Fe(O,OH)$_6$ network nanostructure of rusts formed on weathering steel

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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. Surprisingly "weathering steel" 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.

In order to make clear the corrosion resistance mechanism, the atomic level structure of rust is of great interest. The rust mainly consists of FeOOH, typically α-FeOOH and γ-FeOOH. Their structures are composed of FeO$_6$ octahedrons and intercalated hydrogen (Fig.1). In this study, the change of nanostructures of rusts during corrosion was investigated using x-ray absorption fine structure (XAFS) with a special attention to effects of additional elements.
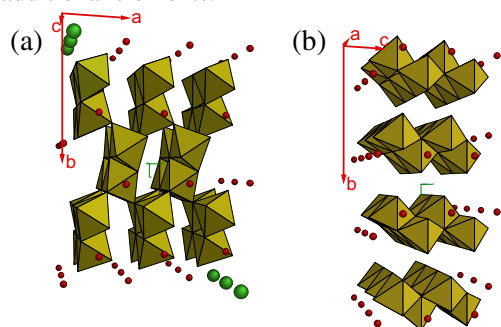

Fig.1 Crystal structures of (a)α-FeOOH and (b)γ-FeOOH.

Experiments

Fe-5 mass % Cr alloy (CR) were prepared and corrodes in sea water and in air for different periods. Rusts formed on the steel surface were analyzed by XAFS, XRD and TEM. Colloidal rusts, which was formed at the sample surface in seawater for several days, were analyzed by a special XAFS cell for a liquid sample. XAFS spectra of rusts formed on the sample surface exposed for a long time were measured in the reflection geometry using a 19-element SSD[1]. XAFS measurement were carried out at BL-12C at PF, KEK, Tsukuba, Japan.

Results and Discussion

Figure 2 shows radial distribution functions (RDF) of rusts formed on the surface under different conditions: 1) CR2W(WET): the colloidal rust formed after corrosion for 2 weeks in seawater, 2) CR2W(DRY): the dried rust of 1), and 3) CR15Y: the rust formed on the CR surface exposed to air indoors for 15 years. The RDF for crystalline α-FeOOH is also shown in Fig.2. The first peaks located at about 0.15 nm in the RDF's are attributed to the first nearest neighbor (1st NN) correlation of Fe-O. The peaks at about 0.27 and 0.32 nm in RDF's

correspond to 2nd NN and 3rd NN correlation of Fe-Fe and Fe-O, respectively. As shown by the 1st NN peaks in all rust samples, the octahedron of Fe(O,OH)$_6$ units are formed in these rusts. However, the heights of the 2nd NN and the 3rd NN peaks in the rusts are weaker than those in α-FeOOH. This suggests that the periodic arrangement of Fe(O,OH)$_6$ units is slightly disordered, compared to that of crystalline α-FeOOH having a long-range order.
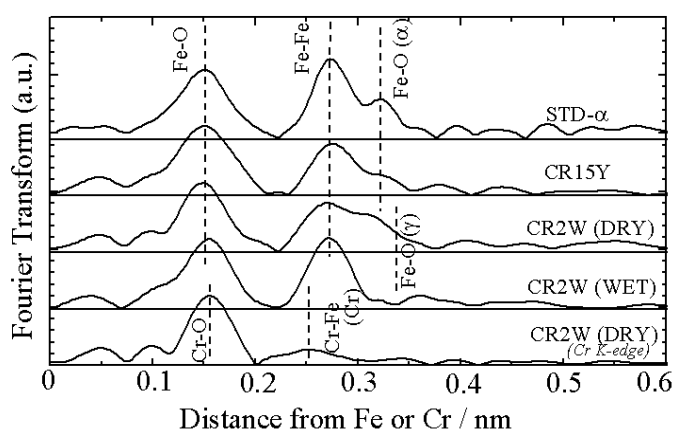

Fig.2 RDF around Fe and Cr of the rusts.

Small but significant differences among these samples were found in the 3rd NN peak region; the 3rd NN peak height in CR15Y is higher than that in CR2W(DRY) and CR2W(WET). In addition, the 3rd NN peak positions in CR2W(WET) and CR2W(DRY) seem to be close to that in γ-FeOOH, while the 3rd NN peak position of CR15Y is near that in α-FeOOH. These results suggest that the Fe(O,OH)$_6$ network of the rust changes depending on corrosion conditions such as its atmosphere and exposing time.

RDF around Cr shows a significant difference. The position of the 2nd NN peak is about 11% shorter than that of around Fe, indicating that Cr occupies a different site in the Fe(O,OH)$_6$ network in the rust.

Additional elements are expected to cause slight but significant differences in evolution of the Fe(O,OH)$_6$ network during corrosion, resulting in different morphology at the final stage. [2].

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