Crystal Plasticity Simulation Considering Oxidation along Grain Boundary and Effect of Grain Size on Stress Corrosion Cracking

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Stress corrosion cracking is a critical concern for light water reactors because it can degrade structural components over a long period. It takes the form of intergranular stress corrosion cracking (IGSCC). Many studies on IGSCC have been conducted over several decades in the past. However, the mechanism of IGSCC initiation and propagation is still not fully understood. In this study, a crystal plasticity model expressing IGSCC is proposed by considering information about the oxidation along the grain boundaries and the failure of an oxide film. From a crystal plasticity finite element analysis and an oxygen reaction-diffusion finite difference analysis based on the presented model, the IGSCC is numerically reproduced, and we discuss the effect of grain size on the crack propagation behavior.

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1. Introduction

Stress corrosion cracking (SCC) in light water reactors (LWRs) has been the cause of significant economic losses as a result of disruptions in power plant availability and the costs associated with SCC mitigation and remediation. Recently, SCC has been found in boiling water reactor (BWR) components, such as core shrouds and primary loop recirculation piping fabricated with low-carbon stainless steels,1,2 as well as in pressurized water reactor (PWR) components, such as the vessel head penetrations, bottom mounted instrument nozzles, and primary water inlet nozzles of steam generators fabricated with Alloy 600 and its weld metals.3–5 Consequently, there is incentive for developing quantitative methods for evaluating the reliability and the remaining SCC lifetimes of structural materials in LWRs. Ford and Andresen proposed a crack growth rate prediction model based on the slip dissolution/oxidation mechanism for SCC.6,7 Shoji et al. proposed a theoretical crack growth rate equation based on a theoretical crack tip strain rate formulation and the asymptotic field by considering the solid state oxidation mechanism.8–11 Bruemmer et al. analyzed a crack tip oxide film using an analytical transmission electron microscope (ATEM) and reported that the mass transport process in a solid state oxide film could be the key element process for crack growth.12 Staehle also discussed the visibility of a film rupture event in a tight crack tip.13 In addition, Fukuya et al. performed detailed observations of the crack tip of an active stress corrosion crack in the highly irradiated Type 316 stainless steel of a pressurized water reactor (PWR), which was initiated in the primary system simulated water. They showed that an oxygen atom could be observed up to a distance of around 10 nm from the crack tip.14 Yamaguchi15 showed that the grain boundary cohesion strength decreased at the $\Sigma 3$ grain boundary of an iron-based coincidence site lattice by the segregation of oxygen atoms. Therefore, a solid state oxidation mechanism might be the critical element process in SCC. Recently, multi-scale modeling has also been performed for the structural materials of a reactor core and the primary coolant components to ensure their safe and reliable operation. In particular, some computational approaches have been proposed for the simulation of intergranular cracks in a polycrystalline aggregate.16–18 The surface of the core shroud of a nuclear reactor is ground to increase the out-of-roundness. Therefore, the surface of the shroud has a severe deformation condition, and the grain size decreases to several microns or less. In the case of the shroud of a nuclear reactor, a crack is generated at the surface of the shroud. SCC in a shroud can be said to start at polycrystalline metals with a grain size smaller than 1 µm, namely, “bulk nanostructured metals”. It is important to evaluate the crack behavior on these bulk nanostructured metals to investigate the SCC of a shroud.

In this work, in order to predict IGSCC numerically, we introduce information about the oxidation along the grain boundaries and the failure of an oxide film caused by deformation localization in a crystal plasticity model. Based on the results obtained from a crystal plasticity finite element (FE) analysis and oxygen reaction-diffusion finite difference (FD) analysis using the presented model, we discuss the effect of the grain size on the crack propagation behavior.

2. Models of SCC

2.1 Oxygen reaction-diffusion equation

In this study, we assume that oxygen atoms diffuse only along grain boundaries, because the value of the diffusion coefficient of oxygen atoms along the grain boundary is larger than that inside the grain. Considering that the movement of oxygen atoms is caused by a potential originating in a stress that is normal to the plane of the grain boundary and that metals are oxidized by the diffusion of oxygen atoms, a reaction-diffusion equation for the oxygen along the grain boundaries can be written as follows

