

## Secondary Ion Mass Spectrometry of Isotope-Labeled Iron Corrosion Products

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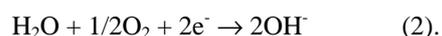
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Secondary ion mass spectrometry (SIMS) has been used for analyzing corrosion products formed on the iron surface by reaction of an iron substrate with aqueous solutions containing two percent sodium chloride. In order to follow a formation process of the corrosion products, hydrogen and oxygen in the aqueous solutions were labeled with stable isotopes, D(<sup>2</sup>H) and <sup>18</sup>O, respectively. Mass spectra of positive and negative ions showed that deuterium was contained in corrosion products formed by reaction with D<sub>2</sub>O solution. On the other hand, <sup>16</sup>O relevant ion peaks as well as <sup>18</sup>O relevant ion peaks were found in corrosion products formed by reaction with H<sub>2</sub><sup>18</sup>O solution. This indicates that oxygen in the corrosion products is mainly composed of oxygen originating from air and oxygen in aqueous solution. A formation process of corrosion products was discussed on the basis of these results.

### INTRODUCTION

Corrosion products of steel, which consist mainly of ferric oxyhydroxides, are formed on the iron surface by atmospheric corrosion at room temperature [1,2]. The atomic scale structure of the corrosion products is likely to be described by linkages of FeO<sub>6</sub> octahedral units containing hydrogen [3,4]. Besides the structure, elemental information is also required to clarify a formation process of corrosion products. For example, ferrous and hydroxyl ions are likely to be formed in non-acid aqueous solution by the following reactions [1,2]:



Consequently, colloidal ferric oxyhydroxides FeOOH are precipitated from ferrous and hydroxyl ions and dissolved oxygen in aqueous solution, through further reactions. However, origins of constituent elements, oxygen and hydrogen, of the ferric oxyhydroxides appear to be unclear.

It should be noted in the above reactions that hydrogen in the corrosion products originates from

aqueous solution, and oxygen comes from water and oxygen molecules in air. When hydrogen and oxygen in aqueous solution are labeled with their isotopes, mass spectra from the corrosion products provide information of the origins of constituent elements of corrosion products. Therefore, the objective of this work is to characterize mass spectra of ions sputtered from the corrosion products by SIMS. The corrosion products were formed by reaction of the iron substrate with aqueous solution, of H<sub>2</sub>O, D<sub>2</sub>O or H<sub>2</sub><sup>18</sup>O, containing two mass percent sodium chloride. Since phosphorus, which plays an important role in corrosion [5], was added to the high-purity material, phosphorus in the corrosion products was also analyzed using SIMS. Formation processes of corrosion products are discussed on the basis of the experimental results.

### EXPERIMENTAL

Iron sheets containing about 0.1 mass% phosphorus alloy of 1 mm in thickness were prepared by rolling. They were polished for analyzing a flat surface using SIMS. The sheets are a starting sample, which is hereafter referred to as Sample S. A drip of

H<sub>2</sub>O, D<sub>2</sub>O or H<sub>2</sub><sup>18</sup>O solution containing 2 mass% sodium chloride was dropped on the surface of Sample S. This is because the water becomes electrolytic by sodium chloride, by which iron is easily corroded. The enrichment of deuterium in D<sub>2</sub>O was 99.9% and the enrichment of <sup>18</sup>O in H<sub>2</sub><sup>18</sup>O was 95%. Corrosion products were formed on the surface of Sample S for about 9x10<sup>4</sup> s. After corrosion, the samples were dried at room temperature. The corrosion products were mostly ferric oxyhydroxides [3]. Then, most of the corrosion products were mechanically removed, as they are thick and non-conductive. The corrosion products remaining near the corrosion front of the iron substrate were analyzed using SIMS. The samples prepared by corrosion reaction with H<sub>2</sub>O, D<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O are referred to as Sample H, Sample D and Sample O, respectively.

