Nitrite and Nitrite/Chloride Solutions at 100°C and 130°C.

The experiment number is shown below each specimen. See Table 1 for details of the experimental conditions.

The specimen opening was sufficiently wide that part of the fracture surface was visible by looking down the machine notch. The crack appeared to have advanced more in the center of

the specimen than at the surface (crack tunnelling). The amount of the tunnelling is greater than observed at room temperature. This suggests that at 100°C the crack advance was inhibited at the surface of the specimen. This is consistent with a decrease in strength of the specimen causing a decrease in the size of the plane strain zone of the specimen. The crack propagation is favoured in the plane strain zone which is now restricted to a small region in the center of the specimen. As shown in Table 1, the surface-crack velocities (SCER) of the specimens tested at 100°C and 130°C are also significantly lower than those rates of the specimens tested at room temperature.

3.2 NITRITE-ONLY SOLUTION

Three experiments at 100°C in nitrite-only solutions were performed using applied currents of: 1 $\mu\text{A}\cdot\text{cm}^{-2}$ (CERT56), 0.01 $\mu\text{A}\cdot\text{cm}^{-2}$ (CERT59), and 0 applied current (OCP CERT57). Comparable experiments, CERT27 (1 $\mu\text{A}\cdot\text{cm}^{-2}$), CERT58 (0.01 $\mu\text{A}\cdot\text{cm}^{-2}$) and CERT32 (OCP), were performed at 22°C.

At an applied current of 1 $\mu\text{A}\cdot\text{cm}^{-2}$, the specimens from experiments CERT56 and CERT27 were discoloured indicating oxidation of the surface. A close visual examination of these specimens showed fine cracks in CERT27 (22°C) that tended to coalesce into larger cracks, whilst CERT56 (100°C) showed only scattered surface dislocations (Figure 6). The extent of SCC and surface crack velocity (i.e., measured SCER) for CERT27 was greater than for CERT56, as shown in Table 1. The SCCF1 value for CERT27 (1.66) is considerably lower than that for CERT56 (4.95). These characteristics indicate the SCC susceptibility decreases as the test temperature increases from 22°C to 100°C.

The effect of low current can be seen by comparing the specimens from CERT59 (100°C, 0.01 $\mu\text{A}\cdot\text{cm}^{-2}$) and CERT57 (100°C, OCP) with the specimens from CERT58 (22°C, 0.01 $\mu\text{A}\cdot\text{cm}^{-2}$) and CERT32 (22°C, OCP). The specimens from experiments CERT59 and CERT57 were blackened whilst CERT32 was only slightly oxidized and CERT58 remained coppery coloured and shiny. CERT59 showed fine surface dislocations near the crack tip while CERT58 showed multiple cracks. CERT32 showed several SCC cracks whilst CERT57 showed some scattered surface dislocations in the crack tip zone. The crack tip was more angular when exposed to the lower temperature (CERT32 and CERT58) and more rounded after exposure to 100°C (CERT57 and CERT59). The measured values for SCCF1 and SCER presented in Table 1 are generally consistent with the appearance of the crack tip and indicate that the degree of SCC is lower at 100°C than at 22°C.

All specimens showed mainly ductile behaviour at 100°C (Figure 6). The specimen from experiment CERT59 (0.01 $\mu\text{A}\cdot\text{cm}^{-2}$) has a rounded cracking zone (Figure 6) indicating ductile tearing. In contrast, the specimen from experiment CERT27 has an angular crack region indicating SCC. Examining the specimens from experiments CERT56 and CERT57 shows angular sides, but a wide opening with some rounding of the crack-tip region. This suggests some degree of SCC for these specimens, but less SCC than observed for the same conditions at 22°C.

The shape of the load curves (Figure 2) were consistent with the visual observations, i.e., the more crack-tip blunting and ductile tearing of the specimen, the flatter the load curve following the maximum. The corrosion potential (Figure 4) for experiment CERT57 showed some initial variation as the load and temperature stabilized, but a stable potential with a slight positive shift

was observed through most of the experiment. The final potential was slightly positive with a value near +0.05 V. The potential for experiment CERT56 ($1 \mu\text{A}\cdot\text{cm}^{-2}$ applied current) showed a steady positive shift in potential and appeared to be reaching a steady value of ~ 0.15 V at 100 h, but at 160 h the potential started a rapid positive shift before stabilizing at a value near 0.4 V. The potential for experiment CERT59 ($0.01 \mu\text{A}\cdot\text{cm}^{-2}$ applied current) showed a consistent negative going shift, and attained a steady value of ~ -0.17 V.

