SIMULATIONS OF METAL DISSOLUTION AND CORROSION

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PROJECT SUMMARY

PERSONNEL

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PROJECT OVERVIEW

Project History

This program was originally funded at MIT (DE-FG02-89ER45388) and was renewed in July 1992 for one year. Between January 1993 and June 1994, work on the renewal program was performed at The Johns Hopkins University under subcontract GC-R-320807and the work described in subsequent sections summarizes progress made during this period.

Significance

The control of metal dissolution processes is important in fields ranging from battery technology to corrosion. Nevertheless, metal dissolution remains a poorly understood class of electrochemical reactions. Although the reaction sequences for dissolution of many metals have been elucidated, kinetic descriptions are based on area averaged values of parameters that describe the relationship between the rate of reaction and the activation energy. Theoretical and experimental research on metal dissolution has focussed traditionally on macroscopic processes and features. However, in the last few years there has been considerable interest in examining these processes on a microscopic scale. In addition, the growth and formation of rough interfaces is of considerable practical importance in surface science and many similarities can be found between material removal processes (e.g. etching, evaporation, and erosion) and material addition processes (e.g. crystal growth, condensation, vapor deposition, and electrodeposition). Over the next few years, results from theoretical modelling of dissolution processes, in conjunction with new experimental techniques such as *in situ* scanning tunnelling microscopy, are expected to provide a new insight into the processes controlling metal dissolution and corrosion.

Objectives

The objectives of this program were to determine the relationship between dissolution kinetics and surface morphology for metal dissolution and corrosion processes. Specific objectives include determination of: (i) the relationship between surface morphology and applied potential, (ii) site population statistics and the contribution of different sites to the total dissolution rate, (iii) the role of surface diffusion in dissolution processes. As a result of our work one paper has been published in Physical Review B [1] and one submitted to Physical Review Letters [2]. Both are appended to this report.

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INTRODUCTION

Over the last few years there has been considerable interest in microscopic aspects of material removal processes in fields such as corrosion, erosion, evaporation, battery technology, electropolishing, and semiconductor etching. Reports of theoretical work related to many of these problems can be found in the literature although metal dissolution is a noticeable exception. For example there are a large number of reports related to theoretical studies of etch pit formation and etching of semiconductors [3]. Very recently, changes in global climates has stimulated research into chemical dissolution of minerals by acid rain and major contributions in this area have been based on theoretical modeling of the dissolution process on a microscopic scale [4-7].

Problems encountered in metal dissolution and corrosion are common to other dissolution processes described by activated complex theory, including dissolution of semiconductors and minerals. In addition, the growth and formation of rough interfaces is of considerable practical importance in surface science and many similarities can be found between material removal processes (e.g. etching, evaporation, and erosion) and material addition processes (e.g. crystal growth, condensation, vapor deposition, and electrodeposition). Critical issues common to all dissolution reactions include the relationship between the surface morphology and the driving term (e.g. potential, concentration, temperature); the role of surface active sites, dislocations, and other heterogeneities to the dissolution kinetics; and the influence of surface diffusion

We have shown [1] that microscopic analysis of electrochemically dissolving metal surfaces via computer simulations can lead to a fundamental understanding of the relationship between surface morphology and dissolution kinetics. Microscopic information on surface processes is not contained in phenomenological equations such as the Butler-Volmer equation, which is commonly used to describe electrode dissolution. In particular, we find that the surface roughness and, consequently, the number of surface active sites, are determined by thermodynamic parameters such as the applied electrode potential. The morphology of surfaces has been shown to be an essential aspect of kinetic processes such as crystal growth and mineral dissolution. Electrochemical processes, however, are fundamentally different in that they feature the presence of very high electrical fields at the interface, which directly affect the surface reactions. To date, treatments of the kinetics of electrochemically dissolving metal surfaces have ignored surface morphology. Over the next few years, results from theoretical modeling of dissolution processes, in conjunction with new experimental techniques such as

STM, are expected to provide a new insight into the processes controlling metal dissolution and corrosion.

TECHNICAL APPROACH
Introduction

The evolution of rough structures on surfaces is observed in a number of important physical and chemical processes in which material is removed from a surface. Examples of such processes are erosion, electropolishing, evaporation, and corrosion [8,9]. Increased understanding of crystal growth has revealed that rough surfaces are also formed during processes in which material is added to the system. The evolution of interface morphologies has therefore been the subject of intense fundamental research, with the aim of understanding and predicting the dynamic and static aspects of roughening, as well as the determination of possible universal characteristics independent of the particular model used.

