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ANALYSIS OF THE EFFECTS OF CORROSION POTENTIAL AND IMPURITIES
ON THE STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL*

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ANALYSIS OF THE EFFECTS OF CORROSION POTENTIAL AND IMPURITIES
ON THE STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL*

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ABSTRACT

Intergranular stress corrosion cracking (IGSCC) of sensitized Type 304 stainless steel (SS) has been a recurrent problem in the high-temperature water environment of boiling-water-reactors (BWRs) over the past two decades. The synergistic effects of environmental and material variables on stress corrosion cracking (SCC) of Type 304 SS were investigated at 289°C by means of constant-extension-rate-tensile (CERT) tests at a strain rate of 1×10^{-6} /s. Correlations among environmental variables (dissolved oxygen and impurity concentrations, viz., H_2SO_4 , steady-state open-circuit electrochemical potential) and the SCC susceptibility parameters have been determined. The extensive results over a wide range of open-circuit corrosion potential conditions were analyzed by a model which accounts for the effects of environmental variables, microstructure (e.g., degree of sensitization) and strain rate. The results are consistent with a slip-dissolution mechanism for SCC. Furthermore, representation of the dependence of corrosion potential and average crack growth rate on the dissolved oxygen concentration of the water by a simple mathematical function, in conjunction with the theoretical model, enables predictions of both strain rate and environmental effects on the SCC susceptibility of sensitized Type 304 SS.

*Work supported by the Office of Nuclear Regulatory Research, U. S. Nuclear Regulatory Commission, Washington, DC.

INTRODUCTION

Sensitized Type 304 SS is susceptible to intergranular stress corrosion cracking (IGSCC) in high-purity water with ~ 0.2 ppm dissolved oxygen at temperatures $\geq 150^\circ\text{C}$ provided the stress level is sufficient to produce some plastic strain rate. The open-circuit electrochemical potential of Type 304 SS under steady-state conditions is a useful parameter for describing environmental effects on IGSCC susceptibility of the steel. For example, at electrochemical potentials corresponding to dissolved oxygen concentrations of < 0.04 ppm in high-purity water, no IGSCC occurs¹ in CERT tests at 289°C and a strain rate of $3 \times 10^{-7}/\text{s}$. It has been demonstrated² that IGSCC can be mitigated in sensitized austenitic stainless steels by means of hydrogen addition to BWR feedwater, which lowers the dissolved oxygen content of the recirculation loop water to < 0.02 ppm and also decreases the electrochemical potential. Impurities (e.g., SO_4^{2-} , NO_3^- , and CO_3^{2-}), if introduced into the recirculating coolant in BWRs by intrusion and degradation of resin fragments or by the exhaustion of ion exchange resins, can aggravate the IGSCC susceptibility.^{3,4} CERT tests have shown that sulfate is one of the most detrimental species at low concentrations (< 0.1 ppm).⁵ Ionic impurities in water can affect the corrosion potential of the steel depending upon the concentration and type of species. This suggests that water conductivity (with some knowledge of the impurity species) and the open-circuit corrosion potential of the steels are appropriate parameters for relating laboratory SCC results to those obtained in a reactor. In addition, the degree of sensitization of the steel has some influence on susceptibility to IGSCC.

This paper describes the synergistic effects of dissolved oxygen and sulfate concentrations on the open-circuit steady-state corrosion potential and the SCC behavior of Type 304 SS, heat-treated to produce different degrees

of sensitization. CERT tests were used because of the high degree of reproducibility of the results and the capability to explore a wide range of variables within a reasonable time period. The results were analyzed by means of a phenomenological model based upon a slip-dissolution process at the crack tip and elastic-plastic fracture mechanics. A model that described the effect of strain rate on SCC^{6,7} was reformulated to account for the effects of environment and material microstructure. The model was then combined with a simple mathematical formulation for the variation of average crack-growth rate with dissolved oxygen concentration in water and corrosion potential to predict both the effects of strain rate and the environment-related parameters on SCC in a quantitative manner. The range of corrosion potential values for the steel in this investigation encompasses the upper- and lower-bound values that are relevant to BWRs, with normal and the alternate hydrogen-water chemistries.

