

## *In situ* observation of pitting of stainless steel by XAFS

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An *in situ* observation technique by XAFS (X-ray Absorption Fine Structures) has been developed for observation of metal corrosion. XAFS spectra were obtained with a special electrochemical cell to elucidate pitting: change of concentrations and structures of ions near the interface of solution and metal. It has been successfully shown that the concentrations of Cr and Br are linearly dependent on the distance from the interface. Also, salt formation at the interface and the hydrolysis reaction far from the interface are indicated.

**Keywords:** XAFS, *in situ*, corrosion, stainless steel, hydrolysis, Cr, Br

### 1. Introduction

In environments containing appreciable concentrations of Cl<sup>-</sup> or Br<sup>-</sup>, in which stainless steels remain essentially passive, they tend to corrode at specific areas and to form deep pits (Uhlig and Revie, 1984). This is called pitting and is a form of localised 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. X-ray absorption and fluorescence techniques have been applied to *in situ* chemistry studies of localised corrosion (Isaacs *et al.*, 1995). However, because of experimental difficulties, there have been few reports on direct observation of structures of ions inside pits.

In this study, 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.

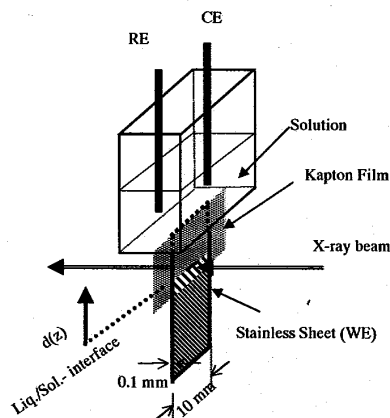
### 2. Experimental

All XAFS spectra were measured by transmission geometry. Standard powders were sandwiched by Kapton tape. Liquid specimens were kept in a plastic bag, and the thickness of the bag was set at an optimum value by a special jig.

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.

The potential of the specimen was kept at 0.8 V vs. a reference electrode (RE; Ag/AgCl) to corrode an entire cross-section of SS sheet. The specimen SS functions as a working electrode (WE) with a counter electrode (CE; Pt). The edge of SS sheet was dissolved down to form a pit before *in situ* experiments were conducted. At the initial stage the current density showed a peak as high as a few 10<sup>4</sup> A/m<sup>2</sup>; it became smaller (5.0 x 10<sup>3</sup> A/m<sup>2</sup>) after a few hrs and then decreases gradually, resulting in formation of a pit with a depth

of a few mm after more than 24 hrs. Then XAFS measurements were performed at different distances from the interface ( $d(z)$ ) by moving the cell. The current density was 1.0 x 10<sup>3</sup> A/m<sup>2</sup>, and the beam size was about 2mm<sup>W</sup> x 0.2 mm<sup>H</sup>. These experiments were carried out at BL-7C at Photon Factory, KEK, Japan.



**Figure 1**

Schematic diagram of *in situ* XAFS measurements conducted for a newly-designed electrochemical cell.

