

In situ Analysis of Solution Chemistry inside the Artificial Crevice of Stainless Steel by X-ray Absorption Fine Structure Measurement

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Chromium and bromide ions inside the artificial crevice of Fe-18%Cr-12%Ni-2%Mo alloy was successfully investigated by the in situ X-ray Absorption Fine Structure (XAFS) measurement. A cross-section of 0.1mm thick stainless steel foil sandwiched with Kapton films attached solution reservoir above contained 1M LiBr solution was dissolved at 0.8V (vs. Ag/AgCl) to form the artificial crevice. When the crevice reached several mm in depth, concentrations and coordination states of dissolved chromium ion and bromide ion were investigated by the transmission XAFS measurement, which was carried out at BL-7C in Photon Factory, KEK, JAPAN. Concentrations of chromium and bromide ions inside the artificial crevice were almost lineally decreased from metal/solution interface towards bulk solution. A concentration of bromide ion at the metal/solution interface was estimated as approximately 10M, which was close to solubility of FeBr₂. Coordination states of dissolved chromium ion and bromide ion were also investigated at different positions from the metal/solution interface inside the artificial crevice, close to interface, the middle of the crevice and close to bulk solution. No change of coordination states of chromium ion was observed. Structures of bromide ion, on the other hand, were changed with positions. Distance between bromide ion and the nearest ion near the interface was shorter than those at middle of the artificial crevice or position close to bulk solution. These results are consistent with a theory that the change of the distance from bromide ion to the nearest atoms might relate to a formation of hydrobromo-complex near the metal/solution interface.

Keywords : crevice corrosion, x-ray absorption fine structure, stainless steel, bromide ion, coordination ions.

1. Introduction

Pitting corrosion or crevice corrosion is the commonest cause of localized corrosion of stainless steels. It is well known that pH inside localized corrosion area is much lower than bulk solution because of hydrolysis of dissolved metal ions and higher chloride concentration which stabilize the growth of localized corrosion. Suzuki et al observed a decrease in pH within artificial pits to 0.6 or 0.8 and a increase in content of chloride ions (6M) for Type304L stainless steel.¹⁾ Acidification of solutions contained in pits and crevices is generally explained by the hydrolysis of salts produced by anodic dissolution of the metal or alloy,²⁾ but the pH values calculated on the basis of the reaction of hydrolysis are considerably greater than those found experimentally. In addition to the effect of hydrolysis, Suzuki et al.,¹⁾ considered the formation of hydrochloro-complex of cations of the dissolved metal leading to a decrease in pH,^{3),4)} however it is difficult to observe formation of these complex inside pit or crevice.

Recently X-ray absorption and fluorescence measurement has become powerful method for the in-situ study of chemical and physical changes during electrochemical and corrosion processes. Isaacs et al.^{5),6)} observed dissolved metal ion concentration inside artificial pit and content of salt films for Type304 SS by using the in situ X-ray microprobe technique.

The authors have been developing in situ XAFS measurement to observe concentration of dissolved metal ions and aggressive anions and coordination states of these ions inside artificial crevice.^{7),8)} In this study, concentration of ions, especially chromium and bromide ions, coordination state of these ions inside the artificial crevice for stainless steels have been investigated by the in situ XAFS measurement.

2. Experimental

Fig. 1 shows schematic diagram of the electrochemical cell for in situ XAFS measurements. A 10mm width x

Fig. 1. Schematic illustration of electro-chemical cell for the in situ XAFS measurement

30mm length x 0.1mm thickness sheet of Fe-18%Cr-12%Ni-2%Mo alloy sandwiched by Kapton films with epoxy glue was attached plastic reservoir above contained 1M LiBr solution. A potential of the steel was controlled by a potentiostat at 0.8V v.s Ag/AgCl reference electrode to corrode entire cross-section of the sample uniformly. After dissolving a few mm depth, XAFS measurements were carried out. All XAFS spectra were measured by transmission geometry shown in Fig. 1. Beam size was 0.1mm height x 10mm width. The electrochemical cell attached with a stage moving X-Y-Z direction by a stepping motor was moved along Z direction to carry out XAFS measurement from dissolving interface to the bulk solution.

