



Short Communication

Formation of magnetite rust particles by reacting iron powder with artificial α -, β - and γ -FeOOH in aqueous mediaHidekazu Tanaka^{a,*}, Ryohei Mishima^a, Nagisa Hatanaka^a, Tatsuo Ishikawa^b, Takenori Nakayama^c^a Department of Chemistry, Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan^b School of Chemistry, Osaka University of Education, 4-698-1 Asahigaoka, Kashiwara, Osaka 582-8582, Japan^c Materials Research Laboratory, Kobe Steel, Ltd., 5-5 Takatsukadai 1, Nishi-ku, Kobe, Hyogo 651-2271, Japan

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ABSTRACT

To simulate the atmospheric corrosion of steels, magnetite (Fe_3O_4) rust particles were prepared in aqueous media containing iron powder (α -Fe) and artificial α -, β - and γ -FeOOH particles at pH = 6.0 and 50 °C for 24 h. The Fe_3O_4 formation was not recognized by treating the iron powder with α -FeOOH. When the iron powder treated with β - and γ -FeOOH, these materials were dissolved to generate Fe_3O_4 and α -FeOOH particles. The amount of formed Fe_3O_4 particles was in the order of β -FeOOH > γ -FeOOH $\gg$ α -FeOOH, which was strongly related to the density and solubility of FeOOH.

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1. Introduction

Atmospheric corrosion products of steels consist of α -, β -, γ -FeOOH, Fe_3O_4 and poorly crystallized iron oxides of which the composition strongly depends on the exposure environment [1]. The β -FeOOH rust is formed in Cl^- -containing environment such as zones where CaCl_2 and MgCl_2 are used as anti-freezing and snow-melting agents and the marine zone including air-borne chloride [1,2]. The α - and γ -FeOOH rusts are mainly generated in the presence of NO_x and SO_x in atmosphere such as coastal and industrial districts [3]. On the other hand, the Fe_3O_4 rust is formed in all environments [3]. It has been reported by Evans and Stratmann et al. that the Fe_3O_4 rust is formed by two routes at wet condition in night: (1) reduction of FeOOH rust with the electron generated by dissolution of steel and (2) reaction of FeOOH with Fe^{2+} in dew condensation water [4–7]. At dry condition in daytime, the formed Fe_3O_4 rust reacts with O_2 and H_2O to produce FeOOH rust. These wet–dry cycles are called as the Evans model. Furthermore, the formation of Fe_3O_4 relates to the corrosion resistance of rust layer on the steels. Hao et al. studied the atmospheric corrosion of MnCuP weathering steel in simulated coastal and coastal-industrial atmosphere and found that the corrosion resistance of rust layer was improved by the increase of α -FeOOH content and decrease of Fe_3O_4 one [8,9]. Also, Qian et al. reported that the

addition of tannic acid suppresses the formation of Fe_3O_4 rust on mild steel in seawater wet/dry cyclic condition [10]. Therefore, understanding the formation of Fe_3O_4 rust is important to clarify the growth of rust layer in atmospheric corrosion of steels. In this respect, several researchers have investigated the formation of Fe_3O_4 rust from FeOOH particles. It is proposed that the γ -FeOOH rust forms at initial stage of corrosion of steel and transforms into Fe_3O_4 one [4–7,11]. Olowe and co-researchers suggested that the Fe_3O_4 is formed by the reaction of FeOOH with Fe^{2+} [12]. Tamura et al. have reported that the γ -FeOOH reacts with Fe^{2+} solution to form Fe_3O_4 rust in aqueous media at pH ≥ 7.3 , while such reaction does not take place on α -FeOOH [13]. Ishikawa et al. synthesized the Fe_3O_4 by treating the α -, β -, and γ -FeOOH particles in aqueous FeCl_2 solution at pH = 3–13 and indicated that the yield of the Fe_3O_4 is in the order of β -FeOOH > γ -FeOOH $\gg$ α -FeOOH, which is strongly dependent of the solubility product of FeOOH in acidic media [14]. Also, Antony et al. reported the transformation of γ -FeOOH into Fe_3O_4 by electrochemical reduction at 25 °C [15]. Although, these studies have not fully considered the dissolution of steels. To clarify more detail of formation of Fe_3O_4 rust, usage of iron powder would give a useful information about growth of Fe_3O_4 rust on the steel because the dissolution of iron powder in aqueous media forms Fe^{2+} and electron.

