

Influence of Metal Ions on the Transformation of γ -FeOOH into α -FeOOH

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The transformation of γ -FeOOH into α -FeOOH in FeSO₄ solutions at 50°C was investigated in two different ways by dissolving Ti(IV), Cr(III), Cu(II), Ni(II), and Mn(II) in the solutions at atomic ratios of metal/Fe of 0-0.1 and adding these metal ions to the γ -FeOOH particles. The transition into α -FeOOH was examined by Fourier transform infrared spectroscopy and X-ray diffraction. Ti(IV), Cr(III), and Cu(II) dissolved in the solutions markedly interfered with the transition into α -FeOOH, whereas Ni(II) and Mn(II) showed no influence. The inhibitory effect of the former three metal ions is ascribed to the protection of γ -FeOOH particles against dissolution in FeSO₄ solution by surface coating with the hydrolysis species of metal ions, because transmission electron microscopy and inductively coupled plasma-Auger electron spectroscopy demonstrated that the conversion proceeds by dissolution and recrystallization. The metal ions added in γ -FeOOH particles due to the decrease in particle size by the addition of metal ions.

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Manuscript submitted July 16, 2003; revised manuscript received February 21, 2004. Available electronically August 11, 2004.

Steel rusts consist of α -, β -, and γ -FeOOH, Fe₃O₄, and amorphous iron oxides of which the composition depends on exposure environment.¹ Weathering steel intended to be free from maintenance is doped with alloying elements such as Cu, Cr, Ni, and Ti to enhance the corrosion resistance; however, the function of alloying metals remains not fully interpreted. Yamashita et al. reported that Cr(III) is incorporated into α -FeOOH to form the stable protective layer of nanosized Cr-substituted α -FeOOH.² Recently, Kamimura and Stratmann revealed that Cr inhibits the cathodic reaction in corrosion.³ We have done a series of systematic investigations on the influences of various metal ions on the formation and structure of α -FeOOH,⁴⁻⁶ β -FeOOH,⁷⁻¹⁰ γ -FeOOH,¹¹ Fe₃O₄,¹¹⁻¹³ and poorly crystallized iron oxides^{14,15} by using artificially synthesized rusts in order to gain comprehensive information on the influence of metal ions. These studies revealed that the influence of the metal ions on the formation and structures of rusts depends on the kinds of metal ions and rust components and suggested that alloying with more than two kinds of metals is effective for formation of a protective rust layer.16

The composition of rusts varies with time by structural transformation of the rust components. The most important transformation is the conversion of γ -FeOOH into α -FeOOH. α -FeOOH is thermodynamically more stable than γ -FeOOH, as is evidenced by the standard free energy of formation, which is 496 J/mol for α -FeOOH and 471 J/mol for γ -FeOOH;¹⁷ thus, α -FeOOH is a more stable rust component than y-FeOOH. For this reason, the mass ratio of α -FeOOH to γ -FeOOH in rusts (α/γ) can be used as a measure of stability and the protective property of rusts, and the corrosion rate of steels in atmosphere was found to be extremely low at $\alpha/\gamma > ca. \ 2.^{18}$ This suggests that promotion of the conversion into α -FeOOH leads to fast formation of stable rusts showing a high resistance to corrosion. However, there have been few reports on the transformation of γ -FeOOH into α -FeOOH despite voluminous studies on the formation, structures, and properties of these FeOOHs.¹⁹ Krause *et al.* have found that γ -FeOOH transforms into α-FeOOH on heating at 150°C in 2 mol/dm³ KOH.²⁰ Nitschmann has reported that γ -FeOOH transforms easily in an aqueous FeSO₄ solution kept at 60°C and concluded that the transformation takes place in the crystal by a topotactic and pseudomorphic process.⁴ After about thirty years, Oosterhout has investigated the effect of α -FeOOH nuclei on the transformation of γ -FeOOH in KOH or FeSO₄ solutions at 70-150°C and detected an appreciable decrease

of particle size after the transformation and a promotion of transformation by adding α -FeOOH nuclei. Thus, the transformation proceeds by dissolution followed by crystallization, and the function of Fe(II) is to increase the dissolution rate of γ -FeOOH in an acidic solution.²² Bechine *et al.* have also reported that γ -FeOOH transforms into α -FeOOH and α -Fe₂O₃ in FeSO₄ solutions at 95-100°C and explained the obtained results by the dissolution and recrystallization mechanism.²³ The electrochemical reductive dissolution of γ -FeOOH enhances the transformation reaction into α -FeOOH.²⁴ However, as far as we know, there is no report on the effects of coexisting metal ions on the transformation of γ -FeOOH into α -FeOOH, except the report by Oosterhout that CoSO₄ showed no influence on the transformation.²²

To explore the anticorrosion function of alloying metals in weathering steels, the effect of metal ions on the structural transformation of rust components should be investigated in addition to the influence of metal ions on the formation and structure of rusts. From this point of view, the present study focused the transformation of γ -FeOOH into α -FeOOH in the presence of various metal ions.

