Oxidation Behavior of Ni$_x$Fe$_{1-x}$(OH)$_2$ in Cl$^-$-containing Solutions

Kyeong Woo Chung and Kwang Bum Kim

Department of Metallurgical Engineering, Yonsei University
134 Shinchon-Dong, Seodaemoon-Ku, Seoul 120-749, Korea

The addition of Ni leads to the formation of protective rust layer on steel and subsequently high corrosion resistance of steel in Cl$^-$-containing environment. α-FeOOH, β-FeOOH, γ-FeOOH and Fe$_3$O$_4$ are formed mainly on steels exposed to Cl$^-$-containing environment. As the first work of this kind, this study reports the influence of Ni on the oxidation behavior of Ni$_x$Fe$_{1-x}$(OH)$_2$ in Cl$^-$-containing solution at two different pH regions(condition I under which the solution pH is allowed to decrease and condition II under which solution pH is maintained at 8) where γ-FeOOH and Fe$_3$O$_4$ are predominantly formed, respectively, upon oxidation of Fe(OH)$_2$. In the presence of Ni(II) in the starting solution, the formation of β-FeOOH was facilitated and the formation of γ-FeOOH was suppressed with increasing Ni(II) content and with increasing oxidation rate of Fe(II). Ni(II) was found to have Fe$_3$O$_4$-suppressing effect under condition II

Keywords : oxidation, protective rust layer, chloride, FeOOH, Fe$_3$O$_4$

1. Introduction

Addition of alloying elements such as Cu and Cr to steels increases the resistance of steels to atmospheric corrosion in SO$_4^{2-}$-containing atmosphere such as industrial region and hence Cu and Cr alloyed steels have been developed as weathering steels.[1] However, these steels show high corrosion rate in Cl$^-$-containing atmosphere such as seashore.[2] Therefore, new weathering steels for Cl$^-$-containing atmosphere are being developed. Recently, Ni alloyed steel is reported to show high corrosion resistance under Cl$^-$-rich environment and has attracted much interest as a new weathering steel.[3),4)]

As the protective rust on steel is reported to be responsible for high corrosion resistance of weathering steel, atmospheric rusting of steel has been a fundamental theme for study in developing weathering steel and the influence of alloying elements on the formation of iron oxides in aqueous solution has been studied extensively in relation to atmospheric rusting of weathering steel. It was reported that Cu and Cr facilitated the formation of α-FeOOH in SO$_4^{2-}$-containing environment and retarded the crystal growth of iron oxide and crystallization, which makes for the formation of a crack-free rust layer in SO$_4^{2-}$-containing environment.[5)-8)] These effects of Cu and Cr induces the formation of fine α-FeOOH which is chemically and electrochemically the most stable among iron oxides and are thought to contribute to high corrosion resistance of Cu and Cr alloyed steels in industrial region. However,

the formation of β-FeOOH, that accommodates Cl$^-$ in its structure, is facilitated in Cl$^-$-containing environment and suppresses the formation of the protective rust layer.[4),9)] Accordingly, development of new weathering steel for Cl$^-$-containing environment has been pursed. Lately, it has been reported that the addition of Ni leads to high corrosion resistance of steel even in Cl$^-$-containing environment. The role of Ni in the formation of protective rust should be the fundamental theme for development of Ni alloyed steel as a new weathering steel for Cl$^-$-containing environment. However, there is a lack of studies on the role of Ni in the formation of protective rust. Genin et al. reported on the oxidation of Ni$_x$Fe$_{1-x}$(OH)$_2$ in Cl$^-$-containing solution, however, their study was concerned about the formation of Green Rust1 (GR1) that is known as an intermediate oxidation product leading to the formation of different types of iron oxides under different oxidation conditions.[10),11)] Cornell et al. reported that Ni retarded the crystallization of Fe(OH)$_3$ in their study about scavenging and immobilizing heavy metal pollutants in waste water.[12)] Nevertheless, these studies could not elucidate the definite role of Ni in the formation of protective rust on Ni alloyed steel.

Several iron oxides such as α-FeOOH, β-FeOOH, γ-FeOOH and Fe$_3$O$_4$ are formed mainly on steels exposed to Cl$^-$-containing atmosphere.[9)] And it is expected that systematic investigation on the effect of Ni(II) on the formation of each oxide in solution should lead to the

elucidation of the role of Ni in the formation of protective rust. It is well known that the aerial oxidation of $Fe(OH)_2$ in Cl^--containing solution yields several iron oxides such as α-FeOOH, β-FeOOH, γ-FeOOH and Fe_3O_4 depending on solution pH;α-FeOOH in basic and slightly acidic pH region, Fe_3O_4 in pH region between 8 and 9, γ-FeOOH in pH region near 7 and β-FeOOH in acidic region.[13), 14)] This work was initiated to investigate the influence of Ni on the oxidation behavior of $Fe(OH)_2$ in Cl^--containing solution of all pH regions with a aim to elucidate the role of Ni in the formation of protective rust on Ni alloyed steel in Cl^--containing environment.