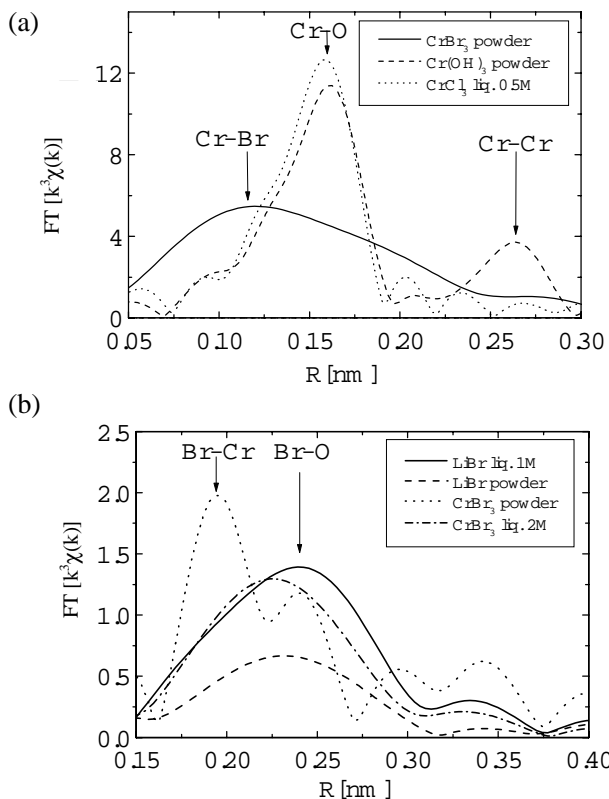
### 3. Results

It is considered that dissolved metal ions such as Fe<sup>2+</sup> and Cr<sup>3+</sup> form a salt layer and that pH is decreased by the hydrolysis reaction inside pits (Isaacs *et al.*, 1995). Then standard specimens are prepared as follows: CrBr<sub>3</sub> and Cr(OH)<sub>3</sub> powders, and LiBr and CrBr<sub>3</sub> liquid with various concentrations. It is expected that metal ions such as Fe<sup>2+</sup> and Cr<sup>3+</sup> form salt with Br<sup>-</sup> near the interface and that ions are surrounded by water molecules (hydrolysis). Fig.2 shows Fourier transforms of (a) Cr-edge and (b) Br-edge spectra of standard specimens.

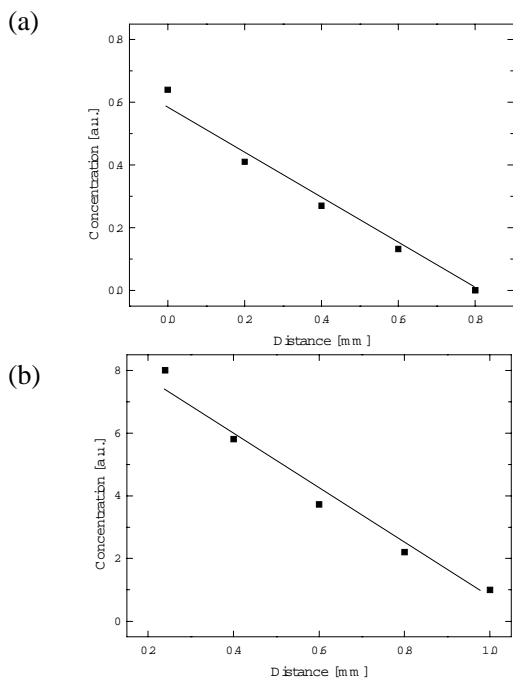
**Powders** : a Cr atom is surrounded by 6 atoms of Br in CrBr<sub>3</sub> and by 6 atoms of O (or OH) in Cr(OH)<sub>3</sub> ; corresponding peaks are indicated in Figs.2 and 3. The broad peak of CrBr<sub>3</sub> can be attributed to its moisture-sensitiveness in spite of the experimental precaution taken.

**Liquid** : As the saturated concentration of salt (FeCl<sub>2</sub>) is about 4-5 M (molar) (Linke, 1958, Isaacs *et al.*, 1995), the salt formed at the interface is expected to be a mixture of FeCl<sub>2</sub> + CrCl<sub>3</sub>; the concentration of CrCl<sub>3</sub> can be estimated to be 4-5×0.168= 0.7-0.8 M in a case of Type 316. The liquid of 0.5 M CrCl<sub>3</sub> and 2.0 M CrBr<sub>3</sub> are chosen as references for the states of saturated salt for Cr and Br edge, respectively. The Fourier transforms of Cr-edge of 0.5 M CrCl<sub>3</sub> show a main peak corresponding to Cr-O (or OH<sub>2</sub>) and a shoulder peak corresponding to Cr-Cl.

Ion concentrations in the pit were investigated by *in situ* measurements of absorption at the edges. Fig.3 shows concentration of ions depends on the distance  $d(z)$  for (a) Cr and for (b) Br. These data were measured for different cells, and the initial depth of pit for (a) was different from that for (b): (a) 1.3 mm and (b) 3.5 mm. It is clearly seen that the concentrations of Cr and Br are linearly



