In-Situ Observation of Metal Surfaces in Aqueous Solutions with an Electrochemical STM* 

Nobuo NAGASHIMA**, Hiroyuki MASUDA*** 
and Saburo MATSUOKA****

In-situ observation at high magnification of materials being damaged by aqueous corrosion and corrosion fatigue is significant in the understanding of these mechanisms. In this study, in-situ observation of Au, Fe, SUS304 steel and SNCM439 steel under potential control in 1%NaCl and 0.1%HNO₃ solutions is performed by STM. The STM image can be observed for all materials both in anodic and cathodic potentials if the proper tunnel bias is applied. In cathodic potentials the STM image does not change with time, while in anodic potentials the STM image changes rapidly unless the material is in a passive condition.

Key Words: Electrochemical STM, Fractography, Bipotentiostat, 1%NaCl, 0.1%HNO₃, Polarization Curve, In-Situ Observation.

1. Introduction

In-situ observation at high magnification of the materials being damaged by aqueous corrosion and corrosion fatigue is significant in the understanding of these mechanisms. However, the surfaces of the materials can't be directly observed in aqueous solutions by an electron probe microscope analyzer (EPMA), Auger electron spectroscope (AES) or scanning electron microscope (SEM), because they work in vacuum.

The scanning tunneling microscope (STM), developed by Binnig et al.(1) in 1982, can be used not only in vacuum, but also in air and aqueous solutions.

Therefore, STM has already been applied to the field of material damage(2,3). In this study, in-situ observation of surface morphology change using STM is performed under potential control in 1%NaCl and 0.1%HNO₃ aqueous solutions for two pure materials of Au and Fe and two steels of SNCM439 and SUS304.

2. Experimental Procedures

2.1 Electrochemical STM

STM in air or vacuum, which in principle consists of a tip and specimen, is not used in an aqueous solution because the faradic current is much greater than the tunnel current between the tip and specimen. Therefore, as shown in Fig. 1, the potentials of the tip and specimen were individually controlled by a bipotentiostat, preparing the reference electrode (RE) and counter electrode (CE) as well as the tip and specimen (WE)⁴. Furthermore, the tip was covered with epoxy resin except for a very small area. As a result, STM observation was conducted under the condition that only the faradic current flowed between the specimen and counter, and that only the tunnel current flowed between the tip and specimen.
The tungsten tip was used in this study. The scanning range of the STM head was $9 \times 9 \times 3 \mu m$ in the $X$, $Y$ and $Z$ directions. The setting range of potential of the bipotentiostat was $\pm 1.999$ V, and the measuring range of the current was between 1 pA and 10 mV. The acquisition of STM data was conducted using a personal computer. The 256x256 points each STM image were taken with a 12-bit A/D converter with a scanning speed of between 2 and 10 Hz in the $X$ direction. A bird's-eye view of 256x128 points was displayed in realtime, because the programming was done by the machine language. The machine language program is much faster than the "Basic" or "C" language program.

2.2 Measurement of polarization properties

The polarization properties were automatically measured with the personal computer. The initial potential was set up at $-1.1$ V (Ag/AgCl) through the D/A converter and was scanned at 120 mV/min toward the final anodic potential. In parallel to this, the current data was taken through the A/D converter.

2.3 Materials and environments

The materials used were two pure metals of Au and Fe and two steels of SNCM439 and SUS304. Au does not corrode in aqueous solution. The Fe was a 60-μm-thick sheet. The grain size on the longitudinal cross section was between 3 and 5 μm as shown in Fig. 2. The size was small enough to enable observation of the corrosion behavior near the boundary by STM head with a scanning range of $9 \times 9 \mu m$ in the $X$ and $Y$ directions. SNCM439 and SUS304 steels were the representatives of low alloy steels and stainless steels in practical use. The surfaces of these materials were finished by polishing with 50-nm-diameter alumina particles.

Test environments were 1% NaCl and 0.1% HNO₃ aqueous solutions. The 1% NaCl solution is an environment which simulates sea water. In the 0.1% HNO₃ solution the grain boundary is selectively attacked.

3. Results and Discussion

3.1 Polarization properties

Before STM observation in the aqueous solutions, the polarization properties of the test materials and the tungsten tip were studied.

