



Reprinted from JOURNAL OF THE ELECTROCHEMICAL SOCIETY
Vol. 136, No. 1, January 1989
Printed in U.S.A.
Copyright 1989

***In Situ* Scanning Tunneling Microscopic Study of the Corrosion of Type 304L Stainless Steel in Aqueous Chloride Media**

Fu-Ren F. Fan and Allen J. Bard*

Department of Chemistry, The University of Texas, Austin, Texas 78712

Scanning tunneling microscopy (STM) (1,2) has been finding growing application for *in situ* surface studies of various substrates immersed in solutions (3-11). Several reports have further demonstrated the possibility of performing the STM imaging under well-defined electrochemical environments, such as under potentiostatic control (12,13). We have recently employed STM for *in situ* investigation of potential-driven phase transition on a nickel electrode in 0.5M sulfuric acid (14).

We demonstrate here the use of STM in the *in situ* study of the corrosion of Type 304L stainless steel (SS) in aqueous chloride media. Such studies can provide very high resolution (ca. nm) topographic images of the cor-

roding substrate, as well as some information about the electronic conductivity of surface phases (14). Note that the topography of corroding substrates can also be probed by scanning potentiometry, although at much lower resolution (15). We also describe the effects of an organic pitting corrosion inhibitor, *e.g.*, N-lauroylsarcosine (NLS), chloride concentration, and pH on the STM images.

Experimental

The STM apparatus used and the method of tip (platinum or iridium-platinum) preparation have been described previously (5,11). The surfaces of the AISI Type 304L stainless steel samples (3 × 5 × 1 mm plates) were mechanically polished to a bright mirror finish, using 0.3 μm alumina powder for the final step, and were degreased in

*Electrochemical Society Active Member.

