Tensile Stress and Plastic Deformation in Aluminum Induced by Aqueous Corrosion

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Abstract

Measurement of near-surface stress generated by metallic corrosion can reveal defects and material property changes relevant to structural degradation by stress corrosion cracking. In this study, stress and topography evolution were characterized during alkaline corrosion of high-purity aluminum. In situ stress measurements revealed tensile increases of the force per width (stress integrated over depth) that scale directly with the sample yield stress. Spectral analysis of the uniform dimpled surface pattern produced by corrosion showed that transient changes of its characteristic wavelength track closely with the force per width. Together, the stress and topography measurements imply that corrosion creates a plastically deformed metal layer. Tensile stress is attributed to the lattice contraction associated with metal vacancies introduced during dissolution. In agreement with this hypothesis, a vacancy diffusion model successfully predicted the time dependence and magnitude of the force response, as well as the observed scaling relation between plastic layer thickness and pattern wavelength. The driving force for vacancy formation is thought to arise from high hydrogen and low aluminum chemical potentials near the corroding surface, the latter imposed by the high dissolution potential relative to the equilibrium potential of aluminum.

1. Introduction

Corrosion processes in combination with external or residual stress can induce embrittlement of structural metals, leading to premature and unexpected failure by stress corrosion cracking (SCC). While SCC has been studied intensively for several decades because of its wide economic significance, critical chemical interactions responsible for corrosion-enhanced degradation have not been fully clarified. In some systems such as high-strength 7xxx series Al alloys, corrosion is accompanied by absorption of hydrogen produced by cathodic water reduction, and SCC may be closely related to hydrogen embrittlement (HE) [1]. SCC and HE of Al alloys has been explained in terms of mechanisms such as hydrogen-enhanced local plasticity (HELP), hydrogen-enhanced decohesion (HEDE) or brittle hydride fracture [2, 3].

Aside from hydrogen defects, several authors suggest that metal vacancies produced during corrosion may influence SCC and HE of various alloys. Vacancies are thought to promote degradation by facilitating dislocation emission or climb at crack tips [4-6], decohesion [7], or void formation [8-10]. Formation of vacancies has been explained by direct injection into the metal by dissolution [4-6, 11], tensile strain or cold work [9, 10]. Also, strong binding of vacancies to absorbed hydrogen can result in dramatically enhanced concentrations of both vacancies and hydrogen near corroding interfaces, potentially assisting failure by HELP and HEDE mechanisms [12-14]. On the other hand, it is thought that vacancy injection during dissolution is kinetically challenged by the appreciable energy barrier to form lattice vacancies, so that high electrochemical potentials at the dissolving surface may be required [15]. Recent advances in atomistic simulations have led to the

development of quantitatively predictive models for SCC and HE that include relevant length scales ranging from crack dimensions down to those of chemical interactions between atoms at crack tips [16-19]. While these models can simulate the detailed effects of defects on embrittlement, there remains a critical need to understand the metal-environment interactions during corrosion that control near-surface concentrations of defects participating in SCC.

In this study, we characterize formation of near-surface defects using in situ measurements of stress changes during corrosion. Hydrogen absorption and vacancy injection respectively expand and contract the metal lattice close to the surface, generating biaxial near-surface stress that in turn induces changes of sample curvature. High-resolution curvature measurements permit sensitive detection of near-surface hydrogen and vacancies during corrosion [20, 21]. Chu and co-workers, using ex situ stress measurements, already found evidence that corrosion-induced tensile stress correlates with SCC susceptibility [22, 23]. The present work focuses on defect generation during uniform alkaline corrosion of large-grain high-purity Al. Such samples avoid complications arising from localized corrosion processes at grain boundaries and second-phase particles. Alkaline corrosion of Al is accompanied by rapid hydrogen absorption [14, 24], as well as formation of large numbers of subsurface nanoscale voids, the latter which may be attributable to condensation of near-surface vacancies produced during dissolution [25-27].

The present experiments employ a new technique, phase-shifting curvature interferometry, with significantly higher curvature resolution than traditional cantilever defection methods [28, 29]. The enhanced curvature resolution permits stress

measurements in relatively thick sheet and foil samples, in contrast to thin metal films typically used for deflection techniques. Thicker samples enable study of material property effects in experiments with extended corrosion exposures. The present measurements revealed large tensile stress increases that scale directly with the sample yield strength. Spectral analysis of the dimpled topography produced by dissolution demonstrated that the characteristic wavelength of this uniform surface pattern scales with corrosion-induced stress, apparently the first indication of corrosion-induced plastic deformation. Model calculations show that both the thickness of the plastically deformed layer and the pattern length scale are determined by the diffusion penetration of vacancies injected by dissolution. The electrochemical driving force for vacancy diffusion-induced tensile stress and plasticity is explained in terms of the high hydrogen chemical potential and low aluminum chemical potential imposed respectively by the metal dissolution and hydrogen absorption processes.

