Available online at www.sciencedirect.com

SCIENCE DIRECT®

Corrosion Science 47 (2005) 2531–2542

CORROSION SCIENCE

www.elsevier.com/locate/corsci

Influence of cations and anions on the formation of β-FeOOH

T. Kamimura [a,*], S. Nasu [b], T. Segi [b], T. Tazaki [b],
H. Miyuki [a], S. Morimoto [b], T. Kudo [a]

[a] *Corporate Research and Development Laboratories, Sumitomo Metal Industries, Ltd., Amagasaki, Hyogo 660-0891, Japan*

[b] *Division of Materials Physics, Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

Received 29 August 2004; accepted 16 October 2004

Abstract

In the presence of cations such as Cr^{3+}, Cu^{2+} and Ni^{2+}, and anions such as SO_4^{2-} and NO_3^-, precipitation of β-FeOOH from Fe^{3+}-solution containing Cl^- by hydrolysis have been investigated by means of X-ray diffraction technique (XRD), Mössbauer spectroscopy (MS) and transmission electron microscopy (TEM). XRD peaks of β-FeOOH were broadened when the cations were added as sulfates, and this tendency for Cr^{3+} was significantly observed. When the cations were added as nitrates, there was no significant change in XRD peaks. Inductively coupled plasma (ICP) analysis showed that only Cr added as sulfate was contained in β-FeOOH. Ni and Cu added as sulfates, and any cations added as nitrates were not contained in it. When β-FeOOH was synthesized with Na_2SO_4, the XRD peaks were broadened. XRD-peak broadening was mainly caused by the coexistence of SO_4^{2-} ion. The incorporation of cations in β-FeOOH is affected by coexistent anions, and the XRD-peak broadening is caused by not only cations but also anions. This behavior has been discussed in association with the stability of Fe^{3+}-complexes in the solution.

---

[*] Corresponding author. Tel.: +81 6 6489 5754; fax: +81 6 6489 5757.
E-mail address: kamimura-tky@sumitomometals.co.jp (T. Kamimura).

0010-938X/$ - see front matter

doi:10.1016/j.corsci.2004.10.014

Keywords: Steel; XRD; TEM; Mössbauer spectroscopy; Rust

1. Introduction

Weathering steels are low alloy steels containing small amounts of Cr, Cu, Ni and P. They are standardized as G 3114 in Japanese Industrial Standards [1] and A588 in American Society for Testing and Materials [2], and have been applied for so many steel structures on land such as bridges because of its superior weatherability. It has been reported that the corrosion products (rust) are dense and tightly adhere to steel surfaces and therefore act as protective coatings. Because of the protectiveness of the rust layer formed on weathering steels, it has been investigated by means of various techniques to elucidate the mechanism of its superior weatherability [3–23]. It is, however, well known that under environments where large amounts of sea salt particles come by air or deicing salts are sprinkled, the so-called protective rust layer is not formed; that is, even weathering steel does not show its superior performance, especially under rain-protected conditions or sheltered conditions where salts accumulate. The characteristics of rust layers formed in such environments are coarse, flaky and less adherent, and therefore they do not show the expected protectiveness. In such rust layers, β-FeOOH is often contained which is not observed for rust formed in industrial and rural environments [24]. It has been reported that the mass fraction of β-FeOOH is proportional to the corrosion loss [25], and these results may indicate why the rust layer is coarse and flaky, and not protective under the existence of large amounts of air–borne salts or deicing salts. Recently, Ishikawa's group has synthesized FeOOH in the laboratory, and reported the influence of the additional elements of Cr, Cu, Ni and Ti, which are added to steels to improve weatherability, on the structures and morphologies [26–30]. However, the formation mechanism of β-FeOOH is not well understood yet.

Under the environments where chloride ion exists, the steel corrodes, and Fe is dissolved as Fe^{2+}. FeOOH is formed from the dissolved Fe^{2+} via various processes such as oxidation, neutralization, hydrolysis and transformation. It has been reported that the above oxidation process of Fe^{2+} is strongly affected by the coexistent cations and anions in the solution [31,32], and therefore we have been focusing on the effect of cations and anions on the structures of hydrolysis products from Fe^{3+}-solution. In the present study, we have especially focused our attention on β-FeOOH. We have synthesized β-FeOOH by a hydrolysis process in the presence of Cu, Cr and Ni ions, and investigated them to clarify the influence of the existence of the cations as well as anions on the hydrolysis process.

2. Experimental

β-FeOOH was, as the basic synthetic method, prepared by hydrolysis of 300 mL, 0.1 mol/L $FeCl_3$ solution at temperature of 80 or 100 °C in a capped 500 mL Pyrex