

A MECHANICAL APPROACH TO THE PREDICTION OF STRESS CORROSION
CRACK INITIATION OF ALLOY 600

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A model aimed at predicting quantitatively the times to crack apparition by stress corrosion is presented. Mechanical variables and the ingress of a chemical species — the nature of which need not be specified — are taken into account, the underlying idea being that SCC is related mainly to the creation of new surfaces due to viscoplastic deformation. The model's sole requirements for a given material are in-air creep test results, the experimental knowledge of a single time to cracking for a known initial stress state and triaxiality. Given these parameters, the model predicts a time to crack apparition under any loading condition at constant stress triaxiality, for any initial stress level and state. The model has been applied successfully to the initiation stage of stress corrosion cracking of Alloy 600 in primary water, where excellent agreement is found between predictions and experimental results.

INTRODUCTION

A primary reason for the difficulties associated with the modelling of SCC is that it is a multifaceted problem. A complete description must take into account the evolution of mechanical and microstructural parameters as well as electrochemical conditions. Furthermore, local (microscopic) quantities may be more appropriate than the global (macroscopic) ones usually obtained experimentally.

A new quantitative model of the initiation stage of SCC is proposed here. The model requires the experimental knowledge of creep parameters in air and only one time to crack initiation for a given material at one temperature for a known initial stress level and initial stress triaxiality. The present approach is original in that it is very simplified, keeping a focus on the evolution of mechanical variables coupled with environmental effects. Questions related to materials sensitivity (grain size, carbon content, grain boundary carbide coverage, surface conditions) are not treated, all these effects being gathered into one identified parameter χ_{mat} . Nevertheless, this model is able to yield results in close agreement with experimental results, as will be illustrated in the case of Alloy 600.

In what follows, a point on the surface of the material in question is considered. General equations describing the point's mechanical evolution and the effect of the environment on this evolution are given first, followed by the law according to which ingress of a chemical species proceeds after creep-induced fracture of the surface oxide scale. Then the hypothesis is made that crack initiation is obtained for a critical value of the concentration of this damaging chemical agent. Results of an application to the crack initiation stage of Alloy 600 in primary water are compared with a compilation of experimental results.

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DESCRIPTION OF THE MODEL

Mechanical Evolution

We are interested here in the long-term evolution of a material's mechanical properties in service, *i.e.* conditions where creep — even at relatively low homologous temperatures — must be taken into account. Experimental creep test results can be expressed by a Bailey-Norton law which relates strain rate $\dot{\epsilon}$ with applied stress σ , temperature T and time t :

$$\dot{\epsilon} = k(T)\sigma^n t^m \quad \text{and} \quad k(T) = k_0 \exp\left(-\frac{E_A}{RT}\right). \quad (1)$$

Creep is heat activated, the effect of temperature T being classically affected to the coefficient k of Eq.(1) — while m and n are considered independent of T — *via* an Arrhenius-type law with activation energy E_A (R is the perfect gas constant). Eq.(1) may be naturally associated to the following viscoplastic creep law with multiplicative hardening, the simplest law accounting for primary creep (σ_{eq} is Von Mises stress, σ_m and σ_d are respectively the hydrostatic and the deviatoric part of stress tensor):

$$\dot{\underline{\underline{\epsilon}}}^{vp} = \frac{3}{2} \dot{p}_v \frac{\underline{\underline{\sigma}}_d}{\sigma_{eq}} \quad \text{and} \quad \dot{p}_v = \left(\frac{\sigma_{eq}}{K(T)}\right)^N p_v^{-\frac{N}{M}}, \quad (2)$$

where the cumulated viscoplastic deformation p_v is defined by: $p_v = \int_0^t \sqrt{\frac{2}{3} (\dot{\underline{\underline{\epsilon}}}^{vp} : \dot{\underline{\underline{\epsilon}}}^{vp})} dt$.

