In Situ Analysis of Pitting Corrosion in Artificial Crevice of Stainless Steel by X-ray Absorption Fine Structure

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A new technique by XAFS (X-ray Absorption Fine Structures) and XANES (X-ray Absorption Near Edge Structures) has been developed for in situ observation of metal corrosion. XAFS and XANES spectra were obtained with a special electrochemical cell to elucidate pitting for stainless steel. A sheet of stainless steel was attached below a reservoir of a specific aqueous environment with thin films. The solution in the reservoir attached to the metal thorough the film, and the solution inside the film corresponds to an artificial pit. X-ray beams pass through the film containing the solution, and XAFS and XANES measurements were performed in a transparent geometry with keeping the specimen at a pitting potential. Measurements were performed for Cr–K, Mo–K, Cl–K and Br–K edges, and changes of concentrations and coordination states of ions were successfully obtained as a function of the distance (d) from the metal/solution interface.

Concentrations of chromium and bromide ions inside the artificial crevice of Fe–18Cr–12Ni–2Mo (mass%) alloy shows a linear dependence on the distance d. Structures of bromide ion were changed with positions; the distance between bromide ion and the nearest-neighboring ion at a position near the interface was shorter than that at a position far from the interface. This indicates the formation of hydrobromo-complex near the metal/solution interface.

The state of molybdenum inside the artificial crevice of Fe–18Cr–12Ni–2Mo (mass%) alloy was investigated using two solutions: LiCl and LiBr. The formation of the [MoO_4(H_2O)_2]^{2-} octahedra was observed in both solutions, but there was observed a significant difference in networking of the octahedral. In LiCl solutions it was similar to that of molybdate ions (MoO_4^{2-}), but in LiBr it was rather different form that of molybdate ions. This shows that the favorable effects of molybdenum can be attributed to the formation of MoO_4^{2-} network near the interface.

KEY WORDS: crevice corrosion; X-ray absorption fine structure; X-ray absorption near edge structures; stainless steel; bromine; chlorine; chromium; molybdenum; ion coordination.

1. 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.\(^1,2\) 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 behavior of stainless steel. X-ray absorption and fluorescence techniques have been applied to in situ chemistry studies of localized corrosion.

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 stabilizes the growth of localized corrosion.\(^2\) 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,\(^3\) but the pH values calculated on the basis of the reaction of hydrolysis are considerably greater than those found experimentally. It was observed a decrease in pH within artificial pits to 0.6 or 0.8 and an increase in content of chloride ions (6 M) for Type304L stainless steel,\(^4\) though an estimated value is about pH \(\approx 1.6\) calculated based on the solubility. This enhancement of pH is reportedly explained by a formation of hydrochloro-complex of cations caused dissolution of metal,\(^5,6\) but there has been little direct observation of it.

Another important issue was effect of additional elements on pitting. Molybdenum is one of the essential elements showing favorable effects on the pitting resistance.\(^2\) Many studies devoted to the influence of molybdenum on the pitting susceptibility of steels, but the exact protection mechanism has not yet been sufficiently explored. In most work, the effect of molybdenum is attributed to formation of complex compounds enhanced by molybdenum: such as metal oxide, oxyhydroxide, and so on.\(^2\) These compounds
are easily expected to be susceptible to experimental conditions, and in situ observation would be essential for understanding the effects of molybdenum. However, because of experimental difficulties, there have been few reports on direct observation of structures of ions inside pits. Recently X-ray absorption and fluorescence measurement has become one of powerful methods for the in situ study of chemical and physical changes during electrochemical and corrosion processes. It was observed dissolved metal ion concentration inside artificial pit and content of salt films for Type304 SS by using in situ X-ray microprobe technique.7,8)

In this study, we have tried to develop an in situ observation technique by XAFS (X-ray Absorption Fine Structures) and XANES (X-ray Absorption Near Edge Structures) measurements conducted on a special electrochemical cell to elucidate pitting in order to measure a change of concentration and coordination states of dissolved metal ions and aggressive anions near the solution/steel interface. 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 and XANES measurements.

