

Local Structure Analysis of the Rust Layer of Weathering Steel

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Introduction

A rust layer formed on a low-alloy steel surface has generally protective ability against corrosives in the atmosphere. The rust layer on weathering steel, which contains small amounts of Cr, P, and Cu, possesses strong protective ability, approximately twice as high as that of carbon steels. The main constituents of the protective rust layer on weathering steel are believed to possess the structure of $\alpha\text{-(Fe}_{1-x}\text{Cr}_x\text{)OOH}$, Cr-goethite[1], which may be formed due to the concentration of Cr in the rust layer after long-term exposure.

It was demonstrated that the increase in Cr concentration in the Cr-goethite results in dense aggregation of small crystals[2]. It was also pointed out that the Cr-goethite possesses cation selectivity[3], therefore impedes the penetration of aggressive corrosive anions such as Cl^- and SO_4^{2-} . These properties can explain the protective ability of the rust layer contains the goethite type phase.

In this work, we measured and analyzed XAFS spectra of Cr-goethite for the aim of discussing the role of Cr on the structure and protective performance of the rust layer.

Experimental

The rust layer examined was formed on the weathering steel containing 0.12C-0.39Si-0.9Mn-0.008P-0.006S-0.36Cu-0.61Cr-0.22Ni-0.014Nb (in mass%) exposed to the atmosphere underneath the girder of a bridge at Yokkaichi, Japan, for 17 years. We also prepared artificial 3mass%Cr-goethite powders for comparison.

The experiments were performed at BL-27B of the Photon Factory(KEK-PF). The spectra of the Fe and Cr K-edges were obtained in the transmission and fluorescence detection modes, respectively.

Results and Discussion

The XAFS spectra of different samples showed a similar feature with the X-ray energy. The oxidation state of Cr in the goethite structure can be estimated to be trivalent, Cr^{3+} , since the obtained absorption edge is 5995eV, i.e., 6eV positive compared to that for metallic Cr. In addition, a well-known pre-edge peak at 5985eV for hexavalent Cr^{6+} ion was not observed in the XAFS spectra. This indicates that no Cr^{6+} is contained in the goethite structure.

Figure 1 shows the Fourier transform (FT) of the Cr K-edge EXAFS spectrum of the rust layer of the weathering steel, and those of the Fe and Cr K-edge EXAFS spectra

of the artificial Cr-goethite. The strongest peak in FT around Cr^{3+} of the rust layer appears at approximately 0.14nm, the phase-shift corrected distance of which is 0.20nm. Because the ionic radius of Cr^{3+} is about 0.07nm, this strongest peak can originate from the nearest neighbor O^{2-} with an ionic radius of 0.13nm. In addition, it should be noted that less correction was obtained above 0.20nm in FT around Cr^{3+} , compared with FT around Fe^{3+} in the artificial Cr-goethite. Therefore, Cr is not positioned simply at the Fe lattice point as a substitute element.

The goethite structure is characterized by the network of $\text{FeO}_3(\text{OH})_3$ octahedra which consists of double chains of octahedra alternating with double chains of vacant site. Experimental results suggest that Cr^{3+} is coordinated with O^{2-} and located in the double chains of vacant sites in the Cr-goethite. If Cr^{3+} forms complex ions with a plural number of O^{2-} , the CrO_x^{3-2x} complex ion can provide negative charge to the goethite structure exhibiting cation selectivity.

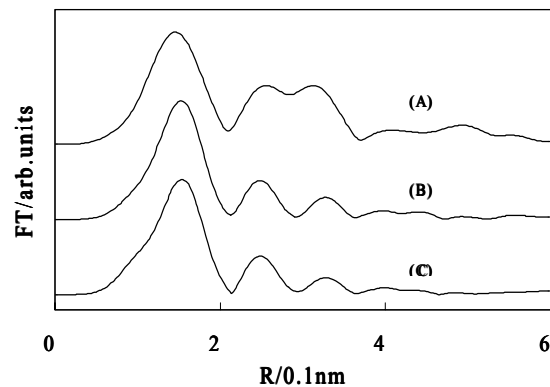


Fig.1 Fourier transformation of k^3 weighted of (A) 3mass%Cr-goethite at Fe K-edge, (B) 3mass%Cr-goethite at Cr K-edge and (C) the rust layer of weathering steel.

References

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