Analysis of Iron Oxyhydroxides and Oxides Converted from Green Rust in Aqueous Solution

Katsuya INOUE, Sang-Koo KWON, Ken’ichi KIMIJIAMA, Kiyoshi KANIE, Atsushi MURAMATSU, Kozo SHINODA, Shigeru SUZUKI and Yoshio WASEDA

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan. E-mail: inoue@mail.tagen.tohoku.ac.jp

(Received on November 24, 2006; accepted on December 20, 2006)

In order to clarify the influence of reaction conditions on the formation of iron oxyhydroxides and oxides obtained from hydroxysulfate green rust (GR), the X-ray diffraction method was used for analyzing the solid particles formed during conversion. GR was synthesized from solutions of ferric sulfate, ferrous sulfate, and sodium hydroxide. The suspension containing GR was oxidized by passing oxygen gas. X-ray absorption spectroscopy and transmission electron microscopy were used for analyzing the chemical state and structure of the solid particles separated from the suspension, respectively. The results revealed that GR was converted primarily to α-FeOOH, and γ-FeOOH and Fe₃O₄ were found to be partially formed during the conversion depending on the temperature and oxygen flow rate. Furthermore, the addition of manganese was shown to enhance the formation of Fe₃O₄. These results indicate that the formation of different structures of iron oxyhydroxides and oxides in an aqueous solution is sensitive to the reaction conditions.

KEY WORDS: green rust; ferric oxyhydroxides; magnetite; aqueous solution; X-ray diffraction; X-ray absorption.
pend on anions such as $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, and $\text{Cl}^-$ that are involved in its formation. In general, GR is classified into two types—green rust one (GR1) and green rust two (GR2)—based on X-ray diffraction (XRD) observations. The structure of GR1 consists of stacks of hydroxide-like sheets of $\text{Fe(OH)}_2$ that alternate regularly with interlayers of $\text{OH}^-$ ions of $A$, $B$, $C$, $C$, $A$, anions and water molecules. In contrast, the structure of GR2 comprises a stacked sequence of the layers of $\text{OH}^-$ ions of $A$, $B$, $A$, stacking. Further, the chemical formula of iron hydroxysulfate green rust ($\text{GR2(SO}_4^{2-})$) is determined as $\text{Fe(II)}_2\text{Fe(III)}_2\text{(OH)}_{12}\cdot\text{SO}_4^2\cdot8\text{H}_2\text{O}$ with a primitive hexagonal cell that includes interlayers composed of two distinct planes of water molecules and sulfate ions.\textsuperscript{16–18}

Thus, although the formation and structure of GR were studied in a number of investigations, the influence of the reaction conditions on the formation of ferric oxyhydroxides and iron oxides obtained from GR by aerial oxidation is unclear. The oxidation processes of GR are very important for understanding the corrosion mechanism, since the species and morphologies of these iron oxyhydroxides and oxides in the corrosion products may be determined by the environmental reaction conditions. Typically, as the corrosion rate of weathering steel is influenced by a layer of corrosion products, an analysis of the structure and morphology of iron oxyhydroxides and oxides is important. Therefore, the role of reaction conditions in the formation of iron oxyhydroxides and oxides from intermediate products of GR in an aqueous solution needs to be investigated. The objective of the present work is to study the influence of the oxidation temperature and oxygen flow rate on the formation of iron oxyhydroxides and oxides obtained from GR in an aqueous solution. The influence of the addition of manganese, which is an important alloying element in steel, on the formation of iron oxyhydroxides and oxides was also investigated.

2. Experimental

2.1. Sample Preparation

The sample used in the experiment was prepared using the following chemicals: special reagent grade ferric sulfate $n$-hydrate ($\text{Fe}_2\text{(SO}_4\text{)}_3\cdot n\text{H}_2\text{O}$, where $n=10.13$ as determined by inductively coupled plasma atomic emission spectrometry), ferrous sulfate heptahydrate ($\text{FeSO}_4\cdot7\text{H}_2\text{O}$), and sodium hydroxide ($\text{NaOH}$) aqueous solution ($8\text{ mol dm}^{-3}$).