2. Experimental

In situ observation techniques using XAFS have been newly developed.9) Figure 1 shows schematic diagram of the electrochemical cell for in situ XAFS and XANES measurements. Sheets of Fe–18%Cr–12%Ni–2%Mo and Fe–18%Cr–20%Ni–5%Mo sandwiched by Kapton films with epoxy glue were attached to a plastic reservoir containing various kinds of solution. The size of sheets is 10 mm width×30 mm length with a thickness of 0.1–1.0 mm which is determined based on the kind of element and its concentration of solution in the crevice. A potential of the steel was controlled by a potentiostat at 0.8 V vs. Ag/AgCl reference electrode to corrode entire cross-section of the sample uniformly. After dissolution of the sheet, the depth of the crevice reached a few mm; XAFS and XANES measurements were then carried out. All XAFS and XANES spectra were measured by transmission geometry shown in Fig. 1. Beam size was 0.1 mm height×10 mm width. The electrochemical cell attached with a stage moving X–Z direction by a stepping motor was moved along Z direction in order to carry out XAFS and XANES measurement at different positions of d(z) from the dissolving interface to the bulk solution. XAFS and XANES measurements were also carried out for LiBr, LiCl solutions, and solutions and powders of chromium chlorides, bromides, oxides, hydroxides as references. XAFS and XANES measurements were performed at beam lines BL-7C and BL-12C at the Photon Factory, KEK, 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 0.8 mm depth; the sheet was Fe–18%Cr–12%Ni–2%Mo and the solution was 1 M LiBr. Concentration was calculated from absorption normalized by standard specimens. When an X-ray beam passes through a medium, its intensity is attenuated exponentially:

\[ I = I_0 \exp(-\mu t) \] .............................(1)

where \( \mu \) is the linear absorption coefficient and \( t \) is the thickness of the media. When the media contains more than a single element, \( \mu \) can be expressed as follows:

\[ \mu = \sum C_i \mu_i \] .............................(2)

\( \mu_i \) and \( C_i \) are the linear absorption coefficient and the molar concentration of the element \( i \), respectively. CrBr3, CrCl3, LiBr, and Na2MoO4 solutions with concentrations of 0.05–5 M were used as the standard specimens. The absorption of the standard specimens was measured for Cr, Br, Cl and Mo edges using the in situ cell under the same conditions as in situ measurements. Absorption inside the pit was measured by in situ experiment; the absorption was normalized by the results of the standards using Eqs. (1) and (2), and the concentration gradient inside the pit was determined.

Figure 2 shows concentration of chromium ion inside the artificial crevice. Concentration of chromium ion was decreased linearly from the dissolving interface to crevice mouth. Concentration of chromium near the interface was found to be about 0.55 M. Estimation of chromium ion con-
centration was based on the measurement of for CrBr₃ solution with different concentration. It was reported that 1.08 M of chromium ion was close to the dissolving interface of an artificial pit for Type304 SS in 0.5 M HCl and 0.5 M NaCl solution, higher than that observed in this study. In the reported 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. Solubility of metal chlorides were estimated as 5.02 M, but 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 2.5 mm depth.

Figure 3 shows concentration of bromide ion inside the artificial crevice. Concentration of bromide ion was also decreased almost linearly from the dissolving interface to crevice mouth. Concentration of bromide at the interface was estimated as about 10 M. Assuming MB₂ as metal bromide, solubility of salt film would be 5 M, which is almost same as that observed for metal chloride. Another source quotes the solubility of FeCl₃ and FeBr₃ at 10°C as 64.4 and 109 g/cm³ or 5.08 and 5.05 M, respectively. From these experimental results, difference of chromium ion concentration at the dissolving interface between in chloride and in bromide shown in the present study should relate to content of chromium in salt films on stainless steels; the content of chromium ion was higher in metal chloride than that in metal bromide.

As shown in Figs. 2 and 3, In the present experiment, concentrations of chromium and bromide ions inside the artificial crevice showed slight deviation form the linear dependence. This is consistent with the other study which showed higher concentrations near the interface and it was reportedly caused by lower diffusion coefficient of ions near the interface. In this study, the deviation was not so clear as reported, which can be attributed to a relatively larger beam size of 0.1 mm in height.

3.2. Coordination States of Chromium and Bromide Ions

In situ XAFS and XANES measurement of chromium and bromide ions were carried out at different positions d(z), from positions near the dissolving interface and near the bulk solution. Each spectrum was analyzed by the REX program (Rigaku Co.). XAFS and XANES spectra of standards specimens were also measured in the same conditions for comparison: LiBr, LiCl, CrBr₃, CrCl₃ solutions with some molar concentration and CrBr₃, CrCl₃ salts etc.

Figure 4 shows a typical results of in situ XAFS measurement : XAFS spectra measured and calculated curve fitting for bromide at d(z)=0.2 mm. The best result of curve fitting was obtained by assuming that bromide is coordinated by Cr and O. At d(z)=3.5 mm, close to bulk solution, on the other hand, the best fitting was obtained for the model that bromide is coordinated simply by oxygen.

