

NONINTEGER DIMENSIONS AND SIMULATIONS IN CORROSION

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SUMMARY

We introduce in this paper a mean field model to estimate the active (fractal) surface involved in corrosion. In the last section we describe a new method to study corrosion from the point of view of computer simulations.

1. INTRODUCTION

Fractals are now a topic of wide interest¹, with applications in all areas of Physics^{2,3} as well as in Chemistry⁴, Biophysics⁵, Meteorology⁶, Civil and Mechanical Engineering⁷, Ecology⁸ and many other disciplines.

In recent years the irregularities in the molecular domain of the surfaces of several organic and inorganic materials have been studied and characterized by Avnir, Farin and Pfeifer^{4,9}. In particular these authors have shown that an increasing number of materials have fractal surfaces, i.e. surfaces with noninteger dimensionalities. As a consequence, it is important to study the chemistry of noninteger dimensions between two and three, since a number of chemical physics phenomena as e.g. adsorption¹⁰ and catalysis¹¹ are heavily dependent upon the nature and geometry of the surface of the material.

Professor Ricardo C. Ferreira, to whom this article is dedicated, has stressed about the increasingly important relationship between Chemistry and Materials Science in our days. Corrosion is an aspect to be considered in the development of a large number of new materials as well as in the current industrial processing of metals, plastics, fibers, ceramics and glasses. Here we discuss the application of fractal concepts to the phenomenon of corrosion. We have two aims in the present work: firstly, a new quantitative estimation of the active surface involved in corrosion is discussed in Section 2. The arguments developed in the following section are certainly useful in heterogeneous catalysis and other chemical processes occurring at surfaces. Secondly, we have introduced in Section 3 for the first time a new approach to study corrosion from the point of view of computer simulation.

2. A FRACTAL MODEL FOR THE ACTIVE SURFACE IN CORROSION

Corrosion is considered in this work as a disaggregation process in which a system reduces its mass M or its number of microscopic constituents c through a mechanism of the type $c + x \rightarrow cx$ occurring at the surface of the system. Here x represents a corrosion agent and cx is a

soluble product. Thus from the kinetic point of view the evolution of M during corrosion can be described by

$$\frac{dM}{dt} = -kM_a, \quad (1)$$

where k depends on macroscopic variables as temperature, pressure and concentration of x . M_a takes into account the effective area of the system available to the chemical attack. Thus eq. (1) assumes that the rate of loss of mass is proportional to an active surface and not necessarily to the total surface. A theoretical estimation of M_a is not a trivial task since most materials have irregular or nonhomogeneous surfaces in a large range of scales. These irregularities are due to structural (microscopic) or mechanical (e.g. cracks, wear) defects. Furthermore, many materials have fractal surfaces^{4,9} and then screening effects are in general important¹².

Here we are interested in the study of corrosion from fractal surfaces free of any type of defects. For a regular (euclidean) tridimensional object of uniform density and free of defects we have surface area \sim volume^{2/3} \sim $M^{2/3}$. In this case we expect that

$$M_a \sim M^{2/3} \sim L^2, \quad (2)$$

where L characterizes the size of the object. From eqs. (1) and (2) we obtain $M_0^{1/3} - M^{1/3} \sim t$. M_0 being the initial mass ($M_0 = M(t=0)$). This behavior is in fact observed for many kinds of corrosion. As an example, Figure 1 illustrates this situation for hot rolled plain carbon steel corrosion¹³ in HCl 2.7M at 80C. On the other hand, for a fractal surface we adopt in this paper the following generalization of eq. (2):

$$M_a \sim L^{d_a}. \quad (3)$$

In principle, the exponent d_a may develop the role of a fractal dimension. One of the aims of this article is the estimation of this exponent. To this end we assume that there is an exponent d_s which scales L and the total number of surface sites N_s according to $N_s \sim L^{d_s}$ at least in a finite interval of L . Euclidean solids have obviously $d_s = 2$; however many compact objects present $d_s > 2$ in relatively wide intervals of scales⁹. The exponent d_s is the fractal dimension of the surface. It is easy to understand that d_s