As the first work of this kind, this study reports the influence of Ni on the oxidation behavior of $Ni_xFe_{1-x}(OH)_2$ in Cl^--containing solution at two different pH regions where γ-FeOOH and Fe_3O_4 are predominantly formed, respectively, upon oxidation of $Fe(OH)_2$.

2. Experimental

$Ni_xFe_{1-x}(OH)_2$ was precipitated by adding adequate quantities of NaOH solution to a mixed solution of $NiCl_2$ and $FeCl_2$ of 0.1M concentration with various ratios of [Fe(II)]/[Ni(II)](=R) ranging from 4 to ∞. All solutions were deaerated with O_2-free Ar gas. Oxidation of $Ni_xFe_{1-x}(OH)_2$ was carried out by the introduction of CO_2-free air at a constant flow rate of 30 ml./min under two conditions; condition I under which the solution pH was allowed to decrease during the oxidation of $Ni_xFe_{1-x}(OH)_2$ and condition II under which solution pH was maintained at 8 during the oxidation of $Ni_xFe_{1-x}(OH)_2$ by addition of 0.1 NaOH solution. For oxidation of $Ni_xFe_{1-x}(OH)_2$ under condition I, ratio of $[Cl^-]/[OH^-]$ in the starting solution was kept constant at 8/7 under which the aerial oxidation of $Fe(OH)_2$ gives rise to γ-FeOOH only.[15)] Evolution of electrode potential with time was monitored with a saturated calomel electrode and a Pt electrode. During the oxidation of $Ni_xFe_{1-x}(OH)_2$, intermediate reaction products were sampled for quantitative analysis of Ni(II) content in the intermediate products. Final products were washed, filtered and dried at 80°C for 6hrs.

Final products were analyzed by X-ray diffractometer(D/Max RINT2000, Rigaku, Japan). X-ray patterns were taken with Cu-K_α radiation and XRD scans were run from 10 to 70° at a scan rate of 0.1°/min. Ni(II) content in intermediate products and final products was determined by Atomic Absorption Spectroscopy(AA6601-F/G, Shimadzu, Japan).

3. Results and discussion

Fig. 1. shows the XRD patterns of the final products formed under condition I. XRD patterns for $R \leq 19$ show strong peaks typical of γ-FeOOH. However, the final products formed for $R \geq 9$ under condition I show the two broad peaks at ca. 35.5° and ca. 53.5°, which indicated that β-FeOOH was formed. Fig. 2 shows the XRD patterns of the final products formed under condition II. XRD pattern for $R = \infty$ displays the peaks of well-crystallized Fe_3O_4 only. However, no Fe_3O_4 was detected when Ni(II) was present in the starting solution. The strong peaks of β-FeOOH as well as γ-FeOOH were observed in XRD patterns for $R \leq 19$, of which the intensity increased with decreasing R. The main phase of the final products depended on Ni(II) content in the starting solution and oxidation conditions. The formation of β-FeOOH was facilitated and the formation of γ-FeOOH was suppressed with increasing Ni(II) content in the starting solution regardless of oxidation conditions. And the formation of β-FeOOH was favored over γ-FeOOH under condition II compared with under condition I for a given value of Ni (II) content in the starting solution. In the presence of Ni(II), no Fe_3O_4 was formed under condition II, which indicates that Ni(II) has Fe_3O_4-suppressing effect.

