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Stochastic Kinetics of Corrosion and Fractal Surface Evolution

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Warning

This paper uses the symbol font for certain Greek letters and mathematical symbols - some browsers may not display these correctly. As a test, the letter that follows in brackets should be a Greek alpha (α). If you do not see this, you should either install the symbol font (this should normally be installed with all versions of Windows™), or use the Acrobat version of the paper (see the Adobe Web site if you need to obtain an Acrobat reader).

Abstract

A kinetic model for general attack is proposed. This model predicts the evolution of a rough surface with a Hausdorff (fractal) dimension that approaches 2.5 as a limiting case. The model predicts a measurable critical length scale, that can be used to determine the time of exposure. Experimental results are shown for 2024-T3 which corroborate the model for the limiting case.

Introduction

Fractal geometry has been found useful for quantitatively describing the irregular shapes associated with fracture surfaces [1-4] and corrosion [5,6]. These studies, particularly those in corrosion, seek to relate the measured "fractal" dimension of the surface to the time or severity of exposure. Though anecdotal evidence suggests a relationship between exposure and "fractal" dimension, and experimental results reinforce this, no quantitative models for the formation and evolution of these surfaces have been proposed in the common literature.

Analysis

From simple rate theory, the rate of the reaction of the surface is nearly linearly related to the chemical potential of the species on the surface, which is related to the local surface curvature. In addition, the electrochemical reaction requires electron transfer across the surface causing local regions of anodic and cathodic reactions. The locations of these reactions are random functions of time and position so that their effect on the overall reaction can be considered as a classical "white noise" source. The rate of surface recession can be expressed as

$$\left(\frac{\partial y}{\partial t}\right)_x = A + \alpha\left(\frac{\partial^2 y}{\partial x^2}\right)_t + \beta W_t(x) \quad , (1)$$

where y is the recession, x is a position vector on the surface, A is the classically defined rate constant for a flat surface, α is proportional to the surface tension, A and β are assumed constants for this system and $W_t(x)$ is an uncorrelated "white noise" function with zero expectation value [7]. Taking the Fourier transform changes the rate model to

$$\dot{Y} = A\,\delta(\omega) - \alpha\omega^2 Y + \beta\hat{W}_t(\omega) \quad , (2)$$

where ω is the (magnitude of the) wave-vector on the surface,

$$Y(\omega,t) = \int_{-\infty}^{\infty} y(x,t)e^{-i\omega\cdot x}\,dx \quad ,$$

$\hat{W}_t(x)$ is a wide-sense stationary, complex, uncorrelated random process [8] and δ (ω) is the Dirac delta-function. Eqn. (2) is a linear stochastic differential equation with the general solution

$$\begin{aligned} Y(\omega,t) &= Y_0(\omega)e^{-\alpha\omega^2 t} + \beta e^{-\alpha\omega^2 t}\int_{s=0}^{t} e^{\alpha\omega^2 s}\,d\hat{B}_s(\omega);\ \omega > 0 \\ &= Y_0(0) + At;\ \omega = 0 \end{aligned} \quad , (3)$$

where $Y_0(\omega)$ is the initial condition for the surface and $\hat{B}_t(\omega)$ is a generalized, complex Brownian motion given by $\hat{W}_t(x) = \frac{dB_t}{dt}$.

The ω = 0 solution is the average rate of reaction for the system. The first term in the ω ≠ 0 solution is the effect of the reaction on the initial surface profile. As expected, the effect of the reaction is to remove all surface asperities and smooth the surface with time. Eventually all surface characteristics are removed completely. The second term in the ω ≠

0 solution is a stochastic (or Ito) integral [9] which has no closed form solution but can be easily estimated numerically. This term generates all of the interesting features of the system in the Fourier domain.

