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Zn^{II}-bearing Green Rust II and Its Spontaneous Transformation into Zn^{II}-bearing Ferrite in Aqueous Solution

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When solutions containing Fe^{II}, Zn^{II}, and SO_4^{2-} ions were oxidized by a mixed gas of air and nitrogen at pH 6.7 (25 °C), a Zn^{II}-bearing green rust II (GR-II), which is a uniform crystalline precipitate with a definite chemical composition, was formed. The mol ratio of Zn^{II}/Fe^{II} in the Zn^{II}-bearing GR-II increased linearly with an increase in the Zn^{II}/Fe^{II} mol ratio in the reaction solution. The distribution coeffient of Zn^{II} between the solid (Zn^{II}-bearing GR-II) and the solution phase is 3.3 times higher than that of Fe^{II}. The Zn^{II}-bearing GR-II was spontaneously transformed into Zn^{II}-bearing ferrite. In this reaction, Zn^{2+} ions in the Zn^{II}-bearing GR-II are preferentially incorporated into the ferrites.

Green rusts (hexagonal crystal), which are composed of Fe^{II}, Fe^{III}, and sulphate or halogenide ions are formed in the course of the atmospheric rusting of iron or mild steel, or in the course of the oxidation reaction of an $Fe(OH)_2$ suspension.[1-3] X-ray crystallographic study of the green rusts has been reported by Bernal *et al.*[1] In the previous paper,[4] we examined the synthesis of a pure green rust II having a definite chemical composition, $(Fe^{3+})_1(Fe^{2+})_2(SO_4^{2-})(OH^-)_{5-2n}(O^{2-})_n$. This green rust II is obtained as a crystalline precipitate from a solution containing Fe^{II} and sulphate ions by air oxidation at pH 6.8 and 25 °C. In this reaction, one mol Fe^{III} ion, formed by the oxidation, combines with two mols of Fe^{II} and one mol of sulphate ions, to form the green rust II. Thus, this is a coprecipitation reaction of the metal ions forming a definite crystalline precipitate. In the present paper, we have studied the coprecipitation reaction of Zn^{II} ions into the green rust II (formation of the Zn^{II}-bearing GR-II). This paper also describes the spontaneous transformation of the Zn^{II}-bearing GR-II into the Zn^{II}-bearing ferrite. Generally, GR-II is considered to be transformed into ferrites only by an oxidation reaction.[4] The spontaneous transformation means that GR-II is transformed into ferrites without oxidation.

Experimental

Chemicals. All chemicals were of analytical grade, and distilled water was used for the preparation of chemical solutions. NaOH solutions were prepared by dissolving NaOH in distilled water through which nitrogen gas had been passed to remove dissolved oxygen.

Apparatus. The reaction vessel described in the previous paper[4] was used.

Chemical Analysis. The Fe^{II} and Fe_{total} contents were determined by the 2,2′-bipyridyl method[5] after dissolving the sample in HCl (1:1). The Zn^{II} content was analyzed by atomic absorption. 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).

Synthesis of the Zn^{II}-bearing GR-II. A solution [0.7 dm³, $FeSO_4\cdot 7H_2O$ (2.5—10.0 g), $ZnSO_4\cdot 7H_2O$ (0—2.5 g), and Na_2SO_4(25 g)] was oxidized with a mixed gas of air and nitrogen [air/N_2=1:1 (1 atm), flow rate; 3.0 dm³ min⁻¹] at pH 6.7±0.05 and 25 °C. During the oxidation, an alkaline solution (0.10 mol dm⁻³) was added to maintain a pH of 6.7. After 40 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 under a nitrogen atmosphere, washed with distilled water freed from oxygen (4 °C), and suspended in distilled water (4 °C). The Zn^{II}-bearing GR-II is stable under a nitrogen atmosphere at temperatures below 4 °C.

For the measurement of the metal ions in the Zn^{II}-bearing GR-II in the course of the air oxidation, 0.005 dm³ of the reaction suspension was transferred under a nitrogen atmosphere to a 0.05 dm³ centrifuging tube chilled in ice water. After centrifuging under a nitrogen atmosphere at 3000 r.p.m for 5 min, the precipitate was washed with cold distilled water freed from oxygen, and the contents of the Fe^{III}, Fe^{II}, and Zn^{II} ions were determined.