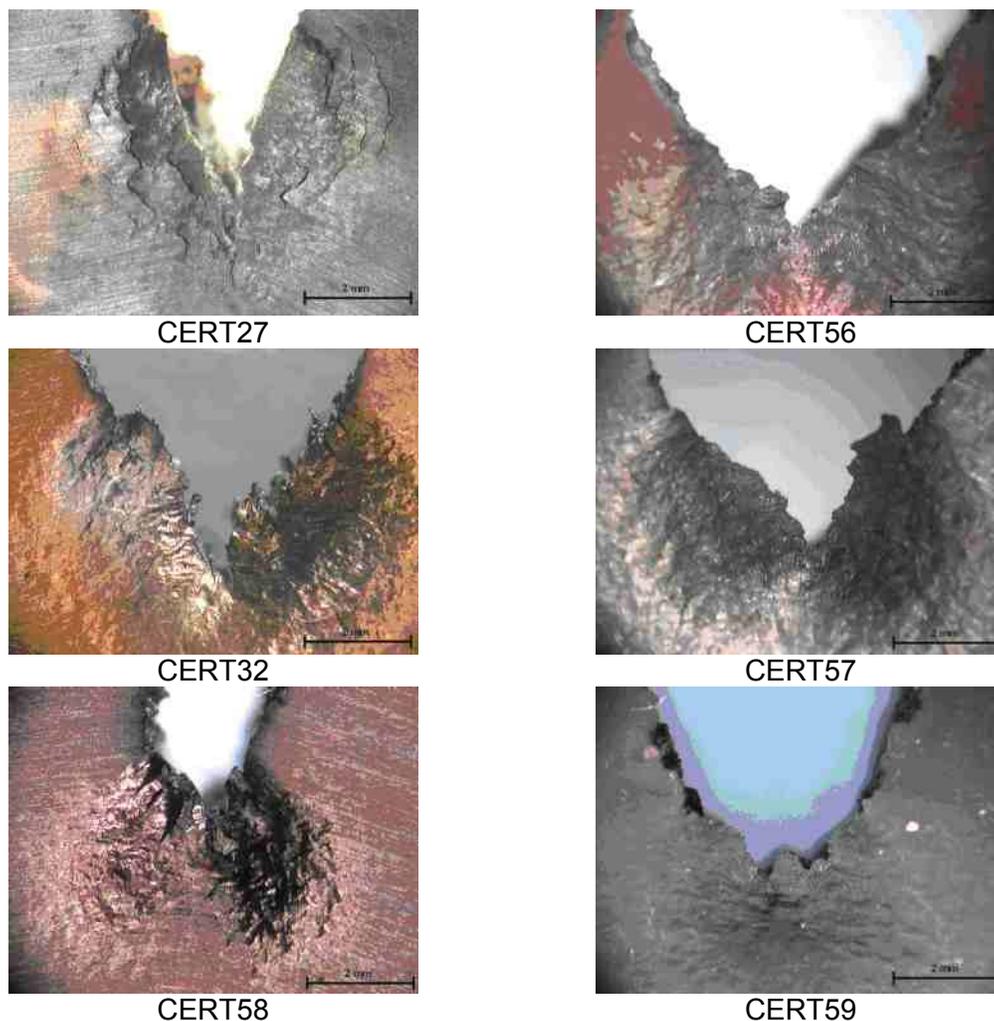


Figure 6: Magnified Images of the Crack Tip Region of Specimens Exposed to Nitrite-Only Environments.

The specimens exposed to 22°C are in the left column and 100°C in the right column. The experiment number is shown below each image. Current applied to the specimens: First row, $1 \mu\text{A}\cdot\text{cm}^{-2}$; second row, $0 \mu\text{A}\cdot\text{cm}^{-2}$; third row, $0.01 \mu\text{A}\cdot\text{cm}^{-2}$.