Experimental

The preparation of γ -FeOOH.—The transition of γ -FeOOH into α -FeOOH in rusts must be affected by the metal ions dissolved from alloying metals into solutions and incorporated in γ -FeOOH particles during their formation. So we prepared two series of γ -FeOOH samples as follows.

The γ -FeOOH particles for studying the influence of metal ions dissolved in solution were synthesized by aerial oxidation of an FeCl₂ solution by bubbling air at a flow rate of 4 dm³/min and 50°C for 2 h. The FeCl₂ solution was prepared by adding 200 cm³ water and 200 cm³ of a buffer solution (pH 7.5) to 300 cm³ of a 0.2 mol/dm³ FeCl₂ solution. The buffer solution was prepared by adding a 0.1 mol/dm³ NH₄OH solution to a 0.1 mol/dm³ NH₄Cl solution up to pH 7.5. During oxidation the solution pH was adjusted to 4.5 by dropping a 0.1 mol/dm³ NH₄OH solution.

The second series of γ -FeOOH samples were synthesized by aerial oxidation of an FeSO₄ solution. 1 dm³ solutions dissolving 0.02 mol FeSO₄ and different metal salts of Ti(SO₄)₂, Cr(NO₃)₃, CuSO₄, and NiSO₄ at metal/Fe atomic ratios varied from 0 to 0.1 were oxidized by bubbling air at a flow rate of 8 dm³/min and 35°C for 3 h, the solution pH being adjusted to 4.5-6.5 by dropping a 2 mol/dm³ butylamine solution throughout the oxidation. The resulting precipitates were separated from solution by filtration with a

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Figure 1. IR spectra of the products by the AS method at different concentrations of $FeSO_4$.

 $0.22 \ \mu m$ Nuclepore, washed with distilled-deionized water, and finally dried at 70°C in air for more than 15 h.

The transition into α -FeOOH.—By using the γ -FeOOH samples thus prepared the influence of metal ions on the transformation into α -FeOOH was examined in different methods of addition of metal ions in solution and γ -FeOOH particle. Hereafter, we abbreviate the addition in solution as the AS method and the addition in γ -FeOOH particle as the AP method.

The transition into α -FeOOH was examined by the AS method as follows. 500 mg γ -FeOOH powders were dispersed in 25 cm³ of 0.3 mol/dm³ FeSO₄ solutions dissolving different metal salts of Ti(SO₄)₂, Cr(NO₃)₃, CuSO₄, NiSO₄, ZnSO₄, and MnSO₄ at different metal/Fe ratios from 0 to 0.1 and treated in a tightly closed 30 cm³ vial at 50°C for 120 h. The metal/Fe is the atomic ratio of metal salt to Fe of FeSO₄. The reason for using Cr(NO₃)₃ instead of Cr₂(SO₄)₃ is a low solubility of the latter. The influence of individual metal salt was inspected by single addition of FeSO₄, NiSO₄, and CuSO₄ at varied concentrations of 0-0.3 mol/dm³ under the condition mentioned previously.

In the AP method, 500 mg of γ -FeOOH particles containing different amounts of Ti(IV), Cr(III), Cu(II), and Ni(II) were dispersed in 25 cm³ of a 0.3 mol/dm³ FeSO₄ solution and treated under the same condition as the AS method. After the treatment in the AS and AP methods, the samples were washed and dried in the same manner as the preparation of γ -FeOOH particles.