XAFS measurements were also carried out for LiBr, LiCl solutions, and solutions and powders of chromium chlorides, bromides, oxides, hydroxides as references.

All the measurements were carried out at BL-7C in Photon Factory, Tsukuba, JAPAN.

3. Results and discussion

3.1 Concentration of chromium and bromide ions inside the artificial crevice

In situ measurement for chromium ion was carried out to investigate concentration inside the artificial crevice of 0.8mm depth. Fig. 2 shows concentration of chromium ion inside the artificial crevice. Concentration of chromium ion was decreased lineally from the dissolving interface to crevice mouth. Concentration of chromium near the interface was found to be about 0.55M. Estimation of chromium ion concentration was based on the measurement of for CrBr₃ solution with different concentration. Isaacs et al observed 1.08M of chromium ion close to the dissolving interface of an artificial pit for Type304 SS in 0.5M HCl and 0.5M NaCl solution, higher than that

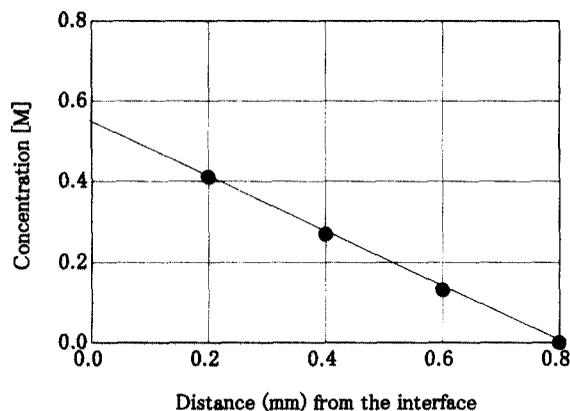


Fig. 2. Chromium ion concentration inside the artificial crevice

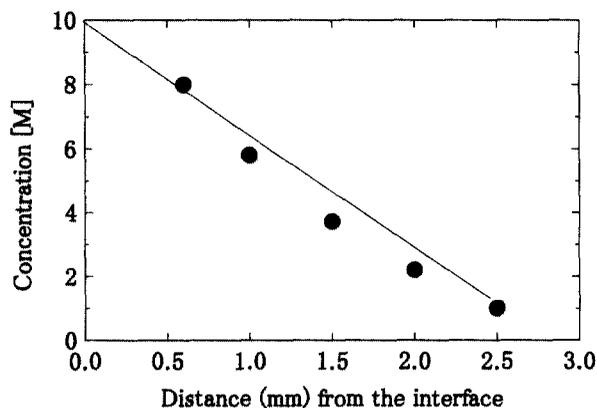


Fig. 3. Bromide ion concentration inside the artificial crevice

observed in this study. In both experiments, stainless steels were dissolving with salt films on the surface, therefore the difference of concentration of chromium ions near the dissolving interface might arise from the difference of solubility of metal chlorides and bromides. According to Isaacs study, solubility of metal chlorides were estimated as 5.02M. Solubility for metal bromide has not been obtained yet. Therefore, measurement for concentration of bromide inside the artificial crevice was carried out when the crevice reaches about 2.5mm depth.

Fig. 3 shows concentration of bromide ion inside the artificial crevice. Concentration of bromide ion was also decreased almost lineally from the dissolving interface to crevice mouth. Concentration of bromide ion at the interface was estimated as about 10M. Assuming MBr₂ as metal bromide, solubility of salt film would be 5M almost same as that observed for metal chloride in Isaacs's work. One source⁹⁾ quotes the solubility of FeCl₂ and FeBr₂ at 10°C as 64.4 and 109 g/cm³ or 5.08 and 5.05M, respectively. From these experimental results, difference of chromium ion concentration at the dissolving interface

observed Isaac's et al in chloride and one estimated in the present study should relate to content of chromium in salt films on stainless steels, higher content of chromium ion in metal chloride than that in metal bromide.