An important feature derived from the results of crystal growth simulations is the distinction between two different mechanisms of growth [10]: at low temperatures, nucleation controlled growth is observed in which stable islands of deposited atoms must be formed and the nucleation process is the rate determining step. Above a certain temperature, T_R, the system enters a continuous growth regime when the nucleation barrier disappears. As a result, the surface becomes rough and atomic clusters of all sizes can be found on the surface of an infinite system. For finite models, the sizes of these clusters, as well as the sizes of the steps, are limited by the sample size.

The roughening temperature is believed to be a function of the external driving force which controls the growth [11]. For large values of the driving force, the transition occurs at temperatures which are lower than the roughening temperature of the system in equilibrium with its vapor. Kinetic roughening has been investigated by several authors [12-15] and it may have important consequences in determining optimal growth conditions to attain a specific surface morphology.

Similarly, we believe that the kinetics of electrochemical processes occurring at a metal-electrolyte interface are dependent on the morphology of the metal surface. If this is the case, then one might expect that information on the kinetics of these processes is left as characteristic structure on the surfaces. All present kinetic theories of electrochemical processes neglect the influence of surface morphology and its fluctuations. In fact, for the case of corrosion, we are

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left with the approach proposed by Wagner and Traud [16] in which the Butler-Volmer equation is applied to a heterogeneous process where the oxidation and reduction reactions originate from different processes. In this approach, the single electrode equilibrium potential is transposed to an open-circuit corrosion potential (E_{corr}) and the exchange current density to the corrosion current (i_{corr}). Under open-circuit conditions, both anodic dissolution and cathodic reduction must occur simultaneously on the metal surface. Therefore, it has been inferred that anode and cathode areas are randomly distributed over the electrode surface. In order to attain a uniform thinning (uniform corrosion), the anode and cathode areas must be dynamic and the accepted concept of uniform corrosion is one of 'shifting' anodes and cathodes. However, the concept of fluctuating anodes and cathodes cannot be built into a phenomenological theory based on the Butler-Volmer equation, which contains no information on local surface properties. For the specific case of driven dissolution, sites with low coordination number are more 'anodic' than sites with high coordination number, in the sense that the former contribute more to the anodic current than the latter. If local properties control the anodic process, we may expect that fluctuations of the surface morphology are coupled with fluctuations on reaction site specificity, and consequently with the shifting of anodes and cathodes.

Several other results from our simulations illustrate the fact that morphological aspects are of importance on electrode kinetics. The width of the interface, for example, is a measure of the correlation between the atoms in the z-direction. We show [1] that this correlation is dependent on the application of an external field. As a consequence of this mechanism, the surface becomes rougher with more low coordination sites. Heusler et. al. [17,18] have experimentally verified that the density of kinks increases with increasing anodic potentials during dissolution of low index planes of iron. Another interesting aspect is the change in the behavior of the width versus anodic potential curve at a characteristic potential, that might be evidence for the existence of a kinetic roughening transition in these systems [1]. We also have shown that the classical picture of dissolution with propagating kink sites along a step is only valid in our model for very low values of potential, and might deserve some further discussion.

Morphological Aspects of Surface Kinetics

Much progress in understanding dissolution kinetics is presently being achieved with studies of weathering and related processes [4-7]. Chemical weathering is the natural

dissolution of minerals in contact with aqueous solutions and it occurs where the chemical composition of the solid is not in equilibrium with the aqueous phase. Due to the importance of weathering in the global cycle of elements, the kinetics of processes at the mineral-water interface are of considerable importance. Recent interest in this area has been stimulated by the accelerated effects of acid rain. Although some issues in this field are still under debate [5], these studies have shown that surface processes control the kinetics of dissolution of oxides and silicates, and that their rates are strongly dependent on the local coordination chemistry at the surface. Experimental data have verified that dissolution of some oxides in acidic solutions follow a proton-assisted mechanism [7] where protons are bound to oxide ions at the surface and weaken the necessary bonds to promote dissolution. Statistical models have been developed [4] in order to calculate the rate of the dissolution reaction. Wehrli [6] carried out computer experiments of oxide dissolution with kinetics based on simulated coordination chemistry of the solid-on-solid model, and it was verified that a constant roughness is generated. Our simulation results [1] on metal dissolution strongly support these conclusions. Furthermore, we have shown how morphologies, and therefore the population of active sites, are strongly dependent on the thermodynamic variables of the system, such as the external applied electrical potential. Wehrli et al. [4] have recently reported anisotropic dissolution kinetics of kaolinite where it was found that the strong anisotropy is due to different mechanisms of protonation of the three distinct crystal surfaces studied, because different geometries expose different active sites.