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\[ \dot{C} = D \nabla^2 C - D \frac{\Omega}{kT} \nabla \cdot (C \nabla \sigma) - KC^2, \]  
(1)

where \( D \) is the diffusion coefficient of oxygen atoms, \( C \) is the concentration of oxygen atoms, \( \Omega \) is the volume per atom, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. Moreover, \( \sigma \) is the normal stress component that applies to a grain boundary, which is expressed by

\[ \sigma = T (n \otimes n), \]  
(2)

where \( T \) denotes the Cauchy stress tensor and \( n \) is the unit vector normal to a grain boundary. In eq. (1), the first and second terms express the phenomena of the diffusion of oxygen atoms and the movement of oxygen atoms caused by the gradient of stress. The third term on the right side represents an oxidation reaction, where \( K \) represents the reaction rate coefficient for the oxidation reaction. The occurrence of a second-order oxidation reaction is assumed in this study. Then, the concentration rate of the metal in the grain boundaries is given by

\[ \dot{M} = -KC^2, \]  
(3)

where \( M \) is the concentration of metal. Equation (3) expresses the decrease in \( M \) originating in the oxidation reaction.

### 2.2 Local criterion of crack progress

When a crack is generated, elastic strain energy is translated into surface energy. In other words, when the density of local elastic strain energy \( E_e \) (the elastic strain energy per unit volume) exceeds the density of surface energy \( E_C \) (the surface energy per unit volume), a crack propagates. The density of elastic strain energy \( E_e \) is given by

\[ E_e = \int T : D^e dt, \]  
(4)

where \( D^e \) is the elastic deformation rate tensor. When considering the decrease in metal atoms caused by the oxidation reaction, we model \( E_C \) such as

\[ E_C = 2e f A \left( 1 - e \frac{M_0 - M}{M_0} \right), \]  
(5)

where \( e f \) is the density of the surface energy per unit area, \( A \) is the area of the generated crack, \( e \) is a numerical parameter expressing the effect of oxidation on cracking, and \( M_0 \) is the initial concentration of the metal. Equation (5) indicates that a crack always propagates when an amount of \( 1/e \) of the metal is oxidized. When \( e > 1 \), \( E_C \) becomes negative with the progress of the oxidation. However, in a situation where a crack is not generated, \( E_C > 0 \) is derived from \( E_C > E_e \) and \( E_e > 0 \).

### 2.3 Model for failure of oxide film

The oxidation films generated on metal surfaces are damaged by the slip deformation of the metal. In order to represent the process where oxygen atoms enter grain boundaries through such damaged oxide films, we propose the model for the failure of an oxide film:

\[ C_S = \sum_\alpha \gamma^{(\alpha)} s^{(\alpha)} \cdot nC_e, \]  
(6)

where \( C_S \) denotes the concentration of oxygen on a metal surface, \( \gamma^{(\alpha)} \) is the slip rate of slip system \( \alpha \), \( s^{(\alpha)} \) is the slip direction vector, and \( C_e \) is the concentration of oxygen in the environment. When eq. (6) is used as the boundary condition of eq. (1), the result indicates that oxygen atoms are allowed to enter grain boundaries from new surfaces generated by slip deformation.

### 3. Crystal Plasticity Model

Information about the stress field can be obtained using the crystal plasticity model proposed by Peirce et al.\(^\text{19}\) The crystal plasticity-type elasto-viscoplastic constitutive equation is written in the form

\[ \bar{\sigma} = \bar{C} : \bar{D} - \bar{C} : \sum_\alpha P_s^{(\alpha)} \gamma^{(\alpha)}, \]  
(7)

where \( \bar{T} \) is the Mandel-Kratochvil rate of the Cauchy stress tensor, \( \bar{C} \) is the anisotropic elastic moduli, \( \bar{D} \) is the deformation rate tensor, \( P_s^{(\alpha)} \) is the Schmid tensor on slip system \( \alpha \), and \( \gamma^{(\alpha)} \) is the slip rate. This slip rate, \( \gamma^{(\alpha)} \), is given by the rate dependent hardening law of Pan-Rice, as follows:

\[ \dot{\gamma}^{(\alpha)} = \dot{\gamma}_0^{(\alpha)} \text{sgn}(\tau^{(\alpha)}) \left| \frac{\dot{\tau}^{(\alpha)}}{\dot{g}^{(\alpha)}} \right|^{1/m}, \]  
(8)

where \( \dot{\gamma}_0^{(\alpha)} \) denotes the referential slip rate, \( \tau^{(\alpha)} \) is the resolved shear stress, \( g^{(\alpha)} \) is the flow stress, and \( m \) is the strain rate sensitivity. The evolution equation of flow stress is represented by

\[ \dot{\gamma}^{(\alpha)} = \frac{h^{(\alpha)}}{\dot{\gamma}^{(\alpha)}} \dot{\gamma}^{(\alpha)}, \]  
(9)