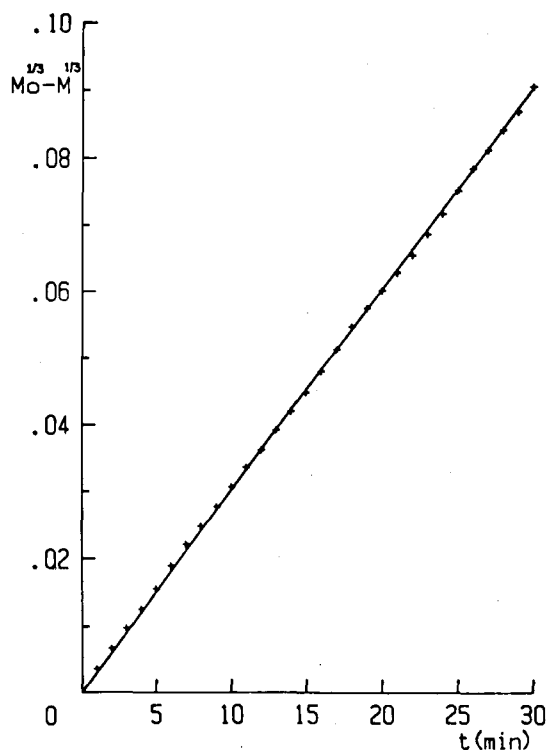


Fig. 1 - Weight loss test for hot rolled plain carbon steel corrosion in HCl 2.7M at 80°C as a function of time. In the ordinate we have plotted $M_0^{1/3} - M^{1/3}$, where M_0 is the initial mass of the sample. The experimental data are denoted by crosses. The good fit obtained with the straight line $M_0^{1/3} - M^{1/3} = kt$ indicates that $d_a = 2/3$ in equation 3 (see Section 2, second paragraph).

lies within the interval $d_T \leq d_s \leq d$, where d_T is the topological dimension of the surface and d is the dimension of the space where the system is embedded¹⁴. Then, for any physical object in the tridimensional space we have in general $2 \leq d_s \leq 3$. Since d_a is connected with the idea of an active surface or unscreened perimeter¹², it is physically plausible to expect a direct relation between d_a and the codimension^{12,15} of d_s , $d - d_s$. If $d_s \rightarrow d$ the surface is extremely folded and a minimum active area or a minimum d_a (for L fixed) is expected in view of the difficult diffusion of the corrosion agent between the folds of the surface. On the other hand, when $d - d_s$ increases we have a progressive unfolding of the surface and so a more satisfactory configuration to the penetration of the corrosion agent (x) in the invaginated regions of the surface is obtained. As a consequence, M_a increases with $d - d_s$ or d_a increases with $d - d_s$ for L fixed. Another important constant to corrosion is the dimension d_p of the x -particles trajectories. This quantity is associated with the scaling relation $N_w \sim \lambda^{d_p}$, where $N_w \gg 1$ is the number of steps of an x -particle random walk needed to reach an average distance λ . Usually $d_p = 2$ for molecules in liquids and gases¹⁶. Other values for d_p may be obtained e.g. through the inclusion of external fields upon the region containing the x -particles. After the introduction of the dimensions d_s , d and d_p we need of the dimension D which appears in the relation $M \sim L^D$ involving the mass M and size L of the system.