We also note that there have been both experimental and theoretical studies of the dissolution of an active metal from a binary alloy containing a second noble metal component. The current - voltage curves for the dissolution of a binary alloy may result in a number of unique features in comparison to the elemental metal. In addition, the surface of a dealloyed layer exhibits a characteristic morphology depending on the alloy composition and solution chemistry. Simulations reported by Sieradzki and Newman and co-workers [19] have been used to demonstrate that dealloying can be described by percolation of the active metal component. In the dealloying problem, the system can be modeled by assigning a dissolution probability of 1 to active metal sites since the chemical potential difference between the two components are more important than electrical terms. For single metal systems, as in our work, dissolution cannot be treated in this way since the dissolution reaction is strongly potential dependent, according to the Butler-Volmer equation.

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Surface Scaling and Phase Transitions

In general, when estimating thermodynamic quantities from numerical simulations of equilibrium statistical mechanics on small systems, one needs to perform a finite size scaling analysis [20]. This analysis is used to search for the dependence of the calculated quantities on the linear dimension, L, of the system under investigation. The quantities can then be extrapolated to values representative of a thermodynamic system.

Since non-equilibrium interface growth processes generally reach steady state conditions with structures that often resemble those of fractals, a general scaling approach [8] has been developed for describing growing interfaces. The importance of this approach is that it determines quantities, i.e. exponents, which are not unique to the process under investigation, but have a universal character independent on the particular features of individual growth model.

The dynamic scaling approach [8] considers a flat surface at t = 0 which is allowed to grow by some pre-defined stochastic growth laws. Information of the surface morphology is controlled by the function h(x,t) which gives the height at the surface position x at time t. For a two dimensional surface, the surface width is measured by:

$$w = \sqrt{\frac{1}{L^2} \sum_i (h_i - \bar{h})^2} \qquad \{1\}$$

where d is the dimension of the surface and $\bar{h}$ is the average height which is given by:

$$\bar{h} = \frac{1}{L^2} \sum_i h_i \qquad \{2\}$$

Initially, the surface roughens as a consequence of the build-up of random fluctuations on h(x,t). The width of the interface therefore grows as a function of time, and is a measure of the correlation among these fluctuations along the growth direction. When the size of the fluctuations become comparable to L, the width reaches a steady-state value. The dependence of w(L,t) on t and L is of the form [8]:

$$w(L,t) \approx L^\alpha \, f(t/L^{\alpha/\beta}) \qquad \{3\}$$

where f is a function such that $f(x) \approx x^\beta$ for $x \ll 1$ and f(x) = constant for $x \gg 1$.

As a result, for small times in the simulation, one expects $w \approx t^\beta$, and after reaching steady-state, $w \approx L^\alpha$. Several estimates for these exponents exist from numerical simulations [12,13,18] and analytical studies [14]. Although results for one dimensional surfaces seem to agree well, some questions on universalities for two dimensional surfaces are still unanswered [8,18].

Our results [1] show that surfaces undergoing driven dissolution show scaling behavior similar to that proposed by equation {3}. The identification of universality classes of rough surfaces given by the exponents may be of practical importance [8,15] in which they characterize possible interfaces. Surface roughness is an important experimental parameter in electrochemistry, principally in studies of impedance measurements. Theoretical and experimental investigations [20-24] have tried to relate the response of rough and fractal-like electrodes to fractal dimensions.

Along with the study of the scaling behavior of growing rough surfaces, the possibility of the existence of a kinetic roughening transition has been investigated by several authors [12-15]. The KRT is the non-equilibrium analog [14] of the equilibrium roughening transition that occurs in interfacial systems at equilibrium, e.g. solid and vapor equilibrium, where smooth facets dominate the morphology at low temperatures, and the surface becomes rough at high temperatures. Perhaps the most convincing evidence for the existence of these transitions during interfacial growth has been published by Amar and Family [13]. They find two growth regimes for low and high temperatures, characterized by distinct exponents.