Since experimental measurements report the power spectral density of the surface profile, plotted on a log-log scale, it seems appropriate to calculate the expectation of the power spectral density (psd) of eqn. (3). Neglecting the initial surface profile (which is identically zero for an initially polished surface anyway) the psd is

$$YY^* = \beta^2 e^{-2\alpha\omega^2 t}\left|\int_{s=0}^{t} e^{\alpha\omega^2 s}\, dB_s(\omega)\right|^2 ;\; Y_0(\omega) = 0 \quad . (4)$$

Using Ito isometry [10], or

$$E\left[\left(\int_\Omega f(t)\,dB_t\right)^2\right] = E\left[\int_\Omega \left(f(t)\right)^2 dt\right]$$

where *E*[ ] denotes the expectation operation, for the complex process in eqn. (3) the result is

$$E\left[YY^*\right] = \frac{\beta^2}{\alpha\omega^2}\left(1 - e^{-2\alpha\omega^2 t}\right) \quad . (5)$$

Figure 1 shows both a numerically generated solution to eqn. (4) and the associated analytical expectation from eqn. (5) for two different times. As can be seen from the figure, the "white noise" term in eqn. (2) excites uniformly across the frequency domain. The high frequency terms are damped by the reaction so that the steady state solution will approach a straight line (of slope -2) on the log-log plot. This would correspond to a surface with a Hausdorff dimension of 2.5.

Discussion

As shown in Figure 1, a knee appears in the transient psd curve for the system. This knee is an apparent transition from slope=0 behavior at long length scales to slope=-2 behavior at short length scales. The position of this knee can be determined by extrapolating the two limiting behaviors at the extremes and equating them to give

$$\lambda = \frac{1}{\omega} = \sqrt{2\alpha t} \quad .$$

This transition length scale can be used as a measure of the time of exposure. It must be kept in mind, however, that long exposures, or for particularly aggressive environments, this length scale can become too long to practically measure. In addition, errors in evaluation of the critical length scale become large at longer exposure times.

Since the system is linear, any change in the spectral content of the "white noise" source will be reflected in the measured psd function. Specifically, if the microstructure of the surface has any texture or intrinsic periodicities on the scale of the measurements, then these will be observed as characteristic periodicities in the measured recession.

It should also be noted that the inclusion of surface curvature effects in the initial kinetic equation admits the possibility of negative recession rates (deposition) in some high curvature areas. This is considered unrealistic, but the inclusion of asymmetric curvature effects limits the tractability of the problem. Numerical simulations that include asymmetric curvature effects have been performed. In all cases, these simulations behave similarly to the model presented above and produce the same Hausdorff dimension for short length scales.

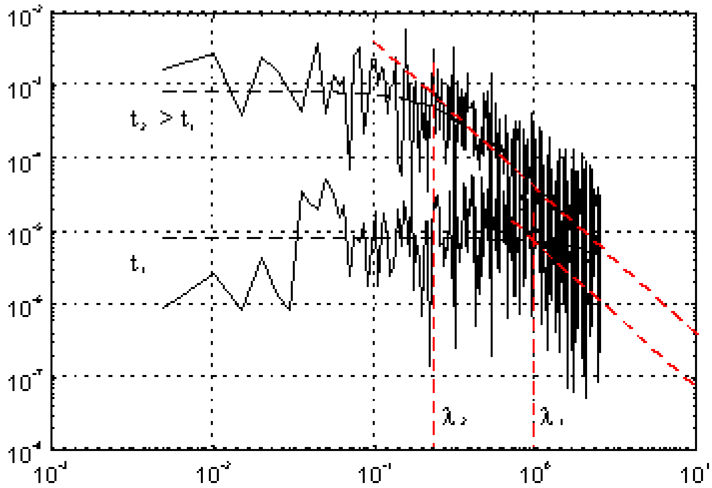

Figure 1. Simulation (solid) and analytical expectation (dashed) of surface profile psd for short and long time.

The samples examined in this study were tensile coupons cut from 2024-T3 sheet. These were then subjected to an ASTM G44 stress-corrosion cracking test, alternate immersion in 3.5% NaCl solution, unloaded for 3 and 6 weeks. Following the exposure, the samples were cleaned according to the ASTM G1 procedure, cleaning in a hot H_3PO_4, CrO_3 and HNO_3 solution followed by a rinse in room temperature HNO_3. The samples were then tested to failure in fatigue. The front and back surface of a representative sample is shown in Figure 2.

Both sides of each sample were studied using a custom-designed, high-precision scanning acoustic microscope (HIPSAM) [11]. The HIPSAM system was outfitted with a 0.635cm diameter, 100MHz transducer with a 0.5cm focal length and set to perform a time-of-flight C-scans to the top surface of each sample. The step size of each scan was 0.05mm along the scan axis and 0.02mm along the index axis. This resulted in a series of bit-mapped surface profile images that could be analyzed with conventional image analysis software.

