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Prediction of PWSCC in Nickel Base Alloys Using Crack Growth *Rate* Models

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Abstract

The Ford/Andresen slip dissolution SCC model, originally developed for stainless steel components in BWR environments, has been applied **to Alloy** *600* and Alloy **X-750 tested** in deaerated pure water chemistry. **A** method is described whereby the crack growth rates measured in compact tension specimens *can* **be** used to estimate crack growth in a component. *Good* agreement **was** found between model prediction and measured **SCC** in **X-750** threaded fasteners over a wide range of temperatures, stresses, and material condition. Most **data** support the basic assumption of **this** model that cracks initiate early in life.

The evidence supporting **a** particular SCC mechanism is mixed. Electrochemical repassivation **data** and **estimates** *of* oxide fracture **strain** indicate **that** the slip dissolution model *can* account for the observed crack growth rates, provided primary rather than secondary creep rates are **used.** However, approximately **100** cross-sectional **TEM** foils of SCC cracks including crack tips reveal no **evidence** of enhanced plasticity or unique dislocation patterns **at** the crack tip or along the crack to support a classic slip dissolution mechanism. No voids, hydrides, or microcracks *are* found in the vicinity of the crack tips creating doubt about classic hydrogen related mechanisms. The bulk oxide films exhibit **a** surface oxide which is often different **than** the oxides found within a crack. Although bulk chromium concentration affects the rate of SCC, **analytical data** indicates the mechanism does not **result** from chromium depletion at the **grain** boundaries. The overall findings support a corrosion/dissolution mechanism but not one necessarily related to slip **at** the crack tip.

Key **terms: Alloy** *600,* Alloy **X-750,** predictive models, mechanism, stress corrosion cracking :

Introduction

This paper describes the application of the slip-dissolution model to the pure water **stress** corrosion cracking **(PWSCC)** of nickel base alloys. **This** model **was** first developed by : D. Vermilyea⁽¹⁾ and later applied to stress corrosion cracking of stainless steel in boiling water reactor conditions by P.Ford and P. Andresen $^{(2,3)}$. The paper covers four aspects of SCC modeling: demonstration that the model **fits** existing Alloy *600* crack growth **data,** demonstration that the model gives reasonable estimates for A600 crack growth rates based

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solely on fundamental inputs, application of the model to predict component **SCC,** and mechanistic considerations.

The conceptual **basis** for the slip dissolution model **assumes** a **stepwise** process of crack advance that *can* be summarized **as follows:**

- Oxide film rupture at the crack tip due to time dependent strain (creep).
- \bullet Bare metal (anodic) dissolution at the crack tip.
- Repassivation at the crack tip due to reformation of the protective oxide. \bullet
- Continued deformation at the crack tip resulting in a new oxide rupture event that repeats the sequence.

Creep strain is the primary variable proposed to control the periodicity of the film rupture events. The **rate** of anodic dissolution and repsivation is determined by the alloy, the nature of its protective oxide, and the environment at the crack tip.

Mathematically, the rate of crack **advance** *can* **be** derived from **Faraday's** law **as** the depth "a" of metal that corrodes electrochemically within an increment of time:

$$
da = \frac{M}{zDF} dQ_f = \frac{M}{zDF} idt
$$
 (1)

where: $da = depth of corrosion (cm)$

 $M =$ molecular weight (g/mole)

 $p =$ density of metal (g/cm^3)

 $z =$ charge on the dissolving metal (equivalents/mole)

 $F =$ Faraday constant (96,500 coulombs/mole)

 Q_f = charge density per film rupture event (coulombs/cm²)

- i = current density at the crack tip (amperes/cm²)
t = time (seconds)
- $=$ time (seconds)

The repassivation current typically follows a power law:

$$
i = i_o(\frac{t}{t})^{-n} \qquad \text{for } t_o < t < t_f
$$

 (2)

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where: i_0 = bare metal current density (amps/cm²)

- t_f = time between rupture events
- **t,** = time at beginning of repassivation
- ⁿ= repassivation **rate** parameter

The incremental growth for each rupture event (i.e., average crack growth rate) is:

$$
V_{CT} = \frac{M}{zpF} \int_{t_a}^{t_f} i_o \frac{(t_o)^{-n}}{t_f} dt = \frac{M}{zpF} \frac{Q_f}{t_f} = \frac{M}{zpF} \frac{Q_f}{\epsilon_F} \dot{\epsilon}_{CT}
$$
 (3)

where: ϵ_f = oxide fracture strain $\dot{\epsilon}_{\text{cr}}$ = crack tip strain rate

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Andresen also developed an empirical relationship which showed that $\dot{\epsilon}_{CT}$ is proportional to the stress intensity factor^{\bar{c}}. The average crack growth rate can be expressed generally as a function of n, ϵ_f , \mathbf{i}_o , and stress intensity factor \mathbf{K}_i :

$$
V_{CT} = A \ddot{\epsilon}_{CT} = A K_l^{4n} \tag{4}
$$

where A and n are parameters which **are** specific functions of the crack tip material and environment combinations.