In principle, we expect that if the codimension $d - d_s > d_p$ all the surface sites of the system will be accessible to x . On the other hand, if $d - d_s < d_p$ the diffusion field associated with x will be screened in a finite

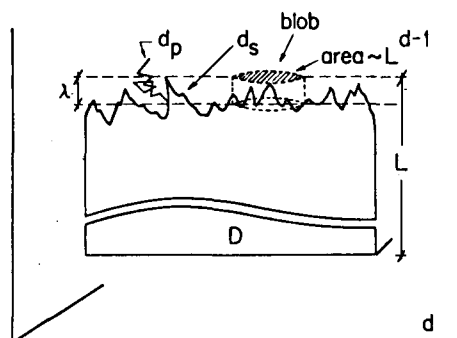


Fig. 2 - Schematic sketch showing the divers dimensions used in the text (Section 2, second paragraph). λ is the average penetration length and L denotes the macroscopic size measured along any space direction.

depth λ (Figure 2). Thus we have for the number N_w of steps of x in the penetration region the relation $N_w \sim \lambda^{d_p}$. To estimate the exponent d_a of Eq. (3) we need to know the dependence of the screening length λ with L . To find this dependence we divide the region near the surface in blobs of height λ and transverse are $A \sim L^{d-1}$ as that shown in Figure 2. Inside each blob we assume that the surface sites are homogeneously distributed with an average density $\sigma = (\text{number of sites}) / (\text{blob volume}) \sim (L^{d_s} / \lambda L^{d-1}) = \lambda^{-1} L^{d_s-d+1}$. We assume again that $N_w \sim 1/\sigma$. Then from the last two scaling relations we obtain $N_w \sim \lambda^{d_p} \sim (1/\sigma) \sim \lambda L^{d-d_s-1}$, or equivalently

$$\lambda \sim L^{(d-d_s-1)/(d_p-1)} \quad (4)$$

Finally we consider that $M_a \sim (\lambda/L)M$ is approximately true for our ends. This relation satisfies the physical requirements $M_a \xrightarrow{\lambda \rightarrow 0} 0$ and $M_a \sim M$ if $\lambda \sim L$. Using the last scaling relation and Eq. (4) we get

$$M_a \sim L^{d_a}, \quad d_a = \frac{(d-d_s-1 + (d_p-1)(D-1))}{(d_p-1)} \quad (5)$$

Thus for $d = D = 3$ and $d_s = d_p = 2$, $M_a \sim L^2$ as frequently assumed and/or observed for many surface processes as that exemplified in Figure 1. However, for $d = D = 3$, $d_p = 2$, $d_s = 5/2$ and $d_s = 3$ we obtain, respectively, the dependences $M_a \sim L^{3/2}$ and $M_a \sim L$, i.e. the number of active surface sites increases more slowly with d_s . For a generic d_s and $d = D = 3$, $d_p = 2$, we have $d_a = (4 - d_s)$. On the other hand, if $d_s = d - 1$, we find that $d_a = D - 1$, indepen-

dently of d_p . This includes the case of corrosion of an Euclidean hypersphere with a smooth well-behaved surface. An interesting example to be studied from the experimental point of view is the corrosion of say an aluminium crumpled surface¹⁷ whose $D = d_s = 5/2$ in $d = 3$. For this situation the predicted active area scales linearly with L .

Although Eq. (5) may in principle be applied to a number of situations, corrosion in physical space is restricted to $d = 3$, $d_p = 2$ and thus the relevant dimensions are only D and d_s . In this particular case $d_a = D - d_s + 1$. However, an infinity of pairs of values (D, d) are possible and this effectively contributes to transform corrosion in a very diversified phenomenon.

3. SIMULATION

In order to simulate corrosion we apply a very simple and practical method, based on the direct use of computer screen storage to model the object being simulated, and screen operations to mimic the interaction between the object and the environment.

In a m by n pixel screen, we represented the object as a (say) black area, against a white background. In the example shown in Figure 3 the cross section of a cylindrical tube (or, equivalently, a two-dimensional annular plate) was "written" on screen storage, and we simulated an attack on the borders of that surface by creating a rain