2. Experimental Methods

Aluminum samples were fabricated from either 1 mm thick sheet of 99.998 % purity (Alfa Aesar), or 25 μm thick foil of 99.999 % purity (Alfa Aesar). Electron backscatter diffraction revealed a typical grain size of 200 to 400 μm in the sheet material. Some of the sheet samples were cold-worked to 0.65 mm thickness using a hand mill. Foils were annealed at 550°C for 52 hr, increasing their grain size to the order of 100 μm . Sample yield stress was estimated from the measured Vickers hardness (Wilson Tukon Hardness Tester) [30]. Usually the aluminum surface was not treated before dissolution. In one experiment, the aluminum sheet was electropolished for 5 min at 30 V in a solution of 20% perchloric acid in ethanol. Alkaline corrosion of the Al samples was at open circuit in aqueous sodium hydroxide solutions. Topographic changes resulting from dissolution were characterized by field-emission SEM (FEI Quanta 250) and atomic force microscopy (AFM, Veeco Metrology Dimension 3100).

Detailed descriptions of the phase shifting curvature interferometry system and procedures used in stress measurements are provided elsewhere [29]. For stress measurements, both sheet and foil samples were cut into rectangular shape (3.5 x 2.5 cm). Only one side of the sample was exposed to the corrosive solution, while curvature changes were determined by interfering light beams reflected on the opposite side. Thus, curvature measurements are not affected by corrosion-induced surface roughening. To produce reflective surfaces for interferometry, gold films were transferred to one side of sheet samples using a template-stripping technique. Foils were bonded with epoxy to silicon wafers, which reflected the light beam and also functioned as elastically stiff

substrates. Curvature and force per unit width changes are related by the thin-film Stoney approximation, $\Delta F_w = \left[E_s h_s^2 / 6(1 - \nu_s) \right] \Delta \kappa$, where ΔF_w and $\Delta \kappa$ are the force per width and curvature change; and h_s , E_s and ν_s are the thickness, elastic modulus and Poisson's ratio of the Al sheet or Si wafer. ΔF_w represents the biaxial in-plane stress σ_{xx} integrated through the sample thickness, relative to that before corrosion, with the x -direction parallel to the Al surface.

3. Results and Discussion

3.1. Stress measurements

All force measurements revealed significant tensile stress increases during alkaline corrosion. Figure 1 compares stress evolution of Al sheet samples in 0.1, 0.5 and 1.0 M NaOH. Force per width in the figure represents the biaxial in-plane stress (σ_{xx} , with x -direction parallel to surface) integrated through the near-surface stress-affected layer, relative to that before corrosion. In the 1.0 M solution, the force increases initially in the compressive direction to a minimum value of to -3 N/m at 0.8 min, after which tensile force begins to accumulate. Force change in the 0.1 and 0.5 M solutions is tensile from the beginning of dissolution. In each solution, tensile force increases for 7 to 17 min until a plateau is reached. The plateau force increases significantly with concentration, but the rate of force increase before the plateau is similar in all three solutions. The rates of both metal dissolution and accompanying hydrogen absorption increase significantly with pH over the range in Figure 1 [24], suggesting that the stress response is controlled directly by the corrosion process.

Since Al has a moderate yield stress on the order of 100 MPa, tensile stress generated during corrosion could induce near-surface plastic deformation of aluminum metal. Figure 2 shows the force per width transient in 1 M NaOH for three samples with close to 99.999% purity but different yield stress: annealed 25 μm foil, 1 mm as-received sheet and the same sheet after cold rolling to 650 μm thickness. The respective yield strengths of the annealed foil, as-received sheet and rolled sheet were estimated as 20, 90

and 120 MPa using Vickers hardness measurements. The force transient of the annealed foil but not the rolled sheet exhibits a compressive minimum of -3 N/m at 1 min, similar to that of the as-received sheet. Both the average rate of tensile force increase and the plateau force increase significantly with yield stress. Indeed, the inset shows that the plateau force per width measured at 15 min scales with the yield stress, suggesting that tensile strain introduced by corrosion may be accommodated by near-surface plastic deformation.