In the present experiment, concentration of chromium and bromide ions inside the artificial crevice showed linear dependence, on the other hand, Isaacs et al observed non-linear relation near the dissolving interface, higher concentration because of lower diffusion coefficient. As a relatively larger beam size as 0.1mm was used in this study, it could not analyze concentration of ions very close to the interface. In consideration of non-linear relation at the interface, estimated concentration of bromide at the dissolving interface might be higher. So micro-beam analysis must be needed to analyze the concentration of ions at the interface.

3.2 Coordination states of chromium and bromide ions

3.2.1 Standard specimens

As discussed above, bromide ion and chromium ion concentrations at the dissolving interface of the artificial crevice reach about 10M and 0.55M, respectively. Therefore, XAFS spectra of LiBr, LiCl, CrBr₃, CrCl₃ solutions with some molar concentration and CrBr₃, CrCl₃ salts etc. were measured as standard specimens. Fig. 4 shows Fourier transforms of Cr edge of CrBr₃ powder, Cr(OH)₃ powder and 0.5M CrCl₃ solution. The broad peak of CrBr₃ can be attributed to moisture-sensitive in spite of precaution taken. Fig. 5 shows Fourier transform of bromide edge.

3.2.2 In situ XAFS measurement of chromium and bromide ions

In situ XAFS measurement of chromium and bromide ions were carried out at different Z positions, close the dissolving interface and bulk solution. Fig. 6 shows the Fourier transforms of Cr-edge spectra of in situ measurements at different d(z) position from the interface for d(z)=0.2mm to close to the bulk solution for d(z)=1.3mm. It is apparent from the results obtained that Cr edge spectra for all d(z) positions showed peaks almost all the same position located between the Cr-Br and Cr-O of the references. As discussed above, observed pH inside pits or crevices are lower than calculated pH owing to hydrolysis reaction of dissolved metals. To explain the difference of pH observed and calculated, the formation of hydrochloro-complex of cations of the dissolved metal leading to a decrease in pH is proposed.^{1),(3),(4)} Based on their model it is presumable that Cr-edge spectra would be changed with different d(z) position, however obtained results were all the same spectra in this measurement. It is believed that it is not easy to detect the change of