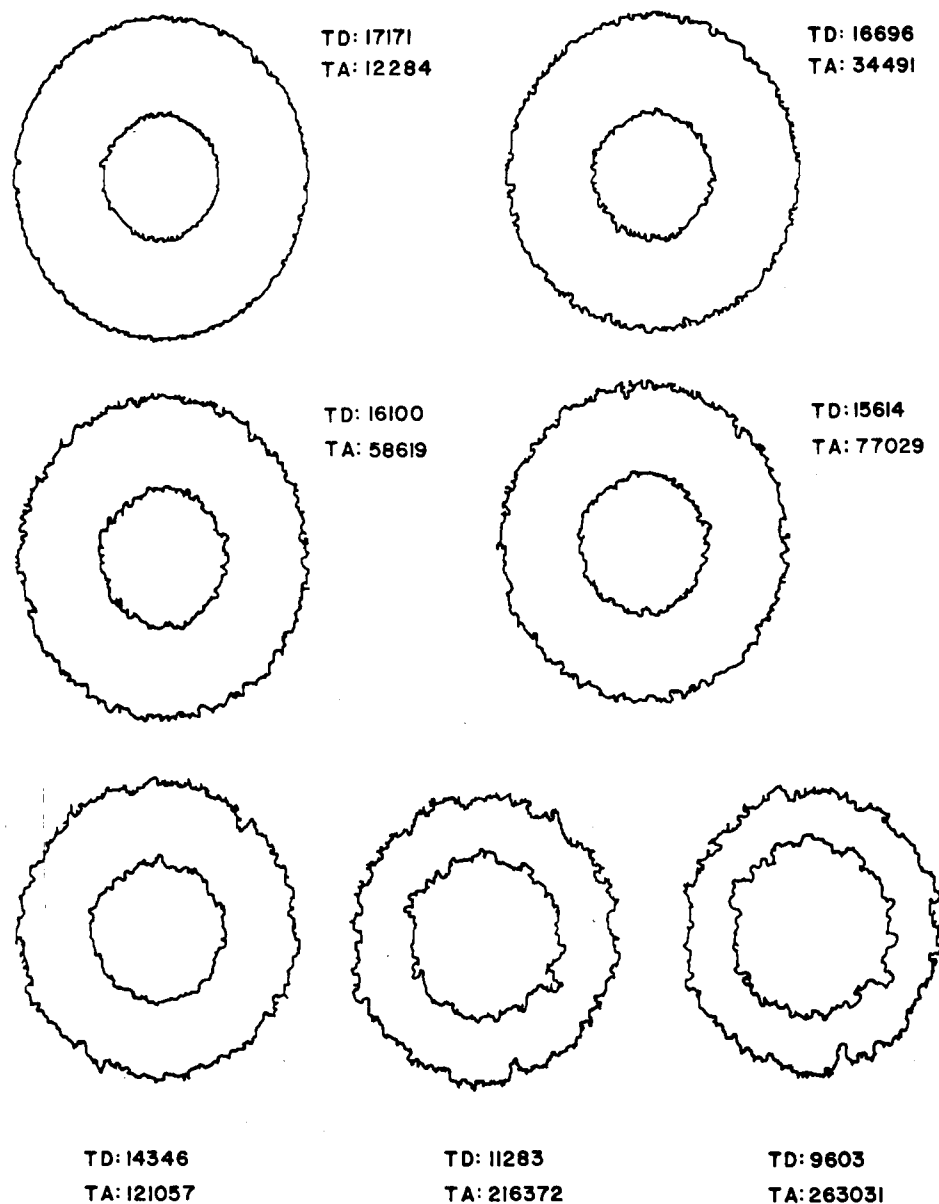


Fig. 3 - These nine snapshots represent several stages of the corrosion of a two-dimensional annular plate built on a square lattice in the plane ($d = 2$) with $ID = 17364$ points using the simulation described in Section 3. TD denotes the actual number of points (or mass) in the plate and TA is essentially the time (see text). In this case ID and TD scales with TA as $(ID)^{1/2} - (TD)^{1/2} \sim TA$ typical of the corrosion of a two-dimensional Euclidean object.

of random homogeneously distributed white pixels. For every white raindrop that fell on to the ground, it only erased a black one if the latter had three or less neighbours. This "rain" is denoted in Figure 3 as TA (Total attack), and as it is evenly distributed in time and space, it can be used as a measure of time in an analysis of the system's dynamic behavior, more exactly TA-physical time (t) x frequency of generation of raindrops.