The abrupt change in behavior of the width parameter as a function of the applied potential, observed in our work [1], may be an indication of such a phase transition in dissolution systems. Guo et al. [12], have studied a growth model in which probabilities are biased by a parameter λ_a (where probability, $P \approx \exp(-\Delta E/kT + \lambda_a)$) corresponding to an external field. When $\lambda_a = 0$, the equilibrium roughening transition is recovered. Simulations at a constant temperature show a phase transition for a fixed value of λ_a. Our model is similar to this, in which the probabilities are biased in the same way.

RESULTS AND DICSUSSION
Introduction
In our work the morphological aspects of corrosion processes are addressed through

computer simulations of dissolving metal surfaces. We have used a solid-on-solid model to describe a metal surface and apply kinetic descriptions of dissolution, indexed over all surface sites. The surface morphology is characterized in terms of the interface width, site population density, and the spectral distribution describing the frequency of characteristic length scales. The characteristic features are compared to existing experimental data and to other models describing equilibrium and dynamic behavior of surface morphology during material removal and growth processes.

The simulation experiments are performed using a Monte Carlo technique. In our model, we have analyzed the case for a simple (001) solid-liquid interface of a defect-free simple cubic crystal. Each occupied site in the lattice is required to be above another occupied site (solid-on-solid model) and the interaction energy between neighboring sites is given by ϕ. Dissolution of the lattice is constrained by a site-dependent form of the Butler-Volmer equation:

$$i_+ = A \sum_q n(q,t) \exp\left(-\frac{\Delta E_{diss}(q)}{kT}\right) \qquad \{4\}$$

where i_+ denotes a positive (dissolution) current and n is the number density of surface atoms of type q at time t. The activation energy for dissolution is given by:

$$E_{diss} = nn \cdot \phi - \eta \, q_0 \qquad \{5\}$$

where nn is the number of nearest neighbor sites, q_0 is the electron charge, and η is the overpotential for dissolution. This expression is equivalent to the definition of an electrochemical activation energy where the electrical term is decoupled from the chemical component (usually incorporated in the constant i_0). This approach supports the simple interpretation of competition between the electric and bonding terms in our simulation. Here, we assume that the chemical component of the activation energy is related to the number of nearest neighbors through an interaction energy, ϕ. The transfer coefficient, α_+, is implicitly assumed to be unity; although lower values can be considered by suitably scaling the potential.

The details of our results using this model can be found in reference [1] appended to this report. Subsequent sections describe approaches developed to address the role of surface diffusion and the influence of local defects such as dislocations in metal dissolution.

Surface Diffusion

Surface diffusion has been studied extensively in surface science and can play an important role in determining the morphology of surfaces in many growth processes, including electrodeposition. For a continuous surface, the chemical potential, μ, of a surface atom is related to the local curvature, κ, by:

$$\mu_\kappa = \kappa \gamma \Omega \qquad \{6\}$$

where γ is the surface tension and Ω is the atomic volume. As a result of the curvature, the flux of atoms from regions of high curvature to regions of low curvature is determined from the Nernst-Einstein equation [25]:

$$J = -\frac{D_s \gamma \Omega v}{kT} \frac{\partial \kappa}{\partial s} \qquad \{7\}$$

where D_s is the coefficient of surface diffusion, s is the arc length, Ω is atomic volume, and v is the number of diffusing atoms per unit area. The curvature term is a geometrical effect for the preferential surface diffusion where, in the absence of an external driving force, the preferred direction of motion is determined by maximizing entropy.

We are exploring the role of surface diffusion by a scaling probability method based on similar approaches used for growth processes. For a given site, we compute the total energy of all nearest neighbor sites and allow surface atoms to jump into a neighboring site with a probability:

$$P_{diffusion} = A \exp\left(-\frac{E_i - E_{i+1}}{kT}\right) \qquad \{8\}$$

where E_i is the energy of the source site and E_{i+1} is the energy of all possible jump sites, calculated from:

$$E_i = nn_i \cdot \phi_1 + nnn_i \cdot \phi_2 \qquad \{9\}$$

The constant A in equation {8} is similar to the pre-exponential constant (D_0) relating the diffusion coefficient and activation energy and incorporates a jump frequency. In the simulations, each a possible jump site is selected randomly and tested for diffusion; if the diffusion probability is lower than a randomly generated probability then the next possible site

is selected. Since surface diffusion is tested after dissolution, the model naturally predicts that diffusion is more important at low driving voltages where the average removal rate is low and the lifetime of a surface atom is long.