EXPERIMENTAL METHODS

The chemical composition (wt %) of Type 304 SS (Heat No. 30956) used in this study is as follows: 18.99 Cr, 8.0 Ni, 1.54 Mn, 0.48 Si, 0.44 Mo, 0.19 Cu, 0.10 Co, 0.10 N, 0.06 C, 0.019 P, 0.007 S, balance Fe. The details of specimen heat treatment and preparation, and the procedure for performing the CERT tests have been described elsewhere^{3,5} and therefore, only a brief description is given here.

The degree of sensitization produced by different heat treatments was quantified by an electrochemical-potentiokinetic-reativation (EPR) technique⁸ and the EPR values ranged from 2 and 30 C/cm². The slow strain rate tests were conducted with an Instron Model 1125 tensile testing machine as well as with a more compliant loading system equipped with a worm gear Jactuator, gear

reducer, and a variable speed motor loading machine. The tests were performed in an autoclave with a once-through water system at a temperature of 289°C, a pressure of 9.0 MPa, and a flow rate of $\sim 10 \text{ cm}^3/\text{min}$. The CERT specimens with a gauge length and diameter of 6.25 and 32.0 mm, respectively, were exposed to water containing controlled amounts of dissolved oxygen with and without 0.1 ppm sulfate added as sulfuric acid. All the tests were conducted at a strain rate of $1 \times 10^{-6}/\text{s}$. An external silver/silver chloride (0.1M KCL) reference electrode, a thermocouple, and platinum and Type 304 SS electrodes were located at the outlet of the autoclave to establish the redox and open-circuit corrosion potentials, respectively, at the test temperature. The measured potentials were converted to the standard hydrogen electrode using the thermocell and liquid-junction potentials.⁹ The potential values for the platinum and stainless steel electrodes changed significantly during the first several hours and reached steady-state values after about 20 h. Therefore, straining of the specimens was initiated after exposure to the environment for ~ 20 h at 289°C.

After the tests were completed, the fracture surfaces were examined by scanning electron microscopy to determine the maximum intergranular or transgranular crack length. The average crack growth rates \dot{a}_{av} were estimated with the assumption that the crack length and strain at crack initiation were small (viz., $a_0 = 1 \text{ }\mu\text{m}$ and $\epsilon_0 = 1.0\%$ where a_0 and ϵ_0 are the crack length and strain at initiation, respectively). The results discussed in this study are not affected significantly by the choice of crack initiation parameters over a wide range of values.

RESULTS AND DISCUSSION

The experimental results in general show that IGSCC in the sensitized Type 304 SS is aggravated by the presence of a 0.1 ppm sulfate added to water as sulfuric acid. The degree of sensitization of the material in the range from 2-30 C/cm², obtained by the EPR technique, has a relatively small effect on SCC in high-temperature water with oxygen levels <0.15 ppm and conductivity values <1.0 μS/cm. The dissolved oxygen concentration or the open-circuit corrosion potential has a dominant effect on SCC in low-conductivity water.

A direct correlation between open-circuit corrosion potential and dissolved oxygen concentration in high-purity water was obtained and this relationship is not significantly affected by the presence of 0.1 ppm sulfate, added as acid. The corrosion potential V of Type 304 SS determined during the CERT tests in both high-purity water and the impurity environments exhibits a characteristic "S" shape, as shown in Fig. 1, when plotted as a function of the logarithm of dissolved oxygen concentration in ppm (i.e., $\log\{O_2\}$). A similar variation of corrosion potential with dissolved oxygen concentration has been observed by other investigators.^{10,11} Logarithmic plots of average crack growth rate as a function of dissolved oxygen concentration were also constructed. As shown in Figs. 2 and 3, the variation of the SCC parameter \dot{a}_{av} with oxygen also exhibits a shape similar to that displayed in Fig. 1 although the details of the curves are different. In addition, it is found that the transition in the "S" curve in both high-purity water and the impurity environment corresponds to a change in the SCC mode from intergranular to transgranular as the oxygen concentration decreases; the transition occurring at ~ 0.1 ppm of oxygen. It is clear that with a decrease in oxygen