The coefficients of Eq.(2) can be obtained from the experimentally determined constants n , m , and k :

$$N = \frac{n}{1+m}, \quad M = -\frac{n}{m}, \quad K(T) = k(T)^{-\frac{1}{n}} (1+m)^{-\frac{m}{n}}. \quad (3)$$

Influence of the Environment

Creep rates have been shown to increase when the material is in contact with water [1, 2]. This may be logically interpreted as due to ingress of a foreign substance into the alloy, be it hydrogen, oxygen, or possibly some other impurity. Alternatively, the effect of the environment might be the injection of vacancies into the metal, the end result being, in all cases, an enhanced creep rate. We make the assumption that when the material is in contact with water, there is a progressive increase of \mathcal{C} , the concentration of such a foreign species in the metal, and that its effect is akin to that of temperature on K in Eq.(2). We thus introduce a function $\mathcal{R}(\mathcal{C})$ such that the creep law becomes:

$$\dot{\underline{\underline{\epsilon}}}^{vp} = \frac{3}{2} \dot{p}_v \frac{\underline{\underline{\sigma}}_d}{\sigma_{eq}} \quad \text{and} \quad \dot{p}_v = \left(\frac{\sigma_{eq}}{K(T)\mathcal{R}(\mathcal{C})}\right)^N p_v^{-\frac{N}{M}} \quad (4)$$

As there is usually some residual presence of the foreign species in the alloy even in the absence of water, the effect of \mathcal{C} on \mathcal{R} is expected to be negligible at low concentration (such that $\mathcal{R}(0) = 1$). $\mathcal{R}(\mathcal{C})$ is *a priori* a decreasing function of \mathcal{C} , in order to enhance creep when \mathcal{C} increases.

Ingress of the foreign chemical species is considered possible only when cracking of the oxide scale occurs, governed by viscoplastic deformation. Considering a small surface

dS , the ingress rate \dot{Q} through this surface dS is then proportional to the creation rate of oxide-free surface $d\dot{S}$. Furthermore, the concentration rate \dot{C} is proportional to \dot{Q}/dS . Since viscoplastic deformation occurs at constant volume, the rate of creation of oxide-free surface is then proportional to the strain rate tensor component ε_{zz}^{vp} , normal to the surface, such that,

$$\dot{C} = \alpha \frac{\langle d\dot{S} \rangle}{dS} = \alpha \langle \varepsilon_{xx}^{vp} + \varepsilon_{yy}^{vp} \rangle = \alpha \langle -\varepsilon_{zz}^{vp} \rangle \quad \text{with} \quad \langle x \rangle = \begin{cases} 0 & \text{if } x < 0 \\ x & \text{if } x \geq 0 \end{cases} \quad (5)$$

Using $(\underline{\sigma}_d)_{zz} = -\sigma_m$ and combining Eqs.(4) and (5) leads to

$$\dot{C} = \frac{3}{2} \alpha \dot{p}_v \frac{\langle \sigma_m \rangle}{\sigma_{eq}} \quad (6)$$

In the case of Alloy 600, the assumptions can be justified as follows:

- the oxide scale is impermeable to the foreign chemical species. Adsorption and diffusion of the foreign chemical species over a limited depth of metal happens immediately following the cracking of the oxide barrier
- the foreign chemical species enters by "waves", the magnitude of which depends on the size of the newly-created oxide-free area; entry stops as soon as repassivation occurs
- cracking of the oxide scale is initiated by intergranular viscoplastic deformation, which therefore constitutes the limiting step of entry (because both repassivation and adsorption/diffusion phenomena occur over a time scale at least an order of magnitude shorter than significant creep).

Furthermore, if repassivation is fast compared to entry of the foreign chemical species into the alloy, the limiting step being the saturation of adsorption sites and/or the diffusion of atoms into the bulk, the constant α — and thereby the proposed mechanism as a whole — will be independent of the repassivation rate.