3.3 NITRITE/CHLORIDE MIXTURES

3.3.1 0.1 mol·L⁻¹ Nitrite Solution with Addition of 0.01 mol·L⁻¹ and 0.001 mol·L⁻¹ of NaCl

Experiments CERT54 and CERT55 were carried out in a 0.1 mol·L⁻¹ nitrite solution with the addition 0.01 mol·L⁻¹ and 0.001 mol·L⁻¹ of NaCl respectively at 100°C, and did not show visible evidence for SCC (Figure 5). The SCC factors were found to be 5.15 and 5.60 for CERT54 and CERT55, respectively (Table 1). The surface-crack velocities (SCER) were approximately 2.0 nm·s⁻¹ for both specimens. The high value SCC factors (i.e., >> 4) and the low surface-crack velocity indicate ductile crack advance and the absence of SCC in these tests. The corrosion potential for CERT54 was slightly negative, but near zero. The noise on the signal could indicate active dissolution, or a competition between film growth and dissolution. The corrosion potential values for CERT55 are suspicious, thus a comparison between the experiments is not possible.

Visually, both specimens were dark. The specimen from experiment CERT55 was black-dark blue compared to CERT54 which was grey-brown, with the area under the grips only lightly oxidized (Figure 5). The crack tips for both specimens were blunted, clearly showing a rounded crack tip and little crack extension (Figure 7).

As shown in Table 1, comparable experiments CERT29 and CERT30 were carried out in a 0.1 mol·L⁻¹ nitrite solution with the addition 0.01 mol·L⁻¹ and 0.001 mol·L⁻¹, respectively at 22°C (Ikeda and Litke 2000). SCC was found in both specimens. The SCC factors (2.70 vs. 1.37) and the SCERs (7.66 nm·s⁻¹ vs. 4.40 nm·s⁻¹) for CERT29 and CERT30 respectively, reinforce the SCC observation. CERT30 had loading difficulties throughout the early stages of the experiment and the extreme calculated values may be biased by the short actual experiment time. CERT29 and CERT30 were both oxidized with a mottled brown covering, but there was no evidence of the heavy black-dark blue colouration seen in the high temperature experiments.

These results indicate that a testing temperature at 100°C would inhibit SCC in 0.1 mol·L⁻¹ nitrite solution at a low NaCl concentration.

3.3.2 Nitrite Solutions (0.01 to 0.1 mol·L⁻¹) with Addition of 0.01 mol·L⁻¹ NaCl

As shown in Table 1, CERT34, CERT33 and CERT29 were carried out in 0.001, 0.01 and 0.1 mol·L⁻¹ NaNO₂ solutions at 22°C, respectively, all with the addition of 0.01 mol·L⁻¹ NaCl (Ikeda and Litke 2000). SCC was found in CERT29, while both CERT33 and CERT34 exhibited mainly ductile tearing. The degree of oxidation of the surfaces increased with increasing NaNO₂ concentrations. Chloride to nitrite ratios of 1 to 1 and 10 to 1 appear to be sufficient to inhibit SCC. However, a chloride to nitrite ratio of 0.1 does not appear to be sufficient to inhibit SCC.