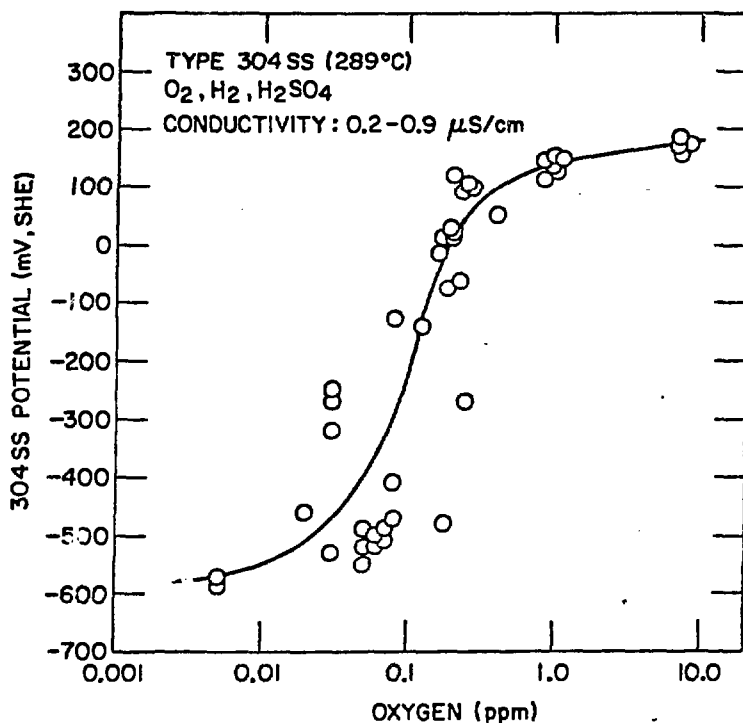


Fig. 1. Variation of Steady-State Open-Circuit Corrosion Potential of Type 304 SS with Dissolved-Oxygen Concentration in an Impurity Environment during CERT Tests at 289°C.

content from 8 to 0.02 ppm or less [or a decrease in corrosion potential from about 180 to -500 mV(SHE)], decreases \dot{a}_{av} by a factor of approximately 6 to 10. This dependence can be incorporated into a theoretical model which quantitatively describes the effect of applied strain rate on the crack growth rate and other SCC parameters in the CERT tests.

The model is based on elastic-plastic fracture mechanics and a slip-dissolution mechanism of crack advance. Since a detailed description is found elsewhere,^{6,7} we include only the essential results relevant to the present study. The model predicts that the crack length and time of failure, a_f and t_f , respectively, are related by an equation of the form

$$a_f = A t_f^{0.5}, \quad (1)$$

where the parameter A is environment- and microstructure-dependent but independent of $\dot{\epsilon}$ in the regime of SCC susceptibility. Equation (1) in conjunction with the following J-integral-based fracture criterion

$$J_c = C a_f \epsilon_f \quad (2)$$

leads to power-law relationships between the SCC susceptibility parameters and $\dot{\epsilon}$. These relations are rewritten in a slightly different form to highlight the environmental effects on SCC as follows:

$$\dot{a}_{av} = (J_c / C \dot{\epsilon})^{-1/3} A^{4/3}, \quad (3)$$

$$a_f = (J_c / C \dot{\epsilon})^{1/3} A^{2/3}, \quad (4)$$

$$t_f = (J_c / C \dot{\epsilon})^{2/3} A^{-2/3}, \quad (5)$$

and

$$\epsilon_f = (J_c \dot{\epsilon}^{1/2} / C)^{2/3} A^{-2/3} \quad (6)$$

where ϵ_f is the failure strain and J_c / C is the fracture-characterizing parameter, which is independent of the environmental variables (and strain rate) but depends on the material and specimen geometry. The value of J_c / C is found to be constant (5×10^{-4} m) for all the data shown in Figs. 2 and 3, which is consistent with the model. Results for the dependence of the various SCC parameters in Eqs. (3)-(6) on environmental conditions are also in agreement with predictions of the model and this is demonstrated as follows.