Ion species from corrosion products were analyzed in a similar manner to a previous work [6]. SIMS measurements were carried out using PHI-6600 with quadrupole-type mass analyzer. An incident beam of 5.0keV Cs<sup>+</sup> ions was irradiated to the sample surface, and positive and negative secondary ions were analyzed from the corrosion products on the sample surface of 0.1 mm square.

Although sputter depth profiling by SIMS is used for characterizing a layered structure of a flat surface, this work stressed mass spectra from the corrosion products to obtain information of ions species.

## RESULTS AND DISCUSSION

### Mass Spectra

In order to distinguish significant effects of the isotopes on the mass spectra, narrow mass spectra of positive ions from Sample H, Sample D and Sample O are shown in Figs.1 (a), (b) and (c), respectively. As the amounts of corrosion products and sodium chlorides remaining on the sample surface are not homogeneous in these samples, relative intensities of different ions of interest should be compared among the different spectra. Ions of one and two in mass number are influenced by residual hydrogen in the UHV chamber and adsorbed hydrocarbon as well as hydrogen and deuterium in ferric oxyhydroxides.

Nevertheless, several differences are observed in oxygen relevant ion peaks: the relative intensity of ions of eighteen in mass number to those of sixteen in mass number in Sample O is clearly higher than those in Sample H and Sample D cases. This implies that <sup>18</sup>O are present in the corrosion products, which were formed by reaction of the iron surface with H<sub>2</sub><sup>18</sup>O solution. It is also interesting to note that <sup>16</sup>O positive ion peak is observed in mass spectra from Sample O, and it will be discussed later.

Isotope ions measured by SIMS are also found in mass spectra of negative ions from Sample H, Sample D and Sample O, as shown in Figs.2 (a), (b) and (c), respectively. A peak of two in mass number is clearly high in Sample D. This peak is assigned to deuterium ions, although ions of hydrogen molecule as the background are observed in Sample H and Sample O. Moreover, the peaks of eighteen and thirty-six in mass number in Sample O are higher than those for Sample H and D, and these peaks are assigned to <sup>18</sup>O<sup>-</sup> and <sup>36</sup>O<sub>2</sub><sup>-</sup>, respectively. Also, the peaks of nineteen in mass number, which is allocated to <sup>18</sup>OH<sup>-</sup>, in Sample O is higher than those for S quadrupole-type mass analyzer. An incident beam of 5.0 keV Cs<sup>+</sup> ions was irradiated to the sample surface, and positive and negative secondary ions were analyzed from the corrosion products on the sample surface of 0.1 mm square. Sample H and Sample D. Phosphorus relevant ions, such as <sup>31</sup>P and <sup>31</sup>PO, are observed in the mass spectra of negative ions. These ion peaks are clearly higher than those for corrosion products formed on the pure iron surface [6]. It is interesting to note that the ion intensity of <sup>31</sup>P<sup>16</sup>O is decreased by an increase of <sup>31</sup>P<sup>18</sup>O in Sample O.

Figure 3 summarizes the intensity ratios of <sup>16</sup>O relevant ion peaks to <sup>18</sup>O relevant ion peaks from the corrosion products, which were formed in H<sub>2</sub><sup>16</sup>O solution and H<sub>2</sub><sup>18</sup>O solution. These ion intensity ratios in the corrosion products formed in <sup>18</sup>O solution are lower than those for the corrosion products formed in <sup>16</sup>O solution by nearly two orders of magnitude. This implies that <sup>18</sup>O constitutes the corrosion products formed by reaction with H<sub>2</sub><sup>18</sup>O solution. However, it should be noted that <sup>16</sup>O relevant ion peaks are still observed in mass spectra from Sample O, as shown in Figs. 1(c) and 2(c).