Crack **Growth Rates**

To assess the applicability of the slip dissolution model to PWSCC of nickel **alloys,** a model was evaluated against an **Alloy** *600* primary water CGR **database.** Figure **1** provides a compilation of **Alloy** *600* CGR **data** from several including **KAPL** generated **data. This data** is edited **to** include only actively loaded specimens to avoid the issue of **stress** relaxation in ; constant displacement specimens. Also shown is the model prediction for CGR vs. K_1 using
repassivation ratio (n) with values of 0.5 and 0.7. The functionality expressed by the Andresen model is in reasonable agreement with the observed trends.

On the basis of **this** fit of the **data** from the slip dissolution model, it was decided **to** examine *5* ! some of the fundamental input parameters of the model **as** further evidence that the model is viable for **PWSCC** application of nickel **base alloys.**

Model Fundamental Parameters

The purpose of this section is to examine the slip dissolution model prediction of Alloy *600* crack growth rates based on the fundamental inputs. The four fundamental inputs (measured parameters) to the slip dissolution model are maximum bare metal dissolution current density (i,,), repassivation rate (n), *creep* rate **(as a** function of applied load), and oxide fracture strain.

Figure 2 shows a plot of log current vs. time for the repassivation of Alloy 600 wire at **288°C (550°F)** in boric acid/sodium hydroxide with pHzss approximately 7.2. These **data** were obtained by stepping the applied potential to -0.711 V_{SHE} after 15 minutes at $-1.5V_{\text{SHE}}$. The plot indicates a lower bound bare metal current density of 3.5 mA/cm² and a repassivation parameter, n ⁿ, of 0.7. Similar results have been obtained using the drop weight method at the *same* potential, indicating that the Alloy *600* oxide found at the test condition is in fact reduced at the test conditions. This repassivation current is equivalent *to* those reported by **Soji"** at **288°C** in 0.01M Na₂MoO₄, but the repassivation time is somewhat faster.

Crack growth rate data for Alloy *600* at **288°C** (550°F) is not available. However, based on the data of Figure 1, a nominal value of 0.3 mils/day at 338° C (640°F) and at a K₁ of 25 ksi $\sqrt{\text{in}}$ **is** a reasonable baseline value to extrapolate to lower temperatures. Apparent activation energies for **PWSCC** of A600 range **from** 15 to **54** KcaVmol depending on **stress** intensity factor and degree of cold work^{9,10}. Extrapolation of 0.3 mils/day at 338°C to 288°C (550°F) with this range of activation energies yields crack growth rates of 0.01 mils/day ($Q = 54$) to 0.1 mils/day $(Q = 15)$.

Figure 3 presents the predicted crack **growth** rate of A600 from the slip dissolution model **as ^a** function of the periodicity of the film rupture. **A** periodic rupture time *(6)* of **about** 550 seconds would be required for **a** crack growth **rate** of 0.1 **mildday,** whereas a **t** of **26,000** results in **^a** calculated rate of 0.01 mils/day.

An oxide fracture **strain** of 0.003, approximately **equal** to the base metal yield **strain,** represents an order of magnitude estimate for *mixed* spinel **oxides** at **80"F,** and it is assumed that **this** value is independent of temperature up to 550°F. For a crack tip strain rate $\dot{\epsilon}_{CT} = \epsilon_f / t_f$, and $\epsilon_f =$ 0.003, the resulting creep strain rate would be calculated to be between 4.2×10^6 to 1.1×10^7 *(sec-').* **These** strain rates are 2-3 orders of magnitude higher than the steady state (secondary) . strain rates predicted by Garud for Alloy $600^{(11)}$. However, with the t_f being between 9.2 minutes and **7.2** hours, primary *creep* appears to be dominant with predicted **strain** rates between $10⁶$ and $10⁸$ (sec⁻¹), which is in agreement with the required crack tip strain rate to maintain the required **crack** growth **rates** predicted by an anodic dissolution mechanism.

The general conclusion **from** this analysis is that the slip dissolution model yields reasonable estimates of Alloy *600* crack growth **rates** based on fundamental input parameters provided **primary** creep **rates are** considered dominant rather than *secondary* creep rates.