The characterization of products.—IR spectra of the products were taken by a KBr method using a Fourier transform infrared (FTIR) spectrophotometer (Nicolet, Protage 460). The sample concentration was 1 mg/500 mg KBr. Powder X-ray diffraction (XRD)



Figure 2. Changes in $X\alpha$ of the products with sulfates of (\bigcirc) Fe(II), (\triangle) Ni(II), and (\square) Cu(II) with metal sulfate concentrations.

patterns were traced by a diffractometer (Rigaku, Geigerflex 2013) with Cu K α radiation (30 kV, 15 mA). The metal content of the particles was assayed by an induction coupled plasma atomic emission spectrometer (ICP-AES, Seiko, SPS1200VR). The samples were dissolved in a concentrated HCl, and the solutions were diluted to a desired concentration by water. The particle morphology was observed by a transmission electron microscope (TEM, JEOL, 200B). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using N₂ adsorption isotherms measured by an automatic adsorption apparatus assembled in our laboratory. Before the adsorption, the samples were degassed under 10⁻³ Torr at 100°C for 2 h.

Results and Discussion

The influence of metal ion dissolved in solution.-Although Oosterhout has reported that FeSO₄ promotes the transition of $\gamma\text{-}\text{FeOOH}$ into $\alpha\text{-}\text{FeOOH}$ but CoSO_4 shows no influence, 22 there is no report on the effect of the other metal ions. Accordingly, we examined the influence of CuSO₄, NiSO₄, and FeSO₄ by the AS method. Figure 1 displays IR spectra of the products at different concentrations of FeSO₄. The spectrum of the product without FeSO₄ shows the bands characteristic of γ -FeOOH²⁵ at 1160, 1020, and 743 cm^{-1} and an additional weak band of $\alpha\text{-FeOOH}^{26}$ at 880 cm⁻¹, being the same as the spectrum of the original γ -FeOOH. Thus, the original γ -FeOOH contains a small amount of α -FeOOH. The massive synthesis of pure γ -FeOOH by aerial oxidation is difficult, because residual Fe(II) facilitates the conversion into α -FeOOH as described previously. It is known that PO₄³⁻ and ethvlenediaminetetraacetic acid (EDTA) inhibit the conversion into α -FeOOH;^{27,28} however, the samples synthesized with these additives is unsuitable for the purpose of the present study due to anxiety that the additives remaining in the particles affect the conversion into α -FeOOH. As seen in Fig. 1, the peaks due to α -FeOOH intensify with the increase in FeSO₄ concentration whereas those due to γ -FeOOH weaken, indicating that the transition of γ -FeOOH into α -FeOOH is promoted by the presence of FeSO₄. The transition into α -FeOOH is quantified by a peak intensity ratio of $I\alpha/(I\alpha)$ $(+ I\gamma) = X\alpha$, where $I\alpha$ is the area intensity of the 880 cm⁻¹ band



Figure 3. IR spectra of the products by the AS method with $CuSO_4$ at varied Cu/Fe.

of α -FeOOH and $I\gamma$ is that of the 1020 cm⁻¹ band of γ -FeOOH. Figure 2 plots $X\alpha$ of the reactions in the presence of CuSO₄, NiSO₄, and FeSO₄ *vs.* concentration of the metal salts. The $X\alpha$ value of the reaction with FeSO₄ steeply rises with increasing the FeSO₄ concentration, whereas those of the reactions with CuSO₄ and NiSO₄ are constant. From this figure it can be clearly conceived that only FeSO₄ promotes the conversion into α -FeOOH. This function of FeSO₄ has been explained by Oosterhout, who considered that the electron transfer from Fe(II) in solution to Fe(III) in γ -FeOOH particles enhances the dissolution of γ -FeOOH particles.²² It goes without saying that the electron transfer from Cu(II) and Ni(II) to Fe(III) does not take place. Consequently, the addition of FeSO₄ is inevitable for the transition into α -FeOOH; hereafter, all experiments used a 0.3 mol/dm³ FeSO₄ solution.

Figure 3 shows IR spectra of the products by the reaction in 0.3 mol/dm³ FeSO₄ solutions dissolving CuSO₄ at different metal/Fe. The absorption bands of γ -FeOOH disappears at metal/Fe = 0, indicating that γ -FeOOH is completely transformed into α -FeOOH without the additives except FeSO₄. However, at Cu/Fe \geq 0.025 the γ -FeOOH bands reappear and intensify with the increase of Cu/Fe, that is, the transition into α -FeOOH is suppressed by adding Cu(II). Figure 4 shows XRD patterns of the products with Cu(II), which demonstrate the inhibitory effect of Cu(II) as well as the IR spectra; with increasing Cu/Fe the diffraction peaks of γ -FeOOH (JCPDS 8-98) increase in intensity and those of α -FeOOH (JCPDS



Figure 4. XRD patterns of the products by the AS method with $CuSO_4$ at varied Cu/Fe.