We are currently comparing our model for surface diffusion to the continuum model developed by Mullins [25,26] in the analysis of thermal grooving. Mullins considered the relaxation of a one dimensional, sinusoidally modulated surface defined by:

$$W(x,t=0) = a \sin (2\pi/\lambda)\, x = a \sin \omega x \qquad \{10\}$$

where W is the amplitude as a function of distance, a is the amplitude, λ is the wavelength and ω is the modulation frequency. Relaxation of the surface, for $a\omega \ll 1$, is given by:

$$\frac{W(x,t)}{W(x,t=0)} = \exp\left(-\frac{D_s\,\gamma\,\Omega^2\,v\,\omega^4\,t}{kT}\right) = \exp\left(-B\,\omega^4\,t\right) \qquad \{11\}$$

where D_s is the surface diffusivity, γ is the surface free energy, Ω is the atomic volume, v is the surface density of atoms, and k and T have their usual meaning.

We have implemented extensive computer simulations of the relaxation of sinusoidally modulated surfaces. The important results can be found in reference [2], appended to this report. The most significant result from this work is that the scaling exponent $z = 4.0$ over a wide temperature range. We conclude that smoothening of modulated surfaces using the SOS model is dominated by fluctuations that allow the systems to sample many configurations which eventually leads to an arrangement that results in the dissappearance of a terrace. This picture is significantly different from the conventional view where curvature is the driving force for the decay.

Defects - Dislocations

Initially, we have considered the role of edge dislocations. The increased strain energy associated with a dislocation core will tend to lower the activation energy of atoms in the vicinity of a dislocation and hence the sites around the core are dissolved preferentially. This effect has a number of important consequences on the surface morphology. First, the preferential dissolution around a dislocation creates a depression, analogous to an etch pit, with a characteristic radius and morphology. Second, the curvature in the depression enhances

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surface diffusion of surrounding atoms toward the center of the dislocation. Diffusion into this region is balanced by the repulsive force of the core preventing surface atoms diffusing into the core itself (this effect is discussed in the next section). The equilibrium morphology of the crystal surface is determined by the pressure due to the strain energy density, directed inwards towards the core, and is balanced by a pressure directed outwards arising from the surface energy.

For metals the elastic energy per unit length of an edge dislocation is given by [27]:

$$E_{dislocation} \approx \frac{\mu b^2}{4\pi} \log \frac{r}{r_0} \qquad \{12\}$$

where b is the Burgers vector, μ is the shear modulus, r_0 is the cut-off distance (nonlinear region), and r is the largest length scale defined by the microstructure (e.g. grain size or distance to the nearest dislocation). Taking the core size as the lattice spacing, $r_0 \approx b$, the change of the strain energy per atomic length of dislocation is obtained by integration of equation {12}:

$$\Delta E_{dislocation} \approx \frac{\mu b^4}{4\pi} \frac{1}{r} \qquad \{13\}$$

Assuming $b \approx 2 \times 10^{-7}$ (cm) and $\mu \approx 10^{11}$ erg cm^{-3}, the strain energy of the dislocation is about 10/r (eV). Introducing this term into the expression for the activation energy gives:

$$E_{diss} = nn \cdot \phi_1 + nnn \cdot \phi_2 - \frac{\mu b^4}{4\pi} \frac{1}{r} - \eta q_0 \qquad \{14\}$$