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Prediction of Component SCC Endurance

KAPL has developed **an** engineering method to relate actual component SCC endurance to laboratory crack growth rates. The needed input **data** consists of measured crack growth rates **as** a function of **stress** intensity factor for the material of interest at the temperature of interest. It is assumed that crack growth **initiates** at time zero in a very small initial flaw. We have generally assumed an initial flaw *size* of O.OOO1" **(O.OOO25** cm) and have found that the calculated crack lengths are fairly insensitive to the initial flaw *size* assumptions. The general process consists of **the** following **steps:**

- Assume initial small flaw *size.*
- Calculate K₁ for initial flaw and given load.
- **•** Calculate corresponding crack growth rate.
- calculate amount of crack growth for an incremental **period** of time at the K,.
- **Advance the crack by the given amount.**
- Recalculate **K,** and repeat the process. \bullet

SCC **data** is **necessary** on both laboratory compact tension specimens and full *size* components for matching material/environment conditions. Such data has been obtained by KAPL for X-750 condition AH. Figure *(4)* presents KAPL crack growth rate **data** on Condition AH **X-750** obtained from **0.4T** *CT* specimens under constant load at 315-360°C **(600-680°F).** Correlating predictions are also plotted against the data. A $K₁^{2a}$ correlation was found to be better than $K₁^{4a}$ for **this** material/environment combination.

The laboratory crack growth rates **and** correlating model has been used to **assess** the SCC of threaded fasteners. **This model** prediction is shown in Figure (5) and is superimposed on the measured **crack** depth **data** for specimens tested at 338°C (640°F). Another prediction and **matching** fastener **data** for 282°C **(540°F)** is shown in Figure (6). Crack lengths in the fasteners were determined by destructive metallographic examination. Figure *(7)* compares the predicted crack lengths to the observed crack length for 88 specimens over a wide range of test conditions with applied stresses from 28 to 103 ksi and test temperatures from 282 to 360[°]C (540 to **680°F).** Good predictive agreement is obtained over a wide range of measured crack lengths (from about 3 to 123 **mils).** The general agreement is within 2X and it is concluded that the CGR modelling process *can* provide reasonable predictions of SCC **in** plant components provided **quality** CGR **data** is available.

Physical Evidence

Figure 8 shows an AEM cross-sectional image of an Alloy 600 specimen tested at 338°C (640°F). The foil preparation process is described in Reference (12). The significant (640°F). The foil preparation process is described in Reference (12). The significant obsemation is lack of indication of any deformation associated with the crack process. Figure 9 shows an SCC crack tip on a grain boundary without carbides with no evidence of voids or grain **boundary** sliding often **associated** with creep. To **date,** more than 100 AEM foils from 50

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separate A600 specimens have been analyzed. We have found no voids, hydrides, or microcracks **ahead** of the crack tip, commonly cited **as** indications of a hydrogen related **SCC** mechanism. The lack of unique deformation associated with the crack tip **casts** doubt on slip or creep **as a** participant in the **SCC** mechanism.

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The bulk oxide **films** exhibit a surface oxide which is often different **than** the oxides found within a crack. Surface oxides are Cr and Ni rich near the metal surface and contain NiO and spinels **in** the outer layers. In **a** number of instances, NiO is found within the crack adjacent to the metal which is not observed **at** the bulk specimen oxidelmetal interface (Figure **10).**

The presence of oxides at the crack tip is **an** indication that oxidation is taking place **as** a result of exposure to the environment. The differing oxides inside the crack **as** compared to the outside surface suggests **a** difference in the environment and/or material **(grain** boundary) **at** the tip. The **changes in** the oxide composition inside the crack suggests non-uniformity in solubility and probably repassivation kinetics. **These** observations taken **as a** whole suggest **an** oxide fracture/dissolution mechanism for crack propagation, but not one associated with slip at the crack tip.

Conclusions

- The slip-dissolution model provides an adequate engineering fit to the measured crack growth rates for Alloy 600 in pure/primary water.
- \bullet Based solely on fundamental inputs, the slip dissolution model gives reasonable **estimates** for A600 crack growth rates, provided primary creep rate values are inputed.
- \bullet *An* **engineering** model (independent of mechanisms) that **uses laboratory** crack **growth** rate **data** provides **a** sound basis to predict the SCC endurance of actual components.
- Issues pertaining to the application of the slip dissolution model to PWSCC of nickel alloys include **lack** of evidence of plastic deformation uniquely **associated with the** crack tip, understanding oxide changes **as** a function of grain boundary microstructure and chemistry, and the **rates** of creep deformation.