3.2. Correlation of topography and stress evolution

In this section we examine the relationship between force evolution and the development of the dimpled or scalloped surface pattern produced by alkaline etching. Examples of scanning electron microscopy (SEM) images after dissolution times of 5 and 20 min are shown in Figure 3 (a, b). Uniformly distributed characteristic dimpled depressions are found which increase in width over time up to 20 min. AFM revealed that the dimple features are concave spherical sections with radius as large as 500 nm. The radius of curvature of the convex ridges between dimples is much smaller, roughly 20 - 30 nm. These ridge and dimple dimensions are typical of patterns produced by etching or chemical polishing of aluminum [31, 32]. Spectral analysis of the SEM images was carried out to determine the characteristic length scales of the dissolution-induced morphology. Figure 3 (c) displays the Fast Fourier Transform (FFT) of the 20 min image in Figure 3 (b). The abscissa and ordinate are the spatial wavenumbers $1/\lambda_x$ and $1/\lambda_y$ of the Fourier modes of the image, where λ_x and λ_y are wavelengths in the horizontal and

vertical directions. The color scale in the transform image is determined by the Power Spectral Density (PSD). The relatively bright spot in the central part of the image contains the modes contributing appreciably to the SEM image contrast. The inclination of the spot is caused by the preferred orientation of dimples along rolling marks on the sheet. Figure 3 (d) represents a line section along the long dimension of the spot in Figure 3 (c). The wavelength of the maximum PSD amplitude along the section corresponds to the characteristic width of dimple features.

Characteristic dimple widths after dissolution of sheet samples are compiled in Figure 4 and compared to the force measurements. The main panel shows the wavelengths on the left axis plotted against dissolution time, while the force transient in 1 M NaOH is plotted for comparison using the right axis. The wavelength increases from 100 nm at 1 min to a stable range of 900 to 1.0 μm reached after 15 min. The transient increase of wavelength closely parallels that of force per width. For the lower NaOH concentrations, the wavelengths measured at 15 min lie below those for 1 M NaOH. However, it is also appropriate to plot these data points at the times at the beginning of the plateaus, based on the constant wavelengths along the force plateau for 1 M NaOH. Figure 4 shows that when this is done, all the wavelength data lie close to a common trajectory. Thus, all experiments initially follow a universal increasing trend of force or wavelength with time until reaching a steady state level, which is larger at higher NaOH concentration. The inset of Figure 4 shows explicitly the linear dependence of force on wavelength for as-received sheet samples.

The scaling of the pattern wavelength with the force change suggests that the dimpled pattern is produced by deformation. The uniformity of this pattern across the

metal surface shows that the surface deformation is distributed uniformly. Therefore, the results of stress and topography measurements establish that (i) corrosion leads to uniform surface deformation, and (ii) this deformation coincides with the development of internal stresses that scale with the sample yield stress (Figure 2). These findings suggests that corrosion produces a uniform surface-adjacent plastically deformed layer. The measured force is dominated by this plastic layer, within which the stress is approximately equal to the yield stress. Similar near-surface plastic layers have been observed to form in Si wafers, as a result of tensile stress induced by dopant diffusion [33]. At steady state, the plastic layer thickness would be given by the slope of the inset graph in Figure 2, $\delta_{ps} \cong F_{ws} / \sigma_Y$, where F_{ws} is the steady state force and σ_Y is yield stress. The similarity of the regression slope of 120 MPa in Figure 4 and the yield stress of 90 MPa suggests that the dimple width and plastic layer thickness are comparable to one another.

According to the plastically deformed surface layer model, the force transients would be interpreted as the increase of the plastic layer thickness with dissolution time. Normalized force defined as the ratio of force per width to yield stress would then estimate the layer thickness at a given time. Figure 5 plots the normalized force during dissolution of the various sample types in 1 M NaOH. The duplicate experiments demonstrate the good reproducibility of the stress measurements. Normalized force transients for sheet and rolled sheet seem to collapse onto the same time dependence, which would support the interpretation of the force transient as plastic layer growth initiating near the onset of dissolution. However, both the steady-state plastic layer thickness and the time to steady state for foil samples are seen to be significantly smaller

compared to sheet. These differences are addressed below with reference to model calculations. Also, Figure 5 shows that electropolishing the sheet prior to corrosion exposure does not significantly affect the force trajectory. Electropolishing Al sheet removes damaged surface layers produced by rolling and surface-segregated impurities such as Pb, while increasing enrichments of bulk noble impurities like Cu [34, 35]. Insensitivity of force curves to these aspects of surface condition is consistent with tensile stress generation by Al dissolution itself.