Spontaneous Transformation Reaction of the Zn^{II}-bearing GR-II. The suspension of the Zn^{II}-bearing GR-II (0.05 dm³, 25 °C) was transferred into 0.4 dm³ of distilled water freed from oxygen (the temperature of the distilled water had been adjusted to get 70 °C after the mixing). The pH of the reaction suspension was adjusted to 10.5 by adding NaOH solution during the reaction. After allowing the reaction suspension to stand at 70 °C under a nitrogen atmosphere for 12 h, the product was isolated by transferring 0.2 dm³ of the reaction suspension to 0.1 dm³ of an oxygen-free acetate buffer solution (pH 4.1, 0.05 mol dm⁻³) to dissolve the metal ions released during the transformation reaction. The product was collected by centrifugation under a nitrogen atmosphere, washed with oxygen-free water and acetone, successively, and dried under a nitrogen atmosphere. The dried product was examined by X-ray diffractometry. The chemical composition was determined after dissolving it in HCl solution (1:1).

Results and Discussion

Formation of the Zn^{II}-bearing GR-II. When the solutions containing Fe^{II}, Zn^{II}, and SO_4^{2-} ions (the Zn^{II}/Fe^{II} mol ratio =0—1.0) were oxidized by a mixed gas of air and nitrogen at pH 6.7 (25 °C), the clear solutions became turbid, and greenish precipitates were formed. The amount of the precipitates in-

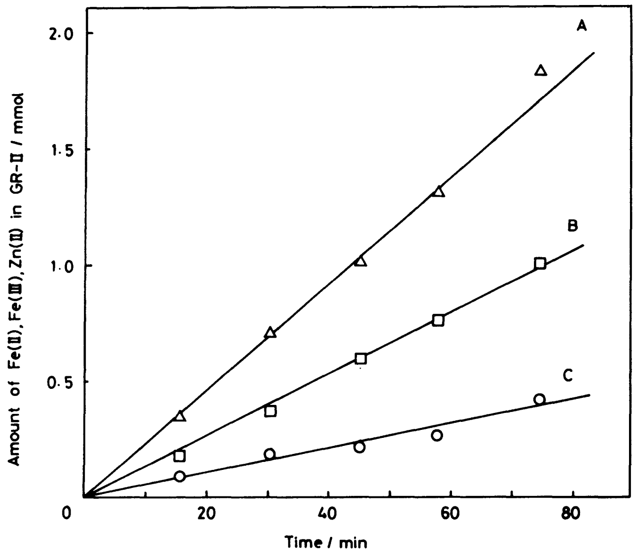

Fig. 1 Time variation of the amounts of Fe^{II}-(Curve A), Fe^{III}(B), and Zn^{II}(C) in the Zn^{II}-bearing GR-II formed during the oxidation reaction. The Zn^{II}/Fe^{II} mol ratio in the initial solution was 0.091.

creased with the oxidation time. Chemical analysis showed that the precipitates contained Fe^{III}, Fe^{II}, and Zn^{II} ions. As shown in Fig. 1, the amount of each metal ion coprecipitated as the greenish precipitates increased linearly with the oxidation time. This shows that the mol fractions of the metal ions in the precipitate are constant; a precipitate with a definite chemical composition was formed. The same results were obtained for the different mol ratios of Zn^{II}/Fe^{II} in the reaction solutions. In the following experiments, we used the greenish precipitates obtained at 40 min of the oxidation time. The X-ray diffraction pattern of the precipitate obtained at 40 min of the oxidation time corresponded to that of the green rust II.[1] In the IR spectrum, strong bands of SO_4^{2-} ion ($1100\,cm^{-1}$) appeared. These results show that Fe^{III} ions formed by the oxidation combine with the Fe^{II}, Zn^{II}, and SO_4^{2-} ions, and form the green rust II, which contains Zn^{II} ions.

The metal mol fraction of Zn^{II} in the Zn^{II}-bearing GR-II increased with an increase in the mol ratio of $Zn^{II}/(Zn^{II}+Fe^{II})$ in the initial solution, as shown by Curve A in Fig. 2. Contrarily, the mol fraction of Fe^{II} decreased (Curve C). However, the mol fraction of Fe^{III} (Curve B) remained nearly constant. The mol ratios of $(Zn^{II}+Fe^{II})/Fe^{III}$ in the Zn^{II}-bearing GR-II (the ratios of the bivalent to trivalent metal ions) are nearly equal to 2:1, which corresponds to the mol ratio of bivalent to trivalent metal ions in the green rust II having no Zn^{II} ions. This suggests that the Fe^{II} ions in the green rust II are preferentially replaced by the Zn^{II} ion. Chemical analysis showed that the chemical composition of the Zn^{II}-bearing GR-II was expressed by $(Zn^{2+})_x(Fe^{2+})_{2-x}(Fe^{3+})(SO_4^{2-})(OH^-)_5$.