The aim of this study was to elucidate the formation of Fe_3O_4 rust by the reaction of FeOOH rust with steel surface. So that, we treated the artificial α -, β - and γ -FeOOH particles in aqueous media containing iron powder (α -Fe) at pH = 6.0 and 50 °C for 24 h. The

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products obtained were characterized by means of XRD and TEM. The present study must serve to illuminate the influence of types of FeOOH rusts on the formation of Fe₃O₄ rust at the surface of steels.

2. Experimental

2.1. Synthesis of α -, β - and γ -FeOOH particles

The α -FeOOH particles were prepared by adding 1.0 mol/dm³ aqueous NaOH solution into 500 ml of 1.0 mol/dm³ aqueous Fe(NO₃)₃ solution up to pH = 12 and aging the formed precipitates at 85 °C for 120 h.

The particles of β -FeOOH were synthesized by aging 0.3 dm³ of 0.1 mol/dm³ aqueous FeCl₃ solution at 85 °C for 24 h.

The γ -FeOOH particles were prepared by aerial oxidation of Fe²⁺ solution as follows. 1000 ml of 0.02 mol/dm³ aqueous FeSO₄ solution were oxidized by bubbling the air at a flow rate of 4 dm³/min and 35 °C for 3 h. During the oxidation, the solution pH was kept ranging from 6.0 to 6.5 by dropping 2.0 mol/dm³ aqueous *n*-butylamine solution.

The α -, β - and γ -FeOOH particles thus prepared were filtered off, washed with deionized-distilled water and finally dried *in vacuo* at room temperature for 16 h. The purity of these FeOOH particles was confirmed by XRD and FTIR.

All the chemicals purchased from Wako Pure Chemical Co. LTD., were reagent grade and used without further purification.

2.2. Synthesis of Fe₃O₄ from FeOOH particles and iron powder

The artificial Fe₃O₄ rust particles were synthesized as follows. 78.5 mg of iron powder (α -Fe, purity = 99.9%, mean particle size = 45 μ m) and 250 mg of synthetic FeOOH particles were dispersed in 0.1 dm³ of deionized-distilled water. Then, the molar ratio Fe/FeOOH was 0.5. After this, the solution pH was adjusted to 6.0 by adding 0.1 mol/dm³ NH₄OH solution and treated at 50 °C for 24 h without stirring. The obtained particles were filtered off, washed with deionized-distilled water and finally dried *in vacuo* at room temperature for 16 h.

2.3. Characterization

The materials thus obtained were characterized by XRD and TEM. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered Cu K α radiation operated at 30 kV and 15 mA. The scanning speed and step were 2°/min and 0.01°, respectively. Particle morphology was observed by a TOP-CON transmission electron microscope (TEM) at 200 kV.

3. Results and discussion

Fig. 1 plots the amount of the products treated with α -, β - and γ -FeOOH particles in aqueous media at pH = 6.0 and 50 °C for 24 h and the solution pH after treating. The amount of the products treated with α -, β - and γ -FeOOH particles is slightly lower than 328.5 mg of initial total amount of FeOOH and iron powder as depicted by dotted line. This infers the dissolution of FeOOH particles and/or iron powder. While, the solution pH is almost unchanged by treating with β - and γ -FeOOH particles, while it raises from 6.0 to 8.2 by the treatment with α -FeOOH. This will be discussed later.