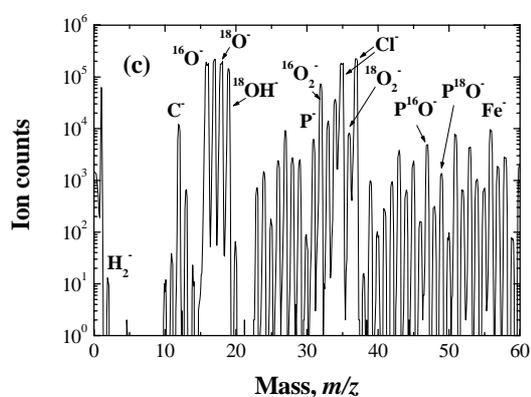
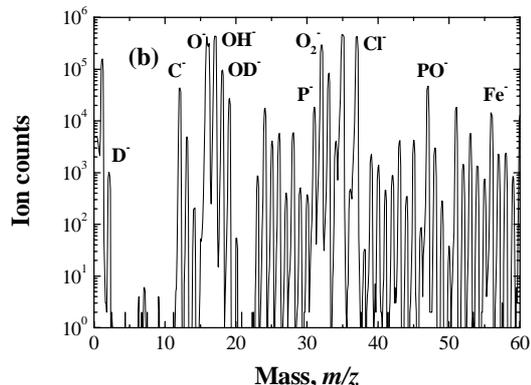
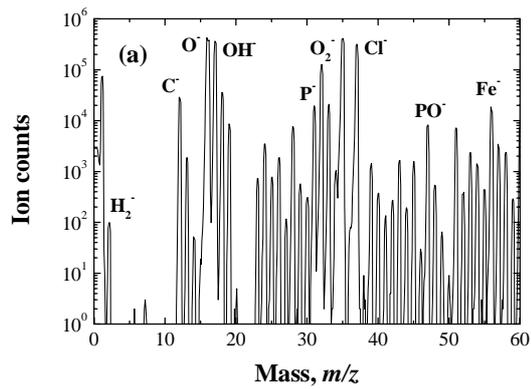
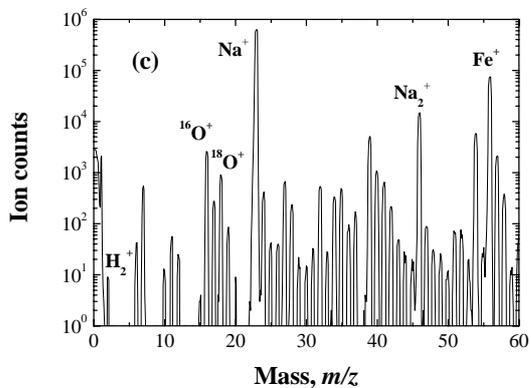
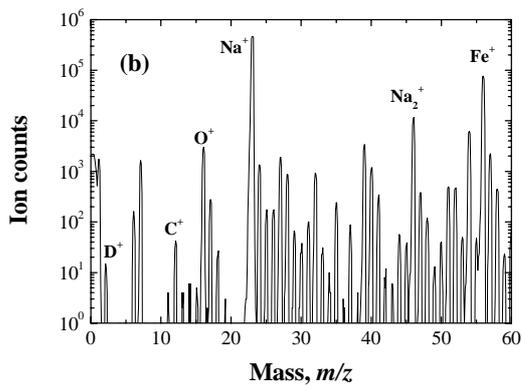
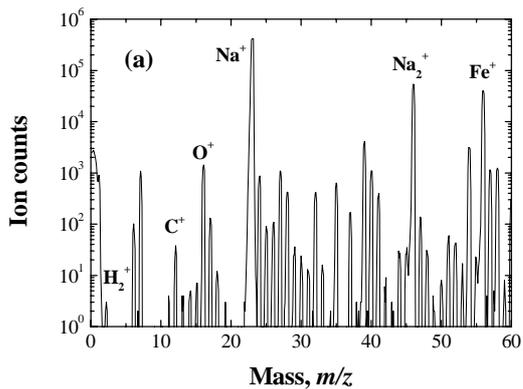


Fig. 1 Mass spectra of positive ions from (a) Sample H, (b) Sample D and (c) Sample O.

