9A, 12C

Fe(O,OH)$_6$ Network Nanostructure of Rusts Formed on 3 mass% Ni-added Weathering Steel

Masao KIMURA*[1], Noriaki Ohta[2], Hiroshi KIHIRA[3], and Masaharu NOMURA[4]
[1] Adv. Tech. Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan
[2] Nippon Steel Technoresearch, Chiba 293-8500, Japan
[3] Steel Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan
[4] Photon Factory, KEK, Tsukuba, Ibaraki, 305-0801, Japan

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].

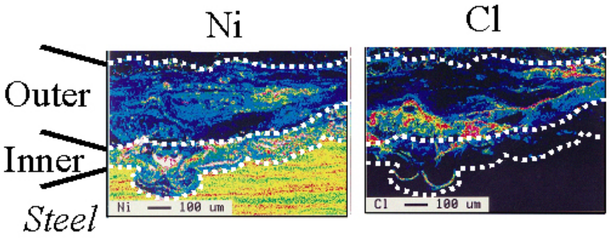
However, a conventional WS shows a good corrosion resistance only when it is exposed under atmosphere containing little air born salt. A new type of WS was developed; the addition of 3 mass % Ni increases the corrosion resistance by a factor more than 10 [3]. In this study, the mechanism has been investigated 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, TEM and XAFS. XAFS spectra of rusts were measured in the reflection 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_3O_4 as small as 10-20 nm in radius by TEM.

XAFS measurements were carried out for the inner and the outer layers of rust and for reference specimens (powders of Fe_3O_4, FeOOH and NiO). Figure 2 shows XAFS oscillation of specimens.

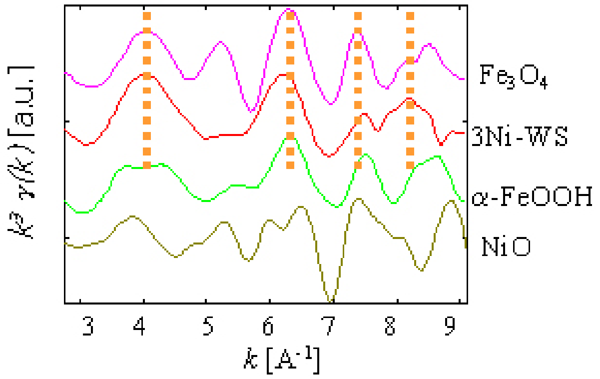


Fig.2 XAFS oscillation of specimens: (from the top) Fe_3O_4 at Fe-K edge, the inner layer of 3Ni-WS at Ni-K edge, FeOOH at Fe-K edge, and NiO at Ni-K edge.

XAFS oscillation of the inner rust, shown by dotted line in Fig.2, corresponds to the octahedral site of the spinel structure of Fe_3O_4. Existence of NiO was not observed by TEM and XRD. These results show that nickel atoms in the rust substitute the octahedral site of Fe_3O_4 and forms Fe_2NiO_4 ferrite.

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_3O_4 (Fe_2NiO_4). Formation of Fe_3O_4 (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 [5].

References

[1] M. Kimura et al: J. Japan Inst. Metals, **66,** 166 (2002).
[2] M. Kimura et al: ISIJ International, **42,** 1534 (2002).
[3] H. Kihira et al: Zairyo-to-Kankyo, **49,** 30 (2000).
[4] M. Nomura: J. Synchrotron Rad., **5,** 851 (1998).
[5] M. Kimura et al: JIM Transactions (submitted,2003)

* kimura@re.nsc.co.jp