17-536) weaken. The pattern of the sample before the reaction shows no peak of α -FeOOH different from the IR spectrum, which is due to a lower sensitivity of XRD than FTIR.

To compare the influences of the metal ions, $X\alpha$ of the reactions with different metal ions is plotted *vs.* metal/Fe in Fig. 5. Interestingly, $X\alpha$ does not decrease on adding Ni(II) and Mn(II), while the addition of Zn(II), Cu(II), Cr(III), and Ti(IV) decreases $X\alpha$ or impedes the transition into α -FeOOH, markedly for the latter three metal ions. The inhibitory effect seems to be caused by interfering with the dissolution of γ -FeOOH and the recrystallization of α -FeOOH, which are possible mechanisms of the conversion into α -FeOOH. However, no diminution of particle size and drop of crystallinity was observed after the reactions with Cu(II), Cr(III), and Ti(IV) as confirmed by TEM and XRD. This strongly suggests that these metal ions inhibit the dissolution of γ -FeOOH particles,



Figure 5. $X\alpha$ changes of the products by the AS method with (\bigcirc) Ti(IV), (\triangle) Cr(III), (\square) Ni(II), (\bullet) Cu(II), (\blacktriangle) Mn(II), and (\blacksquare) Zn(II) metal salts with metal/Fe of the starting solutions.

Table I. Hydrolysis	constants (K)	for $Me^{n+} + H_2O$
$= \operatorname{MeOH}^{(n-1)+} + \operatorname{H}^+$	and precipitation	pH of metal ions at
25°C.		

Metal ion	Κ	pH
Ti(IV)	-1.8 ^a	<1
Fe(III)	-2.4	2.0
Cr(III)	-3.7	4.7
Cu(II)	-8.0	6.0
Zn(II)	-9.1	7.0
Fe(II)	-9.3	7.5
Ni(II)	-10.5	8.0
Mn(II)	-10.6	8.0

^a
$$\text{Ti}(\text{OH})^{3+} + \text{H}_2\text{O} = \text{Ti}(\text{OH})^{2+}_2 + \text{H}^+.$$

despite the coexistence of Fe(II) assisting the dissolution. It was confirmed that without Fe(II) all the metal ions including Ni(II) and Mn(II) did not affect the morphology and crystallinity of γ -FeOOH particles (the data not shown here). Therefore, we can infer that Zn(II), Cu(II), Cr(III), and Ti(IV) interrupt the dissolution of γ -FeOOH particles by Fe(II) and protect the γ -FeOOH particles from dissolution in the FeSO4 solution. Such stabilization of γ -FeOOH particles may be explained by considering that the γ -FeOOH particles are coated by the hydrolysis species of the added metal ions. The formation of the hydrolysis species depends on the hydrolysis constants (K) of the metal ions shown in Table I.^{29,30} Ti(IV), Cr(III), and Cu(II), which inhibit the transition into α -FeOOH, show a larger K than Ni(II) and Mn(II) exhibiting no influence. For more easily understanding this relation, $X\alpha$ at metal/Fe = 0.05 is plotted against K in Fig. 6. It is noteworthy that Ni(II) and Mn(II) with K less than -9.3 of Fe(II) show $X\alpha = 1$ and do not interfere with the transition into α -FeOOH, whereas $X\alpha$ of Ti(IV), Cr(III), and Cu(II) with K more than -9.3 is less than unity and these metal ions impede the conversion. This fact is a convincing evidence for the stabilization of γ -FeOOH particles in FeSO₄ solution by the surface coating.

It has been reported that the crystallization of α -FeOOH is impeded by Ni(II), Cu(II), Cr(III), and Ti(IV) coprecipitating with



Figure 6. Plots of $X\alpha$ of the products by the AS method at metal/Fe = 0.05 *vs.* the hydrolysis constant (*K*) of the added metal ions.



Figure 7. Plots of metal/Fe of the particles formed by the AS method with (\bigcirc) Ti(IV), (\triangle) Cr(III), (\square) Cu(II), (\spadesuit) Ni(II), (\spadesuit) Zn(II), and (\blacksquare) Mn(II) metal salts *vs.* metal/Fe of the starting solutions.

