In-situ Electrochemical Atomic Force Microscopy with Atomic Resolution of Ni(110) in Neutral and Alkaline Aqueous Solution

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Bare and anodically oxidized Ni(110) surfaces in 0.05 kmol m⁻³ Na₂SO₄ (pH = 6.5) and 0.01 kmol m⁻³ NaOH (pH = 12) aqueous solution have been investigated by in-situ electrochemical atomic force microscopy (EC-AFM) with atomic resolution. We have succeeded in in-situ observation of unreconstructed Ni(110)-(1 × 1) structures in both 0.05 kmol m⁻³ Na₂SO₄ and 0.01 kmol m⁻³ NaOH solution. Under passive region, we have observed well-ordered structures differing from those of the bare surfaces and we found that surface structure of nickel is of considerable practical importance for corrosion control. Scanning tunneling microscope (STM) and atomic force microscope (AFM) are one of the most powerful tools to investigate the structure of metal surface not only in vacuum,¹²) but also in aqueous solution. Various investigations have been carried on the surface structures of Ni single crystals in aqueous solution by ex situ¹³⁻⁴) and in-situ⁵⁻⁷) STM, and there has been a gradual accumulation of experimental data for the structure of both Ni substrate and the oxide layer, especially in sulfuric acid solution (pH < 3.0). For example, Suzuki et al.⁷) has succeeded in in-situ observation of bare and oxidized surfaces of Ni(100) and Ni(111) with atomic resolution by means of electrochemical STM (EC-STM). Ex situ⁵⁻⁷) and in-situ¹) STM investigations revealed the epitaxial relationship between the Ni substrate and the oxide layer, as well as those structures. This epitaxial relationship was confirmed by in-situ X-ray scattering study of Magnussen et al.⁸)

On the other hand, the atomic resolution images of oxide layers formed on Ni(100) have been also observed in alkaline aqueous solution (pH = 14) by in-situ EC-STM,⁵) however, the observation of bare surface of nickel single crystals with atomic resolution has not been succeeded yet in neutral or alkaline solution. It is probably because of difficulty of complete removal of electrochemically-formed oxides, which is called “steady state oxides”, in neutral and alkaline solution⁹) and/or of imaging instabilities of EC-STM at reduction region of oxides.⁵) EC-AFM is also one of the tools which can observe the surface in-situ in aqueous solution. In our previous work,¹⁰) we have succeeded in the removal of oxide layer formed in air on Fe(110), which is also one of the base metals, and in the in-situ EC-AFM observation of bare and anodically oxidized surface of Fe(110) with atomic resolution in sodium sulfate neutral solution.

In this paper, in-situ EC-AFM observation of bare and anodically oxidized Ni(110) surfaces with atomic resolution in 0.05 kmol m⁻³ Na₂SO₄ (pH = 6.5) and 0.01 kmol m⁻³ NaOH (pH = 12) aqueous solution under potential control is presented.

2. Experimental

Ni(110) samples were prepared from a Ni single crystal rod (99.99%, Monocrystal). Orientation of the samples was verified within ±1° by Laue backscattering method. After mechanically polished, the samples were etched electrolytically at 1 A cm⁻² for 10 min at −30°C in a solution composed of 70 mL of phosphoric acid, 10 mL of sulfuric acid and 30 mL of MilliQ-water (>18 MΩ). In-situ EC-AFM images are taken in a contact mode by Nanoscope E (Digital Instruments, Inc.) equipped with a potentiostat. The details of this EC-AFM have been described elsewhere.¹⁰) The electrolytes used were 0.05 kmol m⁻³ Na₂SO₄ (pH = 6.5) and 0.01 kmol m⁻³ NaOH (pH = 12), which were prepared from NaOH (Merck, Suprapur), Na₂SO₄ (Wako, Superior) and MilliQ-water. The electrolytes were deaerated with N₂ gas for more than 2 hours before the experiments. The reference electrode used here was the Hg/Hg₂SO₄ electrode (0.65 V vs. normal hydrogen electrode; NHE), to which all potential was referred in this paper.