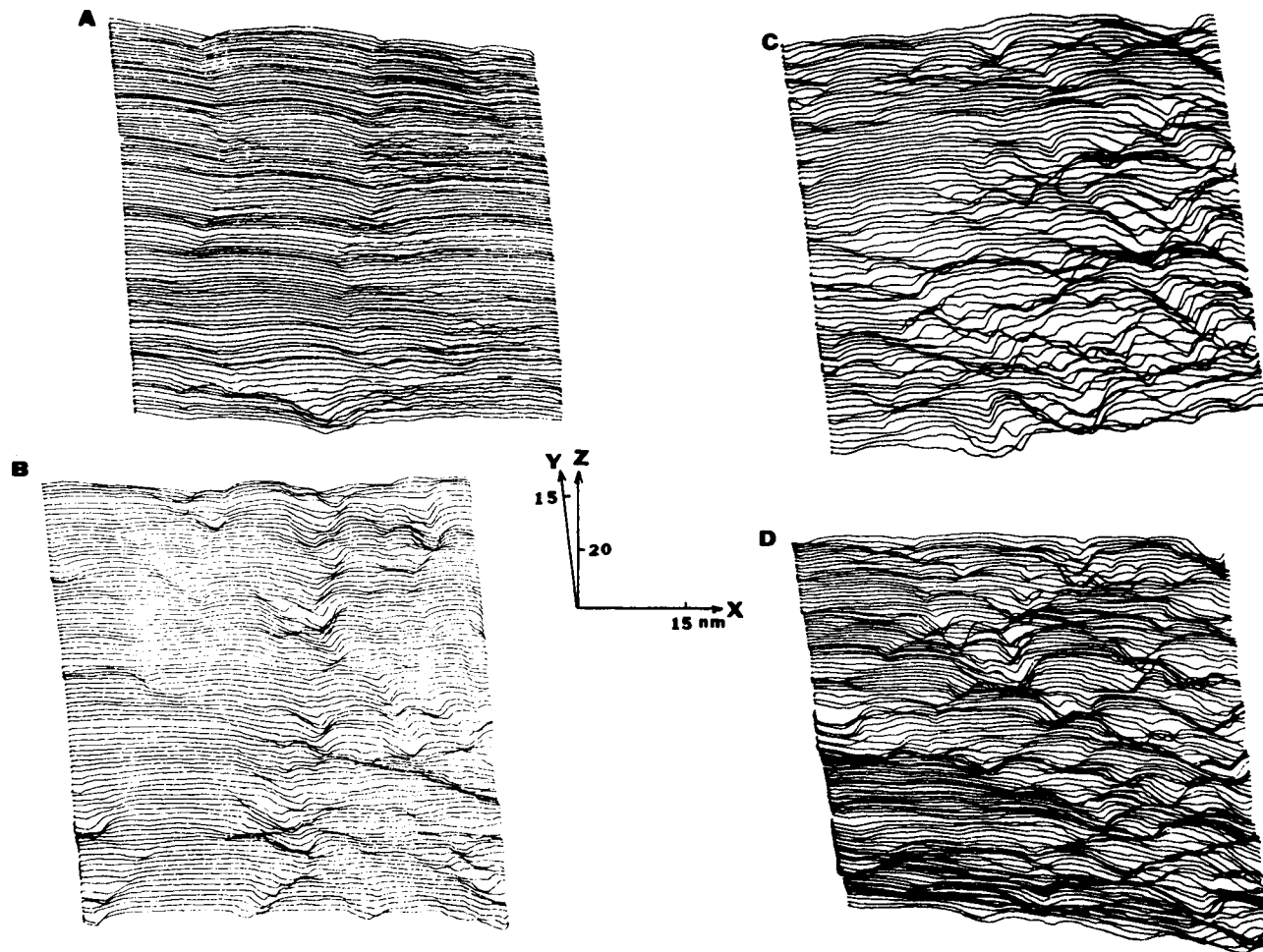


Fig. 1. STM images of a 304L stainless steel sample in a solution containing 0.2M Na_2SO_4 , 0.2M NaCl, and 0.2M sodium acetate (buffered at pH ca. 5.2). The images were taken at different immersion times: (A) 1; (B) 2; (C) 5; (D) 17h. Tunneling current, 0.5 nA; tunneling voltage (tip vs. sample), 50 mV.

methanol, then rinsed thoroughly with Millipore reagent water (resistance > 18 M Ω). All solutions were prepared from purified reagent water and reagent-grade chemicals and were not deaerated. All STM images were taken at a tunneling voltage (tip vs. sample) of 50 mV and a tunneling current of 0.5 nA. The residual electrochemical current, obtained with the tip far (μm) from the sample, was usually less than 50 pA. Typical STM scans taken were of areas $60 \times 60 \text{ nm}$ to $100 \times 100 \text{ nm}$. The lateral (X - Y) resolution was 2 \AA and the Z-resolution better than 1 \AA .

Results and Discussion

STM of SS in chloride media.—STM images of SS samples immersed in electrolyte solution at various times were obtained. In Fig. 1 a sequence of four STM images is shown, which suggests that the corrosion of 304L SS in a 0.2M aqueous NaCl solution buffered at pH 5.2 is initiated at the edges or defect sites. This sequence of images was taken without disturbing the sample and presumably at the same location. However, because of fundamental limitations of the STM technique [discussed previously (1)], especially for samples in liquids, such as small thermal drifts, we cannot be certain that the images for long-term immersion (C and D) are at precisely the same location as those for the short-term immersion (A and B). In all cases the scans shown are representative of those of the sample after a given immersion time, based on observations of a number of samples. Before this series of experiments was initiated, the STM was allowed to thermally equilibrate in 0.2M Na_2SO_4 solution for ca. 2h, to minimize thermal and mechanical drifts in short-term (ca. 1h) experiments. The STM images taken of a freshly polished sample in this solution (or in air) are rather poor (similar to that shown in Fig. 4D), suggesting that the surface is covered by a thin in-