3.3. Stress generation mechanisms

In this section, we discuss the origin of the stress changes accompanying corrosion. Compressive stress during the first minute of dissolution in some experiments can be explained by volume expansion caused by absorption of hydrogen interstitials [21], which occurs at high rates during alkaline corrosion [14, 24, 36]. Tensile stress increases at later times are caused by lattice contraction resulting from corrosion. Contraction contributed by diffusion of atoms from grain boundaries, while potentially significant in thin films [37], should be of minor importance in the present experiments because of the large grain size of the Al samples. Volume contractions would also be induced if dissolution creates metal vacancies replacing metal atoms [14, 36, 38], as the vacancy volume is 35 % smaller than that of Al atoms [39]. A near-surface vacancy concentration of 7×10^{-3} would be sufficient to produce elastic stress equivalent to the yield stress. As mentioned above, vacancy injection is consistent with evidence from positron annihilation spectroscopy (PAS), transmission electron microscopy (TEM) and

SEM that shows extensive formation of near-surface voids during alkaline dissolution [25-27]. More than 10^8 cm^{-2} voids of width 10 to 20 nm were detected within a depth of about 80 nm after dissolution of Al foils in 1 M NaOH [27]. PAS measurements at dissolution times up to 20 min revealed voids, suggesting continuous generation of vacancies during the present experiments.

Prior theoretical work indicates that attractive hydrogen-vacancy interactions can lead to vacancy formation in Al at high hydrogen concentration. Density functional theory (DFT) calculations indicate that hydrogen occupancy of as many as 12 octahedral interstitial sites neighboring the vacancy is energetically favorable [8, 12, 13, 40]. Thermodynamic models based on DFT-derived energetics indicate that large concentrations of vacancy-hydrogen defects should be present at equilibrium with the hydrogen concentrations on the order of 0.1 at. % typically found during alkaline corrosion [12-14, 24, 36]. Proximity to the metal surface may further enhance vacancy formation [41]. Fukai and co-workers found experimental support for H-induced vacancy formation in a number of metals at high temperatures and H_2 pressures [42]. We showed that hydrogen trapping at vacancies induced by hydrogen absorption can help explain hydride formation during alkaline dissolution [43]. On the contrary, other evidence suggests that hydrogen interactions alone would not account for the observed tensile stress increases. Recent stress measurements during cathodic polarization in acid solutions found near-surface concentrations of hydrogen on the order of 0.1 at. % similar to that during alkaline corrosion, but detected only compressive stress due to interstitial hydrogen. In addition, the thermodynamic models show that Vac-H defects at equilibrium with high hydrogen concentration consist of multiple H atoms at interstitial

sites around the vacancy [12]. Recent DFT modeling of H-vacancy interactions in Ni demonstrates that the formation volume of such defects is likely to be positive [44]. Creation of these equilibrium Vac-H defect would then result in volume expansion and compressive stress. Accordingly, it is unlikely that tensile stress generation as observed in the present experiments can be explained only in terms of elevated near-surface hydrogen concentration.

To reconcile the observed tensile stress with the high concentrations of both vacancies and hydrogen near the corroding surface, it is necessary to additionally consider effects of metal dissolution on subsurface defects. The primary anodic reaction during corrosion is the oxidation of Al atoms to form Al^{+3} ions incorporated into the $\text{Al}(\text{OH})_3$ surface film; at the same time, aluminate ions dissolve from this film into the saturated alkaline solution [45]. Also, analytical evidence from Secondary Ion Mass Spectroscopy and Atom Probe Tomography (APT) indicate continuing formation of aluminum hydride (AlH_3) during alkaline dissolution [46, 47]. The presence of hydride at the $\text{Al}/\text{Al}(\text{OH})_3$ interface is consistent with findings that the pH-dependence of the dissolution potential tracks closely with that of the Nernst potential of hydride oxidation [48, 49]. APT images of the interfacial region indicated that hydride is dispersed at the nanoscale, as opposed to being segregated in isolated domains, thus implying that the same electrochemical potential applies at both Al and AlH_3 sites [50]. Expressing this potential in terms of both the Al and AlH_3 oxidation reactions yields the constraint,

$$\mu_{\text{Al}} - \mu_{\text{Al}}^0 = 3F \left(E_{\text{Al}}^0 - E_{\text{AlH}_3}^0 \right) + 3F\eta \quad (1)$$

where μ_{Al} is the Al atom chemical potential, E_{Al}^0 and $E_{AlH_3}^0$ are the standard potentials of Al and AlH_3 oxidation to $Al(OH)_3$, and η is the kinetic overpotential for Al oxidation. Equation 1 assumes that both $Al(OH)_3$ and AlH_3 are at their standard chemical potentials, as implied by the close proximity of the dissolution potential to the Nernst potential of hydride oxidation. The standard potential difference in Equation 1 is -0.6 V in Equation 1 [48, 51], while a study of alkaline dissolution kinetics on fractured Al surfaces suggests that η is limited to values of about 0.1 V [52]. Therefore $\mu_{Al} - \mu_{Al}^0$ in Equation 1 is about -1.5 eV. This μ_{Al} deficiency is more than twice the formation energy of bulk vacancies in Al [13], and therefore by itself would produce large equilibrium vacancy concentrations. In the dissolution experiments, vacancy formation is additionally promoted by the elevated hydrogen concentration.