where \( h^{(\alpha)} \) is the hardening modulus. Various models for \( h^{(\alpha)} \) have been proposed by many researchers, e.g., a model based on the geometrically necessary dislocation density.\(^\text{20}\) In this study, to simplify the calculation, we apply the following function of the total slip, \( \gamma \), to the hardening modulus, \( h^{(\alpha)} \):

\[ h^{(\alpha)} = h_0 \text{sech}^2 \left( \frac{h_0}{\tau_s - \tau_0} \gamma \right), \]  
(10)

where \( h_0 \) is the initial hardening ratio, \( \tau_s \) is the saturated value of the resolved shear stress, and \( \tau_0 \) is the initial flow stress.

### 4. Results and Discussions

#### 4.1 Computational model

In a crystal plasticity FE simulation, a polycrystal of stainless steel under a plane strain condition is assumed and the number of grains is (a) 225 for a fine grain model or (b) 900 for a coarse grain model [see Fig. 1]. The initial width and height of the specimen are 120 and 30 µm, respectively. Delaunay triangulation is adopted for the meshing of the FEM to express inhomogeneity in the shape of the grains. The number of elements used for the FEM is (a) 397972 or (b) 395621. The initial crack depicted by the bold line in Fig. 1 occurs along the initial grain boundary. The length of this initial crack in the horizontal direction is 6 µm. Two types of hardening parameters are used here, i.e., (a) \( \tau_0 = 150 \text{ MPa}, \tau_s = 240 \text{ MPa}, \text{ and } h_0 = 500 \text{ MPa}, \) for a
Note that the area of the generated crack is

\[ \text{area}_{\text{crack}} = \frac{1}{2} \times \text{length}_{\text{crack}} \times \text{width}_{\text{crack}} \]

and numerical parameters are given by

\[
\begin{align*}
D &= 0.017 \text{ m}^2/\text{s}, \\
K &= 1000 \text{ m}^2/(\text{mol} \cdot \text{s}), \\
D_e &= 11.1 \text{ m}^2/(\text{s} \cdot \text{MPa}), \\
2\varepsilon r A &= 8 \text{ MPa}, \\
M_0 &= 140.6 \text{ kmol/m}^3, \\
\gamma_0 &= 0.001 \text{s}^{-1}, \\
m &= 0.005
\end{align*}
\]

Note that we assume that the diffusion and reaction of oxygen occur only along the initial grain boundaries. Therefore, eq. (1) is discretized using finite difference method (FDM) by adopting line elements along the initial grain boundaries. Only the right side of the specimen is exposed to the environment, and the initial oxygen concentrations in the environment and material are 0.001 mol/m$^3$ (about 30 ppm) and 0 mol/m$^3$, respectively. The oxygen concentration at the surface of the specimen is calculated using eq. (6), and this value is used as a boundary condition for the reaction-diffusion eq. (1). As a result of the generation of a crack, the connection between the FEM nodes along the grain boundaries is cut, and in this case, the density of the elastic strain energy expressed by eq. (4) exceeds the density of the surface energy represented by eq. (5). Both the energy densities are calculated at each node of the FEM. The average value of all the elements contacting a node is used as the density of the elastic strain energy at the node. On the other hand, the density of the surface energy is obtained at lattice points of the FDM, which coincide with the FEM nodes.