Fe(III).^{6,31} Especially, the hindrance with Cu(II) is most effective, presumably due to the Jahn Teller effect distorting the octahedron of Cu(II) coordinated by O^{2-} and OH^{-} .³² However, in the previous study α -FeOOH was synthesized at a high pH, ≥ 12 , so that the added metal ions were nearly precipitated with Fe(III). In the present study the solution pH after the reaction was less than ca. 3. Table I lists the theoretical precipitation pH of the metal ions at 0.01 mol/dm³ calculated from the solubility products of metal hydroxides and the ion product of water.²⁹ According to this table only Ti(IV) can precipitate with Fe(III). However, metal ions with different precipitation pH are frequently coprecipitated by induced precipitation due to adsorption and occlusion of hydrolysis species of metal ions showing a higher precipitation pH. To confirm the coprecipitation with Fe(III), we determined the metal ion content of the formed particles by ICP-AES. Figure 7 plots metal/Fe of the formed particles against that of the starting solutions. The metal/Fe of the particles is on the order of Ti(IV) > Cr(IV) > Cu(II) > Zn(II)> Ni(II) > Mn(II), being well equivalent to the order of K and precipitation pH in Table I. Note that the particles formed with the metal ions impeding the transition into α -FeOOH show a high metal/Fe ratio, which is evidence of the surface coating. The products with Ti(IV) show an extremely high Ti/Fe ratio due to a partial

= 0.05.



500nm Figure 8. TEM images of the particles formed by the AS method with

Ti(IV), Cr(III), Ni(II), Cu(II), Mn(II), and Zn(II) metal salts at metal/Fe

Figure 9. TEM images of the particles before and after reaction by the AP method with $NiSO_4$ at varied Ni/Fe.

dissolution of Fe(III) from γ -FeOOH particles, because the solution pH after the reaction with Ti(IV) of 1.6-1.9 depending on Ti/Fe was lower than 2 of the precipitation pH of Fe(III) but higher than that of Ti(IV). Ni(II) and Mn(II) not affecting the conversion into α -FeOOH show less metal/Fe of the formed particles and smaller *K* than the metal ions impeding the conversion, and a higher precipitation pH than Fe(III). Consequently, the surface coating with the hydrolysis species of Ti(IV), Cr(III), and Cu(II) stabilizes the γ -FeOOH particles in FeSO₄ solution. Ni(II) and Mn(II) do not inhibit the conversion into α -FeOOH due to less surface coating, and further, they are almost uncontained in the formed α -FeOOH particles because of their higher precipitation pH than Fe(III). These results can be explained by the dissolution and recrystallization mechanism of the transition into α -FeOOH.

For further verification of the transition mechanism discussed previously, we observed the morphology change of the particles by the reaction. Figure 8 displays the TEM images of the particles before and after the reaction in a 0.3 mol/dm³ FeSO₄ solution dissolving different metal ions at metal/Fe = 0 and 0.05. The original γ -FeOOH particles before the reaction are aggregates of thin plates. The reaction at metal/Fe = 0 or only with Fe(II) produces small needle α -FeOOH particles. The similar needle α -FeOOH particles are formed by the reactions with Ni(II), Mn(II), and Zn(II). The reactions with Ti(IV), Cr(III), and Cu(II) do not noticeably change the particle morphology, and the thin γ -FeOOH particles remain after the reaction, through a few needle α -FeOOH particles are visible. Similar to FTIR and XRD, TEM demonstrates that γ -FeOOH converts into α -FeOOH by dissolution and recrystallization.

The influence of metal ion contained in particles.—The influence of the metal ions contained in the γ -FeOOH particles was studied by the AP method. Figure 9 displays the TEM images of the γ -FeOOH particles containing Ni(II) at Ni/Fe = 0-0.1 before and after the reaction. The particles before the reaction get smaller with the increase of Ni/Fe due to the interruption of particle growth by Ni(II). The particles become smaller after the reaction with the increase of Ni/Fe corresponding to the particles before the reaction; smaller particles give smaller ones. As described later, γ -FeOOH was completely transformed into α -FeOOH at Ni/Fe ≥ 0.01 . A glance at this therefore indicates that γ -FeOOH converts into α -FeOOH by a solid-state transition, being different from the AS method, but this was denied by measuring the metal content of the particles before and after the reaction, as discussed later. The result that smaller α -FeOOH particles result from smaller γ -FeOOH ones can be inter-



Figure 10. Plots of $X\alpha$ of the products by the AP method with (\bigcirc) Ti(IV), (\triangle) Cr(III), (\square) Ni(II), and (\bigcirc) Cu(II) metal salts *vs.* metal/Fe of the particles before the reaction.

preted by the inhibitory effect of Ni(II) on the particle growth of α -FeOOH.⁶ The similar trend was found in the addition of the other metal ions.

