

State of Chlorine in Rusts Formed on 3 mass% Ni-added 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. 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 chlorine which is thought to enhance corrosion.

Experiments

3 mass % Ni-added WS (3Ni-WS) was prepared and has been exposed in costal atmosphere (Kimitsu, Chiba, Japan) for 9 years under two conditions; the specimen experienced (A) a short and (B) a long time of corrosion. β -FeOOH, as a reference, was prepared by hydrolysis of FeCl_3 . 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 by total electron yield [4]. XAFS measurements were carried out at BL-11A at PF, KEK, Tsukuba, Japan.

Results and Discussion

After the corrosion for 9 years, enrichment of nickel and copper 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 copper is lower than that of the inner layer. The "protective" inner layer is composed of fine grains as small as a few nm.

XAFS measurements were carried out for the inner and the outer layers of rust and for a reference powder of β -FeOOH. Figure 1 shows XANES spectra around Cl-K edge. It has been shown that energies of edge are different among specimens; it is the largest for the synthetic powder of β -FeOOH and the lowest for 3Ni-WS(A).

The β -FeOOH contains a lot of chlorine which become free Cl^- ions when the specimen gets wet. Its high edge-energy can be attributed to a weak bonding of chlorine and " $\text{Fe}(\text{O},\text{OH})_6$ network [1,2]". This is also the case for the outer layer of 3Ni-WS(B). However, the inner layer of 3Ni-WS(A) shows a lower edge-energy, suggesting that chlorine is more tightly bound to the network, which may be close to a crystalline phase of β -FeOOH (Fig.2).

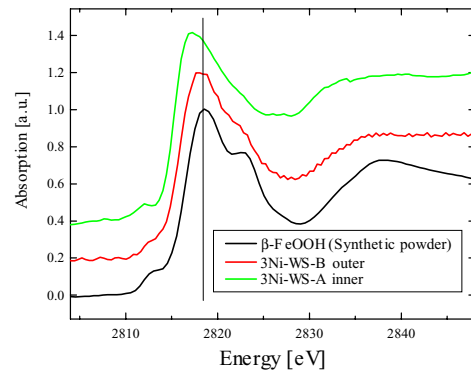


Fig.1 XANES spectra around Cl-K edge: (from the top) β -FeOOH (synthetic powder), 3Ni-WS(B), and 3Ni-WS(A).

It is expected that the chlorine in the rust formed on 3Ni-WS is less active in corrosion than a conventional WS. This may be caused by formation of Fe_3O_4 (Fe_2NiO_4), which produces a negative charge in the inner layer [5]. This means that the state of chlorine and its effects on corrosion can be controlled by an alloy designing.

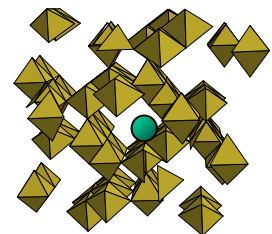


Fig.2 Atomic structure of a crystalline β -FeOOH. A green sphere shows a chlorine atom.

References

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