

Dynamic DXAFS study of iron species near a metal/liquid interface

Yasuhiro NIWA^{1*}, Yasuhiro INADA¹, Masaharu NOMURA¹, Masao KIMURA²
¹KEK-PF, Tsukuba, Ibaraki 305-0801, Japan
²Adv. Tech. Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan

Introduction

The stainless steels are known to remain essentially passive in environments, but the existing Cl^- and Br^- species tend to corrode many materials including the stainless steels at specific areas and to form deep pits. This is called as pitting by a localized corrosive attack [1,2]. It is very important to observe the state and concentration of metal and anionic species under various conditions (pH, electrochemical potential, temperature, etc.) in an aqueous solution to understand the pitting behavior of stainless steel. The dispersive XAFS (DXAFS) method is a suitable technique to study *in situ* the localized corrosion occurred near the metal/liquid interface. We have carried out the *in-situ* observations for the Fe species by means of the time-resolve DXAFS instrument and the electrochemical cell, which was made to clarify a change of concentration and coordination structure of dissolving metal ions from stainless steel and existing anions near the solution/steel interface [3]. The electrochemical cell can be a model of the artificial crevice for stainless steels under dissolving condition, and thus the change of the coordination structure around the Fe species has been dynamically investigated by using the DXAFS technique.

Experiment

A schematic diagram of electrochemical cell for the *in situ* DXAFS measurements is shown in figure 1. The liquid phase was 1.0 mol kg^{-1} aqueous solution of LiBr. The used stainless steel was type 304, which contains 18 wt% of Cr, 12 wt% of Ni, and 2 wt% of Mo in Fe. An electrochemical potential of the stainless steel was controlled by a potentiostat at 0.8 V versus Ag/AgCl electrode to corrode the interface uniformly. The DXAFS measurements were carried out at NW2A beamline using an Si(111) bent crystal (Bragg-type) polychromator with the bending radius of 2 m and a photo diode array (PDA) detector with the CsI(Tl) phosphor. The rapid addition of the electric potential to stainless steel was used as a trigger to start the DXAFS measurements.

Results and Discussion

The dissolving processes of the Fe species have been successfully measured in the aqueous phase closed to the solution/steel interface. The change of the XAFS spectrum of Fe is shown in figure 2. At the beginning, the absorption edge due to the Fe species in the aqueous phase is not observed, but the absorption K edge of Fe appears quickly after the addition of the electrochemical potential and increases gradually. The shapes of the

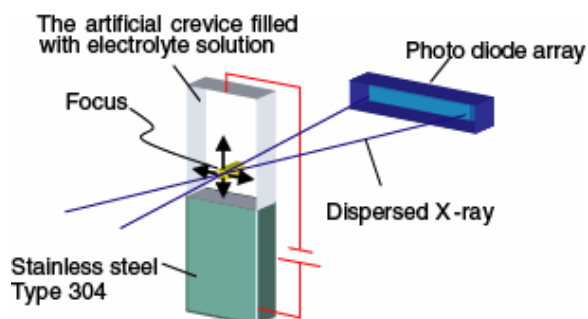


Fig. 1 Schematic illustration of electrochemical cell. The potential of stainless steel was controlled by a potentiostat at 0.8 V vs. Ag/AgCl electrode.

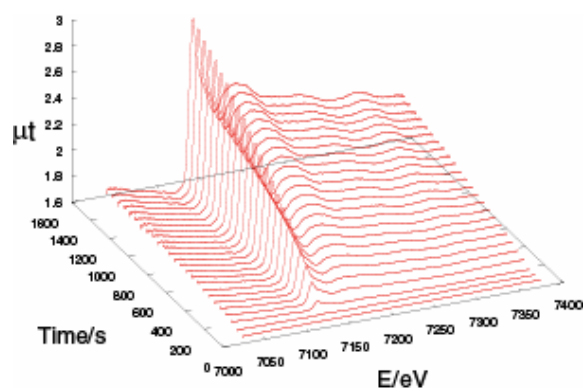


Fig. 2 Change of the Fe K-edge XAFS spectra after the addition of the electrochemical potential.

XANES spectra are almost unchanged and are quite similar to that of the aqueous solution of $\text{Fe}(\text{ClO}_4)_2$. It has been clarified that the dissolved Fe species are assigned to be divalent. The EXAFS analyses demonstrate that the chemical species of Fe^{2+} are found to be $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ with the Fe–O bond length of 210 pm within 30 min after the start of dissolution.

We will measure the DXAFS spectra of other metal species, which are contained in the stainless steels, and Br^- ion under same conditions, and will elucidate the corrosion mechanisms by understanding the dissolving process.

References

- [1] H. H. Uhlig et al., Corrosion and Corrosion Control, 3rd ed., John Wiley & Sons, Inc., New York, (1984).
- [2] Z. S. Smialwska, Pitting Corrosion of Metals, National Association of Corrosion Engineers, Houston, 145, (1986).
- [3] M. Kimura et al., ISIJ international, 42, No. 12, 1399 (2002).

* yasuhiko.niwa@kek.jp