CEMS study of corrosion products formed by NaCl aqueous solution

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Abstract Conversion electron Mössbauer spectroscopy was used to study corrosion products by NaCl aqueous solution. A drop of the solution is put on an iron foil and the foil is left at RT. During the evaporation of the solution, corrosion products are formed. Conversion electron Mössbauer spectra were taken at temperatures between 15 K and room temperature (RT). In the Mössbauer spectra a ferric doublet is observed at RT, but sextets are found at 15 K. These results show that the corrosion product mainly consists of γ - FeOOH and a small amount of β - FeOOH is noticed. As NaCl concentration increases, the corrosion layer becomes thick and β-FeOOH / γ - FeOOH ratio increases slightly. Consequently, it has been concluded that the produced amount of β- FeOOH increases more rapidly than that of γ - FeOOH with increasing NaCl concentration.

1 Introduction

Conversion electron Mössbauer spectroscopy (CEMS) is a powerful tool for characterizing corrosion products because the Mössbauer spectrum can be observed without separating the corrosion products from the substrate materials. Corrosion products formed on an iron foil by the sulfuric acid water have been investigated with CEMS at low temperatures [1, 2]. From the results of previous studies, the corrosion products mainly consist of α-FeOOH, γ-FeOOH and γ-Fe$_2$O$_3$. But in a marine environment β-FeOOH is observed in the corrosion products [3], where chlorine ions exist. Though the Néel temperature of β-FeOOH is reported to be 299 K, a reduction of Néel temperature is often observed due to the existence of interstitial water molecules [4]. Thus, its Mössbauer spectrum measured at room temperature (RT) shows a ferric doublet which can not distinguish from that of

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Fig. 1 CEM spectra of corrosion products by 0.01 M NaCl solution. Sextets A-C are due to iron foil, γ-FeOOH and β-FeOOH, respectively
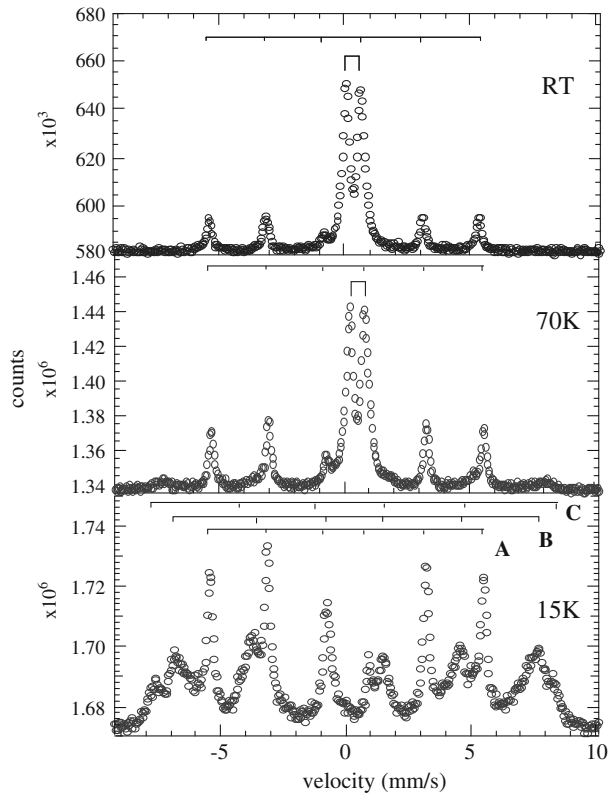
γ-FeOOH. Furthermore the corrosion products consist of a lot of small particles, so that ferric doublets are mostly observed in a Mössbauer spectrum at RT due to their superparamagnetism. Therefore, in order to investigate the properties of corrosion products in detail, it is necessary to measure a Mössbauer spectrum at low temperatures.