In summary, the discussion in this section argues that in the alkaline corrosion process there are two important driving forces for vacancy formation: elevated μ_H and deficient μ_{Al} . Our recent stress measurements on cathodically polarized Al suggest that high μ_H alone would produce compressive stress associated with hydrogen interstitials and possibly vacancies bound to multiple H atoms [21]. On the other hand, the deficient μ_{Al} imposed by the high potential of Al dissolution would tend to promote high concentrations of vacancies with a reduced hydrogen binding, consistent with volume contraction and tensile stress as revealed by the present measurements.

3.4. Prediction of diffusion penetration of vacancies

To test the vacancy injection hypothesis, the penetration depth of vacancy diffusion was estimated and compared to the plastic layer thickness from stress measurements. Injected vacancies would diffuse into the metal, generating a defect layer which grows in thickness over time until a steady state is reached at which the rates of vacancy formation and removal by dissolution are balanced. As a first approximation, we do not include stress effects on diffusion, since stress gradients should be damped within the plastic layer. Thus, the concentration of vacancies evolves according to the diffusion equation, $\partial C_v / \partial t = D_v \partial^2 C_v / \partial z^2$, where z is the depth coordinate on a stationary reference frame and D_v is the vacancy diffusivity. The vacancy concentration at the dissolving metal surface is taken as a constant value C_0 as implied by Equation 1, and the concentration is set to zero both initially and at large depths. Transforming to dimensionless variables $\tau = v_d^2 t / D_v$, $x = v_d (z - v_d t) / D_v$, and $c_v = C_v / C_0$, where v_d is the approximately constant dissolution velocity, the diffusion equation becomes $\partial c_v / \partial \tau - \partial c_v / \partial x = \partial^2 c_v / \partial x^2$, and the boundary condition at $x = 0$ is $c_v = 1$. Model calculations show that the vacancy concentration profile evolves to a steady-state exponential shape in which diffusion and dissolution are balanced, $c_v(\tau \rightarrow \infty) = e^{-x}$ (Figure 6). The defect layer thickness $x_D(\tau)$, defined by $c_v(x_D) / c_v(x = 0) = 0.2$, increases to a steady state value of 1.5 reached at a time of $\tau_s \cong 4$. The steady state defect layer corresponds to the force plateaus in Figures 1-2 and 5.

The vacancy diffusion model was used to predict the main features of the experimental force transients. First we consider the different force evolution of sheet and foil samples in Figure 5. The dimensional defect layer thickness at steady state is

inversely proportional to the dissolution rate, $\delta_{ds} \cong 1.5D_v/v_d$. Noting that the dissolution rate of foil in 1 M NaOH (190 nm/min) [24] is larger than that of sheet (131 nm/min), the steady state defect layer thickness of foil should be smaller by a factor of 131/190 or 0.69. This ratio is nearly the same as the ratio of normalized forces in Figure 5. The dissolution rate also influences the time to steady state, $t_s \cong 4D_v/v_d^2$, which should be smaller for foil than sheet by a factor of $(131/190)^2$ or 0.48. Indeed, according to Figure 5, the experimental times to steady state of foils are about one-half those of sheet. The model also rationalizes the dependence of the force transients in Figure 1 on NaOH concentration. The vacancy diffusivity was estimated from both t_s ($D_v \cong v_d^2 t_s / 4$) and the steady-state force F_{ws} ($D_v \cong v_d F_{ws} / 1.5\sigma_y$). Table 1 shows that these two methods result in closely similar diffusivity values at the three NaOH concentrations, which are also on the same order of magnitude as the vacancy diffusivity extrapolated from high temperature measurements, $4 \times 10^{-16} \text{ m}^2/\text{s}$ [53-55]. The agreement between force transients and model calculations is compelling evidence that vacancy diffusion accounts for the observed tensile stress evolution. The increase of diffusivity with pH in Table 1 is likely caused by factors neglected in the present simplified model, such as effects of stress or vacancy complexation on diffusion. The last column of Table 1 shows that the steady-state pattern wavelength and plastic layer thickness are comparable at all three NaOH concentrations tested.