Figure 3 shows the polarization properties of all the materials in 1% NaCl solution. The potential was measured on the bias of the reference electrode of Ag/AgCl. The free corrosion potentials of Au and SUS304 steel were $-0.1$ and $-0.4$ V, respectively. The SUS304 steel exhibited a plateau current density region corresponding to the passive state. Free corrosion potentials of Fe and SNCM439 steel were between $-0.5$ and $-0.4$ V. Above the free corrosion potential, anodic dissolution occurred. In the cathodic potential region, a plateau current density region corresponding to the oxygen diffusion limited current density was observed in all test materials.

Figure 4 shows the polarization properties of all the materials in 0.1% HNO₃ solution. For SUS304 steel, the free corrosion potential was higher in 0.1% HNO₃ than in 1% NaCl solution and a passive state was observed in the anodic region. In Fe and SNCM439 steel, the current density was much greater in 0.1% HNO₃ solution than in 1% NaCl solution and
the plateau current density corresponding to the oxygen diffusion limited current density was observed in the cathodic region.

Figures 5 and 6 show the polarization properties of the tungsten tip in 1% NaCl and 0.1% HNO₃ solutions, respectively. The free corrosion potential was near −0.3 V in the 1% NaCl solution. It was necessary that the faradic current flowing in the tip should be one order less than the tunnel current to obtain a good STM image. Accordingly, the tip potential should be set between −0.4 and −0.1 V near the free corrosion potential of the tip. Similar results were seen in the 0.1% HNO₃ solution.

3.2 STM observation in aqueous solutions

3.2.1 STM images in 1% NaCl solution

Figure 7(a) and (b) show STM images of Au in air and 1% NaCl solution, respectively. In air, the good STM images have been obtained under the condition of the tunnel current of \( I_t = 1 \) nA and the tunnel bias of \( V = 10 \text{ mV} \). In Fig. 7(a), a good image was obtained under \( I_t = 1 \) nA and \( V = 8 \text{ mV} \), where the corrugation corresponding to the marks polished by the alumina particles of 50-nm in diameter was observed. In the 1% NaCl solution, a good image was also obtained under the similar conditions of \( I_t = 1 \) nA and \( V = 4 \text{ mV} \) (Fig. 7(b)). The tunnel bias \( V \) was given by \( V = E_w - E_t \), because the specimen potential \( E_w \) and the tip potential \( E_t \) were individually controlled by the bipotentiostat in the solution.

Figure 8 shows STM images of SUS304 steel at the passivation region in the 1% NaCl solution under the conditions of \( I_t = 1.93 \) nA, \( E_s = 80 \text{ mV} \), \( E_w = 0 \text{ mV} \) and \( V = E_w - E_t = -80 \text{ mV} \). Figure 8(a) shows the image at the beginning of STM observation, and Fig. 8(b) shows the image after 6 minutes. These images are almost the same because the observation was conducted at the passive region where the low values

Series I, Vol. 35, No. 4, 1992

JSME International Journal
of current density, $I_w$, such as 0.16 and 0.18 nA were measured. The slantwise corrugation was considered to be introduced by the alumina polishing, similar to the case of Au in Fig. 7(a). However, the height of corrugation was much smaller for SUS304 steel than for Au, because the scales in the Z direction were 132 and 44 nm for Au and SUS304 steel, respectively. This is because SUS304 steel is harder than Au.

Figure 9 shows STM images on the longitudinal cross section of Fe at the anodic region in 1% NaCl solution. The observation conditions were $I_i=1.85$ nA, $E_i=-250$ mV, $E_w=-500$ mV and $V=-250$ mV. Figures 9(a) and (b) are the images at the beginning of observation and after 2 minutes, respectively.