Figure 5 shows the Fourier transforms of Cr–K edge spectra of in situ measurements at different d(z) positions: d(z)=0.2 mm (near the interface), d(z)=0.8 mm and d(z)=1.3 mm (close to the bulk solution). It is apparent from the results obtained that Cr–K edge spectra 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. Based on their model it is presumable that Cr–K 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 de-
tect the change of 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. Fourier transforms of spectra of bromide ions at different $d(z)$ position are shown in Fig. 6. In contrast with the spectra of chromium, Br–K edge spectra differs as $d(z)$ position. The peak shifts toward a larger $R$ as the distance $d(z)$ increases.

These results show the change of the complex structure inside the pit. Figure 7 shows a schematic illustration of change of ion-complex structures inside the artificial crevice suggested by this study.

3.3. Effects of Molybdenum on Pitting

In situ measurement for chromium ion was carried out to investigate concentration inside the artificial crevice of 5.5 mm depth; the sheet was Fe–18%Cr–20%Ni–5%Mo and the solution was 1 M LiCl and LiBr. XAFS and XANES spectra were measured for determination of the molybdenum state inside the artificial crevice.

XAFS and XANES spectra of a Na$_2$MoO$_4$ solution, which was reported to play a significant role, were measured using the in situ system in the same conditions for comparison. Figure 8 shows (a) Fourier transforms of XAFS spectra at Mo-edge and (b) XANES spectra at Mo–K edge of 0.1 M Na$_2$MoO$_4$ solution. The first peak in Fig. 8(a) can be attributed to two types of coordination of $O_2$ and $H_2O$ towards Mo ions. In other word, MoO$_4^{2-}$ ions form the network of distorted octahedra of [MoO$_4$(H$_2$O)$_2$]$^{2-}$, which is consistent with the result by XAFS and anomalous X-ray scattering. The network of [MoO$_4$(H$_2$O)$_2$]$^{2-}$ octahedra attributes to the pre-peak around at $E$=20 000 eV in XANES spectra as shown in Fig. 8(b), which is found only in Na$_2$MoO$_4$ solution and not in MoO$_2$ and MoO$_3$ oxides.

Figure 9 shows XANES spectra at Mo-edge of in situ measurement for LiCl and LiBr at $d(z)$=0.1 mm, and a Na$_2$MoO$_4$ solution. In situ observation has successfully shown that the state of molybdenum in pitting; the edge energies of the pre-peak around at $E$=20 000 eV both in LiCl and LiBr are quite similar to that of Na$_2$MoO$_4$, showing
the formation of a complex similar to the network of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ octahedra. However the intensities of the pre-peak around at $E=20,000$ eV show significant difference between in LiCl and LiBr. The intensity was stronger in LiCl and LiBr. This shows that the complex formed in the crevice in LiCl is similar to that of the network of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ octahedra but it has a different configuration in LiBr. Therefore, it is expected the formation of the network of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ octahedra is depressed in LiBr, which was also shown by analysis of XAFS spectra.

The depression of formation the network of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ may play a significant factor of less effectiveness of Mo in LiBr than in LiCl. It was shown that stainless steel of Fe–18%Cr–(12–15)%Ni–(0–5)%Mo shows a larger increase in pitting potential in chloride than in bromide with increased Mo content, and the initiation process was supposed to play an important role in pitting.\(^{14}\) It is also reported that a small amount of Ni addition changes the network configurations of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ octahedra in aqueous solutions.\(^{13}\) The results of in situ observation suggests that bromine, which is known as one of elements easily “bridging” atoms, occupies a specific site in the network of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ octahedra and depress the evolution of the network. Thus, the favorable effect of molybdenum could be attributed to the formation of the network of $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$; near the interface the form of a single $[\text{MoO}_4(\text{H}_2\text{O})_2]^2-$ octahedron may not be effective in prohibition of pitting.

4. Conclusions

(1) An in situ observation technique by XAFS (X-ray Absorption Fine Structures) and XANES (X-ray Absorption Near Edge Structures) has been developed for observation of solution chemistry inside the artificial crevice. Concentrations and coordination state of chlorine, bromine, chromium, and molybdenum ions inside the artificial crevice were successfully investigated by in situ XAFS and XANES measurement with a special electrochemical cell.

(2) Concentration of chromium and bromide ions were decreased lineally from dissolving interface to bulk solution inside the artificial crevice of Fe–18Cr–12Ni–2Mo alloy. Concentration of chromium and bromide ions at the interface was estimated as 10 M and 0.55 M, 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.

(4) The state of molybdenum inside the artificial crevice of Fe–18Cr–20Ni–5Mo alloy was investigated for two solutions: in LiCl and LiBr. The structures near the interface showed a significant difference; it was similar to that of molybdate ions ($\text{MoO}_4^{2-}$) in LiCl but was rather different from a molybdate ion ($\text{MoO}_4^{2-}$) in LiBr.

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