3.5. Morphological stability analysis

In this section, we examine whether morphological stability analysis based on vacancy diffusion-induced plastic flow predicts the observed scaling of pattern wavelength with plastic layer thickness. Since plastic deformation accommodates strain induced by vacancy diffusion, we relate the metal lattice velocity at the interface to the vacancy diffusion flux, $\mathbf{v} \cdot \mathbf{n}_I = \frac{1}{3} f_v \Omega \mathbf{J}_v \cdot \mathbf{n}_I$. Here $\mathbf{n}_I$ is the interface normal vector, f_v is the fractional lattice contraction of vacancies, and Ω is the molar volume of aluminum atoms. The interface velocity is augmented by the lattice velocity,

$$\mathbf{v}_I \cdot \mathbf{n}_I = v_d + \frac{1}{3} f_v \Omega \mathbf{J}_v \cdot \mathbf{n}_I, \text{ where } v_d \text{ is the dissolution velocity. } v_d \text{ is given by}$$

$v_d = \Omega R_{Al} / (1 + f_v C_0)$, where R_{Al} is the metal dissolution rate and C_0 is the vacancy concentration at the interface. At the scale of the dimpled pattern, R_{Al} should be spatially uniform, since the solution diffusion layer thickness is much larger than the dimple height [56]. Given a constant C_0 , the diffusion flux and thus the interface velocity are enhanced on valleys and reduced at peaks, thereby causing interface perturbations to grow. Thus, plastic flow driven by vacancy diffusion destabilizes the flat interface. Restricted vacancy diffusion beneath ridges in the dimple pattern further explains observations of preferential nucleation of voids near ridges [27].

Pattern formation during dissolution requires the existence of a stabilizing process along with destabilizing plastic flow. Given the high interface curvature at ridges, we suggest that surface energy considerations would tend to stabilize the interface by promoting plastic flow toward the bulk metal. Surface forces would be significant when the capillary pressure in the metal is comparable to the yield stress. This is indeed the case, as the ridge radius of curvature of order 10 nm and the surface free energy of order

1 N/m indicate a capillary pressure of 100 MPa, the same order of magnitude as the yield stress of the Al samples. We capture this in a simple way by appending a curvature-dependent term to the interface velocity,

$$\mathbf{v}_I \cdot \mathbf{n}_I = v_d \left(1 + a\kappa\right) + \frac{1}{3} f_v \Omega \mathbf{J}_v \cdot \mathbf{n}_I \quad (2)$$

The parameter a is a length parameter expressing the sensitivity of the interface velocity to curvature. The local surface curvature is defined by the two-dimensional Laplacian operator as $\kappa = \nabla_I^2 z_I$, where $z_I(x, y, t)$ is the local interface position. Note that $v_d a \kappa$ is interpreted as an enhancement of plastic flow, despite the grouping of this factor with the dissolution velocity.

We again assume as a first approximation that vacancy diffusion is driven primarily by concentration as opposed to stress gradients. Thus, the vacancy diffusion flux in equation 2 is calculated from the vacancy concentration distribution as determined by the diffusion equation, $\partial C_v / \partial t = D_v \nabla^2 C_v$, where C_v is the vacancy concentration. The contribution of the small lattice velocity to diffusion is neglected. The boundary conditions for C_v are $C_v = C_0$ at $z = z_I$ and $C_v \rightarrow 0$ as $z \rightarrow \infty$.

The linear stability approach is used to model the response of the interface profile $z_I(x, y, t)$ to small perturbations. Accordingly, C_v and z_I are perturbed slightly from the basic state condition of steady-state dissolution of a flat metal surface:

$C_v(x, y, z, t) = \bar{C}_v(z) + C'_v(x, y, z, t)$, where the overbar denotes the basic state and the prime indicates the perturbation. To solve for the basic state concentration, the reference

frame is changed to that of the dissolving interface, $\zeta = z - \bar{z}_I(t)$. The time dependence of $\bar{z}_I$ is given by $\bar{z}_I = v_I t$, where the basic state interface velocity is $v_I = v_d / (1 - f_v C_0 / 3)$. The basic state vacancy concentration profile is the same as in the one-dimensional diffusion model, $\bar{C}_v(\zeta) = C_0 \exp(-v_I \zeta / D_v)$. The time dependence of the perturbed variables is determined by linearizing the model about the basic state. In terms of dimensionless variables, the linearized diffusion equation is $\partial C' / \partial \tau - \partial C' / \partial s = \nabla^2 C'$ where $C = C_v / C_0$, $s = v_d \zeta / D_v$ and $\tau = v_d^2 t / D_v$. The interface boundary condition is derived by writing C at the perturbed surface in terms of the value at the reference plane $s = 0$,

