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Microscopic characterization of corrosion morphology: A study in specular and diffuse neutron reflectivity

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Abstract

Detailed morphologies of the exposed surface of a Ni film vis-à-vis a buried interface below it have been determined by diffuse (off-specular) neutron scattering (DNS) and specular neutron reflectometry (NR). The exposed surface shows distinct morphological changes with respect to the buried interface, due to corrosion. The results demonstrate the strength of DNS in obtaining morphology of hidden interfaces and exposed surfaces simultaneously.

Keywords: Neutron reflectometry; Interface roughness; AFM; Corrosion

Corrosion kinetics brings in roughening and morphological changes on an exposed surface. Various physical and chemical interactions on an exposed surface constitute, which is broadly termed as corrosion [1]. Corrosion is the prime cause of deterioration in mechanical strength and surface properties of metals, leading to reduction in lifetime of metallic products. The morphology of a metallic surface under corrosion is a key factor towards the progress of corrosion from the surface to the bulk and the extent of corrosion damage. Depending on the process of corrosion, changes on a surface occur at various length scales. Morphological changes due to pitting at micrometer length scales on surfaces of aluminum and copper films have been studied by diffuse light scattering [2] and diffuse X-ray scattering [3], respectively. A large variety of rough surfaces over a wide range of length scales demonstrate self-affine fractal morphology [4]. We have determined the fractal morphology of the corrosion front at the exposed air–film interface of a Ni film as well as the morphology of an interface buried below the affected surface layer, using diffuse (off-specular) neutron scattering (DNS) and specular neutron reflectometry (NR). Neutron is an ideal tool for studying buried interfaces due to its deep penetrability in most of materials [5]. The present DNS study was undertaken to delineate its strength in obtaining distinct morphology of a hidden interface vis-à-vis the exposed surface. We have also determined the morphology of the exposed surface using atom force microscopy (AFM).

In general, the roughness parameter σ^2 is defined as $\langle (h-\bar{h})^2 \rangle$ the variance of the height (h) distribution on the surface of a thin film. The angular brackets specify an ensemble average. This average roughness, "σ" can be obtained from NR or specular X-ray reflectivity (XR) data in the form of a "Debye–Waller like" factor [6] that multiplies the Fresnel reflectivity R_F of ideally flat interfaces, to give the reflectivity $R(Q)$ of a thin film, $R(Q) = R_F\exp(-Q^2\sigma^2)$, at a momentum transfer Q. The roughness parameter σ, obtained from specular NR, is a convolution of mixing at the interface as well as *true* roughness. Details of in-plane correlation for two points separated by a distance 'r' over all length scales on a self-affine fractal surface is quantified by the height difference correlation function (HDCF) $g(r)$, expressed as [7]

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$$g(r) = \langle (h(r) - h(0))^2 \rangle = 2\sigma^2 \left[1 - \exp\left(-\left(\frac{r}{\xi} \right)^{2H} \right) \right] \quad (1)$$

where ξ is a length, over which the heights remain correlated. H is the Hurst parameter, which describes the fractal dimension D $(= 3 - H)$ of the surface. σ is identical with the parameter that we extract from specular NR or XR and for $r \gg \xi$, $g(r)$ reaches a saturation value of $2\sigma^2$, when the heights become uncorrelated. At short distances, for $r \ll \xi$, $g(r) \sim 2\sigma^2(\frac{r}{\xi})^{2H}$.

There are several techniques that can be used to determine the lateral correlations on surfaces of thin films. These are: scanning tunneling microscopy (STM), atom force microscopy (AFM), DXRS and DNS. Notably AFM and STM allow one a direct view of the film surface by mapping the height of the surface at the air–film interface. Presently NR has been used to determine the density profile of the film and average roughness. DNS has been used to determine HDCF of the interfaces. HDCF for the exposed surface of the Ni film was independently obtained using AFM.