Fig. 2 shows the XRD patterns of the products before and after treatment with α -, β - and γ -FeOOH particles. Pattern a of the product before treating with α -FeOOH possesses the diffraction peaks due to α -FeOOH and α -Fe. No remarkable change in XRD pattern is recognized after treating and new peaks are not detected

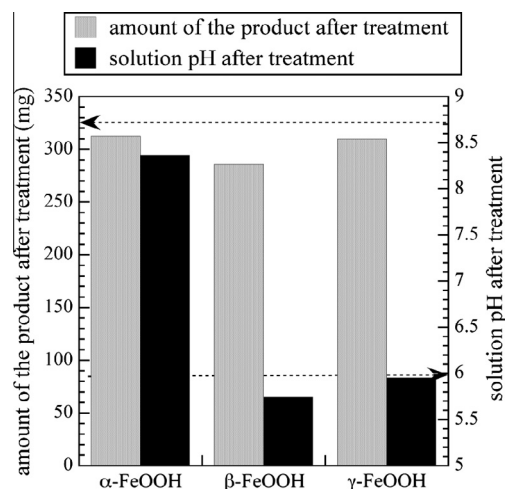


Fig. 1. Plots of the amount of the products and the solution pH after treating with α -, β - and γ -FeOOH. The dotted lines represent the initial total amount of FeOOH and iron powder (328.5 mg) and solution pH (6.0).

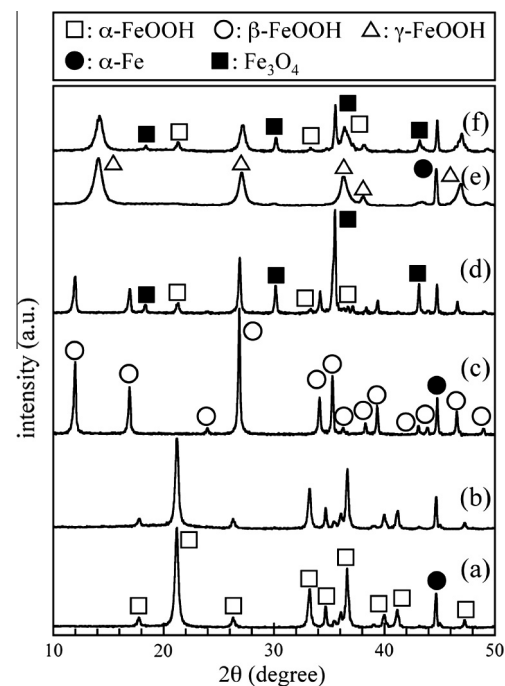


Fig. 2. XRD patterns of the products (a, c and e) before and (b, d and f) after treating with α -, β - and γ -FeOOH. (a and b) α -FeOOH, (c and d) β -FeOOH, (e and f) γ -FeOOH.

(pattern b). By treating with β -FeOOH, the peaks due to β -FeOOH and α -Fe are weakened and new peaks are found at $2\theta = 18.3^\circ$, 21.4° , 30.2° , 33.4° , 35.6° , 36.8° and 43.1° (patterns c and d). These new peaks are assignable to Fe₃O₄ and α -FeOOH. The similar results can be seen for the product treated with γ -FeOOH (patterns e and f). On the other hand, Fe₃O₄ was not formed by the treatment with α -, β - and γ -FeOOH particles in the absence of iron powder at 50 °C and pH = 6.0 for 24 h. These results indicate the formation of Fe₃O₄ by the reaction of β - and γ -FeOOH, and iron powder. More quantitative relationship between the composition of the products and the kind of FeOOH was obtained from the area intensity of XRD peaks. Fig. 3 plots the relative area intensity of α -, β -, γ -FeOOH and α -Fe peaks, and the area intensity of Fe₃O₄ and α -FeOOH formed by the treatment against types of used FeOOH. The area intensity of α -, β -, γ -FeOOH, α -Fe and Fe₃O₄ was respectively estimated from

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