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Ni(II)-Bearing Green Rust II and Its Spontaneous Transformation into Ni(II)-Bearing Ferrites

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When solutions containing Fe(II), Ni(II), and SO_4^{2-} ions were oxidized by a mixed gas of air and nitrogen at pH 7.1 (25 °C), a Ni(II)-bearing green rust II (GR-II), which is a uniform crystalline precipitate with a definite chemical composition, was formed. The Ni(II) content in the Ni(II)-bearing GR-II increased with an increase in the Ni(II) concentration in the reaction solution. The Ni(II)-bearing GR-II was spontaneously transformed into Ni(II)-bearing ferrite under a nitrogen atmosphere without any oxidant. The metal mole ratio of $[Ni(II)/Fe(III)]_{fer}$ in the ferrite increased linearly with an increase in that of $[Ni(II)/Fe(III)]_{grn}$ in the Ni(II)-bearing GR-II (slope=0.193). From this relationship, the spontaneous transformation reaction was described as

$$2(Ni^{2+})_x(Fe^{2+})_{2-x}(Fe^{3+})(SO_4^{2-})(OH^-)_5 \longrightarrow Ni_{0.39x}Fe_{3-0.39x}O_4$$
$$+ (2-1.61x)Fe^{2+} + 1.61xNi^{2+} + Fe(OH)_2 + 2SO_4^{2-} + 4H_2O.$$

This equation shows that Fe(II) ion in the GR-II is more readily incorporated into the ferrites than Ni(II) ion.

The formation and transformation of iron oxides, hydroxide oxides in aqueous systems have been studied by many workers.[1–15] The transformation reaction of γ-FeO(OH) to α-FeO(OH) was studied by Schwertmann and Taylor,[10] Oosterhout,[11] and Inoue et al.[15] Music et al.[1] reported the transformation reaction of β-FeO(OH) to α-FeO(OH). We reported that γ-FeO(OH) is transformed to Fe_3O_4 by the adsorption of Fe(II) ion.[12,13] Green rusts (hexagonal plates), which are composed of Fe(II), Fe(III), and sulfate or halogenide ions, are transformed to iron oxides or hydroxide oxides by oxidation of the Fe(II) ions. Recently,[14] we have found that the green rust II spontaneously transforms into Fe_3O_4 without any oxidation reaction (spontaneous transformation reaction). The term "spontaneous" will be used hereafter to distinguish from the oxidation reaction of the green rust II.

A green rust I is formed by the oxidation of Fe(II) ion in an aqueous solution containing Cl^-, Br^-, and F^- ions, and a green rust II, in that containing SO_4^{2-} ions. In the previous paper,[14] we presented a new method for the preparation of the green rust II having a definite chemical composition; The green rust II with the chemical composition of $(Fe^{3+})(Fe^{2+})_2(SO_4^{2-})(OH^-)_{5-2n}(O^{2-})_n$ was synthesized by air oxidation of Fe(II) ion in an aqueous solution containing a high concentration of SO_4^{2-} ion (the air oxidation method). For the reaction solutions containing Fe(II) and Zn(II) ions, Zn(II)-bearing green rust II's (GR-II) with definite chemical compositons were synthesized by the air oxidation method.[16] The present paper describes the synthesis of the Ni(II)-bearing GR-II's with definite chemical compositions by the air oxidation method, and the spontaneous transformation reaction of the Ni(II)-bearing GR-II's to Ni(II)-bearing ferrites.

Experimental

Chemicals. All the chemicals were of analytical grade, and distilled water was used for the preparation of solutions.

Apparatus. The reaction vessel (1 dm^3) of a separable type flask used in the previous paper was adopted.[14] The reaction solution was vigorously stirred with a magnetic stirring bar. An alkaline solution was added using a pH-stat instrument (TOA Electronics, Model HSM-10A). A teflon tube for the addition of the alkaline solution (ϕ 3 mm×40 cm) was connected to the pH-stat instrument, and the capillary tube (ϕ 0.2 mm×5 cm) was fitted to the end of the teflon tube. The tip of the capillary tube was fixed just above the stirring bar and near the glass electrode. A gas mixer with a gas flow controller was used to mix air and nitrogen.