---

Fig. 8 STM images of SUS304 steel under cathodic potential in 1% NaCl solution. $I_i=1.93$ nA, $E_i=-80$ mV, $E_w=0$ mV and $V=-80$ mV

Fig. 9 STM images of the longitudinal cross section of Fe under anodic potential in 1% NaCl solution. (Left: bird's-eye view, right: 8-bit gray image.) $I_i=1.85$ nA, $E_i=-250$ mV, $E_w=-500$ mV and $V=-250$ mV
The current density of these images due to the anodic dissolution was 4.38 A/m². The scale of 383 nm in the Z direction was very large, as compared with those in Figs. 7 and 8 where STM images on the aluminized surface were shown for Au and SUS304 steel. This means that the anodically dissolved surface was very rough in the microscale. Furthermore, Fig. 9 indicates that the surface morphology was changed by the anodic dissolution within two minutes.

Figure 10 shows STM images of the anodically dissolved surface for SNCM439 steel, obtained under the conditions of $I_i=2.3$ nA, $E_i=-330$ mV, $E_w=-470$ mV, and $V=-140$ mV. The current density, $I_w$, was 1.71 A/m² at the beginning of observation in Fig. 10(a) and 2.75 A/m² after 8 minutes in Fig. 10(b). The two STM images in Fig. 10 indicate an anodic dissolution caused the surface morphological change, similar to the case of Fe in Fig. 9.

Figure 11 shows the STM images of the anodically dissolved surface for SNCM439 steel at very high magnification. However, the observation was done under the cathodic conditions of $E_w=-552$ mV, $E_i=-115$ mV and $I_i=1$ nA after anodic dissolution. The scanning range in X and Y directions was 70 nm, which corresponded to about 250 atoms of iron. This proves that STM can be used at the near-atomic region in an aqueous solution.

3.2.2 STM images in 0.1% HNO₃ solution

Figure 12 shows the STM image of Au in 0.1% HNO₃ solution. The observation was conducted under the cathodic conditions of $E_w=-217$ mV, $E_i=-200$ mV.
and $I_i = 0.64$ nA. Corrugation induced by the alumina polishing was also observed in this solution.

Figure 13 shows the STM images made under the cathodic potential for SUS304 steel. The observation conditions were $E_n = -330$ mV, $E_i = -300$ mV and $I_i = 1.85$ nA. The image in Fig. 13(b) was obtained 6 minutes later than that in Fig. 13(a). These two images show the surface morphological change, although they were observed in the cathodic potential. This may be because the surface of the specimen is covered with a hydraulic oxide film.

Figure 14 shows the STM images seen under the

![STM images of SUS304 steel under the cathodic potential in 0.1%HNO₃ solution.](image1)

![STM images of the longitudinal cross section of Fe under anodic potential in 0.1%HNO₃ solution.](image2)
anodic potential on the longitudinal cross section of Fe. The conditions were $E_w = -141$ mV, $E_r = -210$ mV and $I_r = 1$ nA. The current density was 4.16 and 4.71 A/m$^2$ in Figs. 14(a) and (b), respectively. A profound morphological change was observed within 14 minutes. The grain size on the longitudinal cross section of this metal was between 3 and 5 μm, as shown in Fig. 2. Considering that the scanning range in the X direction is 8 400 nm in Fig. 14, there is at least one grain boundary in the STM images. The big channel appearing in the center of Fig. 14 is apparently the site where the grain boundary is selectively attacked in the 0.1 %HNO$_3$ solution.

Figure 15 shows the STM images for SNCM439 steel under the anodic conditions of $E_w = -420$ mV, $E_r = -390$ mV and $I_r = 1.85$ nA. The current density was 2.26 and 3.20 A/m$^2$ in Figs. 15(a) and (b). Similarly to the case of Fe in Fig. 14, there was a great morphological change between the two STM images within 26 minutes. In particular, it appears that the dissolution strongly occurs at the grain boundary. However, the STM images in Fig. 15 seldom involves the grain boundary because the grain size is about 50 μm.

4. Conclusions

In this study, the surfaces of four metals were observed in 1 %NaCl and 0.1 %HNO$_3$ aqueous solutions using STM. Our main conclusions obtained are summarized as follows.

(1) STM observations were conducted in aqueous solutions, using a bipotentiostat controlling individually the potentials of tip and specimen. The STM images were obtained at regions ranging widely from cathodic potential to anodic potential.

(2) In particular, the surface morphological change with time was observed under anodic potentials for Fe and SNCM439 steel by STM.

These proved that STM is very useful for in-site observation in aqueous solutions at high magnifications.

References