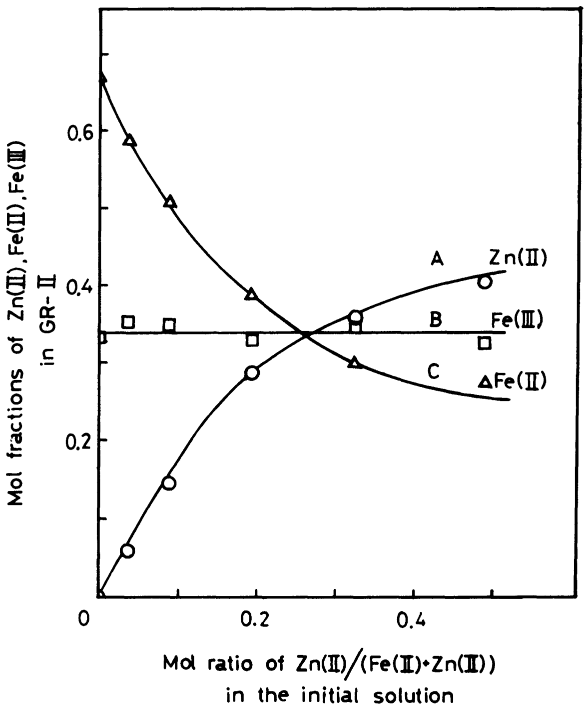

Fig. 2. The relationship between the mol fractions of metal ions (Zn^{II}; Curve A, Fe^{III}; B, and Fe^{II}; C) in the Zn^{II}-bearing GR-II and the mol ratio of $Zn^{II}/(Zn^{II}+Fe^{II})$ in the initial reaction solution. The Zn^{II}-bearing GR-II was obtained at 40 min of the oxidation time.

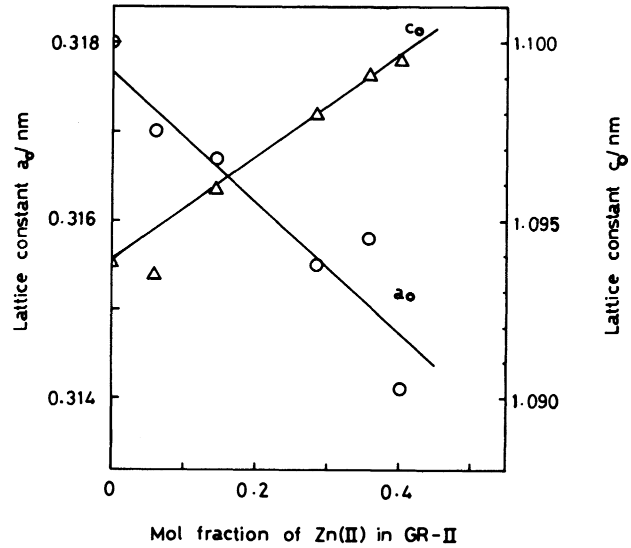

Fig. 3. The relationship between the lattice constants (a_0 and c_0) and the mol fraction of Zn^{II} in the Zn^{II} bearing GR-II.

Figure 3 shows the relationship between the lattice constants and the Zn^{II} content in the Zn^{II}-bearing GR-II. As can be seen here, the lattice constant of c_0 increased with an increase in the Zn^{II} content, but that of a_0 decreased. Since the ion radius of Zn^{2+} is larger than that of Fe^{2+}, it is considered that the Fe^{II} ions arraied along c_0 axis in the green rust II are

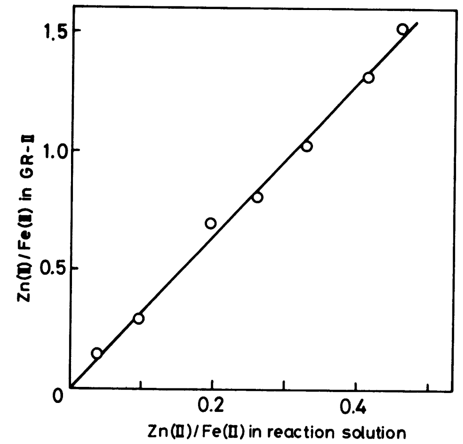

Fig. 4. The relationship between the Zn^{II}/Fe^{II} mol ratio (R_{grn}) in the Zn^{II}-bearing GR-II and those of the Zn^{II}/Fe^{II} mol ratio (R_{sol}) in the initial reaction solution.

preferentially replaced by the Zn^{II} ions.

