In-situ observation of corrosion process by scanning atomic force microscope
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Abstract

This investigation demonstrates that atomic force microscopy (AFM) is capable of performing in-situ nanoscopic visualization of initiation and growth process of localized corrosion in aqueous solutions or in air. The nanoscopic initiation and growth mechanisms of localized corrosion of intergranular corrosion and stress corrosion crack of an austenitic stainless steel and 7XXX series aluminum alloys are discussed based upon nanoscopic in-situ visualization by using AFM.

1 Introduction

Most damage issues in machines and structures are caused by environmentally induced material degradation in an operating environment, including corrosion fatigue and stress corrosion cracking. In order to clarify the fracture and damage mechanisms of these environmentally induced material degradation, serial high-magnification observation of damage initiation and growth processes are necessary.

Scanning tunneling Microscopy (STM), that was first developed in 1982 (e.g. Binning [1]), is revolutionizing the study of surface physics and electrochemical researches (e.g. Masuda [2, 3]). It is capable of imaging nanoscopic topography of surface not only in vacuum but also in air or in aqueous solutions. However, a disadvantage for applying an STM for corrosion studies is that it is not capable of imaging non-conducting surface such as corrosion products. Compared with this, atomic force microscopy (AFM), that was developed in 1986 (Binning [4]), is capable of imaging topography of nonconducting surfaces (Meyer [5]).

This investigation demonstrates that an AFM is capable of performing in-situ nanoscopic visualization of initiation and growth process of intergranular
corrosion as well as stress corrosion cracking of an austenitic stainless steel and aluminum alloys. We also discuss the concerned issues in in-situ visualization in solutions, as well as nanoscopic corrosion damage mechanisms.

2 AFM Probe Microscope and Material Tested

The principles of operation of an AFM are very simple: an extremely, usually atomically, sharp tip made of Si or Si₃N₄ is micromachined at the end of a flexible cantilever. It is then positioned in the close proximity of the sample surface, thereby the cantilever being bend by the atomic force between the tip and sample surface. By using the light lever, an image of topography is then performed by keeping the cantilever deflection constant.

In this investigation, the AFM unit operating in air and/or solutions was connected to the probe station manufactured by Seiko Instrument Industries (Japan), and thereby the in-situ visualization was performed in aqueous solutions. The unit was mounted on an isolator, and the probe station controlled the operation of the unit and the necessary image processing of the acquired images.

The materials tested in this investigation were an austenitic stainless steel type 304 and 7XXX series aluminum alloys, 7N01 and 7075. The stainless steels and 7N01 aluminum alloy were sensitization heat treated, and the 7075 alloy was treated to a peak aging of T6. The samples were ground to #2000 emery paper, and then were polished by 1 μm diamond paste followed by 0.04 μm silica powder. In order to perform in-situ visualization of growth process of stress corrosion cracks, the three-point bending jig was installed in the AFM.

3 Experimental Results and Discussion

3.1 In-situ visualization of growth process of corrosion product in solution

Figure 1 shows bird’s-eye views of the results of in-situ visualization of growth process of corrosion products that were formed on a surface of the 7075 aluminum alloy immersed in a 3.5% NaCl solution. The corrosion products were observed to be piling up near the corrosion product “hills” shown by an arrow in Fig.1(a), which had existed from the beginning of AFM imaging (immersion

![a)](image) In-situ visualization at an initiating stage (Duration is 16min).

![b)](image) In-situ visualization (Duration is 32min).

Fig.1 Three-dimensional visualization of corrosion products that was forming on the sample surface of 7075.
duration: 16min.).

For aluminum alloys, passive films form on the surface, giving relatively superior resistance to corrosion. However, once the films are broken by plastic deformation or the activity of chloride ions, dissolution occurred at that point. In Fig.1, the piling up of corrosion reaction products of aluminum hydroxide of dissolved aluminum and hydroxide ions were visualized by the AFM in an order of nanometer. The contact force between the tip and sample surface is so small that extremely soft sample surface such as corrosion products was imaged in a three-dimensional manner.

### 3.2 In-situ observation of pitting corrosion

Figure 2 shows AFM imaging of pitting corrosion of a sensitized stainless steel (sensitization heat treatment: 650°C for two hours) in a 3.5% NaCl + HCl solution (pH: 1.5): the brightness of each position express the height, and the brightest point corresponds to the highest, and the darkest one the lowest. A gray scale of each image shows the height difference of the highest and the lowest points. At immersion duration of 20 min, extremely small dents could be observed, which are shown by arrows (Fig.2(a)). Figure 2(c) shows the cross section of these extremly small dents, showing that they were in an order of 50 nm in diameter and 5nm in depth. After 11min immersion, these pits respectively grew into so-called corrosion pits (see Fig.2(b)). These indicated that extremely small dents observed at immersion duration of 20 min were the very early stage of the initiation of pitting corrosion.