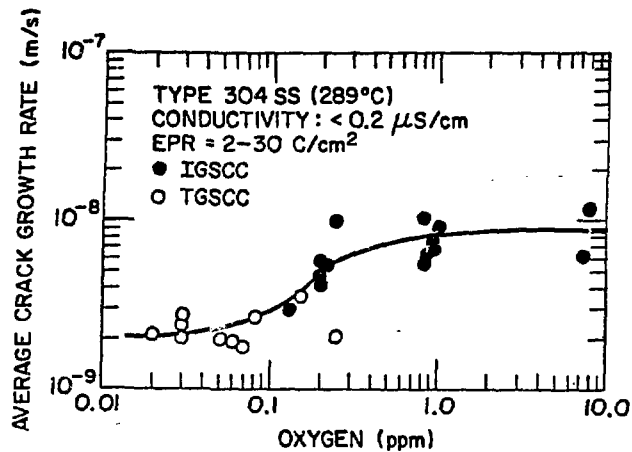


Fig. 2. Average Crack Growth Rate versus Dissolved Oxygen Concentration in Water for the Sensitized Type 304 SS in the High-Purity Environment.

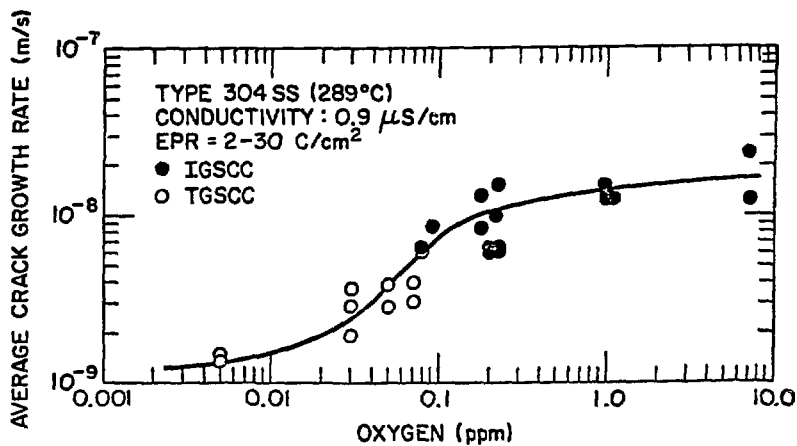


Fig. 3. Average Crack Growth Rate versus Dissolved Oxygen Concentration in Water for the Sensitized Type 304 SS in an Impurity Environment with 0.1 ppm Sulfate as H_2SO_4 .

From the data, the crack-growth-rate constant A [see Eq. (1)] has been calculated from a_f and t_f with the assumption that crack initiation occurs early in life. Log-log plots of \dot{a}_{av} versus A have been constructed to determine whether the data can be described by the model [Eq. (3)]. Figure 4 shows the results in high-purity water for Type 304 SS sensitized to $EPR = 2$ and 20 C/cm^2 . The experimentally determined slope is in satisfactory agreement with the value of $4/3$ predicted by Eq. (3). The results for sensitized Type 304 SS in the impurity environment (Fig. 5) show similar agreement with the model (taking experimental scatter into account). These observations also suggest that CERT results for Type 304 SS over a range of environmental conditions are consistent with a slip-dissolution mechanism for SCC.¹² In both high-purity and impurity environments, the model describing the variation of \dot{a}_{av} with A shows that once the material is sensitized, the degree of sensitization has a relatively small effect on SCC. The dissolved oxygen concentration or steady-state open-circuit corrosion potential has a dominant effect on the SCC behavior. These results are pertinent to the hydrogen-water chemistry that is being considered for use in some BWRs to control the SCC problem. The dependence of other SCC parameters such as a_f , t_f , and ϵ_f on A was also found to be consistent with the model [Eqs. (4)-(6)]. If we can determine, in an analytical fashion, the dependence of A on environment-related variables such as dissolved oxygen content (or corrosion potential), the model can be used to interpolate the SCC susceptibility from one environment to another over the range of potentials that include both the upper- and lower-bound values relevant to operating BWRs. In addition, the model permits the strain rate effects on SCC to be predicted over a wide range, and hence, the capability of the model can be extended. This is accomplished in the following manner.