Iron hydroxysulfate green rust ($\text{GR2(SO}_4^{2-})$) was synthesized by adding $\text{NaOH}$ aqueous solution to an aqueous solution containing ferric sulfate ($\text{Fe}_2\text{(SO}_4\text{)}_3$) and ferrous sulfate ($\text{FeSO}_4$) according to a previous method.\textsuperscript{16–18} First, a 250 mL iron sulfate solution was prepared; it contained $3.750\times10^{-1}\text{ mol dm}^{-3} \text{Fe}_2\text{(SO}_4\text{)}_3$ and $6.250\times10^{-2}\text{ mol dm}^{-3} \text{Fe}^2\text{(SO}_4\text{)}_3$. The proportion of ferric to ferrous ($\text{Fe}(\text{II})/\text{Fe}(\text{III})$) ions was 3, and the total concentration of ferric and ferrous ions was $5.000\times10^{-1}\text{ mol dm}^{-3}$. A 250 mL aqueous solution containing $7.500\times10^{-1}\text{ mol dm}^{-3} \text{NaOH}$ was added to the iron sulfate solution in a reaction vessel at a rate of 5 mL min$^{-1}$ under magnetic agitation with Ar gas bubbling at 5°C. Subsequently, 250 mL of NaOH, corresponding to a ratio of 1.5 between hydroxyl ions and the total number of iron ions ($\text{OH}^-$/[$\text{Fe(II)}+\text{Fe(III)}$]), was added to the solution. At this stage, the precipitate of iron hydroxysulfate green rust—$\text{Fe(II)}_2\text{Fe(III)}_2\text{(OH)}_{12}\cdot\text{SO}_4\cdot8\text{H}_2\text{O}$ ($\text{GR2(SO}_4^{2-})$)—was formed. The suspension containing $\text{GR2(SO}_4^{2-})$ was further bubbled for 1 h with Ar gas to remove the remnant oxygen. $\text{GR2(SO}_4^{2-})$ was washed with Ar-bubbled water by centrifugation; it was then diluted up to 500 mL with Ar-bubbled water in the Duran bottle. The concentration of iron in the solution was $1.875\times10^{-1}\text{ mol dm}^{-3}$; this was used as the standard for $\text{GR2(SO}_4^{2-})$ in this study. The above procedures were performed in a glove box to prevent the oxidation of $\text{GR2(SO}_4^{2-})$. The stoichiometric ratio of $\text{GR(SO}_4^{2-})$ is $\text{Fe(II)}/\text{Fe(III)}=2$ and $\text{[OH}]^{}/\text{[Fe(II)/Fe(III)]}=2$; the superfluous ions in the suspension employed in the preparation of $\text{GR2(SO}_4^{2-})$ were washed away by the centrifugation process that was performed three times.

A reaction cell was used for oxidizing $\text{GR2(SO}_4^{2-})$, as shown in Fig. 2. The reaction cell consists of a 500 mL glass beaker and an airtight glass lid with holes for pH and Pt electrodes, gas inlet/outlet ports, a stirrer port, and a sampling port. The 200 mL suspension containing $\text{GR2(SO}_4^{2-})$ with $1.875\times10^{-1}\text{ mol dm}^{-3}$ iron was diluted up to 500 mL containing $7.500\times10^{-1}\text{ mol dm}^{-3}$ iron. The suspension containing manganese ions was prepared by adding a 50 mL solution containing $3.750\times10^{-1}\text{ mol dm}^{-3} \text{MnSO}_4$ into the $\text{GR2(SO}_4^{2-})$ suspension; the resulting iron concentration was 5 to 100 mol%. The suspension was oxidized in a water bath at 5, 10, 20, 25, and 30°C. The $\text{GR2(SO}_4^{2-})$ suspension was oxidized for over 6 h by passing nitrogen gas containing different amounts of oxygen at a flow rate of 200 mL min$^{-1}$. After a given reaction time, 15 mL of the suspension was sampled and Ar gas was immediately injected into the suspensions to interrupt the oxidation reaction for the purpose of carrying out the measurements. The solid particles separated from the suspension by centrifugation were characterized using different methods. After the final oxidation, the suspension was kept for one day in air and freeze-dried for 48 h to obtain final solid particles.

2.2. Measurements

Samples for XRD measurements were prepared in the glove box by mixing the solid particles separated from the suspension with glycerol in order to prevent their oxidation in air. The crystallographic structure of the particles was
analyzed by XRD measurements performed with Mo Kα radiation of 17.447 keV (50 kV, 30 mA) using Rigaku RINT-2200. The chemical state of manganese in the solid particles was analyzed using the measurements of the X-ray absorption near edge structure (XANES) at the Mn K absorption edge by X-ray absorption spectroscopy (XAS). The apparatus was an in-house X-ray absorption spectrometer (Rigaku R-XAS Looper) equipped with a Ge(220) Johansson-type monochromator. The backgrounds of the XAS spectra were subtracted using the Rigaku REX2000. A transmission electron microscope (TEM, JEOL JEM-1200EX II) was used to observe the particle morphology. In addition, the pH and oxidation reduction potential (ORP) of the GR2(SO4/H2O2) suspensions were monitored as a function of the reaction time by using a TOA DKK IM-55G ion meter.

