Effect of Silicate Ions on Conversion of Ferric Hydroxide to β -FeOOH and α -Fe₂O₃

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Ferric hydroxide (Fe(OH)₃) gel, prepared from FeCl₃ and NaOH solutions, was aged at 100°C in the presence and absence of silicate ions to examine the effect of silicate ions on the conversion process of condensed Fe(OH)₃ gel to iron oxides. The aged suspensions containing colloidal particles in each stage were separated into solid particles and supernatant solutions by centrifugation. X-ray diffraction measurements and transmission electron microscopic observations of the solid particles revealed that β -FeOOH was formed from the Fe(OH)₃ gel and subsequently converted into α -Fe₂O₃, and the addition of silicate ions in the Fe(OH)₃ gel decreased the conversion rate to β -FeOOH and α -Fe₂O₃ particles. IR measurements of the solid particles and inductively coupled plasma analyses of the supernatant solutions showed that the adsorption of silicate ions on specific plane of the solid particles was decisive factor for the suppression of the conversion process.

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1. Introduction

Corrosion products formed on steel surfaces consist mainly of ferric hydroxides, oxyhydroxides, and oxides. The corrosion rate of the steel substrates is strongly affected by these products formed during the atmospheric corrosion processes. Therefore, their structural and morphological control would lead to the design and development of corrosion-resistant steels.^{1,2)} The structure of the corrosion products are correlated with the linkages of the local structure, which is fundamentally described by FeO₆ octahedral structural units.^{1,3)} The FeO₆ units are maintained even in the amorphous state of ferric hydroxide (Fe(OH)₃).⁴⁾ However, their formation mechanism by way of oxidation and oxolation of the FeO₆ units seems as very complicated, because the constitution of the corrosion products is readily changed by various cations and anions contaminated from alloying elements and/or atmospheric exposure. Furthermore, their structure is also influenced by the atmospheric conditions such as temperature and wetting and drying.¹⁾ Thus, their synthesis under the well-defined aqueous solution systems and the characterization of the resulting products are required for the investigation of the corrosion mechanism.

Ferric oxyhydroxides (FeOOH) are main components of the corrosion products. Akaganeite (β -FeOOH), which can be dehydrated and/or dehydroxylated to ferric oxides (Fe₂O₃), is one of the polymorphs of FeOOH. β -FeOOH is known to be formed by hydrolysis of Fe³⁺ species in aqueous media, and β -FeOOH is considered to be the most detrimental to corrosion-resistance of steel because it contains chloride ions (Cl⁻).^{1,2)} Recently, effects of cations and anions on the formation of β -FeOOH particles followed by the conversion to α -Fe₂O₃ particles have been focused. Some elements have been found to strongly influence the formation, structure, and morphology of the β -FeOOH and α -Fe₂O₃ particles in aqueous solution systems.⁵⁻⁷⁾ However,

further experimental studies about the effects of cations and anions on the formation of the corrosion products are essential for the investigation of the corrosion processes.

Silicon (Si) is one of the most important elements of steel and often used as an alloying element so as to improve their corrosion resistance.⁸⁻¹⁰⁾ Silicate ions are formed by oxidation of silicon contained in steel during atmospheric corrosion. However, the influence of silicate ions on the formation of FeOOH is still unclear. These backgrounds prompt us to study the effect of silicate ions on the conversion processes of Fe(OH)₃ to β -FeOOH and α -Fe₂O₃. In this work, the structure and morphology of solid particles, formed during the conversion processes of Fe(OH)₃ in the presence and absence of silicate ions, will be characterized. The adsorption behavior of silicate ions will be also examined.