ulating layer. After the 2h thermal equilibration in Na_2SO_4 solution, a buffered NaCl solution was introduced into the electrochemical cell, and the sequence of STM images was taken. Note that the introduction of the buffered NaCl solution significantly improved the STM images (as described below), perhaps because an electronically insulating surface layer was removed and the surface was always kept conductive by the buffered NaCl solution. As shown in Fig. 1A, an imaged area of $600 \times 600\text{\AA}$ exhibits three recognizable shallow grooves at the top of the image. The middle one proceeds to the bottom and has branches extending to the lower-right corner of the image. An ultramicroscopic (ca. 80 \AA wide) defect is clearly seen at the bottom. As the time proceeds, the surface topography has been progressively altered by corrosion processes. Figure 1B (taken 1h later and ca. 2h after the buffered NaCl solution was introduced) clearly reveals more defects (e.g., pits or steps), mainly along the existing grooves. The surface structure of the sample after long-term immersion has been severely modified. As shown on the right-hand side of Fig. 1D, a mound structure consisting of grains (100-200 \AA in diam) is being formed. This mound structure seems to be the most frequently found stable structure for a long-term corroded sample (see Fig. 2C and D), although step or ridge structures are occasionally observed (see the middle top portion of Fig. 2D). Microscopic examination of the sample surface following experiment 2D also reveals many small pits of diameter ranging from 0.1 to several μm over the entire surface (Fig. 3). These larger microscopic pits are seldom detected by STM. We have attempted to generate a single ultramicropit on stainless steel samples by applying a voltage pulse (ca. 2V) between tip and sample; however, we obtained only a fairly large pit near the tip location. A very large edge, longer than the scan-