### 4.2 Discussion

Figure 3 shows the distributions of the equivalent stress and equivalent plastic strain of model A (t = 49.84 Ms).
cracks. The generated crack propagates to the left from the initial crack tip. Because plastic deformation occurs locally around the crack tip, residual stress exists at the unloaded area along the generated crack, while the plastic deformation region spreads to the left of the crack tip. On the other hand, Kaji et al. performed a quantitative evaluation of the plastic deformation around an SCC crack in Type 316L low-carbon stainless steel in a BWR simulated environment using the electron backscatter diffraction pattern method and showed that around 10–20% of the plastic strain was found at the crack tip and around cracks.\(^{22,23}\) Therefore, concerning the local deformation behavior at the crack tip, the simulation results are consistent with the experimental ones. It is suggested that local deformation at the front of the crack tip affects the configuration of crack propagation. In Fig. 4, the distributions of the equivalent stress and oxygen concentration around the initial crack tip are depicted using contour maps and colors for the grain boundary, respectively. Oxygen atoms enter the grain boundaries from the crack tip [see Fig. 4(a)]. The grain boundaries are corroded by oxidation, and the crack propagates further [see Fig. 4(b)]. Then, crack propagation stops [see Fig. 4(c)]. The same processes are repeated, and another crack propagates further. Because oxygen atoms accumulate around the crack tip where the stress value is high, it can be said that the behavior of oxygen atoms is dominated by the gradient of stress in this model. The stress value around the crack tip increases with the extension of the unloaded area because of crack propagation. Hence, the crack starts to branch off as shown Fig. 3. It is predicted that crack branching such as IGSCC occurs because of an increase in the stress around the cracks originating from crack propagation. Tsukada et al. conducted a post irradiation examination of a sample taken from a stress corrosion cracked region of the outer H6a welded portion of the core shroud from a BWR nuclear power plant and reported that small secondary cracks could be observed around the open main crack with complicated branching. Oxides that mainly consisted of Fe-oxides were observed inside all the cracks, from the opening to the crack tip.\(^{24}\) Thomas et al. characterized stress corrosion cracks in the austenitic stainless steel components from several different BWRs using high-resolution ATEM and showed that the cracking occurred along precipitate-free, non-sensitized grain boundaries in highly strained metals and produced many secondary cracks along intersecting boundaries. Moreover, both open cracks and ones that were filled with oxide were found to contain Cr-rich spinel films along the crack walls and Fe-rich spinel toward the crack centers.\(^{25}\) Therefore, from a crystal plasticity finite element analysis and oxygen reaction-diffusion finite difference analysis based on the presented model, IGSCC with branching secondary cracks that are filled with oxides can be reproduced numerically.

The distributions of the equivalent stress as well as the equivalent plastic strain of models B and C are shown in Figs. 5 and 6, respectively. From Figs. 3 and 5, although the distributions are affected by the initial crystal orientation and shape of the grains, the tendencies of the distributions are similar in cases where the mechanical properties are the same but the grain sizes are different. On the other hand, when the grain size as well as the material properties are different, the distributions of the equivalent plastic strain show different tendencies under similar stress conditions. In the case of Fig. 6(b), plastic deformation occurs only around the crack because of the high yield stress. However, these differences related to the material property and grain size do not affect the shape of the generated crack. Figure 7 shows the relationship between the length of the crack in the horizontal direction and time. We find that the crack propagation rate depends on the hardening parameter and grain size. The first crack propagations of model A and model B, which have the same hardening parameters, occur almost simultaneously. The timing of the first progress of a crack in model C, which has a higher yield stress than the other models, is delayed, because plastic deformation hardly occurs in model C.
stress concentration occurs around the crack tip of model C, whose yield stress is larger than that of model B, because model B can liberate the elasticity energy by plastic deformation. Therefore, it can be said that oxygen can easily concentrate around the crack tip of model C. However, in the present simulations, considering the failure of the oxide film because of slip deformation, because the oxide film of model C is hardly damaged by slip deformation, the amount of oxygen entering the grain boundary is small. On the other hand, the plastic deformation around the crack tip of model B causes the failure of the oxide film. As a result, the invasion of oxygen produces oxides in the grain boundary of model B. When the grain size is small, the rate of cracking is small. The propagation of the generated crack is stopped at the triple junction of the grain boundary in this calculation. In the case of fine grains, a crack is easy to stop with an increase in the volume fraction of the triple junction. These results suggest that the mechanical property of the material and the grain size affect the timing of the first crack and the rate of crack propagation, respectively. In the present calculation, we assume that the grain size is on the order of several microns. The facts that the timing of the first crack is delayed in the case of a high strength material and that the rate of crack propagation is lower when the grain size is small indicates that the IGSCC resistance of ultrafine-grained metals such as bulk nanostructured metals is high.

5. Conclusions

We proposed a crystal plasticity model that considers information about the oxidation along grain boundaries and the failure of the oxide film as a result of slip deformation. A crystal plasticity FE analysis and oxygen reaction-diffusion FD analysis based on the presented model were carried out. IGSCC was numerically reproduced and we discussed the effect of the grain size on the propagation behavior of cracks. The conclusions obtained are summarized as follows.

(1) Introducing the oxygen reaction-diffusion model, the local criterion of crack propagation, and the oxide film failure model into a crystal plasticity model makes it possible to numerically reproduce the generation and propagation of cracks assuming the occurrence of IGSCC.

(2) Although the crack propagation stops at one point, the crack propagates again as a result of the oxidation corrosion of the grain boundary.

(3) The mechanical property of the material and the grain size affect the timing of the first crack and the crack propagation rate, respectively.

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