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In situ observation of pitting of stainless steel by XAFS

Masao KIMURA*, Michio KANEKO, Tamaki SUZUKI
Nippon Steel Co, Futtsu, Chiba 293-8511, Japan

Introduction

In environments containing appreciable concentrations of Cl^- or Br^-, in which stainless steels remain essentially passive, they tend to corrode at specific areas and to form deep pits . This is called pitting and is a form of localized corrosive attack that produces pits. It is very important to observe the state and concentration of metal and chloride ions under various conditions (pH, potential, temperature,...etc.) in an aqueous environment to understand pitting behaviour of stainless steel.

We have tried to develop an *in situ* observation technique by XAFS (X-ray Absorption Fine Structures) measurements conducted on a special electrochemical cell to elucidate pitting: change of concentrations and structures of ions near the interface of solution and metal [1].

Experiments

Fig.1 shows an electrochemical cell for use in an *in situ* observation. A sheet of stainless steel (SS : Type316, Fe-16.8Cr-12.0Ni-2.0Mo wt.%) is attached below a reservoir of 1M LiBr solution acting as an aqueous environment. LiBr was used instead of NaCl because of a limitation of edge-energies. A specimen and the reservoir are joined by a Kapton-box; in other words, the liquid “film” joins the reservoir and a metal edge [2].

Results

Ion concentrations in the pit were investigated by *in situ* measurements of absorption at the edges. Fig.2 shows concentration of ions depends on the distance *d(z)* for Cr. It is clearly seen that the concentrations of Cr and Br are linearly dependent on the distance *d(z)* . This suggests that the dissolution rate can be determined by diffusion of ions.

The structures around Cr were investigated by *in situ* measurements of XAFS spectra at the different distances *d(z)*. A typical result of measurements and curve fitting is shown in Fig.2 for *d(z)*=1.3mm. Calculated curves were obtained by assuming the coordination of Cr-O (the distance: R=0.200nm, the coordination number: N=4.8) .

The propagation of pits is thought to involve the dissolution of metal and the maintenance of a high order of acidity at the pit bottom by the hydrolysis of the dissolved metal ions as follows :

$$M^+Cl^- + H_2O \longrightarrow MOH + H^+Cl^- .$$

The obtained results is consistent with this simple model. In a case of stainless, a salt film containing Cr plays an important role in corrosion, and the information on structures around Cr ion is essential to understand pitting behavior of stainless steel. It has been shown that the *in situ* technique has a potential for understanding the mechanism.

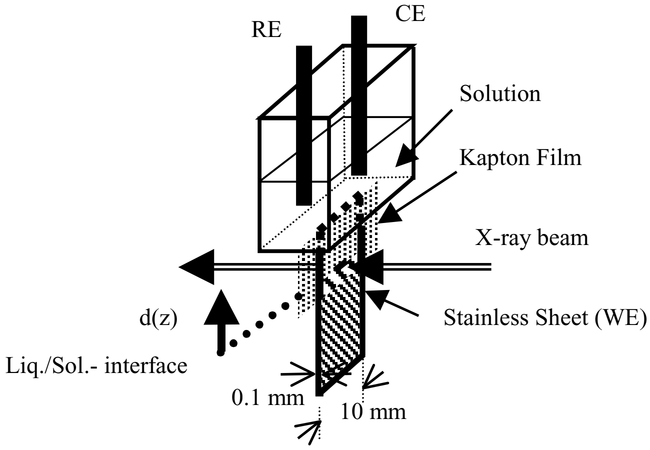

Fig.1 Electrochemical cell for *in situ* observation.

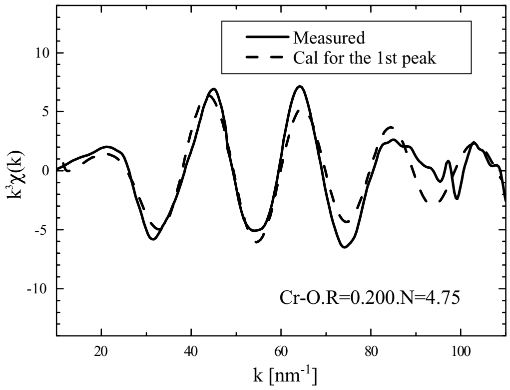

Fig.2 $k^3\chi(k)$ spectra of the observed data and the calculated one fro Cr-edge (*d(z)*=1.3mm) .

References

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[2] M.Kimura et al., J. Synchrotron Rad. 8, 487 (2001).

* kimura@re.nsc.co.jp