The Ni film is a piece of neutron guide tube in Dhruva. It was deposited on float glass substrate by evaporation of Ni under a vacuum of 10^{-5} Torr [8]. The design thickness of the Ni on the glass was 1500 Å. The film has been exposed to atmospheric corrosion for more than fifteen years. The NR and DNS data have been collected on a neutron reflectometer at Dhruva reactor, Trombay [9]. This instrument uses a horizontal $_2He^3$-based linear position sensitive detector (PSD), located normal to the incident beam to capture the reflected intensity. The specular reflectivity pattern was collected as a function of momentum transfer Q_z in Å^{-1}, normal to the plane of the thin film, in a step-scan mode by rotating the vertical sample. The plane of scattering is horizontal for this instrument and off-specular data can be collected in the horizontal plane along the position sensitive detector. This unique arrangement allows us to collect DNS data simultaneously over the channels of the PSD, at any Q_z value. We used the matrix method of Blundell and Bland [10] to generate specular reflectivity pattern of the film with different structural parameters. These parameters were, thickness of the layers, their densities and roughness at the interfaces. A genetic algorithm based χ^2-minimization program [11] was used to fit the experimental data. Fig. 1 shows the NR data (open circles) along with the best fit obtained (continuous line). Our attempt to fit the data assuming a single Ni layers results in a poor fit (triangles in Fig. 1). A two layer model (inset A of Fig. 1) with a low-density top layer at the air–film interface and a layer with bulk density gave the best fit to the data. From the best fit we find that there is a 235 Å thick layer of density 50% (compared to bulk density of Ni) on top of a 1200 Å layer of near bulk density. The Ni film has three interfaces as shown in inset A of Fig. 1: (a) uppermost air–film interface, (b) high-density layer/low-density layer interface and (c) substrate/high-density layer interface. We obtained a layer-averaged roughness parameter σ equal

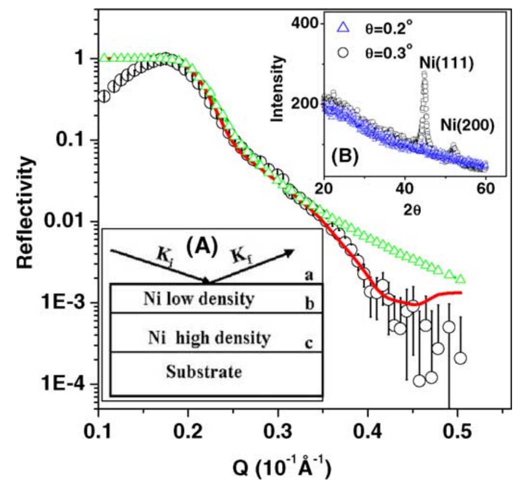

Fig. 1. The specular neutron reflectivity pattern from the Ni thin film sample as function of momentum transfer Q in Å^{-1}. The open circles are the experimental points and the solid line is the best fitted reflectivity pattern. The scatter data (triangles) is the fit for the experimental data, assuming a single Ni layer on glass substrate. Inset A: schematic of the layered structure of the sample. The inset B shows the GIXD data from the sample at two angle of incidence 0.2° and 0.3°.

to 8 Å from the NR data. Presence of the low-density surface layer indicates the progress of corrosion in the bulk of the film. Grazing incidence X-ray diffraction (GIXD) was performed to obtain the chemical structure of the low-density surface layer. GIXD at angles of incidence 0.2° and 0.3° on the sample surface (inset B in Fig. 1) shows the peaks due to fcc Ni at 44.85° (1 1 1 plane) and 52.06° (2 0 0 plane). We did not observe any oxide peaks from the surface layer. Our previous experience [12] indicates that an ultra-thin (~7 Å) oxide (or hydrated oxide) layer forms at the film–air interface, which inhibits further progress of oxidation. Ni and its alloys are widely used as protective coating for their corrosion resistive behavior [1]. In the present case, the loss of density in the top layer of thickness 235 Å, points to propagation of void networks [13] in the Ni film over a period of time and it is not due to any chemical change. Surface morphology of the top passive layer controls the propagation of corrosion in the film. The deviation between the fitted curve and the experimental specular reflectivity data below critical angle of reflection is due to "foot-print effect", which is a purely geometrical effect and does not have any bearing on the physical parameters.

AFM images of the top surface of the sample were obtained using an NT-NDT's Solver P-47 H multimode instrument with a Si_3N_4 tip. The cantilever has a spring constant of 0.6 N/m. We performed the scans in contact mode over scan lengths of about 2 μm. A typical 3-D image of the surface of the film for a scan length of 1.45 μm is shown in the inset of Fig. 2. The AFM data was used to obtain the HDCF for the sample surface as shown in Fig. 2 (open circles). Using Eq. (1) for $g(r)$, we obtained the parameters σ, ξ and H from the AFM data for interface (a). These are 6.5 Å, 760 Å and 0.48 for σ, ξ and H, respec-