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Figure 1. Compilation of Alloy 600 crack growth rate data in high temperature deaerated pure water and Ford/Andresen model correlation for crack growth rate vs. K₁ for 'n' values of 0.5 and 0.7.

Figure 2. KAPL repassivation data on Alloy 600, potential pulse from -1500mV_{SHE} to -711mV_{SHE} at 288°C, deaerated 0.1M boric acid titrated with NaOH to a cell resistance of 105 ohms and pH=7.6 at 25°C.

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Figure 3. Predicted crack growth rate from repassivation data as a function of the periodic oxide rupture time.

Figure 4. Crack growth rate data **for X-750, Condition** *AH* **in high temperature deaerated pure water, constant load 0.4T** *CT* **specimens.**

Figure 5. Model prediction of aack depth based on *CI'* **specimen** data **and oorresponding observations for X-750, Condition** *AH* **threaded fasteners tested in DPW at 640'F.**

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Note: Upper
Bond $1E+D2$ 7. 5 PREDICTED SCC (mils)
په
په \blacktriangleleft 3 $\overline{2}$ C Fastener Design 1, AH $^{\circ}$ + Fastener Design 2. AH $\overline{}$ A Fastener Design 3, BH 5 Fastener Design 4, AH á J. -I ,. **[2](#page-4-0) [3](#page-5-0) [4](#page-6-0)** *[5](#page-7-0)* **[6](#page-8-0) [lE+O1 2](#page-4-0) [3](#page-5-0) [4](#page-6-0)** *[5](#page-7-0) [6](#page-8-0)* **K+02** *9* **OBSERVED SCC (mk)** *t*

[Fire 6.](#page-8-0) Model prediction of uack depth and corresponding for X-750, Condition AH threaded fasrenea tested in DPW at 540°F.

Figure 7. Predicted uack length hsed on *CT* **specimen data versus** ohserved **crack length for wide range of fastener geometries, applied stress, and temperature.**

CRACK CONTAINING BOTH CR AND NI RICH OXIDE AND NIU. CORROSION PRODUCI IN 2CC **FIGURE 10.** OBSERVED AHEAD OF CRACK. NO CARBIDES, VOIDS OR MICROCRACKS **SCC CRACK TIP. FIGURE 9.** CRACK CHANGES DIRECTION DISLOCATION STRUCTURE REMAINS THE SAME. AROUND COMPLEX GRAIN BOUNDARY CONTAINING CR₇C₃ CARBIDES. **ZA 3TON** FIGURE 8. AEM CROSS-SECTIONAL IMAGE SHOWING SCC CRACK PROPAGATING

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 \mathbf{d} 6 CCC Crack

STRESS CORROSION CRACKING INITIATION

- *⁰***502 Double U-bend** & **112 C-ring specimens**
- *⁰***EN62, EN82 weld metal**
- Tested at 600°F, 640°F, 680°F (315, 338, 360°C) for up to 249 weeks
- *⁰***Four strain levels; 10% and 16% for U-bends .45% and 4% for C-rings**

SCC Initiation - **Results**

Thermal treatment of weld metal (1125°F (607°C) for 7 hours)

- *⁰***Beneficial in reducing SCC**
- **^aStatistically 95% confidence of a significant difference**
- 56% of non-thermal treated specimens failed
- *⁰***21% of thermally treated specimens failed**

and the second (19.43 - and 1.539 Part) of \sim

STRESS CORROSION CRACK GROWTH RATE TESTING

- *⁰***3** .4T **precracked compact tension specimens**
- *⁰***EN82 weld metal**
- **Constant load stress intensity of 35 ksivin (38 MPavm)**
- **680°F (360°C) primary water for 108 days** *⁰*

Resul ts/Conclusions

- **Specimens showed a range** of **growth rates** of **0.62 to** 1.08 **niils/day** (1.8 \times 10⁻¹⁰ to 3.2 \times 10⁻¹⁰ m/s) *0*
- **Best estimate SCC growth rate of 0.80 mils/day (2.4** \times **10⁻¹⁰ m/s)**
- *⁰***SCC initiated in less than 16 days**

Characteristics of Weld Metal Used for Crack Growth Rate Specimens

b

0.4T Compact Tension Specimens were oriented such that the notch is perpendicular to the welding passes.

COMPARISON OF SCCGRs FOR EN82 WELD METAL SPECIMENS

Overall Average $\Sigma = 0.80$ $\Sigma = 0.74$

Notes: (1) SCCGR = (Maximum **Crack** Dcpth - **Crack Deptli.at** Detection)/Cracking Time For this calculation, the crack depth **at** detection was assumed to be zero.