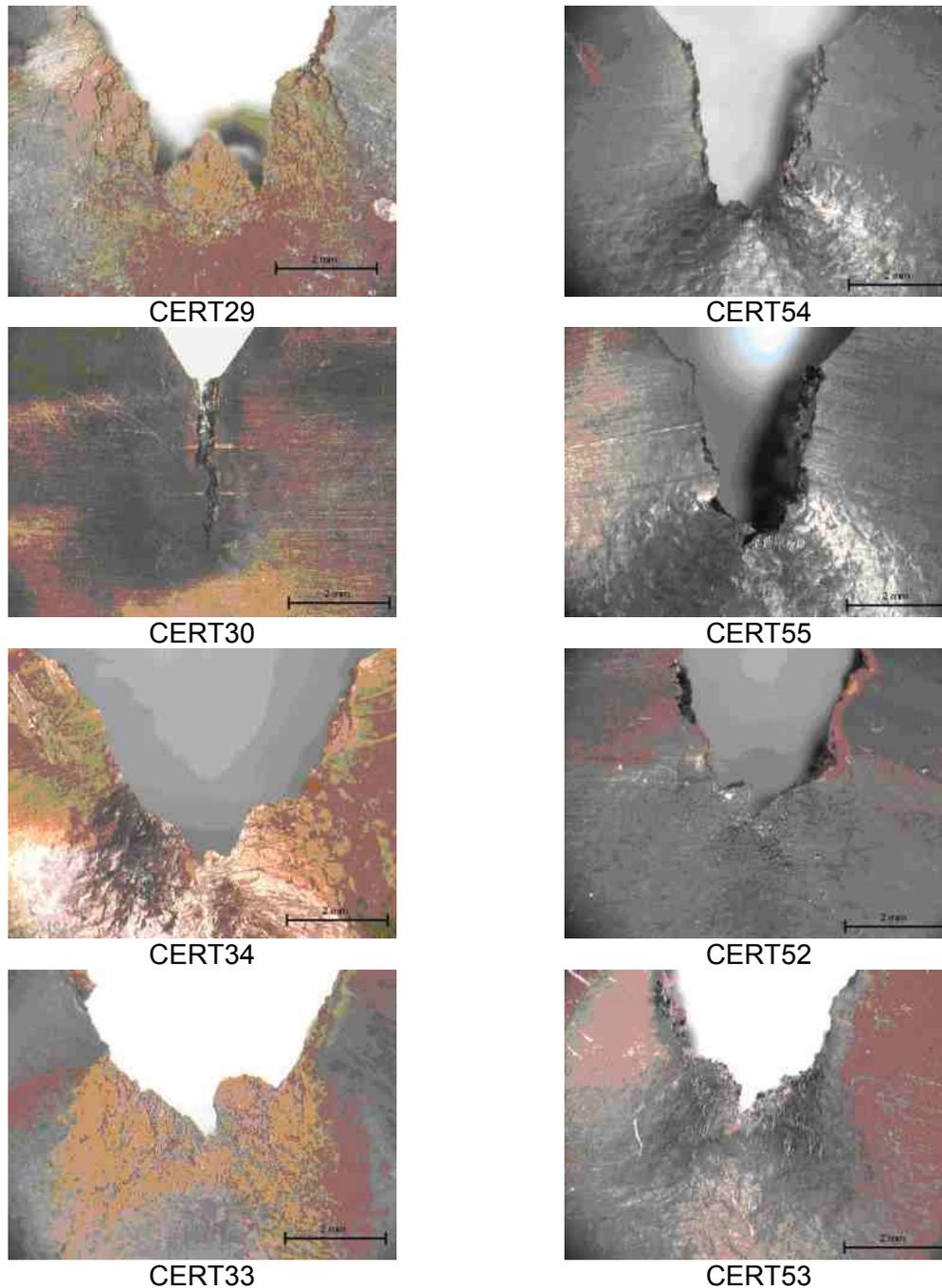


Figure 7: Magnified Images of the Crack Tip Region of Specimens Exposed to Nitrite/Chloride Environments.

The specimens exposed to 22°C are in the left column and 100°C in the right column. The experiment number is shown below each image.

Experiments CERT52, CERT53 and CERT54 were performed in 0.001, 0.02 and 0.1 mol·L⁻¹ NaNO₂ solutions at 100°C, respectively (CERT52 was performed at 130°C) all with the addition of 0.01 mol·L⁻¹ NaCl. The test results are shown in Table 1. The specimens from experiments

CERT52 and CERT53 were oxidized with a more reddish to purple colouration compared to the grey-brown colouration of CERT54. The crack-tips were all rounded, and the specimens showed considerable opening at the crack-mouth, but little extension of the crack length (Figure 7). No SCC was found in these specimens. The SCC factors were 7.10, 5.00 and 5.15, while the SCERs were 1.43, 2.33 and 2.04 nm·s⁻¹ for experiments CERT52, CERT53 and CERT54, respectively. The high value SCC factors (i.e., >> 4) and the low surface-crack velocities indicate ductile crack advance and the absence of SCC in these specimens.