The equation of motion associated with this simulation is identical with Eq.(1). The simulation data show in this case that M_a scales with M as $M_a \sim M^{1/2}$, a scaling relation typical of the corrosion of a two-dimensional

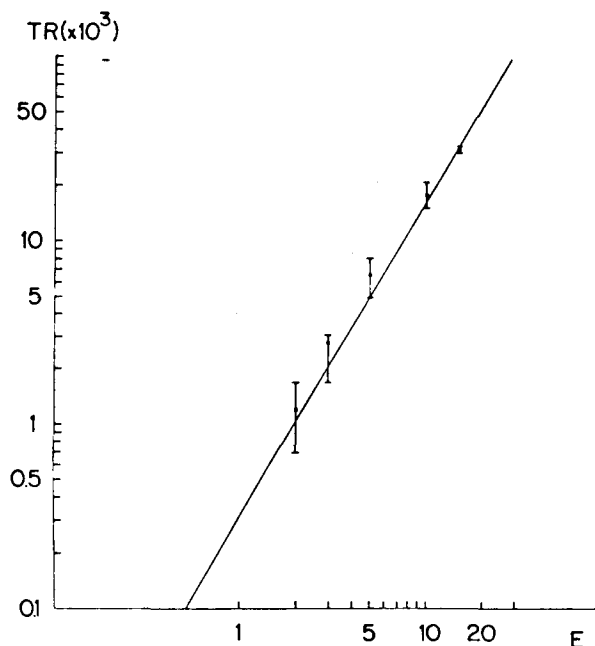


Fig. 4 – Dependence of the rupture time TR (arbitrary units) of the objects which appear in Figure 3, including uncertainty bars, as a function of the initial thickness E (see Section 3, third paragraph).

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1. The term fractal was coined by the mathematician Benoit B. Mandelbrot twenty years ago to designate a set whose its Hausdorff dimensionality strictly exceeds its topological dimension. The interested reader will find detailed information about this concept, accompanied of a number of applications, in Mandelbrot's beautifully illustrated monography THE FRACTAL GEOMETRY OF NATURE (Freeman 1983, San Francisco). An appraisal of this book is made in Science 200, 677-8 (1978) by F. Dyson and in Am. J. Phys. 51, 286-7 (1983) by John A. Wheeler. The chemist certainly will appreciate the article by Pfeifer and Avnir (ref. 4 below) where the role of fractal or noninteger dimensions in Chemistry is discussed.
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($D=2$) Euclidean object whose perimeter behaves as a regular curve of dimension $d_s = 1$. Thus, if we use $D = d = 2$ and $d_s = 1$ in Eq. (5) we obtain $d_a = 1$, independently, of d_p . This implies, in fact, that $M_a \sim L$ or, equivalently, $M_a \sim M^{1/2}$. Then, after integration of Eq. (1) with $M_a \sim M^{1/2}$ we get $(ID)^{1/2} (TD)^{1/2} \sim TA \sim t$, where in the notation of Figure 3 $ID = \text{initial mass} = M_0$ and $TD = \text{mass at time } t = M(t)$. Figure 3 and the simulations reported here show that an irregular (random) surface is not necessarily a fractal. It is interesting to observe the deeply invaginated regions formed in the last two frames of Figure 3: they imply in a local thickness significantly smaller than the mean thickness and may produce catastrophic changes if the system is submitted to some sort of stress. In connection with the last figure we introduce the rupture time TR as the minimal time needed to transform the original annular plate in a simply connected region. In Figure 4 we present TR as a function of the initial thickness E; it is found that TR scales with E as $TR \sim E^{1.73}$. Thus, according this result if the thickness of the wall of a tube submitted to the same corrosion agent from the interior and the exterior is duplicated, the rupture time TR is increased by a factor of 3.3.

Detailed results of extensive simulations in corrosion, as well as in fragmentation, using the method described in this section will be published in a forthcoming paper.

ACKNOWLEDGMENTS

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