Five representative 512x512 pixel regions were selected from each of the resulting surface profile maps. The 2D Fourier transforms of these regions were averaged and the longitudinal and transverse traces were recorded. A representative psd plot of the traces is shown in Figure 3. As can be seen in the figure, the psd follows the predicted trend except in the highest frequency region. These data are for spatial resolutions on the order of a few wavelengths of the excitation (14.9 μm) and are likely due to defocusing and smearing of data over the frequency range.

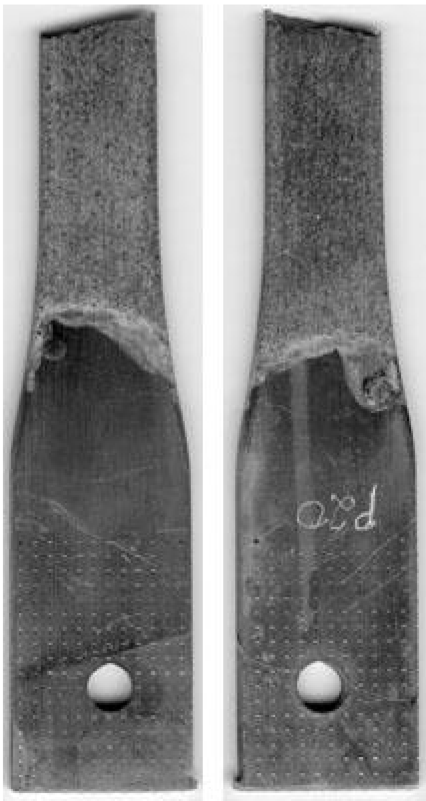

Figure 2. Representative corrosion sample (larger images of left and right figures)

Conclusions

A simple kinetic model for general attack has been described. This model predicts the evolution of a rough surface with a Hausdorff (fractal) dimension that approaches 2.5 as a limiting case. The model predicts a measurable critical length scale, that can be used to determine the time of exposure. Experimental results have been shown for 2024-T3 which corroborate the model for the limiting case.

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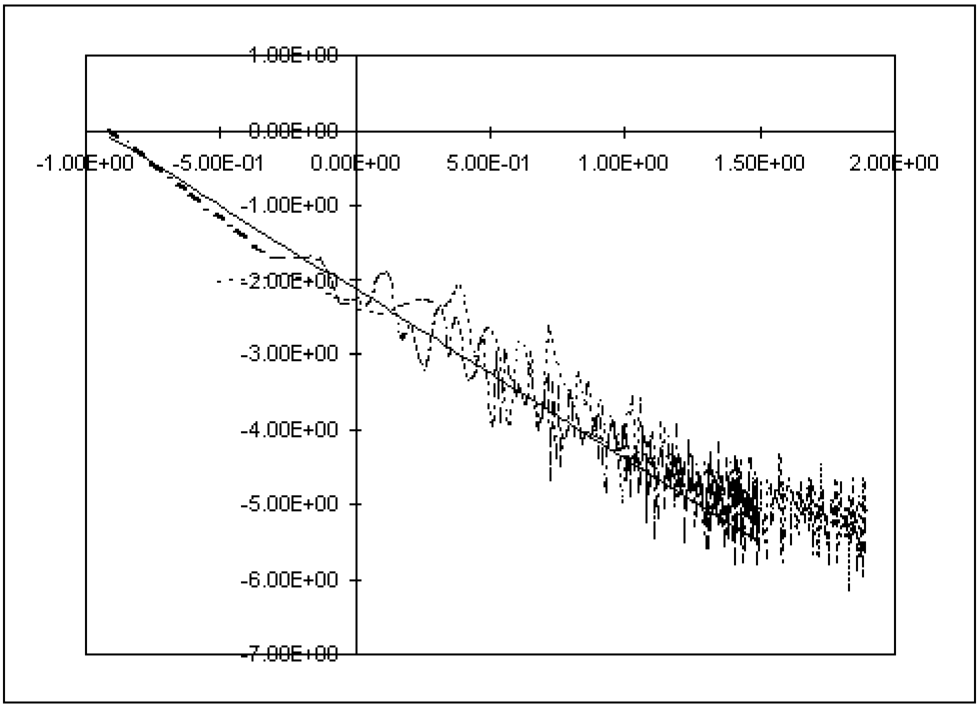

Figure 3. Power Spectral Density (psd) of time-of-flight data for a representative sample in longitudinal (short dash) and transverse (long dash) directions. The straight, solid line has slope=-2.

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