Chemical Analysis. The Fe(II) and Fe_{total} contents were determined by means of the 2,2′-bipyridyl method[17] after dissolving the samples in an HCl solution (1:1). The Fe_{total} was determined after reducing Fe(III) to Fe(II) with hydroxylamine. The content of Ni(II) ions was determined using an atomic absorption spectrometer (Varian Model AA-875). The SO_4^{2-} content was determined by X-ray fluorescence (Toshiba X-ray spectrometer Model AFV 777) from the intensity of sulfur in a $BaSO_4$ precipitate collected on a glass fiber filter (Toyo Roshi GA 100 type). The OH^- content was estimated from the consumed amount of the alkaline solution during the reaction.

Synthesis of Ni(II)-Bearing GR-II. After passing nitrogen gas into a 0.7 dm^3 of the distilled water for 2 h to remove the dissolved oxygen, 25 g of Na_2SO_4, 10 g of $FeSO_4\cdot7H_2O$, and 0—2 g of $NiSO_4\cdot6H_2O$ were dissolved. The pH of the reaction solution was adjusted to 7.1 by adding a 2.0 mol dm^{-3} NaOH solution. The resultant reaction solution was almost transparent and slightly greenish. When the solution was turbid due to the formation of hydroxides, the solution was allowed to stand until the hydroxides dissolved completely. When the deaeration had not been enough to remove the dissolved oxygen, some Fe(III) hydroxide oxides were formed and we could not obtain the GR-II with definite chemical compositions.

The reaction was initiated by passing the mixed gas of air and nitrogen (air/N_2=1:1, flow rate; 3.0 $dm^3\,min^{-1}$) at pH 7.1±0.1 and 25 °C. During the oxidation, an alkaline solution (2.0 mol dm^{-3}) was added to maintain a pH of 7.1. After 20 min, nitrogen gas was passed through in place of the mixed gas, and the reaction vessel was cooled in a water bath chilled with ice. The greenish precipitates formed were collected by centrifugation in a nitrogen atmosphere, washed with distilled water freed from oxygen, and suspended in distilled water. The Ni(II)-bearing GR-II was stable in a nitrogen atmosphere at room temperature.

Electron Microscopy, IR Spectroscopy, and X-Ray Diffractometry for the Ni(II)-Bearing GR-II. A small portion of the Ni(II)-bearing GR-II suspension was taken into an evacuated glass capillary tube, and then sealed. The sample was mounted in a nitrogen atmosphere on a sample holder for electron microscopy. For the IR spectroscopy, the Ni(II)-bearing GR-II was washed with acetone freed from oxygen, dried in a nitrogen atmosphere, and suspended in Nujol. The IR spectrum was taken by a Shimazu IR spectrometer, Model IR 400, using a KBr cell in a nitrogen atmosphere.

Spontaneous Transformation Reaction of the Ni(II)-Bearing GR-II. The suspension of the Ni(II)-bearing GR-II (0.04 dm^3) was transferred in a nitrogen atmosphere to 0.3 dm^3 of a flask with a cap, sealed with Sealon Film (Fuji Co.), and wrapped with a nylon bag to prevent the oxidation. After keeping the flask in the water bath (60 °C) for 12 h, the product was isolated by transferring the reaction suspension to 0.6 dm^3 of a tartaric acid solution (10 w/v%, pH 5.5) and allowing to stand the suspension for 10 h. The product was collected by centrifugation in a nitrogen atmosphere, washed with oxygen-free water and acetone, successively, and dried in a nitrogen atmosphere. The dried product was examined by means of X-ray diffractometry and IR spectroscopy. The IR spectra were measured by the KBr-disc technique.