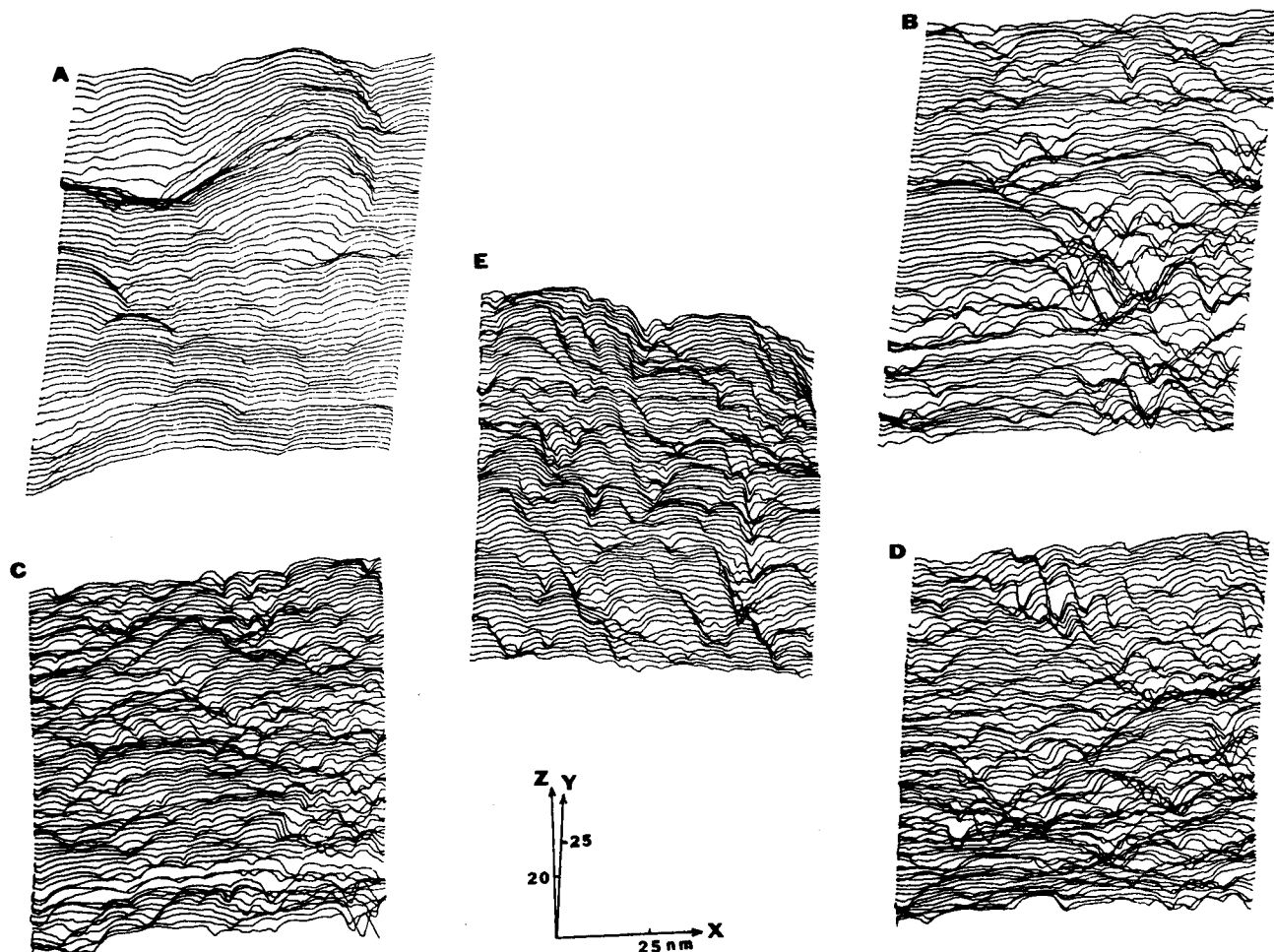


Fig. 2. STM images of 304L stainless steel samples in 0.2M NaCl solutions at different pH and different immersion times. (A) A fresh sample in 0.2M NaCl and 0.01M H_2SO_4 (pH ca. 2) after ca. 15 min; B, C, and D are the continuation of Fig. 1 taken ca. 5h, 1 day, and 2 days after immersion; E is the continuation of A but taken ca. 2h after immersion. Tunneling current 0.5 nA; voltage 50 mV.

ning range (0.1 μm), along one side of the STM image (not shown in this report) was sometimes observed underneath the tip.

Effect of pH.—The corrosion rate of 304L SS in 0.2M NaCl solution, as suggested by Fig. 2E, 1B, and 2B, apparently increases with decreasing pH. This is consistent with the pH dependence of its break-down potential reported by DeBerry *et al.* (16). The surface of a SS sample immersed in 0.2M NaCl solution at low pH (ca. 2) was severely changed even for only ca. 2h immersion (compare Fig. 2E with Fig. 2A). A similarly prepared sample immersed in a solution buffered at pH 5.5 shows much less topography change for the same duration of immersion (see Fig. 1A and B). Figures 1C and 2B clearly reveal that there are still some flat areas on the left-hand side of the images, suggesting that no appreciable corrosion occurs in pit- and edge-free areas, even after ca. 5h immersion.

Effect of corrosion inhibitor, NLS.—In Fig. 4 a sequence of four STM images is shown, which demonstrates the influence of an organic corrosion inhibitor, NLS (16), on the surface topography. We start with a SS sample which had been immersed in 0.2M NaCl solution (pH 5.2) for ca. 4h and exhibits a rough, but easily imaged (*i.e.*, conductive) surface as shown in Fig. 4A. Figure 4B shows a STM image of the same sample taken ca. 30 min after 5 mM NLS has been introduced into the electrochemical cell. The surface topography clearly looks “noisier” than that shown in Fig. 4A. The “noise” level seems to increase with time and a highly disordered image is eventually obtained (see Fig. 4C and D). We have frequently observed these kinds of STM images on chemically contaminated platinum surfaces, such as those with iodine or ester adsorption (11) or on a passivated nickel electrode (14). Wiechers *et al.* (12b) has also recently reported a disordered STM image caused

by electroadsorption of chloride on a gold surface. The experiments performed by DeBerry *et al.* have suggested that NLS is strongly adsorbed onto the SS surface with the possibility that it forms a bilayer structure above a certain critical concentration (ca. 0.5 mM for NLS) (16). To demonstrate the difference in the surface properties of the SS sample in different media, we measured the current response as a function of displacement (14). In NLS-containing solution, the current *vs.* displacement (*i-s*) response is not very reproducible and deviates substantially from ideal tunneling behavior (compare curves 1 and 2 of Fig. 4E). The current rises over a much larger distance than that in an NLS-free solution (curve 1 of Fig. 4E). This suggests that an insulating interfacial layer, of still unknown chemical identity, is formed in NLS-containing solutions. This interfacial layer could act as a physical barrier for the approach of Cl^- to the SS surface (17), or it could change the chemical activity, such as the local pH (18), or the electrochemical activity at the surface, as mimicked by the tunneling experiments. The SEM micrographs of the SS sample taken after this experiment still show no appreciable corrosion, and are similar to those shown in Fig. 3A and C.