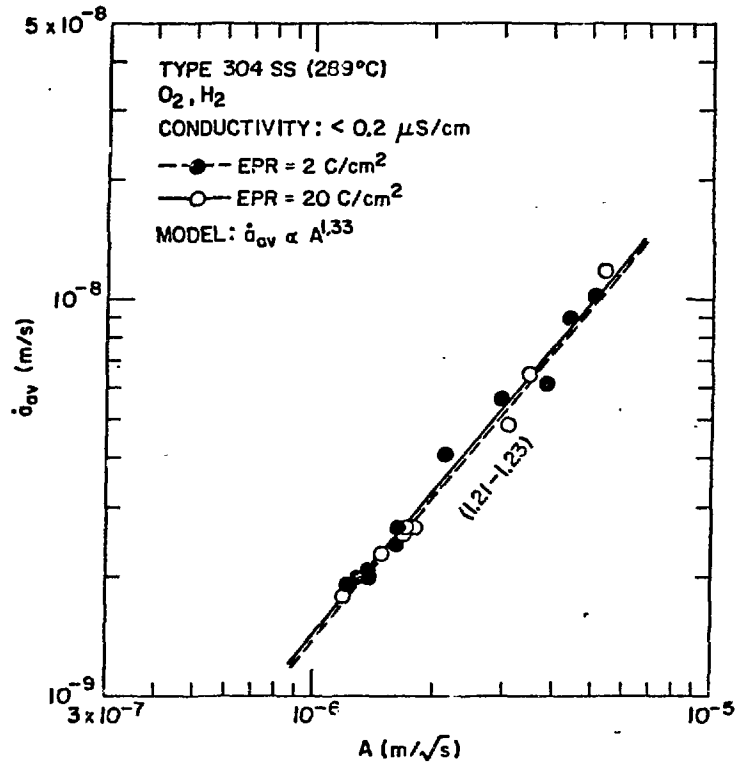


Fig. 4. Variation of Average Crack Growth Rate with the Model Crack Growth Parameter ($A = a_f t_f^{-0.5}$) for Sensitized Type 304 SS in High-Purity Water Containing Different Concentrations of Dissolved Oxygen.

Examination of the characteristic shape for the variation of corrosion potential V with $\log[O_2]$ in Fig. 1 suggests that the dependence can be described by a mathematical function of the following form:

$$V = -\alpha_1 + \beta_1 \tan^{-1} \left(\gamma_1 \frac{\log[O_2]}{\delta_1} \right), \quad (7)$$

where α_1 and δ_1 are the location coordinates (since the symmetry of the curve does not coincide with the value of zero on the axes); β_1 is a scaling factor; and γ_1 is a shape factor (since the details of the "S" shape can vary from a gradual to a sharp transition). Although the approximate value of these coefficients can be determined simply from the properties of the above

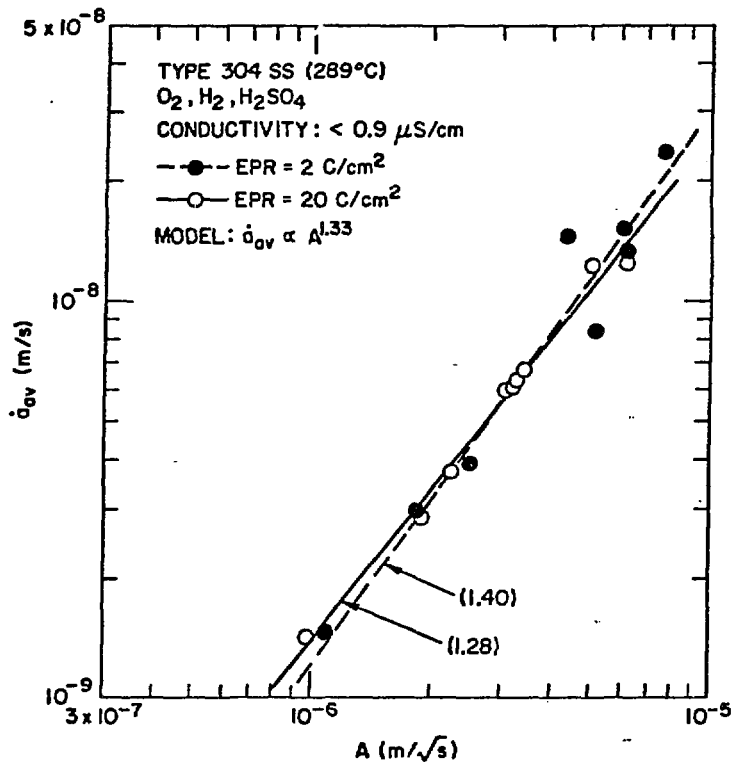


Fig. 5. Variation of Average Crack Growth Rate with the Model Crack Growth Parameter ($A = a_f t_f^{-0.5}$) for Sensitized Type 304 SS in an Impurity Environment with 0.1 ppm Sulfate as H₂SO₄ and Different Concentrations of Dissolved Oxygen.

function, for the present purpose, the values were determined from a nonlinear least-squares analysis of all the data shown in Fig. 1. The values of the four coefficients are listed in Table I. Using Eq. (7) and the values of the constants, the data are well represented by the solid curve in Fig. 1.

