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# State of Chlorine in Rusts Formed on 3 mass% Ni-added Weathering Steel (II)

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## Introduction

Improvement of the corrosion resistance of steel without coating is very important from the viewpoint of life-cycle assessments of materials. Weathering steel (WS) has been developed for the application to bridges without coating. WS, containing a 0.3-0.7 mass% Cr and Cu, forms a protective rust layer after a few years of corrosion under atmosphere and shows a good corrosion resistance [1,2].

However, a conventional WS shows a good corrosion resistance only when it is exposed under atmosphere containing little air born salt. A new type of WS ("the advanced WS") was developed; the addition of 3 mass % Ni increases the corrosion resistance by a factor more than 10 [3]. In this study, the mechanism has been investigated using X-ray absorption fine structure (XAFS) with a special attention to chlorine atoms which are thought to enhance corrosion.

## Experiments

The advanced WS was prepared and has been exposed in costal atmosphere (Kimitsu, Chiba, Japan) for 9 years. Microstructures of cross sections near the surface were investigated by TEM and EPMA. Atomic structures of rusts were analyzed by XRD, TEM and XAFS. XAFS spectra of rusts were measured by total electron yield and X-ray fluorescence[4]. XAFS measurements were carried out at BL-11B at PF, KEK, Tsukuba, Japan. XAFS spectra of reference specimens were also measured for synthesized β-FeOOH, $FeCl_3$ and NaCl.

## Results and Discussion

After the corrosion for 9 years, enrichment of nickel and cupper was found in the inner part of the protective rust formed on the surface of 3Ni-WS. Concentration of chlorine in the inner layer was much lower than that of the outer layer where concentration of nickel and cupper is lower than that of the inner layer. The "protective" inner layer is composed of fine grains as small as a few nm. Protective inner rusts formed on the advanced WS "breathe out" chloride ions [5,6].

XAFS measurements were carried out in order to investigate states of chloride ions that were breathed out from the interface beween the inner rust and the iron substrate. X-ray beam with a size of ca. 1×1 mm irradiates the surface of the outer layer containing chloride ions. XANES spectra around Cl-*K* edge were obtained by measuring X-ray fluorescence (Fig. 1). The results for reference specimens are also shown in Fig.1. It has been shown that features of XANES and edge energies are similar to each other among specimens. This shows that chloride ions in the rust are basically in an ionic state.

There are some differences in a pre-edge region around E=2820 eV in Fig.1. Intensities of the pre peaks are strong for the rust, β-FeOOH and $FeCl_2$. This peak may attribute to Fe-Cl bonding. Therefore chloride ions in the rust may occupy a site near iron atoms. This site is different from the one in β-FeOOH phase. These results suggest that chloride ions in the rust have several states; whereas only one state of chloride ions is reported for an ideal phase of β-FeOOH.

Some states of chloride ions in the rust formed on the advanced WS may be less active in corrosion than a conventional WS. This may be caused by formation of $Fe_3O_4$ ($Fe_2NiO_4$), which produces a negative charge in the inner layer [7].

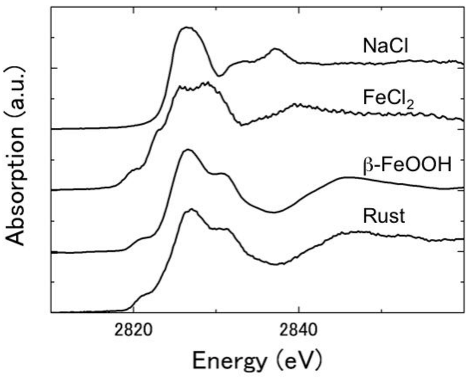

Fig.1 XANES spectra around Cl-*K* edge.

## References

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