

## In situ observation of molybdenum states in pitting of stainless steel

Masao Kimura<sup>1)</sup>, and Michio Kaneko<sup>2)</sup>

<sup>1)</sup>Adv. Tech. Res. Lab., Nippon Steel Corp.,

<sup>2)</sup>Steel Res. Lab., Nippon Steel Corp.,

<sup>1)2)</sup>20-1, Shintomi, Futtsu, Chiba, 293-8511, Japan,

A new technique by XAFS (X-ray Absorption Fine Structures) and XANES (X-ray Absorption Near Edge Structures)<sup>1</sup> has been developed for *in situ* observation of metal corrosion<sup>2,3</sup>. XAFS and XANES spectra were obtained with a special electrochemical cell to elucidate pitting for stainless steel. Special attention was paid to effects of molybdenum on pitting.

Figure 1 shows the electrochemical cell for *in situ* observation. A sheet of stainless steel was attached below a reservoir of a specific aqueous environment with thin films. A thin box made of a film connects the reservoir with the metal, and the solution inside the film-box corresponds to an artificial pit. X-ray beams pass through the film-box containing the solution, and XAFS and XANES measurements were performed with keeping the specimen at a specific potential at beam lines BL-7C and BL-12C<sup>4</sup> at the Photon Factory, Japan.

As a reference, the state of molybdenum in Na<sub>2</sub>MoO<sub>4</sub> solution was investigated by this system. Figure 2 shows radial distribution function (RDF) around Mo obtained by XAFS at Mo-K edge; the first peak can be attributed to two types of coordination of O<sup>2-</sup> and H<sub>2</sub>O towards Mo ions (Fig.3).

The state of molybdenum inside the artificial crevice of Fe-18Cr-20Ni-5Mo (mass%) alloy was investigated using two solutions: LiCl and LiBr. The intensities of the pre-peak around at  $E=20000\text{eV}$ , corresponding to  $[\text{MoO}_4(\text{H}_2\text{O})_2]^{2-}$  octahedron, show significant difference between in LiCl and LiBr (Fig.4).

The formation of the  $[\text{MoO}_4(\text{H}_2\text{O})_2]^{2-}$  octahedron was observed in both solutions, but there was observed a significant difference in networking of the octahedron. In LiCl solutions it was similar to that of molybdate ions ( $\text{MoO}_4^{2-}$ ), but in LiBr it was rather different form that of molybdate ions. This shows that the favorable effects of molybdenum on pitting can be attributed to the formation of  $\text{MoO}_4^{2-}$  network near the interface<sup>2,3</sup>.

<sup>1</sup> B. K. Teo, *EXAFS: Basic Principles and Data Analysis* (Springer, Berlin, 1986).

<sup>2</sup> M. Kimura, M. Kaneko, and T. Suzuki, *J. Synchrotron Rad.* 8, 487 (2001).

<sup>3</sup> M. Kimura, M. Kaneko, and N. Ohta, *ISIJ International* 42, 1398 (2002).

<sup>4</sup> M. Nomura and A. Koyama, in *X-ray Absorption Fine Structure*, edited by S. S. Hasnain (Ellis Horwood, London, 1991), p. 667.

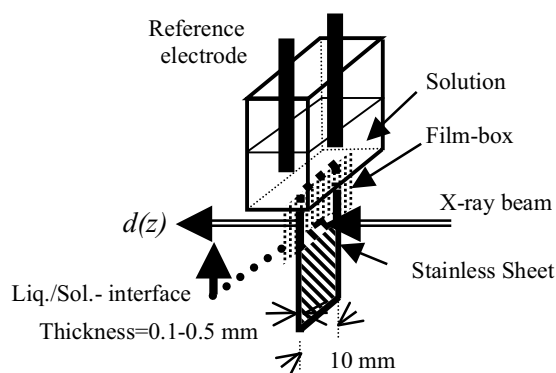


Figure 1 Electrochemical cell for *in situ* observation.

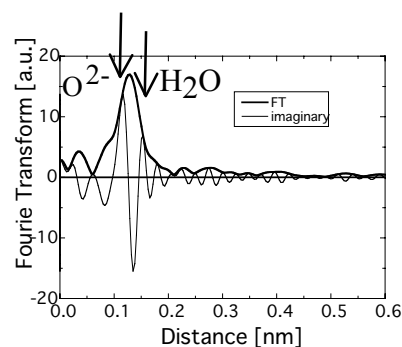


Figure 2 Fourier transforms of XAFS spectra at Mo-edge for Na<sub>2</sub>MoO<sub>4</sub> solution.

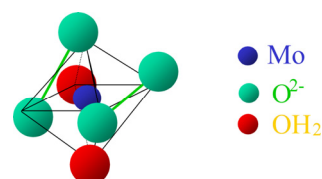


Figure 3 Atomic structure of  $[\text{MoO}_4(\text{H}_2\text{O})_2]^{2-}$ .

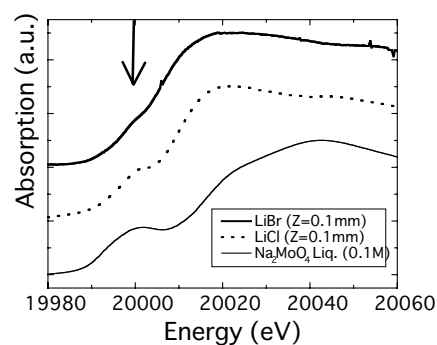


Figure 3 XANES spectra at Mo-edge obtained by *in situ* measurement for LiCl and LiBr at  $d(z)=0.1$ , and a Na<sub>2</sub>MoO<sub>4</sub> solution.