These results appear to indicate that at elevated testing temperatures (100°C and 130°C), the addition of 0.01 mol·L⁻¹ NaCl is sufficient to inhibit SCC. At lower testing temperature of 22°C, the addition of 0.01 mol·L⁻¹ NaCl only inhibited SCC at the lower NO₂⁻ concentrations (0.001 and 0.01 mol·L⁻¹).

4. DISCUSSION

The SCCF1 factor was developed as a simple quantitative measure of SCC to categorize specimens as having brittle-like SCC, ductile tearing, or a mixture of these two behaviours. Small values of the SCCF1 parameter could be used to identify specimens that undergo SCC compared with purely ductile tearing (with large SCCF1 values). This was particularly useful for the experimental series performed in both ammonia and nitrite solutions (Ikeda and Litke 2000, and King et al. 1999b) for which several specimens exhibited brittle-like SCC crack-growth behaviour. A recent analysis of SCCF1 values obtained in acetate solutions (Litke and Ikeda 2006) suggested that when the SCCF1 values are in the range where both SCC and ductile crack growth are present then visual examinations of the specimens must be used to assist in identifying and ranking SCC. Similar to the acetate system, none of the experiments performed at 100°C clearly demonstrated SCC under the conditions used in this study, although some specimens showed more brittle-like crack growth than was observed for purely ductile behaviour observed in the absence of nitrite (COM0301). The SCCF1 factor values for the experiments performed at 100°C were indicative of ductile or mixed SCC/ductile crack growth. The lowest SCCF1 value at 100°C was obtained for experiment CERT56 (SCCF1=4.95), compared to the SCCF1 value obtained for the similar experiment, CERT27 (1.66), at room temperature (Ikeda and Litke 2000). However, visible evidence for some brittle-like crack-growth was observed for experiment CERT56 (Figure 6) despite the large value for the SCCF1 factor. Litke and Ikeda (2006) concluded that intermediate values of the SCCF1 factor do not unambiguously rank the degree of SCC. A visual assessment of the specimens is necessary to determine the degree of specimen ductility under the straining conditions used for these CERT experiments. The degree of roundness of the crack tip can be used to indicate the degree of crack-tip ductility, i.e., the absence of SCC. This visual evidence can be used to qualitatively assess the degree of SCC for specimens where the SCCF1 value no longer provides conclusive evidence for brittle-like crack growth. A similar analysis will be used in this report.

No definitive brittle-like SCC crack growth is suggested by the SCER and SCCF1 data. The larger SCCF1 measured at 100°C compared with the values at room temperature may indicate that the parameter range for ductile tearing had shifted to larger values at 100°C. Alternately, the values may truly indicate an increased ductility of the specimens under these test conditions.

4.1 NITRITE-ONLY SOLUTION

Previously, copper specimens were found to be susceptible to SCC in nitrite-only solution at 22°C. Experiments CERT56 (100°C) and CERT27 (22°C) were performed in 0.1 mol·L⁻¹ NaNO₂ with the application of 1 μA·cm⁻². Crack coalescence virtually disappeared with increasing testing temperature while the amount of oxidation of the specimen increased. More ductile deformation and less SCC was observed near the crack tip suggesting that the susceptibility to SCC and the SCER is lower at 100°C.

A visually comparison of the crack tip region for the experiments performed at room temperature and 100°C as a function of applied current illustrates the increased ductility at the higher temperature (Figure 6). Experiment CERT27 (1 μA·cm⁻²) clearly shows crack growth at room temperature whereas CERT56 shows mostly ductile behaviour at 100°C. Experiment CERT32

(OCP) shows greater ductility at room temperature than CERT27, but still shows a more brittle-like cracking character (i.e., more angular crack-tip) than CERT56 at 100°C. Figure 6 clearly shows the decrease in SCC susceptibility at 100°C compared to room temperature.