Figure 4 shows the relationship between the Zn^{II}/Fe^{II} mol ratio (R_{grn}) in the Zn^{II}-bearing GR-II and those of the Zn^{II}/Fe^{II} mol ratio (R_{sol}) in the initial reaction solution. As can be seen here, R_{grn} linearly increases with an increase in R_{sol}. The distribution coefficients of the partitioned ions (D_f and D_z for Fe^{II} and Zn^{II}, respectively) in solid (Zn^{II}-bearing GR-II) and solution phases are given by

$$D_f = [Fe^{II}_{grn}]/[Fe^{II}_{sol}] \tag{1}$$

$$D_z = [Zn^{II}_{grn}]/[Zn^{II}_{sol}]. \tag{2}$$

From these equations, we obtain

$$R_{grn} = \left(\frac{D_z}{D_f}\right)\frac{[Zn^{II}_{sol}]}{[Fe^{II}_{sol}]}. \tag{3}$$

After 40 min of oxidation time, about 8—10 mol% of the metal ions in the reaction solution was consumed with the formation of the Zn^{II}-bearing GR-II. As a first approximation, the concentrations of the Zn^{II} and Fe^{II} ions in the initial solution are substituted for $[Zn^{II}_{sol}]$ and $[Fe^{II}_{sol}]$ in Eq. 3, then

$$R_{grn} \simeq \left(\frac{D_z}{D_f}\right)R_{sol}. \tag{4}$$

Since the linear relationship in Fig. 4 is considered to be represented by Eq. 4, the slope of the line in Fig. 4 gives the value of D_z/D_f. This value suggests that the distribution coeffient of Zn^{II} between the solid (Zn^{II}-bearing GR-II) and the solution phases is 3.3 times higher than that of Fe^{II}. In general, the term "distribution coefficient" is adopted for the phenomena where substances are distributed between two phases without any chemical reactions. In the precipitation reaction studied here, the metal ions of Fe^{II} and Zn^{II} in the solution phase are transferred into the solid phase accompanying the chemical reactions; the physical meaning of D_z and D_f in Eqs. 1—4 are different from the general meaning of the distribution coeffient.

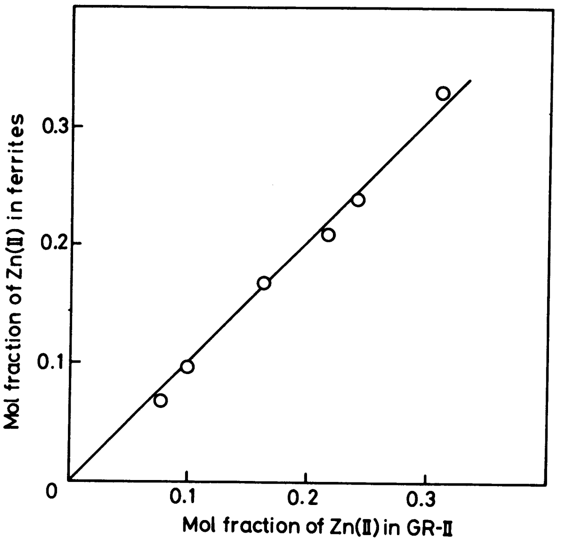

Fig. 5. The relationship between the mol fraction of the Zn^{II} in the Zn^{II}-bearing GR-II and that in the Zn^{II}-bearing ferrites formed by the spontaneous transformation reaction.

Spontaneous Transformation of the Zn^{II}-bearing GR-II into Zn-bearing Ferrites. X-Ray diffractometry showed that the product obtained by allowing the suspension of the Zn^{II}-bearing GR-II to stand under a nitrogen atmosphere at 70°C was a spinel compound. The chemical composition of the product corresponded to a Zn^{II}-bearing ferrite.

Electron microscopic observation showed that the hexagonal particles characteristic of the GR-II changed to spherical or cubic particles characteristic of ferrites. In the IR spectrum of the product, only bands corresponding to the ferrite appeared (strong band at 570 cm^{-1}). Thus, the Zn^{II}-bearing GR-II is spontaneously transformed into the Zn^{II}-bearing ferrite.

The Zn^{II} content in the ferrites increased with an increase in the Zn^{II}-bearing GR-II. Figure 5 shows the relationship between the mol fraction of the Zn^{II} ion $[Zn^{II}/(Zn^{II}+Fe^{II}+Fe^{III})]$ in the ferrites and that in the Zn^{II}-bearing GR-II. As can be seen here, the mol fractions of the Zn^{II} in the ferrites are equal to that in the Zn^{II}-bearing GR-II. This suggests that the spontaneous transformation reaction is represented by

$$\begin{aligned} &2(Zn^{2+})_x(Fe^{2+})_{2-x}(Fe^{3+})(SO_4{}^{2-})(OH^-)_5 + 2H^+ \longrightarrow \\ &\quad (Zn_x{}^{2+}, Fe^{2+}_{1-x})(Fe^{3+})_2O_4 + xZn^{2+} \\ &\quad + (3-x)Fe^{2+} + 2SO_4{}^{2-} + 6H_2O. \end{aligned} \tag{5}$$

The mol ratio of Zn^{2+}/Fe^{2+} in the Zn^{II}-bearing GR-II $[x/(2-x)]$ is smaller than that in the ferrite $[x/(1-x)]$, suggesting that the Zn^{2+} ions in the Zn^{II}-bearing GR-II are preferentially incorporated into the ferrites in the spontaneous transformation reaction.

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