> (2) **SCCGR = (Maximum Crack Depth - Crack Depth at Detection)/Cracking Time** For this calculation, the **crack** depth **at** detection **for** specimens 7741 and 0726 were determined **by** correlating the total SCC area to the LVDT compliance. Due to a broken LVDT wire, a crack depth at detection could not be calculated for 7742 and was assumed to be zero.

> > **FIGURE 16**

OFFRICANT DATA JOY FEXPLUS CRITICS

Cross sectional (schematic) view of test pipe assembly

Test Parameters

 \bullet

- Autoclave pressure \bullet
- Water temperature \bullet
- Hydrogen overpressure \bullet
- Axial load plus pressure \bullet
- Axial tensile residual stress \bullet
- **Test duration**

2850 psi (20 MPa) 680° F (360°C) 40-60 cc/kg 20.3 ksi (140 MPa) 30 ksi (207 MPa) 78 weeks

ALLOY 600 PIPE WELDMENT STRESS CORROSION TEST

- Axially loaded pipe specimen \bullet
- Nine 3" diameter Schedule 160 Alloy 600 pipe test segments \bullet
- Two heats of piping (good and bad microstructure) \bullet
	- Total of 10 welds

 \bullet

- 8 EN82 welds (2 low, 2 medium, 4 high carbon content) \bullet
	- 2 EN62 welds

SUMMARY OF POST-TEST EVALUATION OF PIPE WELDS

FIGURE 18

HEIRICEAN ED AT GOVE LYPENSE # 61

SUMMARY OF POST-TEST EVALUATION OF PIPE WELDS (CONTINUED)

NOTES: Crack length was established by grinding and polishing incrementally until the crack disappeared.

If no crack length is shown, the crack had disappeared after the first increment (usually 0.020") was removed. All cracks are circumferential unless otherwise indicated.

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- (A) Side of weld with acceptable microstructure base metal NX8908
- (U) Side of weld with unacceptable microstructure base metal · NX8913

Pipe wall thickness = 0.437" nominal

 \sim

FIGURE 18A

OF PRODUCTION COLLECTIVE RESEARCH

Alloy 600 Pipe Weldment Stress Corrosion Test - Continued

Results

 \bullet

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SCC initiation observed in weld metal and HAZ of each weld

EN62 and low carbon EN82 had highest propensity for weld SCC \bullet

Worst HAZ SCC occurred in base metal with bad microstructure

HAZ and base metal cracks initiated from stress concentrators \bullet

> Alloy 600 Pipe Weldment Stress Corrosion Test Longitudinal Section of Pipe Weld

FIGURE 19

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THERMAL BOUNDARY CONDITIONS 45° Weld

Nozzle

Pipe Wall

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 $-0.68 -$

 $0.063 -$

 $1.6 -$

- Air with NC Heat Transfer
- · Exterior Surface of Weld Elements Insulated After Birth
- . Monitor Depth of Molten Zone (40-50 Mils Max)
- Thermal Constraint Equations for Uniform Weld Metal Cooling
- · Internal Heat Generation in Weld Passes
- Timed Weld Element Heat Generation to Model Arc Travel Speed
- Adjusted Heat Generation Function to Match Thermocouple Data

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STRUCTURAL MODEL & BOUNDARY CONDITIONS

- 5056 Nodes, 4227 Hex/8 Elements
- Fixed Supports at Base
- Planar But Not Parallel at Pipe End
- Elastic/Plastic Temperature Dependent **Material Properties**
- Bi-Linear Stress-Strain Curves $[70^{\circ}$ F to 2100 $^{\circ}$ F]
- Kinematic Material Hardening
- Root Gap Set Using 3 Tack Welds
- Deposited 7 Full 360° Passes

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• Chemical Cracking Corroborated Peak Stress Locations

• Cracking at Locations Calculated Above 30-35 ksi

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COMMENT

180[°] Away

Last Wejded Quadrant

Zyglo of Cracking in Regions of
>30-35 ksi Tensile Axial Stress

FIGURE 24

Is Atomic Power Laboratory

CONCLUSIONS

- . Good First Order Effects of Welding Process
- 3D Analysis Necessary for True Weld-Induced Stress Response
- Expect Tensile Stresses in Last Welded Quadrant for Thin Wall Weld
- Axisymmetric Analysis Overpredicts Peak 3D Stresses Near, Weld, **Less Agreement Away from Weld**
- . Through Wall Bending Assumption Not Valid for Stress **Measurement Techniques**

-Knolls Atomic Power Laborator

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