Mössbauer spectroscopic studies of corrosion products by NaCl aqueous solution have been made extensively [5–7]. From these studies corrosion layer can be divided into two groups, the adherent rust and the non-adherent rust. The Mössbauer spectra of the adherent rust were recorded in transmission geometry, where corrosion products were removed from the substrate material by scraping or hitting. But there is possibility to vary the size distribution of corrosion products, which affects the Mössbauer spectrum. In this study in order to characterize the corrosion products formed in the marine environment, a dilute NaCl aqueous solution (0.01–1.0 M) was prepared and corrosion products formed by this solution were investigated with CEMS at low temperatures.

2 Experimental

Natural iron foil washed by acetone was used and NaCl aqueous solution (0.01–1.0 M) was prepared. Samples were prepared in two methods. One is that a drop of the aqueous solution is put on the surface of an iron foil and the foil is left at RT.

Fig. 2 Area ratio at 15 K
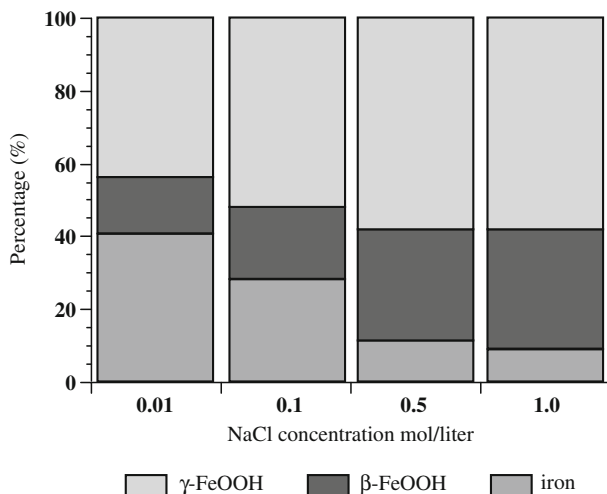
During the evaporation of aqueous solution, corrosion products are formed on the foil surface. Another method is that an iron foil is immersed in the NaCl aqueous solution for several days and dried at RT. During the immersion, corrosion products are formed on the surface.

Conversion electron Mössbauer (CEM) spectra were taken at temperatures between 15 K and RT, with the gas filled proportional counter described elsewhere [8–10]. Hydrogen gas and the 98% He – 2% CH4 gas mixture were used as the counter gas at low temperatures and RT, respectively. The velocity calibration was carried out with a natural iron foil. X-ray diffraction analyses were also performed using a Philips diffractometer (PW1710) with Co Kα radiation.

3 Results and discussion

CEM spectra of the corrosion products formed during the evaporation of 0.01 M NaCl solution in air are shown in Fig. 1. Similar spectra were observed for the corrosion products formed by higher concentration of NaCl aqueous solution. A weak sextet of the iron foil and a ferric doublet are observed at RT. In the spectrum at 70 K the doublet still remains, but at 15 K no doublet is observed and two sextets in addition to that of the iron foil are noticed. The value of hyperfine field suggests that the large sextet is assigned to γ-FeOOH and the small one to β-FeOOH, which is also confirmed by the XRD pattern. Magnetite and α- FeOOH were observed as traces in XRD pattern. Thus, sextets of magnetite and α- FeOOH are small and can not be separated from that of β-FeOOH. The relative area of these sextets are given if Fig. 2. From this figure, it is found that the corrosion layer becomes thicker as the NaCl concentration increases. Assuming that the recoilless fractions of these chemical species are same, a ratio of β-FeOOH to γ-FeOOH is calculated. A plot of the ratio as a function of NaCl concentration is give in Fig. 3. This plot shows that the β-FeOOH / γ - FeOOH ratio increases slightly with increasing of NaCl concentration.

