

In Situ Observation of Corrosion at liq./sol. Interfaces (III)

Masao KIMURA*¹, Noriaki OHTA² and Hiroshi KIHIRA³

¹ Adv. Tech. Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan

² Nippon Steel Technoresearch, Chiba 293-8500, Japan

³ Steel Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan

Introduction

Electrochemical reactions are widely found in applicative as well as fundamental fields, such as corrosion, battery, catalysis and so on. One of its characteristics is that they occur at liquid/solid interfaces. A new system ("EVA"[1,2,3]) was developed for *in situ* observation of reactions at the interface by G-GIXS[4]. In this study, a new system was utilized for *in situ* observation of steel corrosion.

Experiments

In situ measurements were performed for a block specimen of the advanced weathering steel (3.0Ni-0.4Cu-Fe in mass %) [5]. The surface of the specimen was covered with a thickness of ca. 20 μm of diluted artificial seawater and then dried in air at 300 K (Fig.1) using "EVA" system. One wet-dry cycle was about 90 min. X-ray diffraction patterns were measured with $E=12.399$ keV using an image plate at BL-3A at PF, KEK, Tsukuba, Japan.

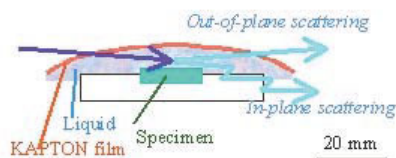
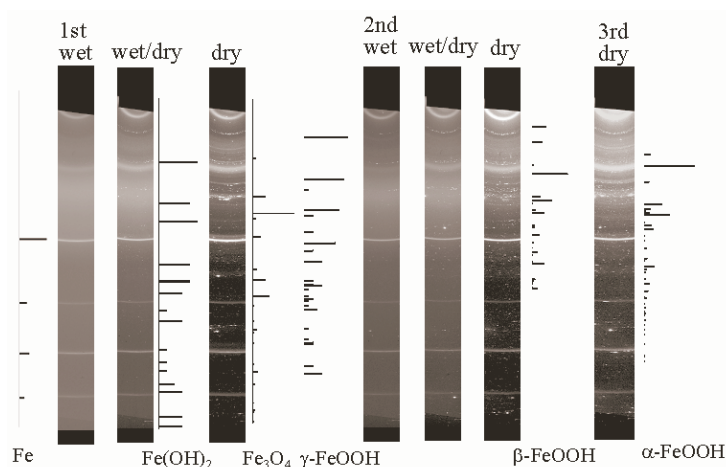


Fig. 1 A sketch of *in situ* cell of the "EVA" system.

Results and Discussion

Figure 2 shows scattering intensities during 1st, 2nd and 3rd wet dry cycles for various t which is time after the seawater covered the surface. The angle of incidence was kept at 1.0 degree. At $t=0$ min. surface was covered by the film of sea water and the diffraction intensities from the substrate (bcc iron) were observed. At $t=33$ min. the surface was still wet but the thickness of sea-water film was less than 20 μm . Formation of $\text{Fe}(\text{OH})_2$ was clearly observed. At $t=91$ min. the surface was almost dry. Diffraction peaks show the formation of $\gamma\text{-FeOOH}$ and Fe_3O_4 .

Fig. 2 Parts of the Debye-rings of XRD from the specimen during the wet-dry cycles: (a) $t=0$, (b) $t=33$, and (c) $t=90$ min. in the 1st wet-dry cycle. (d) $t=95$, (e) $t=125$ min., and (f) $t=165$ min. in the 2nd wet-dry cycle. (g) $t=190$ in the 3rd wet-dry cycle. The horizontal lines show the locations and intensities calculated from reference materials.



Fe_3O_4 , which formed in the 1st cycle, remained in the following wet-dry cycles in the case of the advanced WS (Fig.2). $\beta\text{-FeOOH}$ phase was found in the 2nd and 3rd cycles. After the 3rd cycle, the meta-stable phase of $\gamma\text{-FeOOH}$ transforms into a thermodynamically stable phase of $\alpha\text{-FeOOH}$.

These results showed corrosion reactions on the advanced WS at early stage. When the surface gets wet, dissolved ferrous ions form $\text{Fe}(\text{OH})_2$. In the transition from a wet to a dry state, $\text{Fe}(\text{OH})_2$ transforms into $\gamma\text{-FeOOH}$ and Fe_3O_4 through oxidation by oxygen in air and seawater. Fe_3O_4 remained in the following cycles in the case of advanced WS, whereas Fe_3O_4 was easily oxidized to form $\alpha\text{-}$ and/or $\gamma\text{-FeOOH}$ in a dry cycle in the case of conventional WS [6]. These unique features are deeply relating with high corrosion resistance of the advanced WS [3,7,8].

We would like to thank Drs. T. Mori, M. Tanaka and T. Matsushita at PF for their great supports for experiments.

References

- [1] M. Kimura et al.: PF Act. Rep. #19 Part B, p.227 and #20 Part B, p.202 (2003).
- [2] M. Kimura et al: PF Act. Rep. #21 Part B, p.183, 184, 185 (2004).
- [3] M. Kimura et al: Corrosion Sci. (in print,2005)
- [4] M. Kimura et al.: J. App. Phys., **4**, 2034(2003) .
- [5] H. Kihira et al: Zairyo-to-Kankyo, **49**, 30 (2000).
- [6] M. Kimura et al: J. Japan Inst. Metals, **66**, 166 (2002).
- [7] M. Kimura et al: Procds. of the 13th Asian-Pacific Corrosion Control Conference (Osaka, 2003).
- [8] M. Kimura et al : Procds. of ECS (Honolulu, 2004), ECS PV 2005-14, p133.

* kimura@re.nsc.co.jp