Conclusions

The preliminary results reported here suggest that STM might be a useful complementary technique for the *in situ* study of corroding substrates. Corrosion of SS samples in buffered Cl^- media seems to be initiated at the defect sites or edges and extended corrosion most frequently leads to an observed mound structure, with some scattered steps or ridges, randomly distributed. The corrosion rate of SS 304L samples increases with decreasing pH, which is consistent with the pH dependence of their breakdown potentials (16). The introduction of the organic corrosion inhibi-

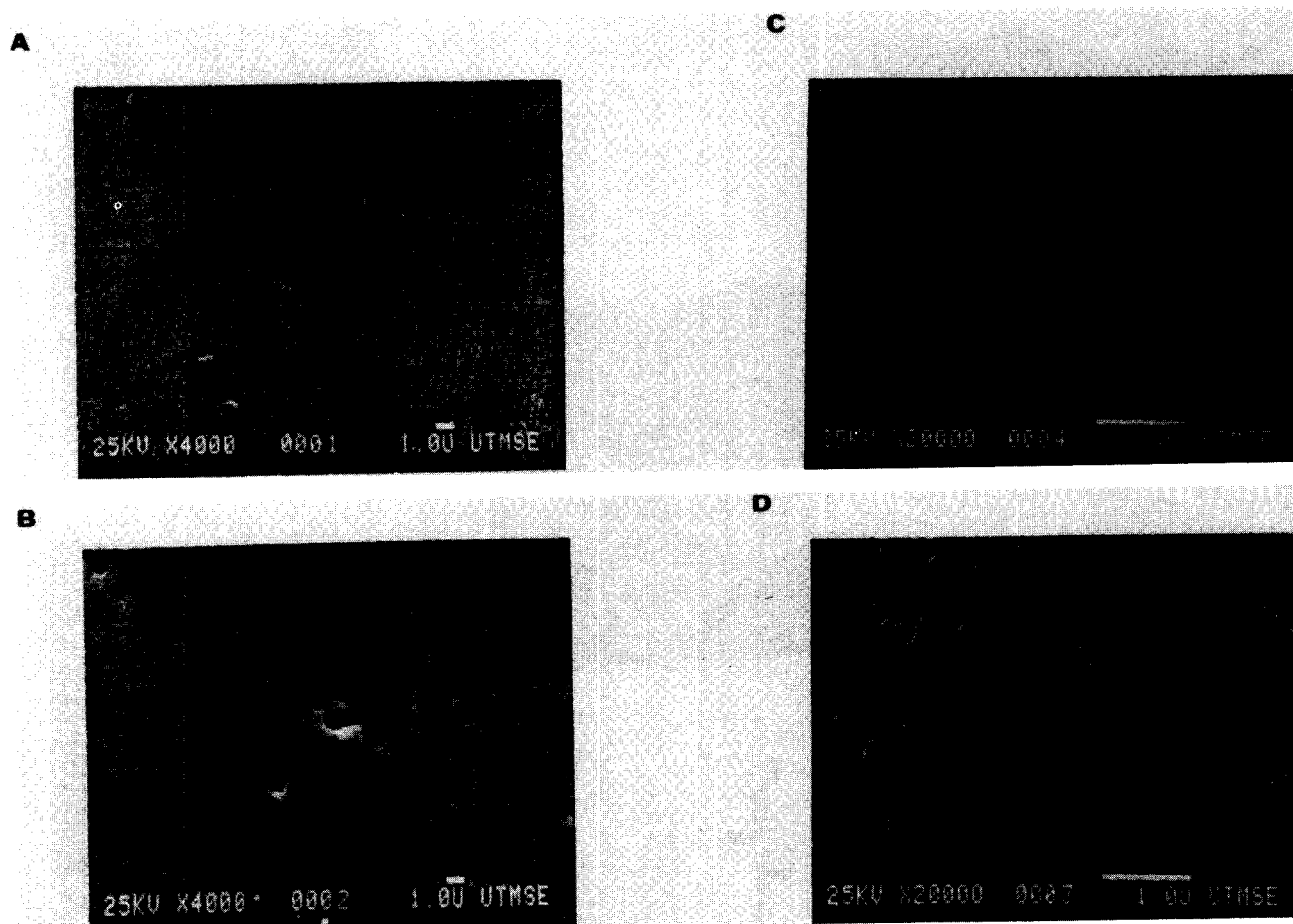


Fig. 3. Scanning electron micrographs of 304L SS samples before (A and C) and after (B and D) immersing in a solution containing 0.2M Na_2SO_4 , 0.2M NaCl, and 0.2M sodium acetate (buffered at pH ca. 5.2 with acetic acid) for 2 days (i.e., after Fig. 2D experiment).

