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$Fe(O,OH)_6$ Network Nanostructure of 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 effects of nickel -addition.

Experiments

3 mass % Ni-added WS (3Ni-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 and TEM and XAFS.

XAFS *in situ* measurements were performed for a block specimen. 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 of rusts were measured in the florescence geometry using a 19-element SSD [4]. XAFS measurements were carried out at BL-9A and 12C at PF, KEK, Tsukuba, Japan.

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 (Fig.1).

The inner layer was found to be composed of fine grains of α-FeOOH and Fe_2NiO_4 as small as 10-20 nm in radius by TEM and XAFS [5,6].

XAFS *in situ* measurements were performed, in order to investigate formation of Fe_2NiO_4 phase at an early stage of corrosion. XAFS spectra were measured during the wet-dry cycles. Figure 2 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. 2. This indicates that nickel atoms substitute iron atoms in the "16d" sites in Fe_3O_4 to form Fe_2NiO_4.

The good corrosion resistance against air-born salinity is attributed to the unique structures of the protective rusts composed of fine α-FeOOH and Fe_2NiO_4. Formation of Fe_2NiO_4 results in negative charge in the inner layer, which prevents chloride ions penetrating from the outer into the inner layer and enrichment of chloride ions is suppressed [7].

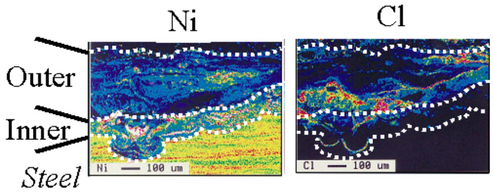

Fig.1 Concentration of Ni and Cl at the cross-section near the rust/steel interface

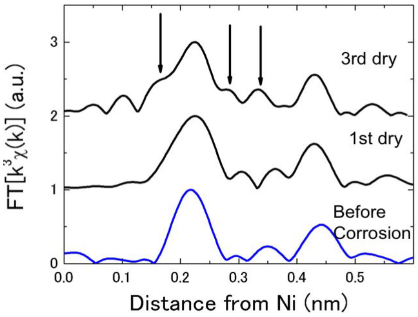

Fig.2 RDF around Ni obtained by *in situ* measurements.

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