Effect of Mechanical Parameters on Primary Water Stress Corrosion Cracking of Nickel-base Alloys

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1. Introduction

Primary water stress corrosion cracking (PWSCC) of nickel-base alloys has become one of the serious problems in the primary water loops of pressurized water reactors (PWRs). Several mechanisms have been proposed to account for the PWSCC behavior of nickelbase alloys in the high temperature water (~300°C). In this study, we consider the slip oxidation model as a potential PWSCC mechanism, and apply this model to the estimation of the crack growth rates quantitatively. A film-rupture / slip-oxidation (SO) process has been proposed to account for SCC of Alloy 600 as a PWSCC mechanism. The rate controlling factors affecting the crack propagation in the SO model are the rupture rate of the oxide film, the rate of repassivation, and the rate of the diffusion of the dissolved metal ions away from the crack tip. The SO model, as proposed by Ford and Andresen [1], has been successful in predicting the crack propagation rate in austenitic stainless steels and lowalloy steels in 288°C water, symptomatic of boiling water reactor systems. Although there are differences in environmental conditions between PWR and BWR, the dissolution of metal atoms plays an important role in the intergranular SCC of any alloys.

The primary objective of the present study is to evaluate the significance of mechanical parameters affecting PWSCC of Alloy 600. Because of the multiplicity of the interacting variables, it is difficult to single out the critical parameter affecting PWSCC. The concept of the crack-tip mechanics, which enables us to determine the crack-tip strain rate analytically, was applied in deriving the crack growth rate (CGR). Emphasis is placed on identifying the parameters that affect the cracking behavior, as well as calculating the CGR of Alloy 600.

2. Modeling of stress corrosion cracking

The SO model relates a crack propagation to the amount of the metal dissolution that occurs on the bare surface when a protective oxide film is mechanically ruptured. This model consists of three processes; 1) rupture of the oxide film, 2) anodic dissolution of the bare metal, 3) reformation of an oxide film (repassivation). Thus, the crack growth rate is equivalent to the rate of a

metal dissolution at the crack tip. The average CGR is given by:

$$\mathbf{s} = \frac{M}{z\rho F} \cdot \frac{\mathbf{i}_{o} \left(\mathbf{t}_{o}\right)^{m}}{\left(1 - m\right)\left(\varepsilon_{f}\right)^{m}} \cdot \left(\mathbf{s}_{t}\right)^{m}$$
(1)

where, M and ρ are the atomic weight and mass density of the crack tip metal, respectively, F is the Faraday constant, z is the number of electrons involved in the oxidation of the metal atom, i_o is the current density dissolved from a bare surface, t_o is the time at which repassivation starts, $\varepsilon_{\rm f}$ is the fracture strain of the oxide-film, and m is the slope of the current-density curve. The factor m is a complex function of several parameters such as electrochemical potential, solution conductivity, pH, etc.

The crack-tip strain rate $\&_{ct}$ in Eq. (1) is an engineering parameter which represents the mechanical contribution to the CGR. A mechanically-based $\&_{ct}$ equation was derived by Shoji [2] using the plastic strain distribution ahead of a growing crack tip, developed by Gao [3] et al., which is given by:

$$\mathbf{\mathscr{E}}_{\text{ct}} = \frac{\beta \, \boldsymbol{\sigma}_{y} \, \mathbf{n}}{\mathrm{E} \left(\mathbf{n} - 1\right)} \left(2 \, \frac{\mathbf{\mathscr{K}}_{I}}{\mathrm{K}_{I}} + \frac{\mathbf{\mathscr{K}}}{\mathrm{r}_{o}} \right) \left\{ \ln \left[\frac{\lambda}{\mathrm{r}_{o}} \left(\frac{\mathrm{K}_{I}}{\sigma_{y}} \right)^{2} \right] \right\}^{1/n-1}$$
(2)

where β and λ are dimensionless constants, σ_v the yield strength, n the strain-hardening exponent in the Ramberg-Osgood power law, E the Young's modulus, K_I the stress intensity factor, and r_o the characteristic distance. In Eq. (2), the variable r_0 represents the characteristic distance ahead of a crack tip where the strain rate should be defined. While the physical significance of r_o still remains unsettled, the best estimate of r_0 is in the order of several µm, which was derived from the inverse analysis. The CGR equation can be obtained by combining two Eqs. of (1) and (2). The CGR equation derived here takes into account all the factors affecting the SCC behavior - load, material properties, and electrode kinetics. Although the SO mechanism may not work in the SCC of Alloy 600, the application of the theoretical equation enables us to predict the CGR in a quantitative way, at least to provide the numerical tool for a future work.

3. CGR calculations

The electrode kinetic and material parameters for Alloy 600, used as a standard set in the CGR calculation, are listed in Table 1. The parameters related to the repassivation kinetics for Alloy 600 are referred from [4].

Table 1Standard electrode kinetic and materialparameters for Alloy 600

Parameter	Value
Atomic weight, M (g/mol)	57.2
Number of equivalents exchanged, z	2.6
Oxidation current density, io (A/mm ²)	0.00015
Repassivation rate, m	0.4
Duration of constant i_o , t_o (s)	0.4
Fracture strain of metal oxide, $\epsilon_{\rm f}$	0.001
Young's modulus, E (GPa)	214
Mass density, ρ (g/cm ³)	8.49
Yield strength, σ_y (MPa)	200
Strain-hardening exponent, n	2
Dimensionless constant, β	5.46
Dimensionless constant, λ	0.106

It is well known that the changes in the mechanical properties of materials affect the SCC behavior, while it is still not clear how to estimate the extent to the cracking rate in a quantitative way. We investigate the CGR changes as a function of the yield strength and the strain hardening exponent of Alloy 600. Different heat treatments and the amount of radiation dose to alloys may lead to changes in the microstructure, which can cause the tensile properties of materials to change. Fig. 1 shows the CGR as a function of the yield strength and strain hardening exponent. In plotting Fig.1, other parameters necessary for the calculation are referred to in Table 1.



Figure 1. Effect of tensile properties (σ_y and n) on CGR as a function of stress intensity

The measured CGR data for Alloy 600, i.e. the changes in the CGR as a function of stress intensity K_I under constant loading, were collected and plotted in Fig. 1 [5]. The collected CGRs were measured in the following conditions: constant load tests with the pre-cracked specimens at 330°C and 350°C in solutions containing LiOH (Li content < 10 ppm) and H₃BO₃ (B content < 1200 ppm) with an oxygen content below 5 ppb. As K_I increases, the CGR increases slowly ranging from 10⁻⁹ to 10⁻⁸ m/s. The two doted-curves in Fig. 1 represent the upper and lower bounds of the CGR which are provided for convenience.

4. Conclusions

In order to quantitatively investigate the effects of the mechanical parameters on PWSCC behavior for Alloy 600, a SCC model on the basis of the SO mechanism was implemented. In mathematically formulating the CGR equations, we applied the crack-tip strain rate \mathscr{E}_{tt} , which is related to the engineering stress and determines the periodicity of the oxide rupture at a crack tip. The calculation results show that the calculated CGRs lie within the measured ones in the steady-state crack growth regimes, albeit with an uncertainty about the kinetics and material parameters.

Parametric study was performed to evaluate the significance of the parameters. Effects of the mechanical parameters on the CGR, especially the yield strength σ_y and strain-hardening exponent n, were examined. In this case, we can estimate the changes in the CGRs due to simultaneous changes in *n* and σ_y . The use of the CGR equations enables us to determine which parameter makes a contribution to CGR changes.

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