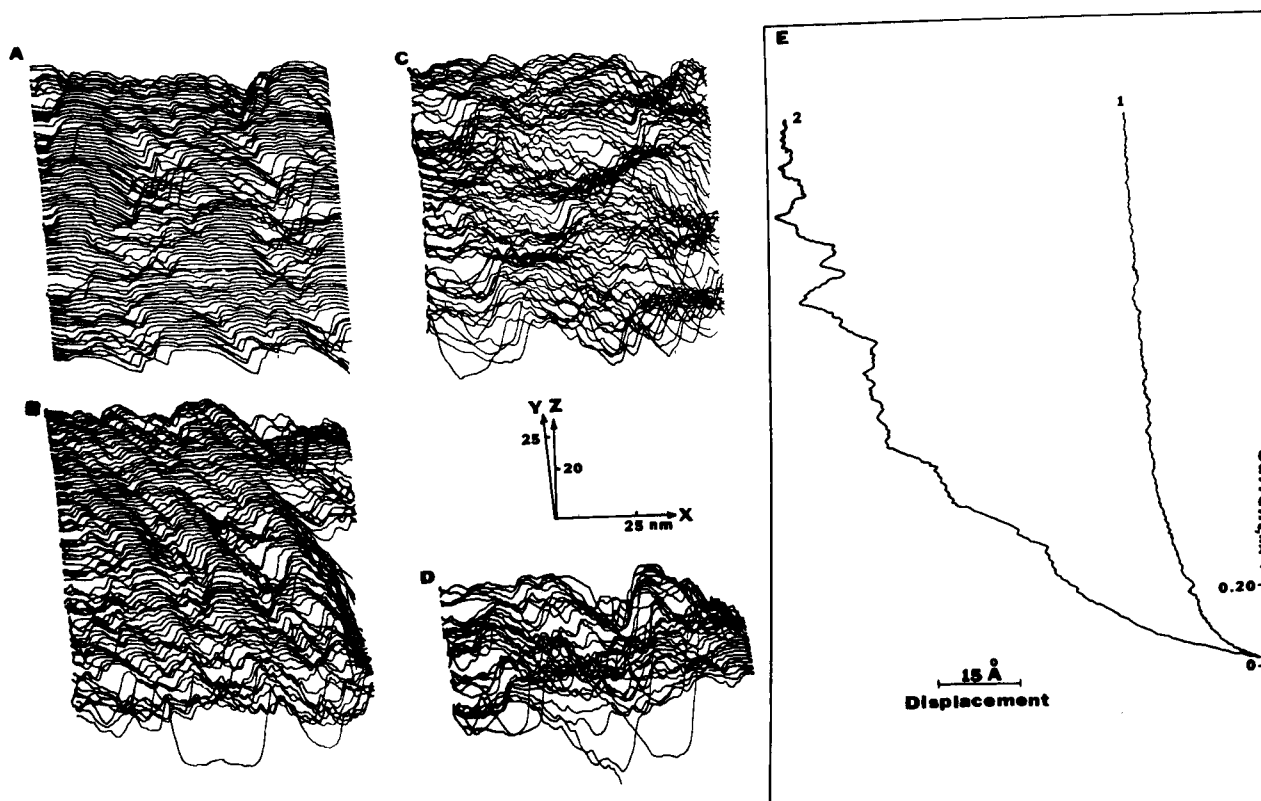


Fig. 4. The effect of NLS on STM images (A-D) and tunneling current vs. tip displacement relationship (E) in a solution containing 0.2M NaCl and 0.2M sodium acetate (buffered at pH ca. 5.2 with acetic acid). (A) No NLS, 4h immersion; (B) ca. 30 min after the introduction of 5 mM NLS; (C and D) 2 and 18h after the introduction of 5 mM NLS; (E) current response to tip displacement: curve 1, after experiment A and curve 2, after experiment D.

