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Scattering length density profile of Ni film under controlled corrosion: A study in neutron reflectometry

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Abstract. We report the density depth profile of an as-deposited Ni film and density profile for the same film after controlled electrochemical corrosion by chloride ions, measured by unpolarized neutron reflectometry. The neutron reflectometry measurement of the film after corrosion shows density degradation along the thickness of the film. The density profile as a function of depth, maps the growth of pitting and void networks due to corrosion. The profile after corrosion shows an interesting peaking nature.

Keywords. Neutron reflectometry; electrochemical corrosion; pitting.

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1. Introduction

Metals such as Ni, Fe, Cr and Ni-based stainless alloys, are protected against corrosion by a passive film [1,2]. Localized interaction of Cl^- with the passivated surface can cause the breakdown of passivity leading to localized corrosion (pitting). Generally, the pitting corrosion process of metals in chloride-containing solutions involves breakdown of the passive film, growth of metastable pits which can re-passivate, and growth of stable pits. Despite a considerable amount of data obtained [1,2] the fundamental aspects of the mechanisms operating in the early stages of pitting (leading to passivity breakdown and growth of pits) still needs to be investigated in detail. In particular, there is no atomic-scale data on the structure and morphology of growth of pits in these early stages of corrosion. Chemical or physical heterogeneities at the surface (such as inclusions, second particles, solute-segregated grain boundaries, flaws, dislocations, or mechanical damage) are favoured locations for pit initiation. Detailed scattering length density depth profile of an as-deposited Ni film and of the same film after controlled electrochemical corrosion was measured by unpolarized neutron reflectometry. The attempt has been to map the propagation of pits in the film due to corrosion. The neutron reflectometry measurements show density degradation along the thickness of film, which maps the growth of pitting and promulgation of void networks along the depth of the film. Interestingly, the density profile of the corroded film shows that the degradation in density is not a monotonic function of depth in the film as one tends to feel intuitively. We find that the density on the surface is lowest due to large number of voids present. It reaches close to the bulk value at a certain depth and then again goes down as we go deeper in the film indicating that the propagation of the voids in the film has progressed to deeper layers (possibly due to network of paths) before layers closer to surface are affected.

2. Experimental details and data analysis

The Ni sample used in the present study had been grown by r.f. sputtering technique at a base pressure of 5×10^{-8} Torr and at a deposition pressure of 4×10^{-3} Torr. A Si(1 0 0) substrate was first cleaned for both organic and inorganic contaminations. Ni layer of thickness about 900 Å was grown on the Si substrate. The sample thickness was monitored by quartz crystal system during growth. The electrochemical passivation and pitting corrosion on sputtered Ni surface was carried out using AUTOLAB-30 Potentiostat/Galvanostat. The electrolyte was made up of analytical grade 0.09 5M NaOH, 0.05 M H_2SO_4 for passivation and 0.05 M NaCl was added later for pit formation. The pH of the electrolyte was maintained at 3, making it strongly acidic. Both pitting and passivation experiments were performed under constant potential conditions and the transient current behaviour was monitored with time. All the potentials mentioned in the text are referred to saturated calomel electrode (SCE). The neutron reflectometry experiments for the as-deposited sample as well as the sample after pitting corrosion were performed *ex situ* at room temperature on the polarized neutron reflectometer at Dhruva, BARC, India [3]. Neutron reflectivity data can be fitted [4,5] using a depth-dependent scattering length density (SLD) profile $\rho(z)$ (where z is the film depth), $\rho(z) = \sum_i N_i(z)b_i$, where the summation is over each type of atom in the system, N is the number density at a depth z and b is the coherent nuclear scattering length. From the neutron reflectivity data, we obtained the number density as a function of depth z, viz. the SLD profile.

3. Results and discussion

Figure 1 shows a typical current transient recorded at 0.5 V_{SCE} after the introduction of chloride. The curve shows an increase of current, which is a characteristic for the formation of stable pits. The current density shows a steep increase from 0.43 to 0.63 mA cm^{-2} within a span of 72 s after introduction of chloride. Thereafter current was found to be constant for a longer duration with fluctuation of smaller amplitude.

Figure 2 shows the unpolarized neutron reflectometry data from as-deposited sample (before corrosion) as well as on sample after corrosion. Closed circles and open circles are the experimental data from the as-deposited sample and sample after corrosion, respectively. The continuous lines are fits to the measured data.

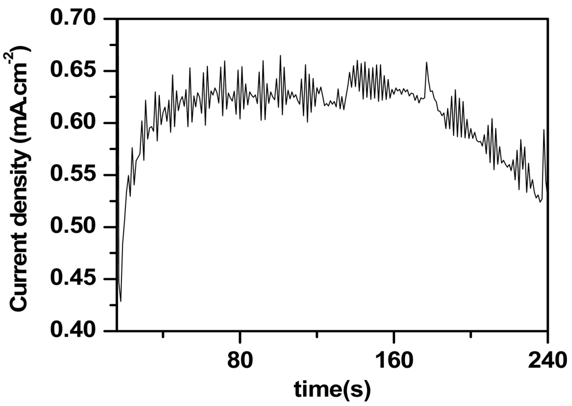

Figure 1. Current transient of Ni film recorded at $0.5\,V_{SCE}$ in 0.095 M NaOH + 0.05 M H_2SO_4 + 0.05 M NaCl solution at pH = 3.0.