The influence of applied current at 100°C can be seen by comparing experiments CERT56 ($1 \mu\text{A}\cdot\text{cm}^{-2}$), CERT57 ($0.01 \mu\text{A}\cdot\text{cm}^{-2}$), and CERT59 (OCP) (Table 1). Comparing the SCER and SCCF1 values for experiments CERT56 (SCER= $2.32 \text{ nm}\cdot\text{s}^{-1}$, SCCF1=4.95) and CERT59 ($4.95 \text{ nm}\cdot\text{s}^{-1}$ and SCCF1 6.28) suggests that the SCC susceptibility increases with increasing applied current or oxidant supply. The visual examination of the specimens shows a greater similarity between experiments CERT56 and CERT57 than between CERT57 and CERT59. The specimen appearance also suggests that experiments CERT56 and CERT57 suffered some SCC, but experiment CERT59 did not (Figure 6).

An examination of the crack-tip following these experiments showed that CERT59 suffered the greatest blunting (rounding of the crack-tip) while CERT56 suffered the least (maintained a more angular relationship between the left and right crack-edges) (Figure 6). The measured corrosion potential was the most negative for experiment CERT59 and most positive for experiment CERT56. In addition, the load decay transient curve was the flattest for experiment CERT59 and the most rapid for experiment CERT56. The more rapid rate of load decrease has been qualitatively correlated with increasing degree of SCC (Ikeda and Litke 2000). The consistency of the trends for these parameters indicates that SCC decreases in the order CERT56>CERT57>CERT59. Since CERT57 is a free corrosion experiment and its SCC behaviour falls between the 0.01 and $1.0 \mu\text{A}\cdot\text{cm}^{-2}$ experiments, then the suggestion is that the corrosion current of copper in nearly deaerated nitrite solutions is between 0.01 and $1.0 \mu\text{A}\cdot\text{cm}^{-2}$.

Cassagne et al. (1990) suggested that pure copper is susceptible to SCC if the oxide film is formed in a particular potential region. The concept of a critical potential for SCC of pure copper was proposed previously by Benjamin et al. (1988). The overall colour of the specimen surfaces for experiments CERT56 and CERT57 are similar, but the images in Figure 5 are not the same because of lighting and printing artefacts. A more consistent lighting is obtained under higher magnification, and the gradation in the colour of the specimens observed in Figure 6 suggests a shift in oxide film formation that may be consistent with change in susceptibility to SCC - the darker (blue) the specimen, the less the susceptibility to SCC. The degree of SCC appears to increase with increasingly positive potential, also consistent with oxide film formation. In contrast, when the potential was negative, consistent with active dissolution of the copper, SCC was not observed (experiment CERT59). The blue colouration may be indicative of a precipitated copper oxide layer. The colouration of the specimens following elevated temperature testing may not be an accurate indication of the film formed at temperature because the film properties may change as the experimental vessel is cooled at the end of the experiment.

The decrease in SCC susceptibility and surface-crack velocity at an elevated testing temperature (100°C) could be explained by the higher testing temperature: a) promoting the formation of more coherent and less SCC susceptible oxide film at the crack tip, and b) decreasing the strength of the copper specimen which lessen the maximum stress intensification possible at the crack tip.

4.2 NITRITE/CHLORIDE MIXTURE

Previous results at room temperature have shown that the SCC susceptibility and surface crack velocity increases with decreasing chloride concentration and increasing nitrite/chloride ratio (Ikeda and Litke 2000). As the chloride and the nitrite concentrations were increased, the SCCF1 value for the specimen also increased, indicating that there was less SCC and more ductile crack growth. As shown in Table 1, SCC at room temperature was suppressed at a nitrite/chloride concentration ratio as low as 0.1. No SCC would occur for a nitrite/chloride concentration ratio less than 1. These results support the suggestion of a threshold nitrite/chloride ratio, below which SCC would not occur (Ikeda and Litke 2000). The corrosion potential shifted to more negative values with increasing chloride concentration, suggesting more uniform corrosion. Consequently, a negative shift in potential was correlated with increasing uniform corrosion and diminishing susceptibility to SCC.