Prediction of Time to Crack Apparition

Crack initiation is supposed to occur when the concentration C reaches a critical value C_c , that depends only on the material. Using Eq.(4), and by integration from 0 to the time of crack initiation t_c , we obtain

$$\int_0^{t_c} \left(\frac{\sigma_{eq}}{K(T)} \right)^N dt = \int_0^{t_c} \mathcal{R}(C)^N p_v^{\frac{N}{M}} \dot{p}_v dt \quad (7)$$

When $\langle \sigma_m \rangle / \sigma_{eq}$ remains constant, and assuming $C(t=0) = 0$, Eq.(6) yields

$$C = \frac{3}{2} \alpha \frac{\langle \sigma_m \rangle}{\sigma_{eq}} p_v \quad .$$

Eq.(7) then reduces to

$$\int_0^{t_c} \left(\frac{\sigma_{eq}}{K(T)} \right)^N dt = \left(\frac{\langle \sigma_m \rangle}{\sigma_{eq}} \right)^{-\frac{N}{M}-1} \chi_{mat} \quad (8)$$

with

$$\chi_{mat} = \left(\frac{3}{2} \alpha \right)^{-\frac{N}{M}-1} \int_0^{C_c} C^{\frac{N}{M}} \mathcal{R}(C)^N dC ,$$

where the criterion $C = C_c$ at $t = t_c$ has been used. χ_{mat} is a scalar material specific constant: it is independent of the time evolution of the system. The time to crack initiation predicted in the case of constant triaxiality is therefore independent of the choice of the function \mathcal{R} .

It then follows directly that:

- When the material is under compressive stress:

$$\langle \sigma_m \rangle = 0, \text{ hence (since } N \text{ and } M \text{ are both found to be positive) } \int_0^{t_c} \left(\frac{\sigma_{eq}}{K(T)} \right)^N dt = +\infty.$$

Therefore no crack appears in this case.

- When the material is under decreasing load (as during a creep test), the time to cracking is necessarily smaller than for constant loading.
- When the material is under constant load and at constant temperature, an expression for the time to crack initiation can be obtained directly as

$$t_c = \left(\frac{\sigma_m}{\sigma_{eq}} \right)^{-\frac{N}{M}-1} \left(\frac{K(T)}{\sigma_{eq}} \right)^N \chi_{mat} , \quad (9)$$

RESULTS FOR ALLOY 600

Comparisons are made with a compilation of experimental results obtained from constant uniaxial load tests and known as the "method of indices", according to which the time to crack apparition t_c may be expressed approximately as [3]:

$$t_c^i = \frac{10000}{I_M I_\sigma I_T} , \quad (10)$$

where the material (I_M), stress (I_σ), and temperature (I_T) indices for Alloy 600 are:

$$I_M = \left\{ \begin{array}{ll} 0.5 & \text{standard} \\ 1 & \text{susceptible} \\ 2 & \text{very susceptible} \end{array} \right\}, I_\sigma = 2.44 \cdot 10^{-11} \sigma^4, I_T = 9.49 \cdot 10^{15} \exp\left(-\frac{22000}{T}\right) \quad (11)$$

with t_c in hours, σ in MPa and T in Kelvin. The coefficients of the creep law (Eq.(1)) have been estimated in air at 350°C (Ref.[4]) as¹:

$$n = 2.00, m = -0.47, \text{ and } k(T) = 2.38 \cdot 10^{-3} \exp\left(-\frac{95000}{8.31 T}\right) . \quad (12)$$

¹A recent work (Ref. [5]) proposes the very different value of 180,000kJ/mol, but for a different expression of (1) including the yield stress.

From Eq.(3), the constants of Eq.(2) are thus:

$$N = 3.77, M = 4.26, \text{ and } K(T) = 17.67 \exp\left(\frac{47500}{8.31 T}\right) . \quad (13)$$

For this case of uniaxial load tests, the stress triaxiality σ_m/σ_{eq} is equated to 1/3, and Eq.(9) becomes:

$$t_c = \left(\frac{404600}{\sigma^{3.77} \exp\left(-\frac{21570}{T}\right)}\right) \chi_{mat} . \quad (14)$$

For materials of different susceptibility to stress corrosion cracking, χ_{mat} must be identified. For example, at 350°C, for a reference material with $I_M = 1$ and $\sigma = 450$ MPa, the time to crack apparition obtained from Eq.(10) is $t_c = 2284$ hours. χ_{mat} is thus identified using Eqs.(9,13), giving $\chi_{mat} \approx 5.10^{-8}$.

