Transactions of the Korean Nuclear Society Autumn Meeting
Gyeongju, Korea, October 24-25, 2013

Structural analysis of Ni/NiO-water interface using X-ray reflectivity

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1. Introduction

Passive films on the surface of metals and alloys take very important role of self-protection against corrosion in aqueous environments. Transition metals including Cr, Fe, and Ni formed protective ultrathin oxide or hydroxide layers. However, breakdown eventually occurs when exposure very aggressive environments such as chloride or lead contained solution. The structural information at solid-water interface is crucial to electrical double layer and ion exchange on metal or alloy surface. For this reason, investigating the interfacial structure at solid-water interface is very important to understand the corrosion or oxidation behavior on the metal or alloy surface.

Various studies have been revealed the surface structures of Ni single crystals in aqueous condition by ex-situ [1,2] and in-situ [3,4] Scanning Tunneling Micro-scope (STM), X-ray-scattering [5], and electro-chemical STM study[6]. These test revealed the epitaxial relationship between Ni substrate and the oxide layer as well as those structures. However, still the resolution of the initial structural data of interface between water and pre oxidized Ni(110) surface is not clear.

Therefore, the objective in this study was to obtain detailed structural data between pre-oxidized Ni(110) and water interfaces to investigate the mechanism of growth the passive film formed on Ni(110) by In-situ high energy X-ray reflectivity study and simulated atomistic model.

2. Methods and Results

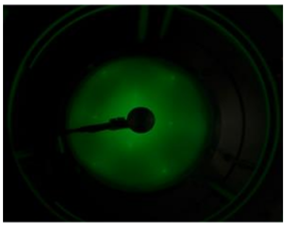
2.1 Sample treatment

A Ni(110) single crystal from a Ni single crystal rod(99.99%, fabricated by Princeton Scientific Corp.) was used. The orientation of the specimen was verified within ±0.01° and the diameter and thickness is 10.00mm and 1.00mm, respectively. The Ni(110) was mechanically polished with alumina powder and then electropolished To improve the surface crystallinity of Ni(110) which is very important to high energy X-ray reflectivity, surface annealed in reduction condition by ultra-vaccum chamber. Figure 1 shows the overall view of the ultra -high vacuum chamber at UNIST. The annealing was conducted with hydrogen gas injection.

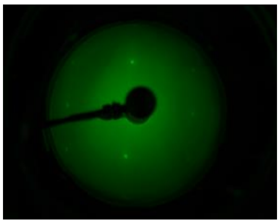
Figure 1. overall view of the UHV chamber at UNIST

The surface condition was observed using Low Energy Electron Diffraction (LEED) after each annealing cycle. Figure 2 shows the LEED images after each annealing cycle.

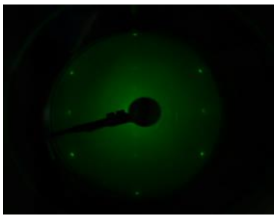
After the 1st cycle, as shown in figure 2(a), LEED image shows diffraction pattern of Ni (110) single crystal. The intensity of the spot is increase as increase the cycle. After 3rd, the spots show brightest intensity and the subsequent cycle appeared to improve the surface crystallinity further.



(a) 1cycle



(b) 2 cycle



(c) 3 cycle

Figure 2. LEED images after (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle.

2.2 X-ray Reflectivity Measurements

After the successful surface pre-treatment, X-ray measurement at room temperature was conducted at 5ID-D beamline at Advanced Photon Source (APS) by Dr. Changyong Park of Carnegie Institution of Washington through collaborating efforts. Figure 3 shows an overview of the X-ray beamline.

For reference data, Crystal Truncation Rod(CTR) measurement which one of high energy x-ray reflectivity measurement was conducted for Ni(110)-helium gas interface at room temperature. Figure 4 shows the mounted sample stage on the x-ray facility used in study. The blue tubes used to inlet and outlet of the helium gas

CTR data for Ni(110)-helium gas result obtained and it is shows that the CTR data is measurable with low errors even at lower intensity region. This CTR data also confirms that

the surface pre-treatment procedure developed for Ni(110) was suitable for the surface X-ray study.

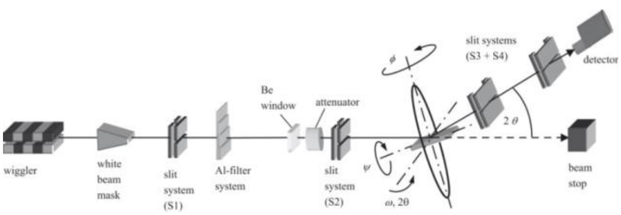


Figure 3. Overview of the X-ray beamline [7]

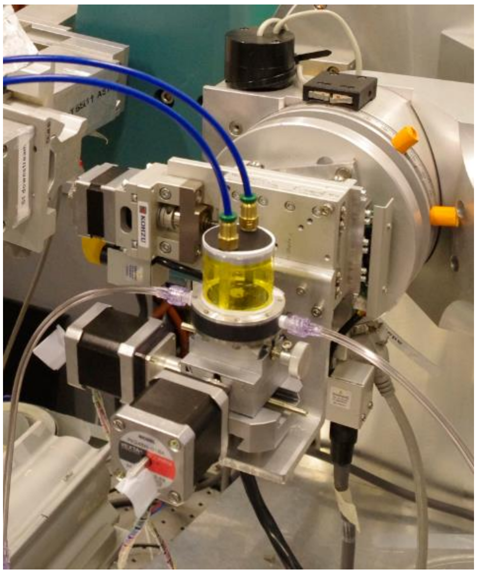


Figure 3. Mounted sample stage used in this study

3. Conclusions

The surface treatment procedure to increase the surface crystallinity was developed to surface x-ray reflectivity measurement. The CTR data shows the surface pre-treatment procedure developed for Ni(110) was suitable for the surface X-ray study. Synchrotron X-ray experiments and analyses will be continued to identify the surface interface between Ni(110), water, and solution contained lead.

ACKNOWLEDGMENTS

This work was financially supported by the I-NERI program organized by the National Research Foundation (NRF) of Korea in support of the Ministry of Science, ICT & Future Planning (MSIP).

REFERENCES

[1]. Maurice, V. Talah, H. and Marcus P. Surf. Sci. 284, 431-436 (1993)
[2]. Maurice, V. Talah, H. and Marcus P. Surf. Sci. 304. 98-108 (1994)
[3]. Yau, S.L., Fun, F., Moffat, T. P. and Ard, A.J. J. Phys. Chem. 98 5493 – 5499 (1994)
[4]. Zuili, D. Maurice, V. and Marcus, P. J. Electrochem. Soc. 147 1393-1400 (2000)
[5]. Magnussen, O.M., Schere, J., Ocko, M. and Behm, R.J., J. Phys Chem. B 104 1222-1226 (2000)
[6]. Suzuki, T. Yamada, T. and Itaya, K., J. Phys. Chem. 100 8954-8961 (1996).
[7] Genzei Ch. Denks I.A. Gibmeier J. Klaus M. and Wagener G. Nucl. Instrum. Meth. A 23-33 (2007)