### 3.3 In-situ observation of intergranular corrosion

Figure 3 shows serial AFM imaging (c) Cross section of nanoscopic corrosion pit shown in Fig. 2(a). All dimensiona are in nm

(a) Immersion duration: 20min  
(b) Immersion duration: 31min

Fig.2 In-situ visualization of pitting corrosion of SUS304 in a 3.5% NaCl solution.
of intergranular corrosion of a sensitized austenitic stainless steel in a 3.5% NaCl + HCl solution (pH: 1.5). These demonstrate that three aligned corrosion pits along the grain boundary of 80 nm in depth and 100 nm in diameter were coalescing with each other, through the slender groove shown by an arrow. These pits were growing along the grain boundary, not in the depth (z) direction. This indicates the coalescing of aligned corrosion pits along the grain boundary led intergranular corrosion.

3.4 In-situ observation of SC crack
In-situ visualization of stress corrosion (SC) crack of the sensitized 7N01 aluminum alloy was performed. For this purpose, the sample was mounted on the three-point bending jig, and in-situ observation of SC crack growth was performed. For this Al alloy, it was rather difficult to perform in-situ imaging of SC cracks in a 3.5% NaCl solution, because the crack grew relatively fast and was covered with thick corrosion products. However, it was noteworthy that the SC crack, which was introduced in a 3.5% NaCl solution, grew also in air. This showed that in-situ, clear AFM visualization of crack shape was possible in air under better condition of no piling up of corrosion products over a crack. An SC precrack was then introduced in a 3.5% NaCl solution, and in-situ AFM visualization was performed in air.

Fig.3 In-situ visualization of intergranular corrosion of SUS304 in a 3.5% NaCl + HCl solution (pH = 1.5).
(a) Visualization of stress corrosion precrack tip introduced in a 3.5% NaCl solution.
(b) Visualization of stress corrosion crack growth.
(c) Visualization of stress corrosion crack growth
Fig. 4 In-situ visualization of stress corrosion crack of 7N01 by AFM in air.

3.4.1 SC crack growth along grain boundary perpendicular to tensile stress
Figure 4 shows AFM images of the growing SC intergranular crack (crack length: about 5 mm), where the grain boundary was almost perpendicular to the tensile stress. The topographies of deformed crystal surfaces ahead and behind the crack were symmetric against the grain boundary, indicating that the crack grew in pure Mode I loading even from microscopic standpoints. The crack grew successively, turned to the right at the triple grain boundary, and again grew along the grain boundary.

Figure 5 shows the loci of the crack tip observed by the AFM in the Cartesian coordinate. The loci agreed with the crack shape after the test. In Fig. 5, the
(a) Visualization of stress corrosion precrack tip introduced in a 3.5% NaCl solution.

(b) Topography of Fig.6(a).

(c) Visualization of stress corrosion crack growth.

(d) Topography of Fig.6(c).

Fig.6 In-situ visualization of stress corrosion crack of 7N01 by AFM in air. Time interval of the imaging was almost constant, indicating that the crack growth rate decreased with approaching the triple grain boundary. The average growth rate was about 3.3 nm/s, and the crack grew continuously in the order of microns.

3.4.2 SC crack growth along the grain boundary inclined to tensile stress

Figure 6 shows the AFM images of the growing SC crack (crack length: about 7 mm) along the grain boundary that inclined to the tensile stress. Before the Mode I crack opening of the growing crack from the upper right hand corner approached the triple grain boundary, the crack opening was observed at the triple grain boundary (see Fig.6(a)). This indicates that the initially existing crack (crack ①) grew in the mixed mode of Modes I, II and III as far as the triple grain boundary. In fact, Fig.6 shows that not only Mode I displacement but also Modes II and III displacement was observed for the crack. The crack ② was also inter-
granular crack.

Figure 7 shows the loci of the observed crack tip by the AFM. The direction of tensile stress parallels the x-axis (abscissa). Figure 8 shows the relationship between time and crack length, which was measured along the individual growing direction. From the figure the grain “C” was detaching from the grains “A” and “B” with crack extension, and the average growth rate of the crack ① was about 2.4 nm/s, whereas the rate was 3.9 nm/s for the crack ②. These show that the growth rate of the crack ② was higher than that of the crack ①, because the crack ② grew along the grain boundary almost perpendicular to the tensile stress, and therefore the crack grew in pure Mode I loading, whereas the crack ① grew in the mixed mode of Modes I, II and III. In fact, no Mode II and III displacement was observed for the crack ②.

4 Conclusion

This investigation demonstrates that AFM is capable of performing in-situ, nano-sscopic and topographic visualization of initiation and growth processes of localized corrosion. This investigation yielded the following conclusions.

1. AFM is capable of performing in-situ nanoscopic visualization of corrosion damage including corrosion product forming, intergranular corrosion and stress corrosion cracking. The contact force between the tip and sample surface is so small that very soft sample surface such as corrosion
products can be imaged with an AFM.

AFM has very high resolution, and the very early stage of pitting corrosion with 50 nm in diameter and 5nm in depth can be visualized.

3. Intergranular corrosion was formed by coalescence of aligned pitting corrosion which initiates along grain boundaries.

4. The crack growth rate of intergranular SC crack of an aluminum alloy decreased with approaching the triple grain boundary. The growth rate under Mode I loading was higher than that under a mixed loading mode.

References