3. Results and Discussion

3.1 Ni(110) in 0.05 kmol m⁻³ Na₂SO₄ aqueous solution (pH = 6.5)

Cyclic voltammograms (CVs) for Ni(110) in 0.05 kmol m⁻³ Na₂SO₄ aqueous solution with sweep rate of 50 mV s⁻¹ are shown in Figs. 1. Figures 1(a)–(d) are those...
with the anodic reversal potential of $-1.0$, $-0.8$, $-0.6$ and $-0.4$ V, respectively. These CVs are practically consistent with the potentiostatic I-V curves for Ni electrodes in the anodic polarization reported in the previous work.\(^9\) In the anodic polarization in Figs. 1(a)–(c), there are two anodic peaks at $-1.15$ V ($A_1$) and at $-0.95$ V ($A_2$), followed by a current plateau. In the cathodic polarization in Figs. 1(a)–(c), there are two cathodic peaks at $-1.35$ V ($C_2$) and $-1.45$ V ($C_1$), followed by the hydrogen evolution peak. From these CVs, it can be stated that the peak $C_1$ corresponds to the reduction of the peak $A_1$, and the peak $C_2$ corresponds to the reduction of both the peak $A_2$ and the current plateau. When the anodic reversal potential increases from $-0.6$ to $-0.4$ V, the shape of the CV (Fig. 1(d)) changes as follows; the heights of the peak $A_2$ and the current plateau decrease, the peak $A_2$ shifts to negative potential, the peak for hydrogen evolution shifts to positive potential, and a new anodic peak, which may be identical with the peak $A_1$, appears at $-1.25$ V ($A_3$). Figure 2 shows that the height of the peak $A_2$ decreases abruptly when the anodic reversal potential is more positive than $-0.5$ V. Once the stable oxide, which is called “steady-state oxide” by MacDougall and Cohen,\(^9\) is formed, the shapes of CVs become different from those shown in Figs. 1(a)–(c). These results indicate that the stable oxide is formed on the bare surface of nickel at the potential $\geq -0.5$ V. These results also indicate that the total charge for the peaks $C_1$ and $C_2$ in Figs. 1(c) approximately corresponds to the reduction of an oxide layer. Therefore, we have carried out the charge consumption measurements for the peaks $C_1$ and $C_2$ more than 5 times and a charge of $1.3 \pm 0.3 \text{ mC cm}^{-2}$ was consumed for these peaks. Assuming that all of this charge was consumed for the reduction of an oxide layer consisting of NiO(110), this charge density approximately corresponds to the reduction of $5.0 \pm 1.2$ monolayers of Ni(110) ($\approx 0.7 \pm 0.2$ nm), because a charge of $0.26 \text{ mC cm}^{-2}$ was required for the oxidation of a monolayer of NiO(110).

We have also investigated the Ni(110) samples by in-situ EC-AFM. Immediately after the electrochemical etching as described in the experimental chapter, the samples were transferred in air to the electrochemical cell for EC-AFM. Immediately after the electrolyte is introduced into the cell, the electrode potential was kept at $-1.5$ V for 10 min while the surface was scanned by the AFM cantilever continuously. This procedure results in the observation of an well-ordered surface. Figure 3(a) shows an unfiltered EC-AFM image ($7 \text{ nm} \times 7 \text{ nm}$) of Ni(110) surface, accompanied with a magnified and filtered image ($1 \text{ nm} \times 1 \text{ nm}$), obtained at $-1.5$ V in $0.05 \text{ kmol m}^{-3}$ Na$_2$SO$_4$ aqueous solution after the procedure described above. The protrusions in the filtered image have the nearest and next nearest distances of $0.25 \pm 0.02$ nm and $0.35 \pm 0.02$ nm. Assuming that the protrusions correspond to each Ni atoms, this structure is consistent with Ni(110)-(1 $\times$ 1) structure.

After the EC-AFM image of Fig. 3(a) was acquired, stepping the potential from $-1.5$ to $-0.8$ V, which was more positive than the oxidation peak ($A_2$) in Fig. 1, didn’t yield the appearance of any well-ordered structure. When we stepped the potential from $-0.8$ to $-0.5$ V, where the formation of the stable oxide is predicted in CVs in Fig. 1, we observed a new well-ordered structure. Figure 3(b) shows an unfiltered EC-AFM image ($7 \text{ nm} \times 7 \text{ nm}$) of Ni(110) surface, accompanied with a magnified and filtered image ($1 \text{ nm} \times 1 \text{ nm}$), at $-0.5$ V in $0.05 \text{ kmol m}^{-3}$ Na$_2$SO$_4$ aqueous solution. In the filtered image, we can see two perpendicular arrows of periodical protrusions with $0.30 \pm 0.02$ nm and $0.42 \pm 0.02$ nm. This structure corresponding to O atoms (or Ni atoms) on NiO(110). Figure 4 shows a schematic illustration of orientation relationship between Figs. 3(a) and 3(b). We found that the atomic rows along the [001] and [110] directions of NiO(110) oxide layer were parallel with those along the [001] and [110] directions of NiO(110) substrate, respectively.

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**Fig. 1** Cyclic voltammograms for Ni(110) electrode in 0.05 kmol m$^{-3}$ Na$_2$SO$_4$ aqueous solution (a) from $-1.6$ to $-1.0$ V, (b) from $-1.6$ to $-0.8$ V, (c) from $-1.6$ to $-0.6$ V, or (d) from $-1.6$ to $-0.4$ V vs. Hg/Hg$_2$SO$_4$ with sweep rate of 50 mV s$^{-1}$.