tor, NLS, into buffered Cl^- solutions produces a highly disordered surface structure that exhibits nonideal tunneling behavior. The tunneling current resembles that seen with the formation of insulating interfacial layers and is probably caused by strong adsorption of NLS and bilayer coverage of the SS surface. The combination of STM with other techniques, such as ellipsometry or other spectroscopic techniques, to elucidate the chemical identity of this interphase layer should be interesting and requires further development. Other applications of STM to studies of corroding substrates might include rapid estimates of corrosion rates, e.g., by measuring topographical changes in the surface ($\text{\AA}/\text{min}$). While STM at the present state of its development is useful in giving a qualitative picture of the electronic conductivity of surface films and interfacial barrier heights to electron tunneling, further developments [e.g., the measurement of $d(\log i)/ds$ (13) and di/dV , where s is the tip displacement and V , the substrate potential] are needed to characterize the surface layers better.

Acknowledgments

The support of this research by the Robert A. Welch Foundation, Office of Naval Research, and Texas Advanced Research Project is gratefully acknowledged. We appreciate the assistance and advice of Dr. David DeBerry.

Manuscript Aug. 25, 1988.

The University of Texas at Austin assisted in meeting the publication costs of this article.

REFERENCES

- G. Binnig and H. Rohrer, *Helv. Phys. Acta*, **55**, 726 (1982).
- G. Binnig and H. Rohrer, *Surf. Sci.*, **126**, 236 (1983).
- B. Drake, R. Sonnenfeld, J. Schneir, P. K. Hansma, G. Slough, and R. V. Coleman, *Rev. Sci. Instrum.*, **57**, 441 (1986).
- R. Sonnenfeld and P. K. Hansma, *Science*, **232**, 211 (1986).
- H.-Y. Liu, F.-R. F. Fan, C. W. Lin, and A. J. Bard, *J. Am. Chem. Soc.*, **108**, 3838 (1986).
- S. Morita, I. Otsuka, T. Okada, H. Yokoyama, T. Iwasaki, and N. Mikoshiba, *Jpn. J. Appl. Phys.*, **26**, L1853 (1987).
- R. Sonnenfeld and B. C. Schardt, *Appl. Phys. Lett.*, **49**, 1172 (1986).
- B. Drake, R. Sonnenfeld, J. Schneir, and P. K. Hansma, *Surf. Sci.*, **181**, 92 (1987).
- K. Itaya and S. Sugawara, *Chem. Lett.*, 1927 (1987).
- K. Itaya, K. Higaki, and S. Sugawara, *ibid.*, 421 (1988).
- F.-R. F. Fan and A. J. Bard, *Anal. Chem.*, **60**, 751 (1988).
- (a) P. Lustenberger, H. Rohrer, R. Christoph, and H. Siegenthaler, *J. Electroanal. Chem.*, **243**, 225 (1988); (b) J. Wiechers, T. Twomey, D. M. Kolb, and R. J. Behm, *ibid.*, In press.
- A. Gewirth and A. J. Bard, *J. Phys. Chem.*, **92**, 5563 (1988).
- O. Lev, F.-R. F. Fan, and A. J. Bard, *This Journal*, **135**, 783 (1988).
- See, for example, (a) H. S. Isaacs and M. W. Kendig, *Corrosion*, **36**, 269 (1980); (b) H. S. Isaacs and B. V. Yas, in "Electrochemical Corrosion Testing," ASTM STP 727, F. Mansfield and V. Bertocci, Editors, p. 133, Am. Soc. for Testing and Materials (1978).
- (a) D. W. DeBerry and A. Viehbeck, *This Journal*, **133**, 30 (1986); (b) D. W. DeBerry, in "Surfaces, Inhibition, and Passivation, Vol. 86-7, E. McCafferty and R. J. Brodd, Editors, p. 3, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1986).
- K. C. Tsai and N. Hackerman, *This Journal*, **118**, 28 (1971).
- J. R. Galvele, *ibid.*, **123**, 464 (1976).

