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In situ XAFS observation of corrosion during wet-dry cycles

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Introduction

Improvement of corrosion resistance of steels without coating is important from the viewpoint of life-cycle assessments of structures. Weathering steel (WS) has been developed for such applications especially to bridges. WS, containing a 0.3-0.7 mass% Cr and Cu, forms a protective rust after a few years of exposure to atmosphere to show 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. Thus the advanced WS was developed; the addition of 3 mass % Ni increases the corrosion resistance to a large extent [3]. The mechanism has been investigated using various techniques including synchrotron radiation [4-6]. In this study, effects of nickel and chlorine were studied by *in situ* XAFS observation during wet-dry cycles.

Experiments

In situ XAFS measurements were performed for a block specimen of the advanced WS (3.0Ni-0.4Cu-Fe in mass %). The surface of the specimen was covered with a thickness of *ca.* 20 µm of diluted artificial seawater and then dried in air at 300 K. One wet-dry cycle was about 90 min. XAFS spectra around Ni K-edge were measured in the florescence geometry using a 19-element SSD at BL-12C [7] at PF, KEK, Tsukuba, Japan. XAFS spectra around Cl K-edge were measured in the florescence geometry by total electron yield and X-ray fluorescence at BL-9A [8] and BL-11B [9] at PF, KEK, Tsukuba, Japan.

Results and Discussion

XAFS spectra were measured during the wet-dry cycles. Figure 1 shows the radial distribution function (RDF) around Ni obtained by *in situ* measurements. Before corrosion begins, nickel and iron atoms are in a solid solution (an alloy). As corrosion progresses, RDF around nickel shows additional peaks as shown by the arrows in Fig. 1. This indicates that nickel atoms substitute iron atoms in the “16d” sites in Fe_3O_4 to form Fe_2NiO_4.

Formation of Fe_2NiO_4 at an early stage of corrosion changes properties of rust. Rust formed on the advanced WS shows a negative charge when wet, whereas that on the conventional WS shows a positive charge [3,5].

This unique feature of rust prevents chloride ions approaching the rust/steel interface [5]. Change in XAFS spectra around Cl K-edge showed that chloride ions changed from a state similar to NaCl into that of β-FeOOH during the wet-dry cycles. This shows that chloride ions which are forced away form the rust/steel interface by Fe_2NiO_4, are stabilized in a netowork of $Fe(O,OH)_6$ octahedra and forms a β-FeOOH (Fig.2).

In situ XAFS observation successfully showed crucial information on the good corrosion resistance of the advanced WS. It can be attributed to formation of Fe_2NiO_4 and β-FeOOH during wet-dry cycles.

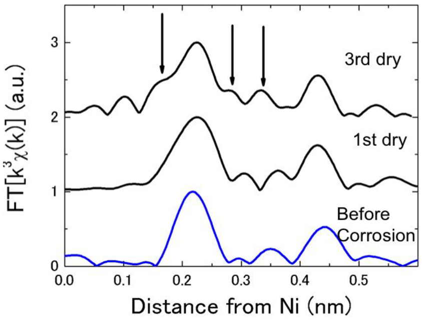

Fig.1 RDF around Ni obtained by *in situ* measurements.

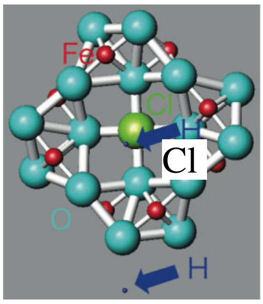

Fig.2 Atomic structure of β-FeOOH. A chloride ion (green) is located in the center of $Fe(O,OH)_6$ octahedra.

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