**Fig. 2** Height of the anodic peaks ($A_2$) in the CVs for Ni(110) electrode in 0.05 kmol m$^{-3}$ Na$_2$SO$_4$ aqueous solution as a function of the anodic reversal potential.
3.2 Ni(110) in 0.01 kmol m\(^{-3}\) NaOH aqueous solution

Cyclic voltammograms for Ni(110) in 0.01 kmol m\(^{-3}\) NaOH aqueous solution (pH = 12) are shown in Fig. 5. Figures 5(a)–(b) are those with the anodic reversal potential of 0.6 and 0.4 V, respectively. These CVs practically agree with those reported in the previous works.\(^{5,11}\) In Fig. 5(a), there are two anodic peaks at 1.15 V (A\(_1\)) and at -0.95 V (A\(_2\)), and two cathodic peaks at -1.35 V (C\(_1\)) and -1.45 V (C\(_2\)). When the anodic reversal potential increases from 0.6 to -0.4 V, the shape of CV changes as shown in Fig. 5(b). This result may indicate that the stable oxide is also formed in alkaline solution at the potential \(\geq -0.5\) V.\(^{11}\) We have also carried out the charge consumption measurements for the peaks C\(_1\) and C\(_2\) more than 5 times. The consumed charge is almost the same as that in neutral solution, that is, a charge of \(1.3 \pm 0.3\) mC cm\(^{-2}\) was consumed for these peaks. Assuming that all of this charge was consumed for the reduction of an oxide layer consisting of NiO(110), this charge density approximately corresponds to the reduction of 5.0 ± 1.2 monolayers of Ni(110) (\(\approx 0.7 \pm 0.2\) nm), because a charge of 0.26 mC cm\(^{-2}\) was required for the oxidation of a monolayer of NiO(110).

3.2 Ni(110) in 0.01 kmol m\(^{-3}\) NaOH aqueous solution (pH = 12)

CVs for Ni(110) in 0.01 kmol m\(^{-3}\) NaOH aqueous solution with sweep rate of 50 mV s\(^{-1}\) are shown in Fig. 5. Figures 5(a)–(b) are those with the anodic reversal potential of -0.6 and -0.4 V, respectively. These CVs practically agree with those reported in the previous works.\(^{5,11}\) In Fig. 5(a), there are two anodic peaks at -1.15 V (A\(_1\)) and at -0.95 V (A\(_2\)), and two cathodic peaks at -1.35 V (C\(_1\)) and -1.45 V (C\(_2\)). When the anodic reversal potential increases from -0.6 to -0.4 V, the shape of CV changes as shown in Fig. 5(b). This result may indicate that the stable oxide is also formed in alkaline solution at the potential \(\geq -0.5\) V.\(^{11}\) We have also carried out the charge consumption measurements for the peaks C\(_1\) and C\(_2\) more than 5 times. The consumed charge is almost the same as that in neutral solution, that is, a charge of \(1.3 \pm 0.3\) mC cm\(^{-2}\) was consumed for these peaks. Assuming that all of this charge was consumed for the reduction of an oxide layer consisting of NiO(110), this charge density approximately corresponds to the reduction of 5.0 ± 1.2 monolayers of Ni(110) (\(\approx 0.7 \pm 0.2\) nm), because a charge of 0.26 mC cm\(^{-2}\) was required for the oxidation of a monolayer of NiO(110).

Figure 6(a) shows unfiltered (7 nm x 7 nm) and filtered (1 nm x 1 nm) EC-AFM images of Ni(110) surface at -1.5 V in 0.01 kmol m\(^{-3}\) NaOH aqueous solution after the same procedure for neutral solution. The protrusions of the filtered image are 0.30 nm and 0.42 nm, which is almost the same as in Fig. 3(a), indicating that this structure corresponds to Ni(110)-(1 x 1). After the EC-AFM image of Fig. 6(a) was acquired, we shifted the potential from -1.5 to -0.8 V, which was more positive than the oxidation peak (A\(_2\)) in Fig. 5. However, no well-ordered structure was observed at that potential. When we stepped the potential to -0.5 V, where the formation of the stable oxide is predicted, we observed a new well-ordered structure (Fig. 6(b)), which is
characterized by three-fold symmetry with interatomic distance of 0.32 ± 0.02 nm. This structure is similar to \(\beta\)-Ni(OH)\(\_\) (0001). Figure 7 shows a schematic illustration of orientation relationship between Figs. 6(a) and 6(b). We found that the atomic rows along the [110] and [110] directions of \(\beta\)-Ni(OH)\(\_\) (0001) oxide layer were parallel with those along the [001] and [110] directions of Ni(110) substrate, respectively.

### 4. Conclusion

*In-situ* EC-AFM was used to investigate bare and anodically oxidized Ni(110) electrodes in 0.05 kmol m\(^{-3}\) \(\text{Na}_2\text{SO}_4\) or 0.01 kmol m\(^{-3}\) NaOH aqueous solution under the control of potential. After the electrochemical pre-treatment, we have succeeded in *in-situ* observation of unreconstructed Ni(110)- (1\(\times\)1) structures in both 0.05 kmol m\(^{-3}\) \(\text{Na}_2\text{SO}_4\) and 0.01 kmol m\(^{-3}\) NaOH solution. Under passive region, we have observed well-ordered structures differing from those of the bare surfaces and it was concluded that NiO(110) films were formed in 0.05 kmol m\(^{-3}\) \(\text{Na}_2\text{SO}_4\) solution, whereas \(\beta\)-Ni(OH)\(\_\) (0001) films were formed in 0.01 kmol m\(^{-3}\) NaOH solution. Table 1 shows orientation relationships relationship of the surface structures on the anodic oxide layers and the substrates.

### REFERENCES