3. Results and Discussion

3.1. Conversion to Iron Oxyhydroxides and Oxides

Figure 3 shows the XRD patterns of particles obtained from GR2(SO4/H2O2) in the aqueous solution. The samples were oxidized by passing nitrogen–21% oxygen gas at a flow rate of 200 mL min⁻¹ at 20°C for 0, 10, 30, 50, and 90 min. The backgrounds observed in these patterns are likely to be attributed to the remnant water in the samples and glycerol. These results revealed that GR2(SO4⁻²) was converted to α-FeOOH particles through the dissolution and precipitation of ferrous and ferric ions in the aqueous solution. The formation of α-FeOOH was initiated by oxidizing the suspension for 10 min. Most of the diffraction peaks for the particles oxidized for 30 min were attributed to the structure of α-FeOOH, whereas the diffraction peaks of GR2(SO4⁻²) were not detected in the particles. As the conversion from GR2(SO4⁻²) to α-FeOOH was completed by oxidation for 90 min, it was considered as the final product of the oxidation of GR2(SO4⁻²) in the present work.

The XRD patterns of the particles obtained from GR2(SO4⁻²) in the aqueous solution are shown in Fig. 4. The samples were the particles that were oxidized by passing nitrogen–21% oxygen gas for 90 min at 30, 25, 20, 10, and 5°C. While GR2(SO4⁻²) was completely converted into α-FeOOH by oxidation at 20°C and 25°C, Fe₃O₄ was partially detected in the particles formed at 30°C and γ-FeOOH was partially formed at 5°C and 10°C. These results implied that the species of iron oxyhydroxides and oxides formed in the aqueous solution depended on the temperature of the aqueous solution. As the amount of oxygen dissolved into the aqueous solution depends on the temperature of water, it may be a factor controlling the formation of different iron oxyhydroxides and oxides.

Figure 5 shows the XRD patterns of particles obtained from GR2(SO4⁻²) in the aqueous solution; these particles were oxidized by passing nitrogen–21% oxygen gas for 90 min at 25°C and 30°C, and nitrogen–2.5% oxygen gas at 25°C and 30°C for 360 min. The results show that the amount of magnetite formed at a slow flow rate of oxygen was large and the amount of magnetite formed at 30°C was larger than that formed at 25°C. Since magnetite does not contain hydrogen, it is formed through a deprotonation process of iron hydroxyls, which plays an important role in the formation of magnetite. Thus, the deprotonation process should be investigated to clarify the formation of magnetite as the oxygen flow rate and reaction temperature affect the deprotonation process of iron hydroxyl.
3.2. Effect of Manganese Addition on Conversion

In order to study the influence of manganese on the formation of magnetite, manganese sulfate was added to the solution. Figure 6 shows the XRD patterns of particles obtained from GR2(SO$_4^{2-}$/H$_{11}$O$_2$) containing 5 mol% manganese ions to the total iron and pure GR2(SO$_4^{2-}$) in aqueous solution. The ions were oxidized by passing nitrogen gas containing 2.5% oxygen at 30°C for 360 min. The XRD pattern of the particles obtained from GR2(SO$_4^{2-}$) and containing 5 mol% manganese ions was broader than that of particles from pure GR2(SO$_4^{2-}$), which was considered to be caused by the adsorption of sulfate ions on the particles. The amount of magnetite was increased by the addition of manganese ions into the solution, indicating that it enhanced the formation of magnetite.

Transmission electron micrographs of the above particles formed from GR2(SO$_4^{2-}$) containing 5 mol% manganese ions to total iron and pure GR2(SO$_4^{2-}$) are shown in Figs. 7(a) and 7(b), respectively. Since the shape of pure $\alpha$-FeOOH particles is known to be spindle-like,²,6 the spherical particles are magnetite. The particle sizes of magnetite obtained from GR2(SO$_4^{2-}$) containing manganese tend to be larger than those from pure GR2(SO$_4^{2-}$). This tendency indicates that the particle growth of magnetite is affected by manganese ions in the aqueous solution.

In order to investigate the chemical state of manganese in the magnetite particles containing manganese, the X-ray absorption near-edge structure at the Mn K absorption edge of particles obtained from GR2(SO$_4^{2-}$) containing manganese and from reference samples were measured, as shown in Fig. 8. The reference samples were MnO, Mn$_2$O$_3$, and MnO$_2$. The spectra show that manganese in the magnetite particles formed in the present experiment was primarily divalent, although some deviation from the reference spectrum of MnO was observed. As magnetite contained divalent iron ions, the divalence of manganese in the magnetite particles is related to the enhancement of magnetite formation in the precipitation process.