Results and Discussion

Synthesis of Ni(II)-Bearing GR-II. When the mixture of air and nitrogen gas was passed through the reaction solution, greenish precipitate was formed, and its amount increased with the oxidation time. The X-ray diffraction pattern of the precipitate obtained corresponded to that of the green rust II.[4] In the IR spectrum strong bands of SO_4^{2-} ion (1100 cm^{-1}) appeared. In the electron micrograph, hexagonal plate particles characteristic of the green rust II were observed. Chemical analysis showed that the greenish precipitate contained Fe(II), Fe(III), and Ni(II) metal ions. The metal mole fraction of Ni(II) in the greenish precipitate increased with an increase in the mole ratio of Ni(II)/Fe(II) in the initial reaction solution, as shown by Curve A in Fig. 1. Contrarily, the mole fraction of Fe(II) decreased (Curve C). However, the mole fraction of Fe(III) (Curve B) remained nearly constant. Table 1 shows the mole ratio of bivalent metal ions [Ni(II)+Fe(II)] to trivalent ions [Fe(III)] in the greenish precipitates. The mole ratios are nearly equal to 2:1, which corresponds to that of Fe(II) to Fe(III) ions in the green rust II having no other metal ions.[14] This suggests that the Fe(II) ions in the green rust II are preferentially replaced by the Ni(II) ions. As seen from Fig. 1, the Ni(II)-bearing GR-II having a Ni(II) mole ratio above 0.33 could not be obtained even from a solution of high Ni(II) concentrations. This suggests that only one out of the two Fe(II) ions in the GR-II can be preferentially replaced by Ni(II) ion. The Chemical analysis showed that the chemical composition of the Ni(II)-bearing GR-II was given by $(Ni^{2+})_x(Fe^{2+})_{2-x}(Fe^{3+})(SO_4^{2-})(OH^-)_5$.

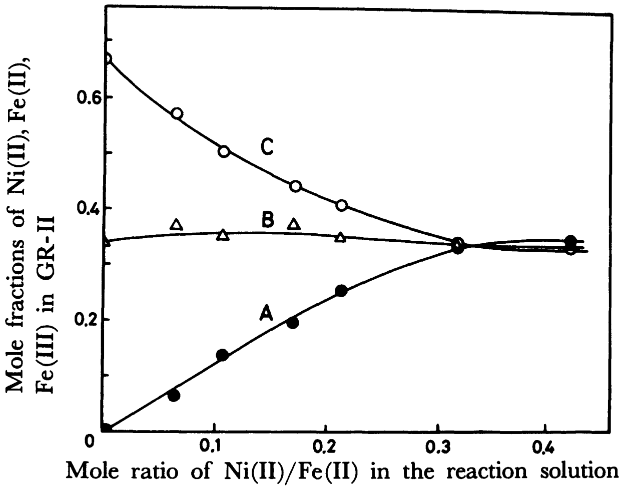

Fig. 1. The relationship between the mole fractions of metal ions [Ni(II); Curve A, Fe(III); B, and Fe(II); C] in the Ni(II)-bearing GR-II and the mole ratio of Ni(II)/Fe(II) in the initial reaction solution.

Table 1. Ratio of Bivalent Metal Ion [Fe(II)+Ni(II)] to Trivalent Metal Ion [Fe(III)] in the Ni(II)-Bearing GR-II

Mole ratio of Ni(II)/Fe(II) in the reaction solution	[Fe(II)+Ni(II)]/Fe(III) in the Ni(II)-bearing GR-II
0.0635	1.72
0.106	1.82
0.169	1.76
0.212	2.19
0.317	2.07
0.423	2.18

Formation of Ni(II)-Bearing Ferrites From the Ni(II)-Bearing GR-II. The X-Ray diffraction pattern of the black precipitate formed from the Ni(II)-bearing GR-II by the spontaneous transformation corresponded to that of a spinel type compound. Electron microscopic observation showed that the hexagonal particles characteristic of the GR-II changed to shperical or cubic particles characteristic of ferrites. In the IR spectrum, only bands corresponding to the ferrite appeared (strong band at 570 cm^{-1}). Thus, the Ni(II)-bearing GR-II spontaneously transformed into a Ni(II)-bearing ferrite in a nitrogen atmosphere without any oxidant (spontaneous transformation reaction).