Although the crack growth data in Figs. 2 and 3 can also be described by a similar function, to extend the versatility of the model we consider the model crack-growth parameter $A (= a_f t_f^{-0.5})$ and its variation with dissolved oxygen concentration in water as follows:

TABLE I. Coefficients in Equations Used to Describe the Variation of Open-Circuit Steady-State Corrosion Potential V and Crack Growth Rate Constant A for Sensitized Type 304 SS (EPR = 2 to 30 C/cm²) with Dissolved Oxygen Concentration in 289°C Water

Relation ^a	Conductivity (μS/cm)	α	β	γ	δ
V vs log[O ₂]	0.2-0.9	216.0	273.0	3.38	0.10
log[A] vs log[O ₂]	0.2	5.61	0.20	2.45	0.22
log[A] vs log[O ₂]	0.9	5.70	0.39	1.30	0.03

^aV in mV, O₂ in ppm, A in m/√s.

$$\log A = -\alpha_2 + \beta_2 \tan^{-1} \left(\gamma_2 \frac{\log[O_2]}{\delta_2} \right) \quad (8)$$

The values of the constants for material sensitized to different degrees and tested in two environments (high-purity water and water containing 0.1 ppm sulfate) are also given in Table I. Equations (3) and (8), in conjunction with $J_c/C = 5 \times 10^{-4}$ m, were used to describe the crack-growth data. As can be seen from Fig. 6, agreement between the predicted and experimental average crack-growth rates is good. Although the functional relationship of A versus [O₂] is useful, the dependence of A on the open-circuit corrosion potential may be more advantageous since in reactor-type environments, corrosion potential is not only affected by the dissolved oxygen but also by the different impurity species. The variation of A with corrosion potential for Type 304 SS is obtained by combining Eqs. (7) and (8) and is given by

$$\log A = -\alpha_2 + \beta_2 \tan \left\{ \gamma_2 \left[\frac{1}{\gamma_1} \tan \frac{(V+\alpha_1)}{\beta_1} + \log (\delta_1/\delta_2) \right] \right\} \quad (9)$$

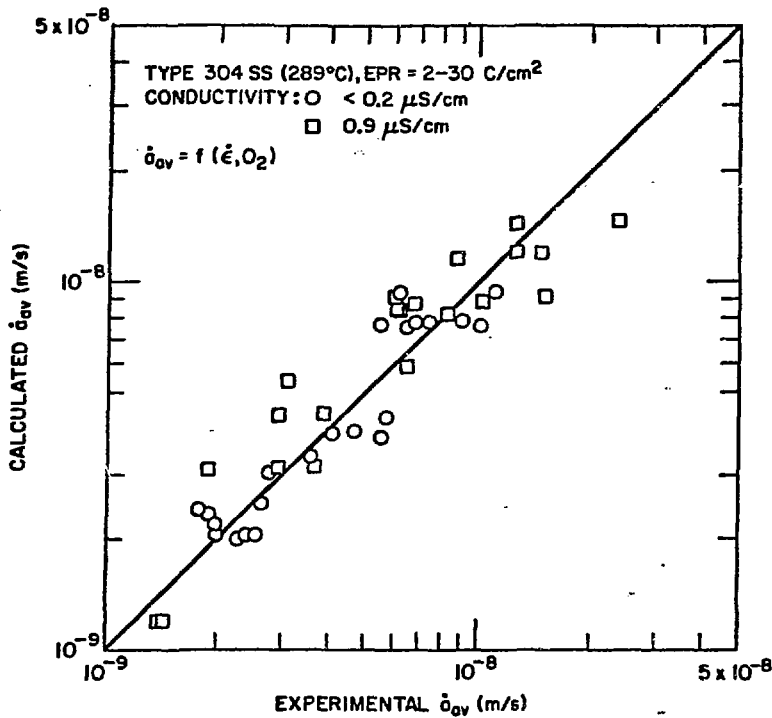


Fig. 6. Comparison between Calculated and Experimental Average Crack Growth Rates when $A (\sim a_f t_f^{-0.5})$ is Expressed as a Function of Dissolved Oxygen Concentration in Water.