The extracted scattering length density profile from unpolarized neutron reflectivity measurements are shown in figure 3. The dash-dot-dot line and continuous line in figure 3 represent the SLD profile from the as-deposited sample and the sample after corrosion, respectively. The thickness and density of the as-deposited Ni film, obtained from NR measurements are 790±10 Å and 8.1±0.3 g/cc, respectively. The density of the film is about 92% of its bulk density. A single layer model of Ni with the above density and thickness, as shown by the dash-dot-dot line in figure 3, was enough to fit the data. The film after corrosion shows a lower critical angle for reflection in the data. Since critical angle depends on the density of the media, overall loss in density of the film due to corrosion is apparent from the lower critical angle of the film after corrosion. The SLD profile for electrochemically corroded sample as obtained from the reflectometry data shows an interesting peaked nature as a function of depth, shown as a continuous line in figure 3.

If one considers that the propagation of the corrosion is solely due to the pit formation by the Cl^- ion in the material, then intuitively one feels that the corrosion front due to Cl^- ion migration should result in a density profile that monotonically increases to bulk density as one goes from the surface of the film to the insides of the film. Instead, the present density profile shows that the density is lowest on the surface of the film and as one goes inside the film, the density rises to a near-bulk value and then again goes down to a lower value in the interior of the film (figure 3). The SLD obtained from neutron reflectometry suggests that Cl^- ions are able to reach deeper in the film before some of the surface layers are affected. This is possible if there are pre-existing void networks in the film before the chloride ion is introduced. The increase in density and the subsequent decrease as one goes deeper in the film can be attributed to the void pathways for chloride ions in the film. The experiment throws light on this interesting aspect of corrosion propagation in a Ni film. The top 200 Å thickness has a SLD of 3.35×10^{-6} Å^{-2} in the film after corrosion. The SLD of NiO is approximately 2.60×10^{-6} Å^{-2}. The lower density on the surface could be due to the formation of non-conducting NiO as well as due to pit formation. NiO layer might have resulted during the passivation of the film before addition of chlorine.

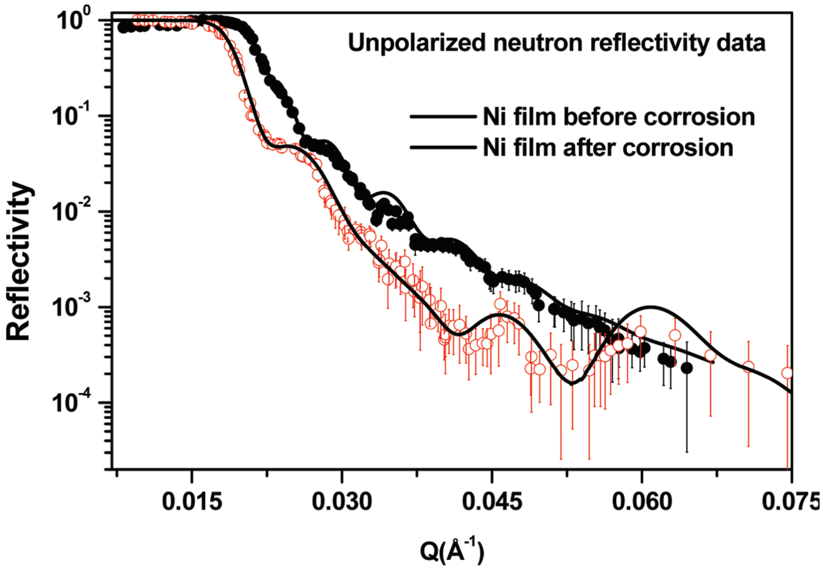

Figure 2. Specular unpolarized neutron reflectometry measurements on sample before (filled circles) and after (open circles) corrosion. Continuous lines are fit to measurements.

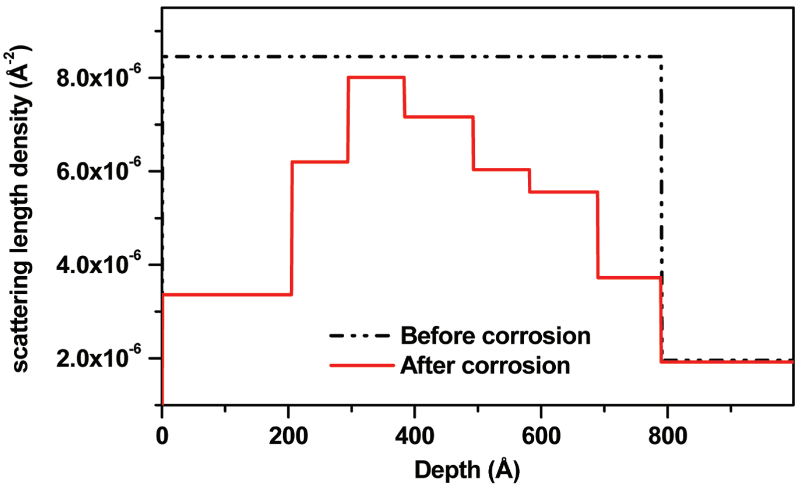

Figure 3. Scattering length density (SLD) profile of the sample extracted from fit to unpolarized neutron reflectivity measurements. Dash-dot-dot line is SLD profile of the as-deposited (before corrosion) sample whereas continuous line is SLD profile of the sample after corrosion.

4. Summary and conclusion

A Ni film grown by rf sputtering has been corroded using electrochemical method. The layered structure before corrosion as well as after corrosion has been studied by neutron reflectometry technique. The scattering length density profile of the corroded film suggests the growth of pitting and promulgation of void networks along the depth of the film, which changes the scattering length density along the depth of the film.

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