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A new approach to combating corrosion of metallic materials

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ABSTRACT

In this study a new approach that is based on creating surface patterns on metallic surfaces has been used to decrease corrosion in nickel. Patterns of holes with specific diameters (D) and inter-hole spacings (L) were created by laser ablation on nickel and potentiodynamic polarization corrosion tests were carried out in a 0.5 M H_2SO_4 solution. The corrosion potential, E_{Corr}, and current density (I_{Corr}) were determined and compared for different ratios of (D/L). Energy dispersive spectroscopy (EDS) was performed on the surface of the samples to investigate the chemical composition, specifically the oxygen content of different regions of the patterned area before and after corrosion testing. By creating such patterns we are able to produce a surface with heterogeneous wetting properties, to decrease the surface energy and to decrease the contact area between the liquid and the substrate. As a result of the surface patterning a significant improvement of corrosion properties of nickel surface has been achieved. Patterned surfaces showed better corrosion resistance compared to the polished reference samples. In addition, it has been shown that for a few specific patterns the corrosion resistance can be increased by orders of magnitude.

1. Introduction

Corrosion is the degradation of a material's properties over time due to environmental effects [1]. Approaches available for controlling corrosion include the application of protective coatings, the addition of inhibitors, alteration of an alloy chemistry to make it more resistant to corrosion, and the treatment and modification of the surface of a metal to increase its resistance to corrosion [2]. An alternative solution for controlling corrosion is the reduction of the contact area between the affected surface and the corrosion agent/electrolyte. Due to the surface nature of the corrosion phenomenon a reduction in the contact surface should lead to a significant reduction in the overall corrosion rate. A possible approach to reduce the contact surface between a solid and a fluid is by achieving heterogeneous wetting at the solid–liquid interface. Heterogeneous wetting, known as the Cassie–Baxter state [3–5], is a suspended state where air/vapor is assumed to be trapped in the grooves of the surface, i.e., the liquid contacts with the composite surface of both air and solid (Fig. 1).

The challenge in forming heterogeneous interfaces from hydrophilic materials lies in designing surface topographies that will lead to stable air/vapor entrapment [6,19]. There are two main parameters that are important for creating heterogeneous solid–liquid interfaces. One is the topology of the surface and the other is the nature of surface layer [7]. The mechanism of roughness-induced heterogeneous wetting is complicated and involves effects over various length scales. The composite interface is fragile, since transition to a homogeneous interface is irreversible, and therefore the stability of a composite interface is crucial and should be addressed for the successful development of corrosion resistant surfaces.

A patterned surface with composite heterogeneous solid–liquid–air interface is notable as it has the features of liquid repellency and low surface energy. These two attributes have vast potential in various applications such as anti-sticking, self-cleaning, wettability improvement, anti-fouling, anti-corrosion, friction reduction, and heat transfer enhancement [4,8–13].

As a result, recent studies have focused on designing patterned surfaces by various experimental methods. With rapid improvements in micro/nanofabrication techniques, it is now becoming possible to control and tailor micro/nanoscale structures on solid surfaces to achieve a suitable surface topology [8]. These surfaces have been successfully fabricated on various metallic substrates, such as stainless steel, Cu, Al, Zn and Ti [14,15]. Numerous methods have been developed to fabricate patterned surfaces, such as lithographic patterning and etching (including plasma etching, laser etching, and chemical etching) [15]. Electron beam lithography can provide a resolution of 10 nm but the technique is limited by low throughput and high sample cost. Photolithography has been extensively used for fabrication of patterned surfaces due to its ease of repetition and capability of large area fabrication. Unfortunately, the minimum feature size is limited by the diffraction limit [10]. Laser ablation is one of the more promising methods of surface patterning [16,17]. Laser ablation has also the ability of generating

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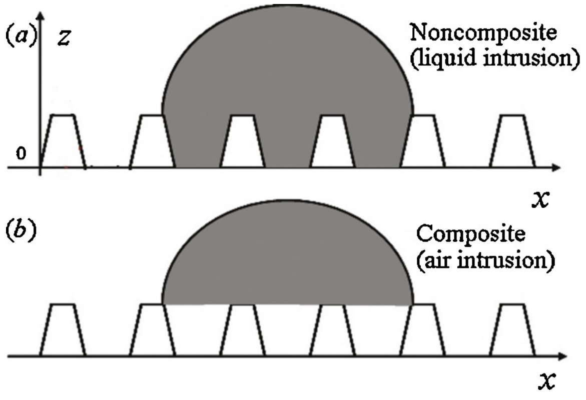


Fig. 1. A typical 2D microtexture: (a) noncomposite; (b) composite.

complicated structures without the need of a photomask, and can work in different environments [10]. By controlling the energy density, laser ablation can be applied to process metals, ceramics, and polymers [16].