2. Experimental

Reagent-grade ferric chloride hexahydrate (FeCl₃·6H₂O), sodium hydroxide aqueous solution (10 mol dm⁻³), and sodium orthosilicate *n*-hydrate (Na₄SiO₄·*n*H₂O (*n* = 3.4 determined by ICP measurement)) were used as received. The method to prepare β -FeOOH and α -Fe₂O₃ particles was fundamentally identical to the previous one.¹¹⁻¹⁵⁾ The FeCl₃ solution was filtered through 0.20 μ m millipore filter to remove insoluble particulates. Aqueous NaOH solution (5.4 mol dm⁻³) was added to 2.0 mol dm⁻³ FeCl₃ aqueous solution containing Na₄SiO₄·*n*H₂O (*n* = 3.4) more than 10 min at 0°C under agitation (300 rpm) to make initial pH of Fe(OH)₃ gel fixed value ranged 4.8 to 5.2 since the addition of silicate ions was found to increase pH of the resulting gels.¹⁶⁾ The concentration of silicate ions was adjusted to be 0, 0.050, and 0.100 mol dm⁻³, which was corresponding to 0, 5.0, and 10.0 mol% based on the ferric ions, respectively. The highly viscous 1.0 mol dm⁻³ Fe(OH)₃ gel was formed through these processes, and then aged at 100°C for different time from 4 h to 14 days, in order to study influence of silicate ions on the conversion processes of the Fe(OH)₃ gel to the β -FeOOH and α -Fe₂O₃ particles. After a

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given aging time, the suspension was cooled to room temperature by running water. Solid particles were washed with the combination of centrifugation of 18000 rpm for 30 min and dispersion with doubly distilled and deionized water for two times, and then freeze-dried.

The crystallographic structures of the obtained solid particle samples were identified by Rigaku RAD-B RINT 2000 system using Ni-filtered Cu K α irradiation (36 kV, 20 mA). Morphologies of the solid particles were observed by using a transmission electron microscope, JEOL JEM-1200EX II with an acceleration voltage of 60 kV. The pH value of the supernatant solution separated from the suspension was recorded with TOA DKK pH meter HM-60G. Inductively coupled plasma (ICP) equipment, Perkin-Elmer Optima 3300, was used to examine concentration of ferric and silicate ions in the supernatant solutions.

3. Results and Discussion

3.1 The conversion of Fe(OH)₃ by aging at 100°C

Fe(OH)₃ suspensions with 0, 0.050, and 0.100 mol dm⁻³ Na₄SiO₄ were aged at 100°C for periods from 4 h to 14 days. Figure 1(a) shows the XRD patterns of the solid particles separated from the aged suspensions without Na₄SiO₄. The aging periods are 4 h, 6 h, 24 h, and 14 days, respectively. These patterns indicate that β -FeOOH particles are formed from the Fe(OH)₃ gel by aging for 4 h, but the line broadening of the diffraction peaks suggests that they are poorly crystalline. The β -FeOOH particles started to be

converted to α -Fe₂O₃ particles by aging for 6 h. All diffraction peaks of the solid particles aged for 24 h are assigned as the α -Fe₂O₃ structure, indicating the complete conversion to α -Fe₂O₃.

In the presence of 0.050 mol dm⁻³ Na₄SiO₄, XRD profiles of the solid particles show that the conversion from the Fe(OH)₃ gel to the β -FeOOH particles is remarkably suppressed by the addition of silicate ions, as shown in Fig. 1(b). α -Fe₂O₃ particles converted from β -FeOOH particles, which are observed by aging for 6 h in the absence of silicate ions, emerge by aging for 24 h in the presence of silicate ions. The β -FeOOH particles are converted to the α -Fe₂O₃ particles completely by aging for 14 days. Remarkable difference of structural changes by the addition of silicate ions is observed in the solid particles with 0.100 mol dm⁻³ Na₄SiO₄, as revealed in Fig. 1(c). The conversion of the Fe(OH)₃ gel to the β -FeOOH and α -Fe₂O₃ particles is completely suppressed by silicate ions increased to 0.100 mol dm⁻³, although the XRD intensity is slightly increased with aging time. Any diffraction peaks of β -FeOOH and α -Fe₂O₃ are not detected and line broadening of the diffraction peaks indicates that they are poorly crystalline like amorphous phase.