When we used the Ni(II)-bearing GR-II's with various Ni(II) contents, the Ni(II)-bearing ferrites having various Ni(II) contents were formed by the spontaneous transformation reaction. Their chemical compositions are given by Fig. 2 [ternary diagram (FeO–Fe_2O_3–NiO)]. The broken line connecting Fe_3O_4 and $NiFe_2O_4$ shows the stoichiometric composition of

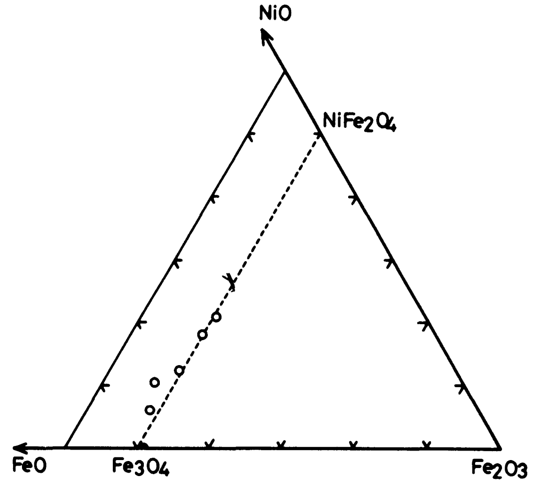

Fig. 2. Chemical compositions (FeO–Fe_2O_3–NiO system) of the Ni(II)-bearing ferrites formed from Ni(II)-bearing GR-II by the spontaneous transformation.

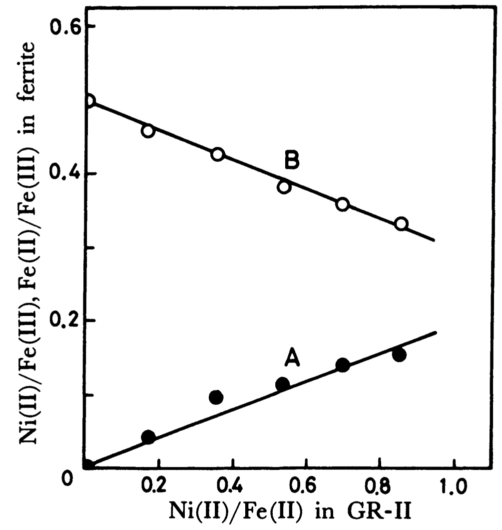

Fig. 3. The relationship between the mole ratios of $[\mathrm{Ni(II)/Fe(III)}]_{\mathrm{fer}}$ (Curve A) and $[\mathrm{Fe(II)/Fe(III)}]_{\mathrm{fer}}$ in the Ni(II)-bearing ferrites and the mole ratio of $[\mathrm{Ni(II)/Fe(III)}]_{\mathrm{grn}}$ in the Ni(II)-bearing GR-II.

the Ni(II)-bearing ferrites. As can be seen here, the chemical compositions of the Ni(II)-bearing ferrites formed by the spontaneous transformation are nearly stoichiometric with respect to oxygen. The limitation in the Ni(II) content in the ferrites is due to the fact that there is a limitation in the Ni(II) content in the Ni(II)-bearing GR-II as described above.