At the elevated testing temperatures used in this study, all test specimens exposed to chloride (CERT53, CERT54, and CERT55 at 100°C and CERT52 at 130°C) exhibited ductile crack growth (Figure 5) and no SCC for any chloride concentration or chloride/nitrite concentration ratio investigated. The SCC factors were large (>5) with correspondingly small SCER (approximately $2 \text{ nm}^\circ\text{s}^{-1}$). The high SCC factors and low surface-crack velocities indicate that the copper specimens tested at elevated temperatures were subjected to only ductile crack growth driven by the experimental apparatus and not SCC. Visual examination of the specimens after SCC tests verified that significant ductile deformation occurred at the crack with no SCC (e.g., Figure 7). The ductile deformation and crack growth were driven by the constant extension of the specimen.

In contrast to room-temperature testing, the inhibitive effect of chloride on SCC appeared to be enhanced by the elevated testing temperatures. For example, at 100°C in a $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaNO}_2$ solution with $0.001 \text{ mol}\cdot\text{L}^{-1} \text{ NaCl}$, no SCC and a high SCCF1 value (5.60) were observed. This result can be compared to the result from a similar test at room temperature where SCC was present and the SCCF1 value was 1.37. Furthermore, at elevated temperature, SCC was still inhibited at the lowest nitrite/chloride concentration ratio of 0.1. The results appear to suggest that SCC is inhibited at a smaller chloride concentration at elevated temperature than at room temperature. However, a clear chloride concentration effect cannot be determined because the chloride concentration at the end of experiment CERT56 (no chloride added initially) was near that for CERT54, and was thought to be due to chloride leakage from the reference electrode during the experiment. A potential transient was observed in experiment CERT56 which may have been caused by the increasing chloride concentration during the test (Figure 4).

In comparison to room-temperature testing, elevated temperatures would increase the rate of uniform corrosion of copper. The crack advance requires sufficient stress (or an intensification of stress) at the crack tip. This stress drives the SCC crack growth. The stress gradually increases with time as the crack-mouth is opened by the constant extension of the sample. As the crack mouth opens, the load at the crack tip increases until the crack lengthens and the load is relaxed. For SCC conditions, the crack advance is by a brittle-like crack growth mechanism. However, if copper material is removed by dissolution, and if the material is removed from the crack tip faster than stress intensification at the crack tip can advance the crack, then SCC will not occur. Therefore, the increasing corrosion rate of copper in elevated temperature chloride environments would diminish SCC.

The negative shift in potential observed at room temperature indicated an increased rate of uniform corrosion with increasing chloride concentration (Ikeda and Litke 2000). Unfortunately, experimental difficulties prevented a similar analysis at 100°C because only one experiment containing chloride provided meaningful potential data. The negative potential for experiment CERT54 (Figure 4) is consistent with a more active behaviour, but further electrochemical data are required to confirm this assessment.

The surface-crack velocities in nitrite solution and nitrite/chloride mixtures are slower at 100°C than at room temperature (Table 1). At elevated testing temperature, the copper specimens were not subjected to SCC and the ductile crack grow rate was only driven by the experimental apparatus.

5. CONCLUSIONS

In this study, Constant Extension Rate Tests (CERT) of stress corrosion cracking (SCC) on oxygen-free phosphorous-doped (OFP) copper specimens were performed at elevated temperatures of 100°C and 130°C in nitrite-only solutions and in various nitrite/chloride mixtures. In summary, the findings of this work are:

1. The extent of SCC and the surface-crack velocity in nitrite-only solutions are much smaller at 100°C than at room temperature;
2. No SCC was displayed by the copper specimens exposed to the nitrite/chloride mixtures at temperatures above 100°C; and
3. The SCC susceptibility increases with increasing current in nitrite-only solutions.

The inhibiting effect of chloride on SCC was larger at the elevated testing temperatures when compared with room temperature. SCC was inhibited at lower chloride concentrations and nitrite/chloride concentration ratios. All specimens tested at elevated temperatures displayed ductile cracking and no SCC.

This study suggests that the SCC susceptibility, extent of SCC, and crack velocity of OFP copper will be suppressed at elevated testing temperatures compared to the behaviour at room temperature. Therefore, the general SCC behaviour of copper in nitrite-only and nitrite/chloride environments at elevated temperatures may be conservatively assessed by performing appropriate SCC tests at room temperature.

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