The morphological changes of the solid particles with aging time were observed by TEM to compare the structural results obtained by XRD with the morphology of the solid particles. Figure 2 shows TEM micrographs of the solid particles obtained in the presence of 0, 0.050, and 0.100 mol dm⁻³ Na₄SiO₄. The TEM micrographs of the particles without silicate ions (Fig. 2(a)) aged for 6 h exhibit pseudocubic α -Fe₂O₃ particles of black contrast start to be formed actively like the XRD profiles. The solid particles aged for 24 h consist of only α -Fe₂O₃ particles about 200 nm in diameter in accordance with the results of XRD profiles. On the other hand, the formation of the α -Fe₂O₃ particles is initiated by aging for 24 h and finished by aging for 14 day in the presence of 0.050 mol dm⁻³ silicate ions. Although the results corresponded to the formation of pseudocubic α -Fe₂O₃ particles in previous works,^{11,12} the conversion rate to α -Fe₂O₃ particles is decreased as silicate ions concentration increased. A remarkable difference is found in the final size and morphology of the solid particles by the addition of silicate ions. Ellipsoidal particles are obtained by aging for 24 h. They grow about 500 nm in particle long axis in the suspension with 0.050 mol dm⁻³ Na₄SiO₄ by aging for 14 days, which is larger than the particle size obtained in silicate-free system. They were assigned to the α -Fe₂O₃ structure in the XRD patterns. In contrast, β -FeOOH and α -Fe₂O₃ particles are not observed in the suspensions as the concentration of silicate ions increased to 0.100 mol dm⁻³ which are aged even after 14 days. Thus, the addition of 0.100 mol dm⁻³ silicate ions considerably suppressed the conversion of Fe(OH)₃ to β -FeOOH and α -Fe₂O₃. The formation of the ellipsoidal α -Fe₂O₃ particles by the addition of 0.050 mol dm⁻³ can be explained by the specific adsorption of silicate ions on the α -Fe₂O₃ particles. Such morphological control using anisotropic crystal growth inhibition by the specific adsorption has been observed in previous reports.^{13,17-19} In the case with 0.100 mol dm⁻³ silicate ions, the crystal growth inhibition effect by the adsorption might be strongly suppressed the formation of α -Fe₂O₃ particles.

Fig. 1 XRD patterns of solid particles during the conversion process from 1.0 mol dm⁻³ Fe(OH)₃ gel to β -FeOOH and α -Fe₂O₃ particles with (a) 0, (b) 0.050, and (c) 0.100 mol dm⁻³ Na₄SiO₄ aged at 100°C for (i) 4 h, (ii) 6 h, (iii) 24 h, and (iv) 14 days.

Fig. 2 TEM micrographs of solid particles obtained from the suspension with (a) 0, (b) 0.050, (c) 0.100 mol dm⁻³ Na₄SiO₄ by aging for (i) 4 h, (ii) 6 h, (iii) 24 h, and (iv) 14 days.

3.2 pH Changes by aging at 100°C

In order to obtain information complementary to the formation of the β -FeOOH and α -Fe₂O₃ particles in the condensed Fe(OH)₃ gel, pH of the supernatant solutions separated from the aged suspensions of each stage was measured at room temperature. Figure 3 shows the pH values of the supernatant solution with 0, 0.050, and 0.100 mol dm⁻³ silicate ions as a function of the aging time. In the supernatant solution without silicate ions, pH continues to decrease rapidly from the initial stage to the final stage during the conversion process with increasing aging time. On the other hand, pH value of the supernatant solutions with 0.050 and 0.100 mol dm⁻³ silicate ions increases from 0 to 4 h. For the suspensions with 0.050 mol dm⁻³ silicate ions, the rate of pH decrease is drastically reduced from 0 h to 12 h and a subsequent meta-stable stage is observed newly in aging time from about 12 h to 24 h, in which Fe(OH)₃ gel is converted to β -FeOOH particles. After then, pH again decreases by aging over 24 h up to 4 days and a stable stage is observed in aging over 4 days. During the stage with pH decrease, the β -FeOOH particles are converted to the α -Fe₂O₃ particles, as revealed by XRD measurements. The pH decrease can be explained by the lower solubility of α -Fe₂O₃ than Fe(OH)₃ and β -FeOOH, that is, the lower solubility products of α -Fe₂O₃, [Fe³⁺][OH⁻]³.¹⁸⁾ Significant pH changes due to the formation of β -FeOOH and α -Fe₂O₃ are not observed in the supernatant solutions with 0.100 mol dm⁻³ silicate ions, as shown in Fig. 3.