$$C|_{s'_I} = \bar{C}|_0 + C'|_0 + \left. \frac{d\bar{C}}{ds} \right|_0 s'_I \quad (3)$$

where s'_I is the perturbed dimensionless interface position. Since C at s'_I and $\bar{C}$ are both one, equation 7 becomes $C'|_0 = -d\bar{C}/ds|_0 s'_I = s'_I$. Using a similar expansion for the concentration gradient, the perturbed interface position is shown to evolve according to

$$\frac{ds'_I}{d\tau} = -\frac{1}{3} f_v C_0 \left(\left. \frac{\partial C'}{\partial s} \right|_0 + \left. \frac{d^2 \bar{C}}{ds^2} \right|_0 s'_I \right) + A \nabla_1^2 s'_I \quad (4)$$

where $A = a v_d / D_v$. The perturbed variables are represented as Fourier modes, e. g. $C' = \hat{C}(z) \exp(\beta \tau + i \mathbf{k} \cdot \mathbf{x})$, where $\mathbf{k}$ is the dimensionless wavenumber vector with components k_x and k_y . The solution for the amplitude of the perturbed concentration is found to be $\hat{C} = \hat{s}_l \exp\left[-\left(1 + \sqrt{1 + 4\beta + 4k^2}\right)s/2\right]$. Substituting for the concentration gradient into the perturbed interface motion equation (4) leads to a quadratic algebraic equation relating the growth factor β to system parameters,

$$\frac{6\beta}{f_v C_0} + \frac{6Ak^2}{f_v C_0} + 1 = \sqrt{1 + 4\beta + 4k^2} \quad (5)$$

The stability characteristics of the dissolving interface are determined by the roots of equation 5, $\beta(A, f_v C_0, k)$. One of these roots is always negative, while the other becomes positive for certain parameter ranges, indicating unstable behavior. The domains of stability and instability are the regions respectively above and below the curve in the inset of Figure 7, showing the critical $A/f_v C_0$ as a function of dimensionless wavenumber. Instability is found at sufficiently small values of $A = a v_d / D_v$, which controls stabilizing flow at ridges. The critical value of a therefore scales with the product of the vacancy diffusion length D_v / v_l , the vacancy contraction $f v$, and the interface vacancy concentration C_0 . As the measured tensile force indicates that C_0 is smaller than 10^{-2} , the critical a value is much smaller than the vacancy diffusion length. For all values of the system parameters, the inset of Figure 7 indicates unstable and stable behavior at low and high wavenumbers, respectively. This is because the vacancy

diffusion length controls destabilizing large-scale vacancy diffusion, while the relatively smaller length parameter a controls the stabilizing effect of enhanced dissolution at ridges.

Figure 7 shows examples of dispersion curves predicted by linear stability analysis. The growth factor β is plotted against the wavenumber for three values of the parameter $A/f_v C_0$. Each curve exhibits a non-monotonic wavenumber dependence, with positive maxima at small k and crossover to negative β values at the critical wavenumbers in the inset plot. The fastest growing wavenumbers typically identify the wavelength of emergent patterns. Significantly, the pattern wavelength scales with the vacancy diffusion length, i. e. $\lambda \sim D_v/2\pi v_l$. This correspondence of length scales is the same as that implied by the experimentally observed relationship between wavelength and plastic layer thickness in Table 1. Patterns with the same $D_v/v\lambda$ ratio as that found experimentally are obtained near the limiting $A/f_v C_0$ ratio of 2 at large wavelength. In addition, the small values of A associated with the pattern suggest that the magnitude of the effective capillary length a is no larger than about 10 nm. This estimate compares favorably with both the observed ridge radius of curvature and the capillary length estimated from the yield stress and surface free energy. The apparent agreement with experiment of both the pattern length scale and the capillary length is evidence that the dimpled pattern arises from plastic deformation accommodating tensile strain induced by vacancy diffusion.

The present morphological stability model predicts dimpled surface patterns in a given system when metal vacancies are generated at the surface. Since uniform corrosion processes produce similar dimpled or scalloped surface patterns on a variety of metals,

the scope of vacancy-induced plastic flow may extend beyond aluminum [57-61]. If so, our approach of combined stress and topography measurements would be expected to reveal the expected scaling relationships between plastic layer thickness and pattern length scales. Vacancy-induced plastic deformation might also explain TEM observations of enhanced dislocation activity near dissolving surfaces on brass and stainless steel [62, 63]. These systems exhibit enhanced susceptibility to stress corrosion cracking, raising the possibility discussed above that vacancy injection may play a direct role in the SCC mechanism. Vacancies generated near crack surfaces during SCC would also efficiently trap absorbed hydrogen, dramatically enhancing the local H concentration so as to activate HEDE and HELP hydrogen embrittlement processes. In addition to mechanistic implications for SCC and HE, the present results show that corrosion processes can produce defective and presumably weakened surface layers that may be precursors for crack initiation. Detection of such layers, if possible, may provide valuable early indications of stress corrosion cracking susceptibility prior to the catastrophic propagation stage.