Figure 10 plots $X\alpha$ determined in the same way as the AS method vs. metal/Fe of the γ -FeOOH particles before the reaction. The product at metal/Fe = 0 shows $X\alpha$ of 0.37, less than 1.0 of $X\alpha$ obtained by the AS method (Fig. 5), which is due to the difference in particle size of these samples. From observing the TEM pictures in Fig. 8 and 9, the original γ -FeOOH particles in the AS method (Fig. 8) are smaller than the particles before reaction at metal/Fe = 0 in the AP method (Fig. 9), so that the former is more soluble in the FeSO₄ solution and easily transforms into α -FeOOH than the latter. As seen in Fig. 10, $X\alpha$ is increased by the addition of all the metal ions. The addition of Cr(III) and Ni(II) abruptly increases $X\alpha$ up to 1.0 at a low metal/Fe of 0.01 and effectively promotes the conversion into α -FeOOH, but Ti(IV) does not prominently increase $X\alpha$. Because the solubility of the γ -FeOOH particles must affect the conversion into α -FeOOH by dissolution, the size of the γ -FeOOH particles used in the AP method was estimated from the specific surface area determined from N₂ adsorption isotherms, because the reliable mean particle size was difficult to measure from the TEM pictures of the particles with an irregular shape. The addition of the metal ions increased the specific surface area of the γ -FeOOH particles, that is, it decreased the particle size. Figure 11 plots $X\alpha$ vs. the specific surface area, which quite resembles Fig. 10 showing the relation between $X\alpha$ and the metal/Fe of the particles before the reaction. $X\alpha$ increases with the specific surface area, that is, smaller γ -FeOOH particles more easily convert into α -FeOOH, strongly supporting the dissolution and recrystallization mechanism.

If the conversion into α -FeOOH proceeds in the particles by a solid-state transition, the metal content of the γ -FeOOH particles should not vary during the conversion. To confirm this, the metal/Fe ratios of the particles before and after the reaction are shown in Fig. 12. The products with Ti(IV) and Cr(III), of which the precipitation pH is close to that of Fe(III), shows the equivalent metal/Fe ratio before and after the conversion, whereas the metal/Fe ratio of the products with Cu(II) and Ni(II) after the reaction is less than that before the reaction. It becomes more apparent that the transition takes place by the dissolution of γ -FeOOH and the recrystallization of α -FeOOH. The metal ions once dissolved into the solutions are



Figure 11. Plots of $X\alpha$ of the products by the AP method with (\bigcirc) Ti(IV), (\triangle) Cr(III), (\square) Ni(II), and (\bullet) Cu(II) metal salts *vs.* specific surface area of the particles before the reaction.

incorporated again in the formed α -FeOOH particles, affecting the particle growth of α -FeOOH.

Conclusions

The transformation of γ -FeOOH into α -FeOOH in FeSO₄ solution was influenced by the metal ions dissolved in solution. Cu(II), Cr(III), and Ti(IV) in solutions markedly interfered with the transformation, but Ni(II) had no affect. These metal ions added to γ -FeOOH particles promoted the transition into α -FeOOH by reducing the particle size; Ni(II) most effectively enhanced it. Therefore,



Metal/Fe of particle before reaction, atomic ratio

Figure 12. Plots of metal/Fe of the particles formed by the AP method with (\bigcirc) Ti(IV), (\triangle) Cr(III), (\square) Ni(II), and (O) Cu(II) metal salts *vs.* metal/Fe of the particles before the reaction.

among the metal ions used in the present study Ni(II) is thought to be most effective in promoting the transition into α -FeOOH. This finding allows us to infer that the anticorroding function of the alloying metal elements is not only to promote the formation of thermodynamically stable α -FeOOH rusts but also to reduce the particle size and crystallinity of α -FeOOH rusts, leading to the formation of compact and stable rust layers. The information presented in this article provides understanding of the anticorroding effect of allowing metals in weathering steels, because the transition of γ -FeOOH into α -FeOOH rusts is an important process concerning the stabilization and protective nature of rusts.

Acknowledgment

The authors are grateful to Masao Fukusumi of Osaka Municipal Technical Research Institute for help with the TEM observations. This study was partly supported by the Grant-in-Aid for Science Research Funds (B) from the Ministry of Education, Science, Sports and Culture, Japan.

Osaka University of Education assisted in meeting the publication costs of this article.

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