**Figure 2** Fourier transforms of (a) Cr-edge and (b) Br-edge spectra of standard specimens.

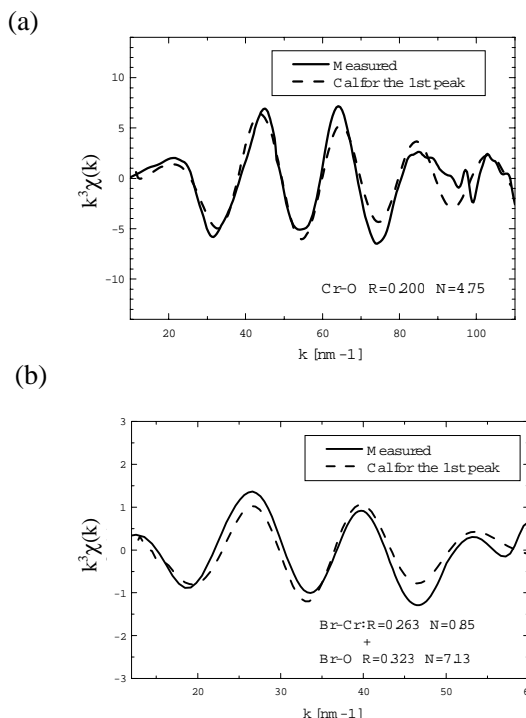


**Figure 3** Concentration of ions depends on the distance from the interface ( $d(z)$ ): (a) Cr and (b) Br.

dependent on the distance  $d(z)$ . This suggests that the dissolution rate can be determined by diffusion of ions (Isaacs *et al.*, 1995).

The structures around Cr and Br were investigated by *in situ* measurements of XAFS spectra at the different distances  $d(z)$ . Typical results of measurements and curve fitting are shown in Fig.4 for (a) Cr-edge ( $d(z)=1.3\text{mm}$ ) and (b) Br-edge ( $d(z)=0.2\text{mm}$ ). Calculated curves were obtained by assuming the coordination of (a) Cr-O (the distance:  $R=0.200\text{nm}$ , the coordination number:  $N=4.8$ ) and (b) Br-Cr ( $R=0.263\text{nm}$ ,  $N=0.9$ ) + Br-O ( $R=0.323\text{nm}$ ,  $N=7.1$ ).

Fig.5 shows the Fourier transforms of (a) Cr-edge and (b) Br-edge spectra of *in situ* measurements. Cr-edge spectra for all  $d(z)$  show peaks almost all at the same position located between the Cr-Br and Cr-O of the references (Fig.2(a)). The distance obtained by curve fitting of the data is 0.20 nm, and the coordination number is about 5-6 (Fig.4 (a)).



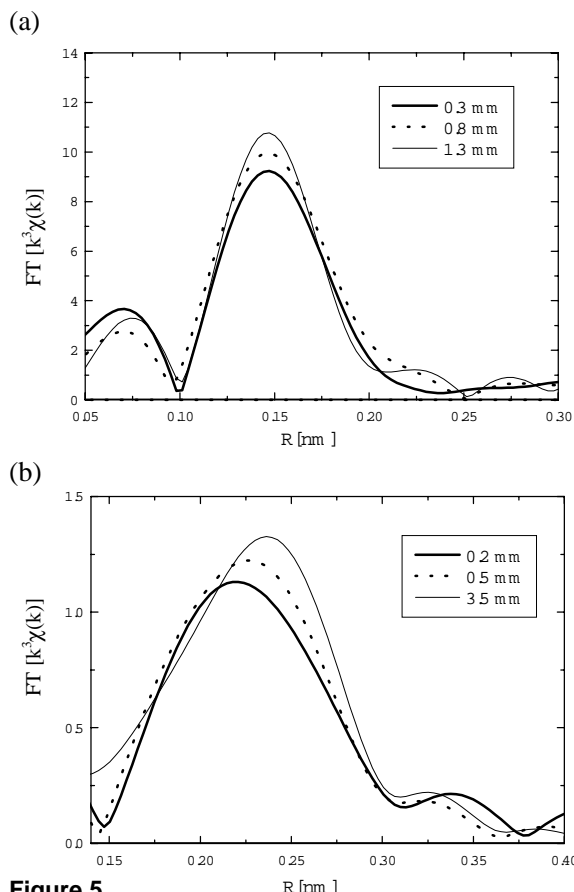
**Figure 4**  $k^3\chi(k)$  spectra of the observed data and the calculated one: (a) Cr-edge ( $d(z)=1.3\text{mm}$ ) and (b) Br-edge ( $d(z)=0.2\text{mm}$ ).