Equations (3) and (9) were used with the appropriate values for the coefficients to construct Fig. 7, which shows a comparison between the predicted and experimental crack-growth rates \dot{a}_{av} . The agreement is satisfactory despite the existence of slightly more scatter in the results than found in Fig. 6.

It is important to point out that in Figs. 6 and 7, prediction of SCC susceptibility over a wide range of environmental variables and EPR values for the material is based on experimental results. Extrapolation of the SCC behavior beyond the range of corrosion potentials in this study is not required for BWR environments. Another application of the model and analysis

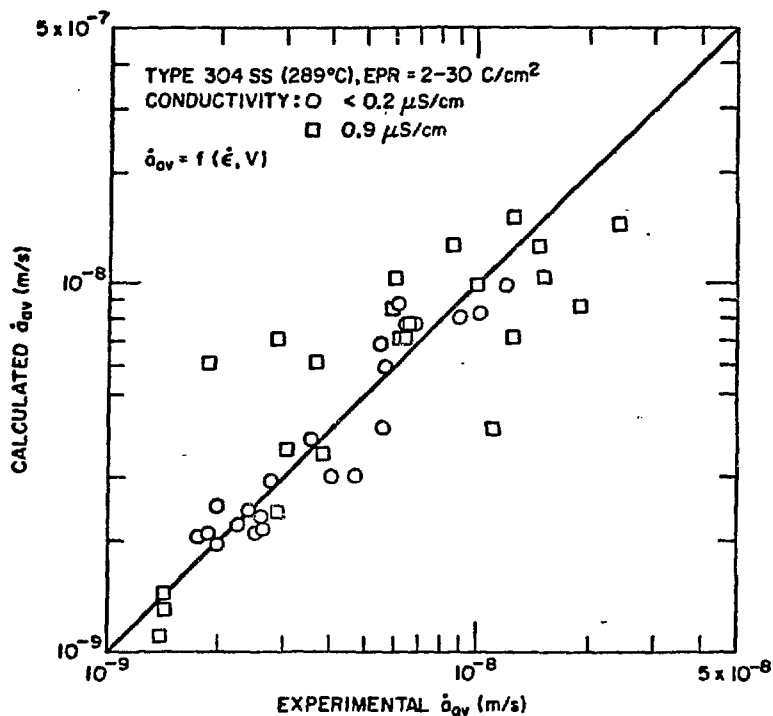


Fig. 7. Comparison between Calculated and Experimental Average Crack Growth Rates when $A (\sim a_f t_f^{-0.5})$ is Expressed as a Function of Open-Circuit Corrosion Potential.

lies in comparing SCC susceptibility not only in terms of \dot{a}_{av} but also in terms of other CERT parameters such as t_f , a_f , and ϵ_f , including the effect of strain rate on these parameters as well. Additional tests, now in progress, will examine the affects of strain rate below $10^{-6}/s$. Finally, the model and analysis of the SCC results for Type 304 SS are useful in comparing similar results obtained at different laboratories, including in-reactor data on different heats of material over a wide range of experimental conditions (i.e., oxygen, impurities, and strain rate). The correlations are expected to result in a better understanding of the synergistic effects of environmental, material, and mechanical loading variables on SCC pertinent to material performance in BWRs.

SUMMARY

The investigation of the synergistic effects of sulfate and dissolved oxygen concentrations in 289°C water and the degree of sensitization on the SCC susceptibility of Type 304 SS in CERT tests at a strain rate of $1 \times 10^{-6}/s$ suggests that the dissolved oxygen concentration governs the SCC behavior as well as the corrosion potential of the steel in the low-conductivity environments ($<1.0 \mu S/cm$). A model derived from a slip-dissolution mechanism of crack advance and elastic-plastic fracture mechanics can account for the environmental effects on SCC susceptibility. The model was used to develop analytical expressions for the dependence of SCC on dissolved oxygen concentration and corrosion potential as well as strain rate. The capability of the analysis to predict the effect of strain rate on SCC over a wide range of corrosion potentials was discussed in relation to comparison of the present results with those of other investigations, including information from in-reactor SCC experiments.

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