4. Conclusions

This article reports stress measurements on Al sheet and foil samples during alkaline corrosion using phase-shifting curvature interferometry. The use of these bulk samples permitted study of material property effects on stress generation during extended corrosion exposures. The measurements reveal tensile force increases that scale with the yield strength. Coupled stress and topography changes strongly suggests that both are associated with plastic deformation. Spectral analysis of SEM images shows that the characteristic wavelength of the dimpled or scalloped surface topographic pattern produced by dissolution remains comparable to the plastic layer thickness interpreted from stress measurements. It was proposed that tensile stress in the metal is produced by lattice contraction associated by metal vacancies injected during dissolution. The driving force for vacancy injection arises from the low aluminum chemical potential and elevated hydrogen chemical potential, imposed respectively by the high electrochemical overpotential and hydrogen absorption rate during metal dissolution. The large overpotential is in turn associated with simultaneous Al and hydride oxidation reactions during corrosion. In support of the hypothesis that vacancies induce tensile stress and plastic deformation, we showed that vacancy diffusion controls the transient penetration of the plastic layer into the metal, and hence the time dependence of the measured force. Further, morphological stability analysis showed that the scaling relationship of the topography wavelength and plastic layer thickness is consistent with plastic deformation controlled by vacancy diffusion.

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Table 1. Estimates of vacancy diffusivity from stress measurements for Al sheet.

Symbols: C NaOH concentration; v_d dissolution velocity; t_s time to force plateau; F_{ws} force at plateau; $D_v(t_s)$ vacancy diffusivity estimated from t_s ; $D_v(F_{ws})$ vacancy diffusivity estimated from F_{ws} .

C M	v_d nm/min	t_s min	F_{ws} N/m	$D_v(t_s)$ m ² /s	$D_v(F_{ws})$ m ² /s	$D_v/v_d\lambda$
0.1	31	7.0	31	2.8×10^{-17}	4.2×10^{-17}	0.13
0.5	71	10	64	2.1×10^{-16}	3.2×10^{-16}	0.35
1.0	131	16	90	1.1×10^{-15}	1.7×10^{-15}	0.60

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Figure 1. Effect of NaOH concentration on force per width evolution during open-circuit alkaline etching.

Figure 2. Force evolution of Al foil (●), sheet (▲) and rolled sheet (○) during dissolution in 1 M NaOH. The main panel shows examples of force transients of samples with different yield stress. The inset demonstrates linear relationship between plateau force F_{ws} and yield stress σ_Y (circular symbols are used for clarity). The slope of the linear regression fit is 1.00 μm .

Figure 3. Image analysis of dissolution topography. (a), (b), SEM images after dissolution in 1 M NaOH for 5 and 20 min, respectively. (c) Image representing power spectral density of SEM image in (b). (d) Power spectral density plotted along the line in (c). Arrow indicates the characteristic pattern wavelength.

Figure 4. Characteristic wavelengths of dimple patterns after alkaline dissolution of Al in 1 M NaOH (●), 0.5 M (■, □) and 0.1 M NaOH (◆, ◇). The main panel shows wavelengths (left axis) of samples after different dissolution times. Solid symbols are plotted at the measurement time, open symbols at the time of the beginning of the force plateau. Force transient in 1 M NaOH is shown on right axis. The inset shows the relationship of force per width and wavelength, with the solid line a linear regression fit.

Figure 5. Evolution of normalized force of various samples during dissolution in 1 M NaOH. Normalized force is the measured force per width divided by the yield stress.

Figure 6. Vacancy concentration profiles calculated by the one-dimensional diffusion model. The ordinate and abscissa are respectively is the vacancy concentration normalized with the surface concentration C_0 , and the dimensionless depth relative to the dissolving interface. The parameter is dimensionless time (see text for definitions).

Figure 7. Results of linear stability analysis. Main panel shows examples of dispersion curves for various values of $A/f_v C_0$ (parameter in plot). Values of f_v and C_0 are 0.35 and 0.001. Inset illustrates critical conditions for instability. Unstable and stable behavior respectively are predicted below and above the curve.

Figure 1

Figure 2

Figure 4

Figure 5

Figure 6

Figure 7