In contrast with this, Br-edge spectra differ as  $d(z)$  differs; the peak shifts toward a larger  $R$  as the distance  $d(z)$  increases. This shift may result from the change in coordination of Br. The curve fitting of the spectrum at  $d(z)=0.20\text{mm}$  showed a result for the model where Br is coordinated by Cr and O (Fig.4 (b)) better than that where Br is coordinated simply by O. But the curve fitting for  $d(z)=3.50\text{mm}$  showed that Br is coordinated simply by O.

#### 4. Discussion

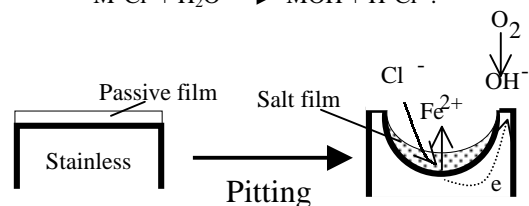
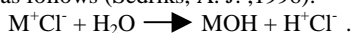
These results suggest that the  $\text{Cr}^{3+}$  ion is coordinated by OH and  $\text{H}_2\text{O}$  in the pit and that some of the ligands are exchanged by  $\text{Br}^-$  especially near the interface, which are clearly seen by Br-edge spectra. These facts indicate the formation of  $\text{CrBr}_3$  salt near the interface. This is consistent with a report on existence of a salt film with a thickness of about  $10\ \mu\text{m}$  obtained by *in situ* observation of fluorescence (Isaacs *et al.*, 1995).

At this stage, it was rather difficult to obtain the quantitative value of the number of coordination and the distance of Cr and the ligands from the *in situ* XAFS spectra in spite of intensive efforts. One of the main reasons for this is the difficulty of preparing a flat and smooth interface; it tends to become rough after dissolving for a long time. Further, the limitation of a beam size is another factor.

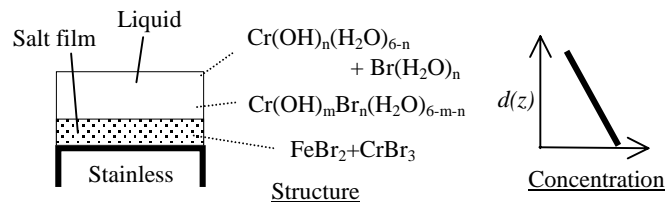


**Figure 5** Fourier transforms of (a) Cr-edge and (b) Br-edge spectra of *in situ* measurements

The results of *in situ* measurements are discussed in terms of corrosion mechanism. The initiation of pits on an otherwise fully passive stainless surface requires that the corrosion potential exceed the critical potential, which is caused by the existence of various ions, pH, temperatures, and so on (Fig.6). In this study, such a corrosion potential is simulated by applying the potential of 0.8 V vs. RE in solution containing Br<sup>-</sup>. 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 (Sedriks, A. J., 1996):



**Figure 6** Schematic illustration of the pit initiation and growth.



**Figure 7** Schematic illustration of pitting shown by *in situ* measurements.

In the experiments, the formation of a pit was simulated (Fig.7). The dissolution of metal and the hydrolysis reaction occurs at the interface located at  $d(z)=0$ , and cathodic reaction proceeds at CE. This makes it possible to prepare a flat interface for *in situ* measurements, which have shown the linear dependence of concentrations of Cr<sup>3+</sup> and Cl<sup>-</sup> on  $d(z)$  and the formation of the salt films (FeBr<sub>2</sub>, CrBr<sub>3</sub>, NiBr<sub>2</sub>) at the interface (Fig.7).

The change of structure, first revealed by *in situ* observation, is consistent with that of proposed model (Isaacs *et al.*, 1995; Uhlig and Revie, 1984; Sedriks, A. J., 1996). The salt film containing Cr plays an important role in corrosion. Ion migration across the salt could affect its composition. Salt layers have been considered to be porous from diffusion and electromigration. Further experiments are necessary to improve the model and understand the pitting mechanism, and the *in situ* technique has a potential for it.

### 5. Conclusion

A novel technique in corrosion science has been developed. This technique has successfully shown that the concentration gradient and the change in the structure of ions inside a pit are a function of the distance from the interface. Further experiments are planned to investigate effects of additional elements in stainless steel.

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