Fig. 3 β-FeOOH / γ-FeOOH ratio as a function of NaCl concentration
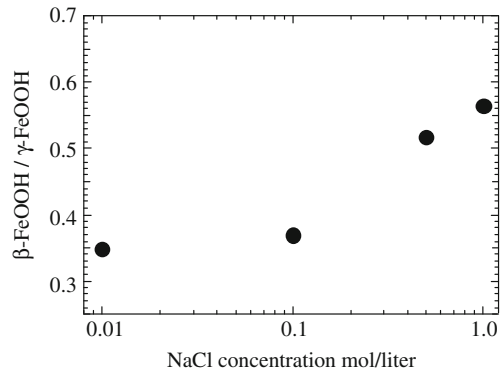
Fig. 4 CEM spectra of adherent layer on the iron foil. Sextet A is due to iron foil and sextets B, C are due to magnetite
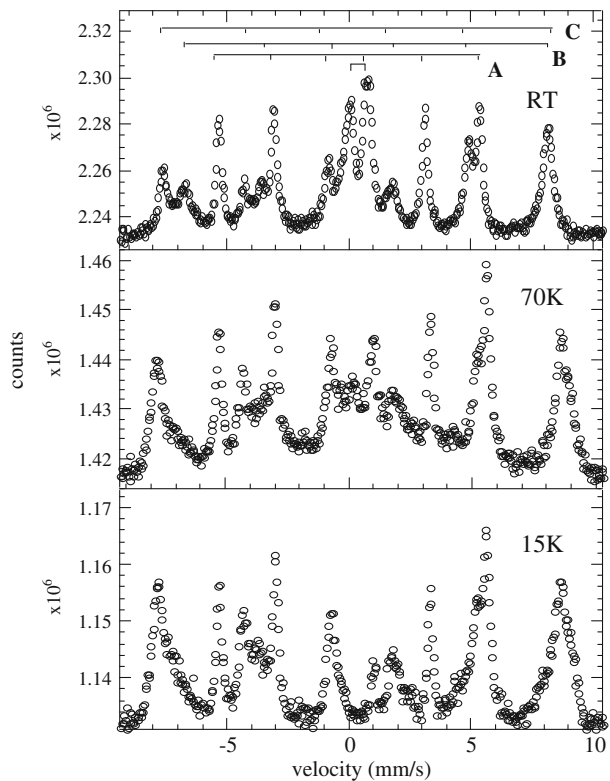
In the case of immersion samples, corrosion products can be divided into two layers. The colour of the outer layer is light brown and that of the inner layer is black. The outer layer is not adherent and easy to remove from the substrate material in the solution. The inner layer is adherent and its CEM spectra are shown in Fig 3, where the iron foil was immersed in 0.01 M NaCl for two weeks. In RT spectrum, one doublet and two sextets in addition to that of the iron foil are observed. Hyperfine fields and isomer shifts of these sextets suggest that they are

due to magnetite, corresponding to iron atoms in A and B sites respectively. The isomer shift of the doublet is 0.35 mm/s, which indicates this doublet is ferric. But its quadrupole splitting is 0.7 mm/s which is larger than that of γ-FeOOH. In the XRD pattern of this sample, the peaks of magnetite are found and γ-FeOOH is observed as trace. In 70 K spectrum, the intensity of the doublet becomes much smaller than that in RT spectrum, and in 15 K the doublet disappears. If this doublet is due to γ-FeOOH, the intensity of doublet in 70 K must be similar to that in RT [1]. Therefore this doublet can not assign to γ-FeOOH. Since the fine powder of magnetite shows superparamagnetic relaxation [11], this doublet assigns to superparamagnetic magnetite (Fig. 4).

4 Conclusions

In the case of corrosion products formed by the evaporation of NaCl aqueous solution, corrosion products consist of γ-FeOOH and β-FeOOH. The β-FeOOH / γ-FeOOH ratio becomes large as NaCl concentration increase, which indicates that the produced amount of β- FeOOH increases more rapidly than that of γ - FeOOH with increasing NaCl concentration. In the case of immersion sample, the adherent layer on the foil consists magnetite including the superparamagnetic small particles.

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