3.3 Changes in the concentrations of iron and silicon species by aging

Concentrations of iron and silicon species in the supernatant solutions as a function of the aging time are shown in Fig. 4. In any cases, iron species are not detected by ICP analyses in the initial stage, but the concentrations are

Fig. 3 Changes in pH of the solution in the suspension with 0, 0.050, and 0.100 mol dm⁻³ Na₄SiO₄ as a function of aging time at 100°C.

drastically increased after aging about 6 h in the absence of silicate ions. It is due to decrease of pH by the formation of the α -Fe₂O₃ particles, as shown in Fig. 3 and Fig. 1(a). The concentration is slightly decreased by further aging at 100°C, and approached to a steady-state after aging for 4 days. However, the increase in the concentration of iron species by aging is delayed between 24 h and 2 days by the presence of

Fig. 4 Changes in concentrations of iron and silicon species in the supernatant solution with 0, 0.050, and 0.100 mol dm⁻³ Na₄SiO₄ as a function of aging time at 100°C.

0.050 mol dm⁻³ silicate ions. During this period, conversion from β -FeOOH to α -Fe₂O₃ is observed (Fig. 1(b)). Such increase in the concentration of iron species is not observed in the supernatant solution with 0.100 mol dm⁻³ silicate ions.

In the case with 0.050 mol dm⁻³ silicate ions, the drastic change of the silicon concentration from 0 to 0.004 mol dm⁻³ after aging for about 24 h is observed. It is corresponding to the formation of the α -Fe₂O₃ particles. Silicon species could not be detected in the supernatant solution of the system with 0.100 mol dm⁻³ silicate ions. The result indicates that all of the silicate ions added in each system are totally used in the initial stages, regardless of their addition amounts, by the complexation with the Fe(OH)₃ gel and/or adsorption on the solid particles. Then, in the case with 0.050 mol dm⁻³ silicate ions, less than 10% silicate ions were released into the supernatant solutions by the formation of the α -Fe₂O₃ particles. Silicate adsorption amount on β -FeOOH can be higher than α -Fe₂O₃. Thus, the influence of silicate ions can be explained by that the silicate ions suppress the formation of direct precursors of β -FeOOH and α -Fe₂O₃ and/or reduce the formation rate of the particles. On the other hand, IR measurements of the solid particles in the early stages, obtained in the presence of silicate ions, revealed that the silicate ions were adsorbed on the solid surfaces. The absorption amount was increased with increasing the addition amounts of the silicate ions.

In the present study, we have observed that the suppression of the conversion from Fe(OH)₃ gel to β -FeOOH and α -Fe₂O₃ by the addition of the silicate ions in the aqueous solution systems. However, further detailed characterization and evaluation will be needed to understand the role of silicate ions completely.

4. Conclusions

Powder XRD, TEM, pH, IR measurements, and ICP analyses have been used for characterizing influences of silicate ions on the conversion of Fe(OH)₃ gel to solid particles of β -FeOOH and α -Fe₂O₃ by aging. Main concluding remarks obtained from this work are as follows:

- (1) The addition of silicate ions drastically suppressed the conversion of Fe(OH)₃ gel to β -FeOOH and α -Fe₂O₃ particles and the conversion of Fe(OH)₃ gel was not observed in the suspensions as the concentration of silicate ions increased to 0.100 mol dm⁻³.
- (2) Silicate ions had remarkably strong affinity with ferric ions and this is considered to lead to the inhibition of the conversion process of Fe(OH)₃ gel to β -FeOOH and α -Fe₂O₃ particles.

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