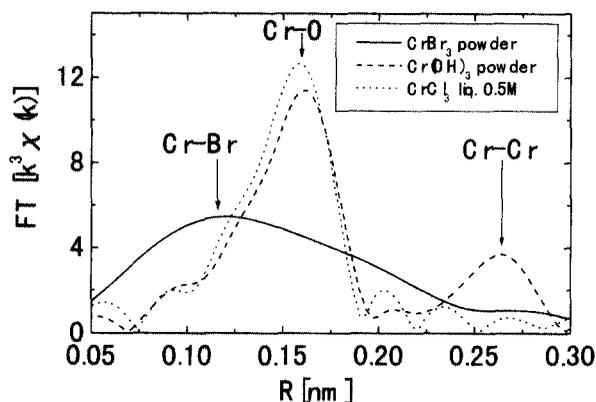


Fig. 4. Fourier transforms of Cr-edge spectra of standard specimens

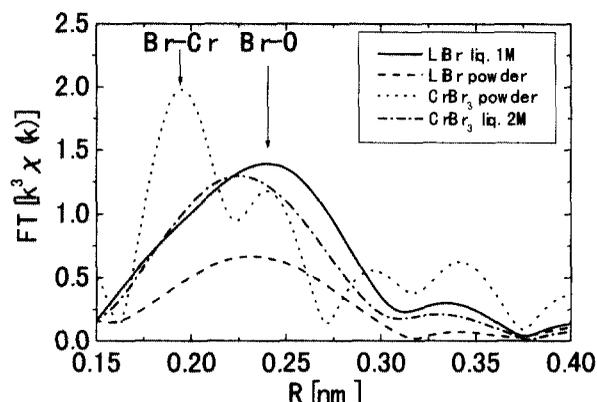


Fig. 5. Fourier transforms of Br-edge spectra of standard specimens

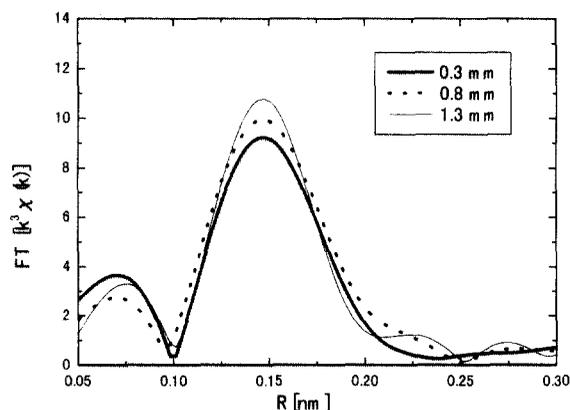


Fig. 6. Fourier transforms of Cr-edge of in situ measurements

coordination state of chromium, because not all coordinated ions are considered to be halide ions. Therefore, it would be difficult to detect the difference of the distance of coordinated atoms or numbers. So, XAFS spectra for bromide ions were examined by in situ measurements.

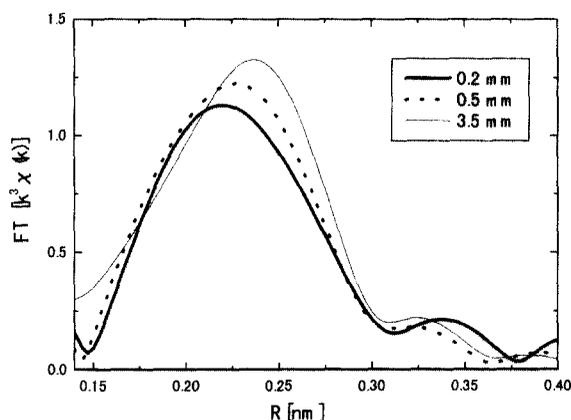


Fig. 7. Fourier transforms of Br-edge of in situ measurements

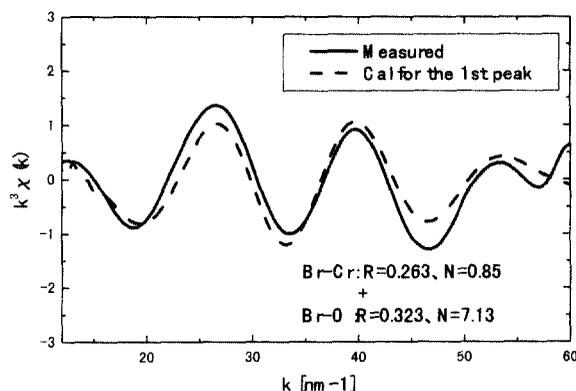


Fig. 8. $k^3 \chi(k)$ spectra of the observed data and the calculated one for Br-edge ($d(z)=0.2\text{mm}$)

Fourier transforms of spectra of bromide ions at different $d(z)$ position are shown in Fig. 7. In contrast with the spectra of chromium, Br-edge spectra differs as $d(z)$ position. The peak shifts toward a larger R as the distance $d(z)$ increases. Fig. 8 shows measured and calculated curve fitting for bromide at $d(z)=0.2\text{mm}$. The curve fitting was well fit to the measured one by assuming that bromide is coordinated by Cr and O. At $d(z)=3.5\text{mm}$, close to bulk solution, on the other hand, the curve fitting was well corresponded with the measured curve based on the model

that bromide is coordinated simply by oxygen.

It is concluded from results obtained by in situ XAFS measurements that hydro-bromo complex might be formed near the interface leading to lower pH than that calculated by simple hydrolysis reaction of metal salts.

4. Conclusions

1) Dissolved chromium ion and bromide ion concentration, and coordinations state of these ions inside the artificial crevice were successfully investigated by in situ XAFS measurement.

2) Concentration of chromium and bromide ions were decreased lineally from dissolving interface to bulk solution inside the artificial crevice. Concentration of chromium and bromide ions at the interface were estimated as 10M and 0.55M, respectively.

3) Coordination state of bromide ion at the interface was different from that close to bulk solution, which might correlate with formation of hydro-bromo-complex at the interface.

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