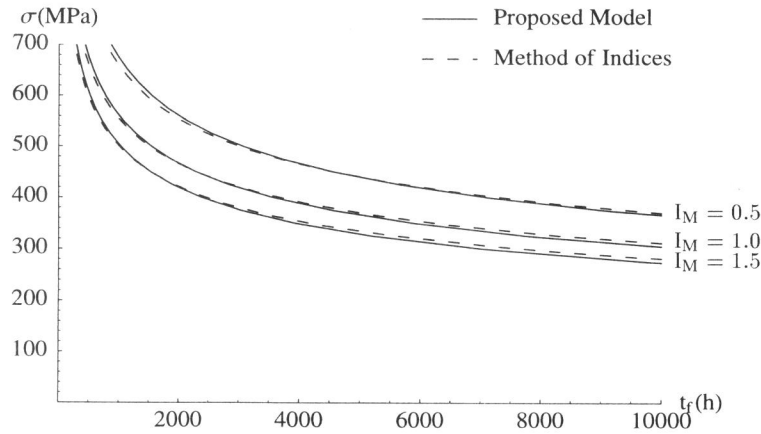


Figure 1: Comparison between results predicted by the present model and average experimental data (method of indices), under constant load conditions, for materials of varying susceptibility.

The predictions of the present model applied to Alloy 600 in primary water for materials of varying susceptibility, are plotted in Figure 1, together with average experimental results. The agreement is seen to be excellent, the model predictions being essentially identical to the mean of experimental test results throughout the whole range of initial stresses. Figure 2 shows results computed for different temperatures. Again, the agreement with experimental observations is excellent.

CONCLUSION

A model able to predict times to crack apparition by stress corrosion has been presented. The main idea is that SCC is related mainly to the creation of new surfaces due to viscoplastic deformation. Only one parameter χ_{mat} needs to be specifically identified for a

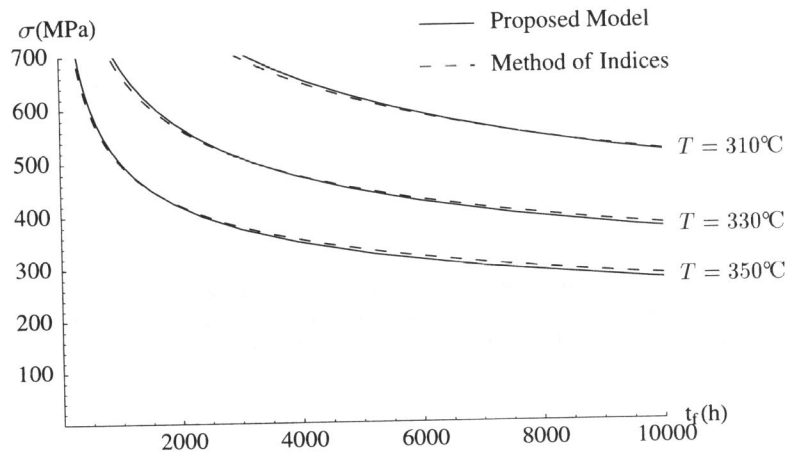


Figure 2: Comparison between results predicted by the present model and average experimental data (method of indices), under constant load conditions, for different temperatures.

given material. χ_{mat} is obtained from experimentally determined in-air creep parameters and one time to cracking by stress corrosion. The model has been applied successfully to the SCC initiation stage of Alloy 600 in primary water. The agreement between predicted and experimental results is excellent for the stress range, temperatures, and material sensitivities of interest. In addition, the model predicts stress triaxiality effects and an influence of the loading mode. The two latter points need additional experimental data to be confirmed.

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