Incorporation of Ni(II) Ions into Ferrites in the Spontaneous Transformation Reaction. Figure 3 shows how the metal mole ratios of $[\mathrm{Ni(II)/Fe(III)}]_{\mathrm{fer}}$ (Curve A) and $[\mathrm{Fe(II)/Fe(III)}]_{\mathrm{fer}}$ (Curve B) in the ferrites change with the metal mole ratio of $[\mathrm{Ni(II)/Fe(III)}]_{\mathrm{grn}}$ in the Ni(II)-bearing GR-II. As can be seen here, the $[\mathrm{Ni(II)/Fe(III)}]_{\mathrm{fer}}$ increases linearly with an increase in the $[\mathrm{Ni(II)/Fe(III)}]_{\mathrm{grn}}$ (contrarily, the $[\mathrm{Fe(II)/Fe(III)}]_{\mathrm{fer}}$ decreases linearly). Since the spontaneous transformation reaction of M(II)-bearing GR-II is generally written by

$$\begin{aligned}&2(M^{2+})_x(Fe^{2+})_{2-x}(Fe^{3+})(SO_4{}^{2-})(OH^-)_5 \longrightarrow \\ &\quad M^{2+}{}_yFe^{2+}{}_{1-y}Fe^{3+}{}_2O_4 + (2x-y)M^{2+} \\ &\quad + (3-2x+y)Fe^{2+} + 2SO_4{}^{2-} + 4H_2O + 2OH^-, \end{aligned} \tag{1}$$

the linear relationship of Curve A in Fig. 3 is given by $y/2=0.193x$. With this, Eq. 1 is rewritten for the Ni(II)-bearing GR-II by

$$\begin{aligned}&2(Ni^{2+})_x(Fe^{2+})_{2-x}(Fe^{3+})(SO_4{}^{2-})(OH^-)_5 \longrightarrow \\ &\quad Ni_{0.39x}Fe_{3-0.39x}O_4 + (2-1.61x)Fe^{2+} \\ &\quad + 1.61xNi^{2+} + Fe(OH)_2 + 2SO_4{}^{2-} + 4H_2O. \end{aligned} \tag{2}$$

As reported previously16) for the spontaneous transformation reaction of the Zn(II)-bearing GR-II, the linear relationship between $[\mathrm{Zn(II)/Fe(III)}]_{\mathrm{fer}}$ and $[\mathrm{Zn(II)/Fe(III)}]_{\mathrm{grn}}$ was obtained. Thus, in the spontaneous transformation reaction, there seems to exist a linear relationship betweeen $[\mathrm{M(II)/Fe(III)}]_{\mathrm{fer}}$ and the $[\mathrm{M(II)/Fe(III)}]_{\mathrm{grn}}$. When the slope of the line of the linear relationship is t, $y=2tx$. To evaluate what bivalent metal ions (M^{2+}) studied here are more readily incorporated into the ferrites in the spontaneous transformation reaction, we compared ratios of $[\mathrm{M(II)/Fe(III)}]_{\mathrm{grn}}$ with those of $[\mathrm{M(II)/Fe(III)}]_{\mathrm{fer}}$. These mole ratios are given by

$$[\mathrm{M(II)/Fe(III)}]_{\mathrm{grn}} = x, \tag{3}$$

and

$$[\mathrm{M(II)/Fe(III)}]_{\mathrm{fer}} = y/2 \quad (=tx). \tag{4}$$

For the ferrites, t and x should range from 0 to 1. The difference, D, bewteeen $[\mathrm{M(II)/Fe(III)}]_{\mathrm{brn}}$ and $[\mathrm{M(II)/Fe(III)}]_{\mathrm{fer}}$ is given by $(1-t)x$. Table 2 shows the relationship bewteen D and t in the spontaneous transformation reaction of the Zn(II)-, Fe(II)-, and Ni(II)-bearing GR-II's. The value of t for Zn(II)-bearing GR-II was evaluated from the data of the previous work (t=0.48).16) For the Fe(II)-bearing GR-II, t=0.25, since $[\mathrm{Fe(II)/Fe(III)}]_{\mathrm{grn}}=2$, and $[\mathrm{Fe(II)/Fe(III)}]_{\mathrm{fer}}=1/2$. As can be seen from Table 2, Zn(II) ion is more readily incorporated into the ferrites in the spontane-