In this paper, the corrosion properties of nickel with a number of surface patterns with different pattern density are studied. The main goal of this study is to detect heterogeneous wetting on the patterned surfaces and determine the effect of this type of wetting on the corrosion properties on metals.

2. Materials and methods

Pure nickel (99.7 wt%) was selected as a model metal. Samples of 1.5 × 1.5 cm size were polished to a standard finish with a roughness that did not exceed 50 nm. Laser ablation with copper bromide (CuBr) laser was used to create the specific patterns. A single pulse with duration of 30 ns was applied to create each hole. During the laser ablation, nitrogen gas (N_2) was blown to protect the surfaces from oxidation, and to clean off debris and melt splashes. The surface textures were created based on repetition of holes in the form of equilateral triangles in both the *X* and *Y* directions. Fig. 2 illustrates the arrangement of the holes, the hole diameters (*D*) and inter-hole spacings (*L*). For easy identification of the samples, the following labeling system has been adopted: *DxLy*, where *x* is the diameter of the hole in μm and *y* is the inter-hole spacing in μm.

The selection of hole diameters and their density is primarily based on the studies of the influence of the surface patterning on the adhesion contact forces [20]. Rashwan et al. [20] have shown that the dispersive component of the adhesion forces (van der Waals forces) can be significantly reduced with proper surface patterning. In the current study, the selected hole's diameter range and surface density are consistent with those showing the greatest reduction in adhesion contact forces in [20].

Corrosion tests were performed using a potentiodynamic polarization method (BioLogic-SP150) in a 0.5 M H_2SO_4 solution at room temperature (24 °C). A conventional three-electrode cell was used in which the nickel coupons were the working electrodes, a standard calomel electrode (SCE) was used as the reference electrode and platinum electrode as the cathode. The applied potential ranged from −0.5 to 0.5 V (with respect to the SCE) with a scanning rate of 1.5 mV/s. Before performing the corrosion tests all samples were stabilized at the open circuit potential (OCP) for 20 min. Corrosion current density and corrosion potential were calculated from the linear polarization resistance curves (LPR) and the Stern–Geary equation (Eq. (1))

$$R_p = \frac{\Delta E}{\Delta I_{\text{app}}} = \frac{\beta_a \beta_c}{2.3 I_{\text{corr}}(\beta_a + \beta_c)} \tag{1}$$

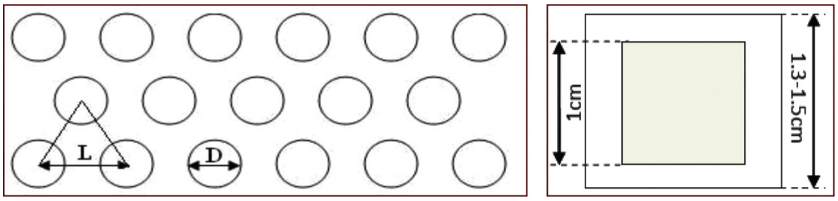
where I_{Corr} is the corrosion current, β_a and β_c are the Tafel slopes of the anodic and cathodic reactions respectively [18].

3. Results

3.1. Corrosion test

Fig. 3 illustrates the polarization curves of the reference and the patterned samples in 0.5 M H_2SO_4 solution at room temperature. I_{Corr} and E_{Corr} were calculated using Tafel extrapolation method (Eq. (1)). The values of the I_{Corr} and E_{Corr} for samples with different hole diameters (*D*) and inter-hole spacings (*L*) are summarized in Table 1.

According to the current density values, I_{Corr}, the corrosion rate (mass-loss rate) in all patterned samples (except for *D*10*L*10), is significantly lower compared to the reference polished sample (REF). The reduction of the corrosion rate in 13 out of 16 patterned samples is between 4 and 500 times. The lowest corrosion rate was measured in two samples: *D*20*L*40 and *D*30*L*60. The magnitude of the corrosion current density is 0.04–0.09 μA/cm^2, which



(D) μm	(L_1)μm	(L_2)μm	(L_3)μm
2	-	4	8
3.5	3.5	7	14
5	5	10	20
10	10	20	30
20	20	30	40
30	30	60	-

Fig. 2. Hole diameters (*D*) and inter-hole spacings (*L*) for surface patterned samples.