The structural transformation from GR to iron oxyhydroxides and oxides in the aqueous solution was studied in the present work, which involves the oxidation of ferrous ions. On the other hand, GR has also been observed to be formed by the reduction of ferric compounds.⁶⁻¹³ Although the reduction–oxidation of ferric and ferrous ions takes place due to their chemical properties in the aqueous solution, the detailed reaction conditions should be understood by further experiments.

3.3. Variations in ORP and pH during Conversion

The ORP and pH of the aqueous solution were measured in order to investigate the formation conditions of different iron oxyhydroxides and oxides. Figure 9 shows the variations in the ORP and pH in the aging GR2(SO$_4^{2-}$) suspensions as a function of the oxidation time. The XRD patterns of particles sampled from the suspension that were aged for different time intervals as shown in Figs. 3(a)–3(e) are shown in Fig. 9(a)–9(e), respectively. In general, the ORP increased during the conversion of GR2(SO$_4^{2-}$) to $\alpha$-FeOOH because ferrous ions were oxidized to ferric ions. Ferric oxyhydroxides may be formed in the solution during the oxidation of ferrous ions in GR2(SO$_4^{2-}$). The ORP
value increased just after the onset of oxidation and was then maintained at an intermediate stage for approximately 20 min during which the α-FeOOH particles have been nucleated from the GR2(SO42−) suspension. It was drastically increased in the following stage in which most of the α-FeOOH particles have been formed. As in the case of the ORP, the pH of the solution containing pure GR2(SO42−) decreased in a few minutes and then remained at a certain level for approximately 20 min. It decreased due to further aging, which have completely precipitated the α-FeOOH particles.

The formation reaction of α-FeOOH from GR2(SO42−) in the aqueous solution has been proposed to be as follows11):

\[
\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}\text{SO}_4 + 3/4 \text{O}_2 \\
\rightarrow 5\text{FeOOH} + \text{Fe}^{2+} + \text{SO}_4^{2−} + 7/2 \text{H}_2\text{O} \quad \text{..............(1)}
\]

The reaction does not indicate any change in the pH during the conversion from GR2(SO42−) to α-FeOOH. However, since the pH varied during the conversion, the reaction was probably associated with the formation of protons. Therefore, although the elemental reaction may be complicated, a possible reaction of the conversion from GR2(SO42−) to α-FeOOH is expressed as follows:

\[
\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}\text{SO}_4 + \text{O}_2 \\
\rightarrow 6\text{FeOOH} + 2\text{H}^{+} + \text{SO}_4^{2−} + 2\text{H}_2\text{O} \quad \text{..............(2)}
\]

When the rate of conversion from GR2(SO42−) to α-FeOOH is high, the pH should decrease rapidly. In these processes, the dissolution of GR2(SO42−) and the precipitation of α-FeOOH are considered to show two stages in which the nucleation and growth of α-FeOOH particles may occur; however, the influence of oxidation conditions on the conversion of to GR2(SO42−) to iron oxyhydroxides and oxides should be further studied.

4. Conclusion Remarks

The influence of oxidation conditions on the formation of ferric oxyhydroxides and iron oxides, of the structure as described for FeO2, obtained from hydroxysulfate green rust (GR2(SO42−)) in an aqueous solution was investigated using XRD, XAS, and TEM. The main conclusions are summarized as follow:

1) During the conversion from GR2(SO42−) particles to α-FeOOH particles, the amount of γ-FeOOH particles were found to be increased by decreasing the reaction temperature, and the formation of magnetite was observed at a high temperature. It is suggested that the reaction temperature is an important factor in the formation of different ferric oxyhydroxides and iron oxides.

2) The formation of magnetite particles was enhanced by reducing the flow rate of oxygen, increasing the temperature, and adding manganese during the conversion of GR2(SO42−) to α-FeOOH. The TEM observations revealed the formation of spherical magnetite together with spindle-like α-FeOOH particles. The XANES spectra indicated that divalent manganese may play an important role in the formation of magnetite.

Acknowledgements

The present authors wish to express their thanks to Prof. E. Matsubara, Prof. K. Sugiyma, and Prof. S. Sato for their valuable discussions with the authors. This work was supported by the Grant-in-Aid for Scientific Research Fund from Japan Society for Promotion of Science (No. 17206075).

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