

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

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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 in atmosphere and shows a good corrosion resistance [1,2].

However, a conventional WS shows a good corrosion resistance only when it is exposed to 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 chloride ions which are thought to enhance corrosion.

Experiments

The advanced WS was prepared and has been exposed in coastal 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 at Cl-K edge were measured by total electron yield and X-ray fluorescence[4]. XAFS measurements were carried out at BL-11B at PF, KEK, Tsukuba, Japan.

Results and Discussion

After the corrosion for 9 years, enrichment of nickel and copper was found in the inner part of the protective rust formed on the surface of the advanced WS. Concentration of chlorine in the inner layer was much lower than that of the outer layer, whereas concentration of nickel and copper 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 [5,6,7].

XAFS measurements were carried out in order to investigate states of chloride ions that were breathed out from the interface between the inner rust and the iron substrate[6,7]. Figure 1 shows XAFS spectra around Cl-K edge of the rust and reference specimens: synthesized β -FeOOH, FeCl₃, and NaCl. The spectra of specimen is similar to that of β -FeOOH, whose structure is shown in Fig.2. It is expected that chloride ions in the rust form networking with Fe(O,OH)₆ octahedrons [8,9].

Detailed analysis has shown that energies of Cl-K edge differ slightly among specimens [8]. That of the inner rust is about 0.9eV higher than those of the outer rust and NaCl. It is expected that chloride ions in the inner is more stable in the "Fe(O,OH)₆ network [1]" than those in the outer rust. This can be attributed to the high performance of the advanced WS [9].

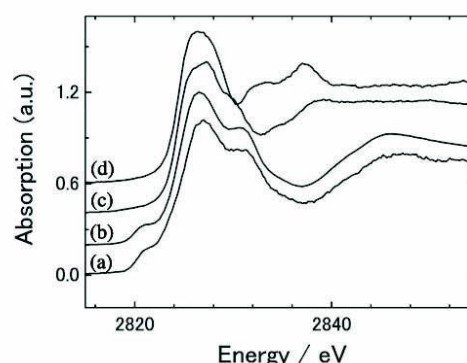


Fig.1 XANES spectra around the Cl-K edge: (a) the specimen after 9 years exposure, (b) β -FeOOH, (c) FeCl₃ and (d) NaCl.

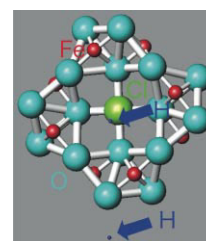


Fig.2 Atomic structure of β -FeOOH. A chloride ion (green) is located in the center of Fe(O,OH)₆ octahedrons.

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