Fig. 2 Mass spectra of negative ions from (a) Sample H, (b) Sample D and (c) Sample O.

This indicates that the corrosion products are mainly composed of oxygen originating from air, in which the abundance of  $^{16}\text{O}$  is 99.7 at%.

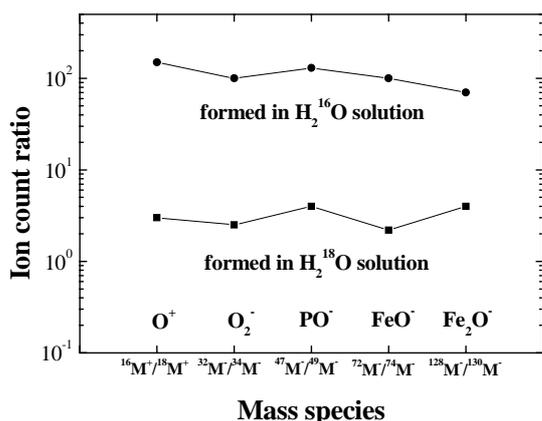


Fig. 3 Intensity ratios of <sup>18</sup>O relevant ion peaks to <sup>16</sup>O relevant ion peaks from the corrosion products, which were formed in H<sub>2</sub><sup>16</sup>O solution and H<sub>2</sub><sup>18</sup>O solution.

### FORMATION OF FERRIC OXYHYDROXIDES

Ferric oxyhydroxides, such as  $\gamma$ -FeOOH and  $\alpha$ -FeOOH, are described by linkages of FeO<sub>6</sub> octahedral structural units. Iron ions of ferrous ions and ferric ions are formed by dissolution of the metallic iron substrate, whereas oxygen are dissolved from air and hydroxyls are formed from the reaction of oxygen molecules with water, as shown in Equation (1). The dissolved iron ions are reacted with hydroxyls and dissolved oxygen to form corrosion products. In this process, oxygen in hydroxyl is <sup>16</sup>O or <sup>18</sup>O, and oxygen in air is <sup>16</sup>O<sub>2</sub> in the formation of in corrosion products Sample O, and therefore the corrosion products in Sample O may contain <sup>16</sup>O and <sup>18</sup>O.

When water containing the corrosion products, H<sub>2</sub><sup>18</sup>O, is evaporated from aqueous solution, the iron ions in the solution become supersaturated to be precipitated. Then, oxygen in air easily penetrates into chinks in ferric oxyhydroxides particles, to form additional corrosion products. This formation process is affected by <sup>16</sup>O<sub>2</sub>. This is the reason why <sup>16</sup>O relevant ions are mainly detected in Sample O. Thus, careful analysis of mass spectra of isotope-labeled corrosion products by SIMS is effective to characterize formation processes of corrosion

products.

### CONCLUDING REMARKS

SIMS has been made for analyzing corrosion products, which were prepared by reaction of an iron substrate with H<sub>2</sub>O, D<sub>2</sub>O or H<sup>18</sup>O solution containing two percent sodium chloride. Main concluding remarks drawn from this work are as follows:

- (1) Hydrogen and deuterium relevant ions from the corrosion products were found in mass spectra of SIMS.
- (2) Systematic oxygen relevant ions, containing <sup>16</sup>O or <sup>18</sup>O, from the corrosion products were found. These results indicate that the corrosion products form from hydroxyl in aqueous solution and oxygen in air, which is main origin of oxygen in the corrosion products.
- (3) Phosphorus relevant ion peaks were detected in the mass spectra from the corrosion products. These results showed that SIMS analysis of isotope-labeled corrosion products is an effective tool for characterizing corrosion processes.

### ACKNOWLEDGEMENTS

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