Table 2. Relationship between D ($[\mathrm{M(II)/Fe(III)}]_{\mathrm{fer}}$-$[\mathrm{M(II)/Fe(III)}]_{\mathrm{grn}}$) and t (Slope of the Linear Relationship between $\mathrm{M(II)/Fe(III)}]_{\mathrm{fer}}$ and $[\mathrm{M(II)/Fe(III)}]_{\mathrm{grn}}$ for the Transformation Reaction of the Zn(II)-, Fe(II)-, and Ni(II)-Bearing GR-II)

GR-II	t	D	$\log K_h$
Zn(II)-Bearing GR-II	0.460	0.540×	−8.96
Fe(II)-Bearing GR-II	0.250	0.750×	−9.5
Ni(II)-Bearing GR-II	0.193	0.807×	−9.86

$x=[\mathrm{M(II)/Fe(III)}]_{\mathrm{grn}}$, K_h; hydrolysis constant of MOH^+.

ous transformation reaction compared with Fe(II) and Ni(II) ions, and Ni(II) ion is the most difficult metal ion to be incorporated. This seems to come from the ease of the hydrolysis of those metal ions, considering the hydrolysis constants (log K_h) of −8.96, −9.5, and −9.86 for Zn^{2+}, Fe^{2+}, and Ni^{2+}, respectively.[18)]

Since the particle shapes of the green rust II (hexagonal plate) and the ferrites (cubic) are different, it is assumed that the spontaneous transformation reaction proceeds via a dissolution-precipitation process. The mole ratio of the hydrolyzed species of the metal ions to the hydrolyzed Fe(II) ions is given by

$$\frac{[\mathrm{MOH}^+]}{[\mathrm{FeOH}^+]} = [\mathrm{M(II)/Fe(II)}]_{\mathrm{grn}} \frac{K_h^{\mathrm{M}}}{K_h^{\mathrm{Fe}}}, \tag{5}$$

where we assumed that the metal mole ratio of M(II)/Fe(II) near the surface of the GR-II, where the reaction takes place, is $[\mathrm{M(II)/Fe(II)}]_{\mathrm{grn}}$. K_h^{M} and K_h^{Fe} are the hydrolysis constants of M^{2+} and Fe^{2+} ions, respectively (in the pH range studied here, the main hydrolyzed species are $FeOH^+$ and MOH^+). On the other hand, from Eq. 1, the mole ratio of $[\mathrm{M(II)/Fe(II)}]_{\mathrm{fer}}$ in the ferrites is given by

$$[\mathrm{M(II)/Fe(II)}]_{\mathrm{fer}} = 2tx/(1-2tx). \tag{6}$$

The mole ratios of $MOH^+/FeOH^+$ evaluated from Eq. 5 for Zn(II) and Ni(II) with x in the range of 0—1, and those of $[\mathrm{M(II)/Fe(II)}]_{\mathrm{fer}}$ evaluated from Eq. 6 derived from the experimental results are given in Table 3. As can be seen here, the values evaluated from Eq. 5 are in fair agreement with those from Eq. 6. This suggests that the hydrolyzed species are preferentially incorporated into the ferrites, and that t can be related to the ease of the hydrolysis of the metal ions released from the green rust II.

The ligand field stabilizing energy (LFSE) would also affect the incorporation of metal ions into the spinel structure in the spontaneous transformation reaction. In theGR-II's, the metal ions occupy the octahedral sites. In the ferrites, Fe(II) and Ni(II) ions situate on the octahedral sites, but Zn(II) ion on the tetrahedral site. This means that differences in LFSE of these metal ions between GR-II's and ferrites are zero, indicating that the data (Table 2) can not be explained satisfactorily by LFSE.

Table 3. Comparison of the Values Evaluated from Eqs. 5 and 6 for Zn(II) and Ni(II) with x in the Range of 0—1

x	Ni(II)		Zn(II)	
	Eq. 5	Eq. 6	Eq. 5	Eq. 6
0.2	0.0484	0.0837	0.384	0.225
0.4	0.109	0.183	0.865	0.582
0.6	0.187	0.301	1.48	1.23
0.8	0.291	0.447	2.31	2.79

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