In our simulations, we define certain x,y co-ordinates (independent of z) as the locations of edge dislocations aligned perpendicular to the surface. In the simulations, equation {14} is used to determine E_{diss} for each site with r, the distance from the dislocation core, determined by the distance to the nearest dislocation. Figure 1 shows an example of the steady state morphology for simulations at two different potentials. The effects described above, can be clearly seen in these surfaces. At lower potentials, the characteristic radius associated with the depressions are smaller than the separation whereas at higher potentials, interaction between the two regions gives rise to a ridge-like feature between them. In future work, the implications of these results on corrosion processes should be investigated.
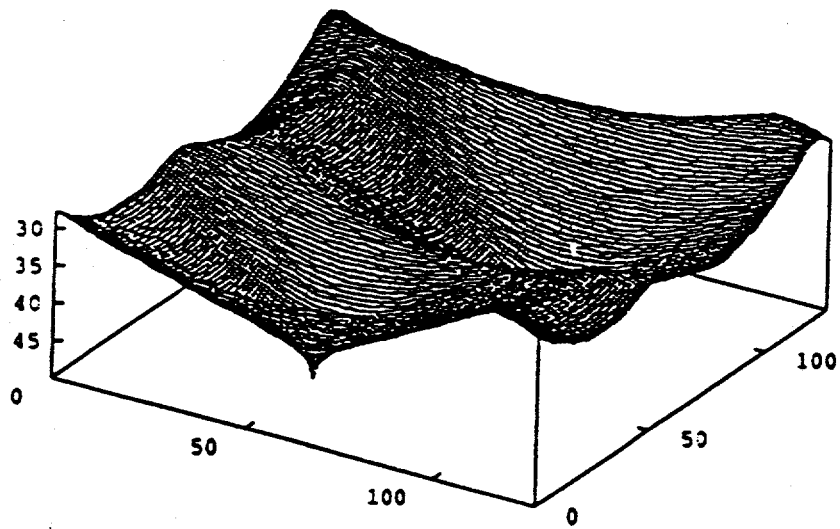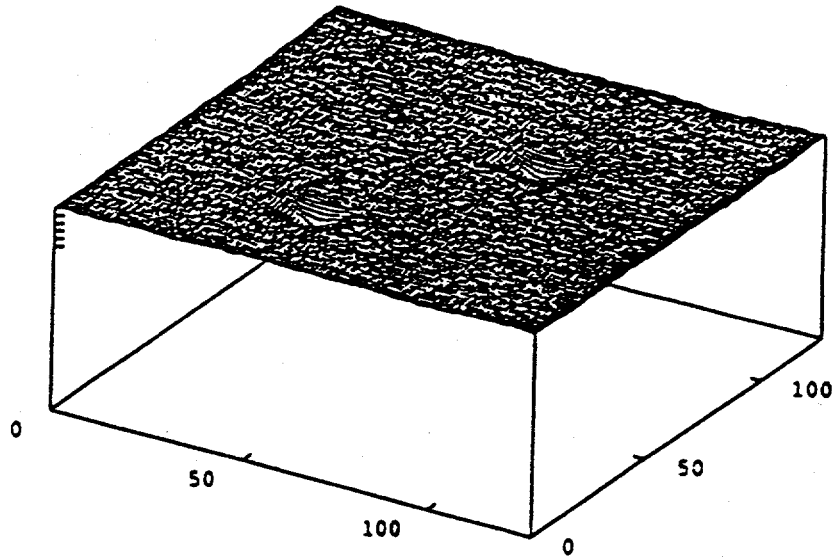
Figure 1. Simulations of metal dissolution on a 128 x 128 lattice with two edge dislocations at η=2 (top) and η=5 (bottom). φ/kT = 1.95; no surface diffusion.

Summary

We developed a discrete kinetic model for the metal/electrolyte interface undergoing dissolution. Simulation experiments were performed on a defect-free, cubic lattice as a function of applied potential; the details of this work can be found in reference [1] appended to this proposal. We observed that with increasing applied potential, the surface roughness, characterized by the interface width and the high frequency spectral density, also increased. As a consequence of this mechanism, the surface becomes rougher with an increase in the concentration of low coordination sites.

In addition, we have observed a characteristic potential above which the interface width became more sensitive to changes in the applied potential, similar to systems undergoing kinetic roughening transitions. Recent experimental data of electrochemically induced surface reconstructions also demonstrate that surface morphology can be influenced by an external field. An important consequence of the surface roughening is that the contribution of different surface sites to the total dissolution current is dependent on potential. We have concluded that the roughening may induce a change in dissolution mechanism from kink propagation at steps at low potentials to a mechanism dominated by more weakly co-ordinated sites at higher potentials.

We have also examined the role of surface diffusion in an SOS model. We have suggested that the smoothening of perturbations is related to the fluctuations in the surface morphology and not due to curvature. These results can be found in reference [2].

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