Fig. 3 and 4 display curves for E_{redox}(redox potential) vs. time of the oxidation reaction of $Ni_xFe_{1-x}(OH)_2$ for $R = \infty$ under oxidation conditions I, where γ-FeOOH was formed only, and for $R = 9$ under condition II, where β-FeOOH was predominantly formed, respectively. The curve for $R = \infty$ under condition I consisted of two stages, where potential sharply increased at the end of the each stage. However, the curve for $R = 9$ under condition II consisted of three stages. It is well known that intermediate products are involved with the formation of γ-FeOOH and β-FeOOH. The formation of γ-FeOOH proceeds through one intermediate product, Green Rust1(GR1, Fe(II)$_3$Fe(III)(OH)$_8$Cl), upon aerial oxidation of $Fe(OH)_2$. On the other hand, β-FeOOH is formed through two intermediate products, GR1 and over-chlorinated GR1.[16)] From these facts and curves for E_{redox} vs. time of the oxidation reaction of $Ni_xFe_{1-x}(OH)_2$, it can be inferred that GR1 and over chlorinated GR1 may be the intermediate products involved with the formation of final products, γ-FeOOH and β-FeOOH. It could be said that the first stage was related with the formation of GR1 irrespective of the final products. And the second stage was related with the formation of γ-FeOOH for $R = \infty$ under condition I. On the other hand, the second stage in curves for E_{redox} vs. time for $R = 9$ under condition II was related with the formation of over-chlorinated GR1 and the third stage with the forma-
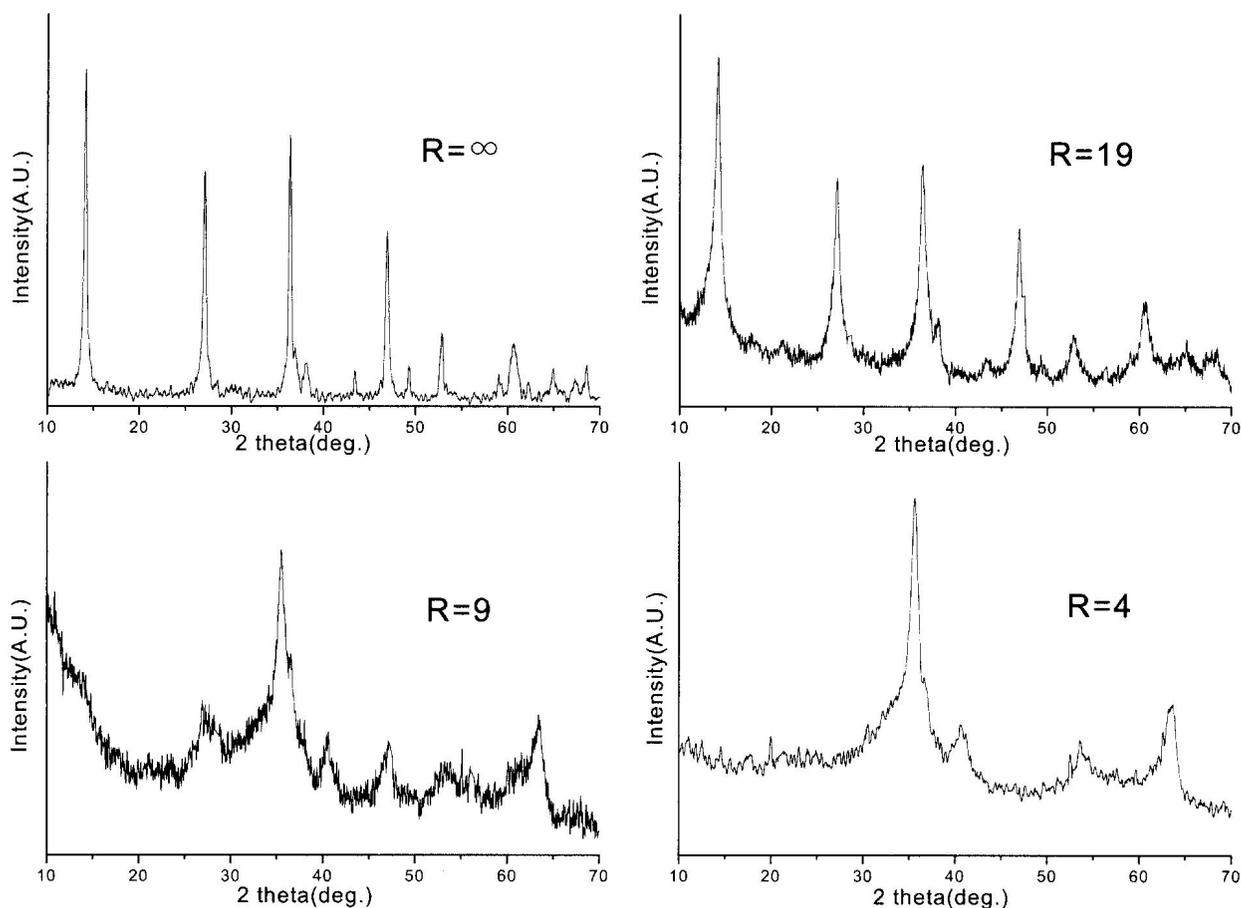
Fig. 1. XRD patterns of final products for different values of R ; oxidation by oxygen under condition I .

tion of β-FeOOH.

Chemical analysis of the final products showed that Ni (II) content in the final products was lower than that in the starting solution.(Table 1) Further, Ni(II) content in the final products varied greatly for a given value of R depending on oxidation conditions. Chemical and phase analysis suggested that Ni(II) content might be closely related to the main phase of the final products. When γ -FeOOH was the main phase of the final product, Ni(II) content in the final products was lower than 1.3 mole% and Ni(II) content in the final products was higher than 6.13 mole% when β-FeOOH was the main phase of the final product. This implies that β-FeOOH can contain more Ni(II) than γ-FeOOH. Buchwald et al. reported that Ni (II) up to 19 wt% could be incorporated into β -FeOOH.[17),18)

Lower Ni(II) content was observed in the final products than in the starting solution. Curves of E_{redox} vs. time indicated that γ-FeOOH was formed through intermediate products. To investigate why and on which stage a dec-

rease in Ni(II) content in oxidation product occurred, sampling of intermediate products was made at two points, t_g and t_m and their chemical analysis was conducted. Sampling time, t_g and t_m, corresponded to the point immediately after the formation of GR1. Fig. 5 shows change in Ni(II) content in oxidation product for R=9 under condition I with time. Ni(II) content in oxidation product at t_g showed the same value as that in the starting solution, however, decreased with time after t_g. As expected, it could be seen that Ni(II) up to 20 mole% was incorporated into GR1, which is in agreement with the study of Genin et al.[10) It could be said that Ni(II) content in oxidation products stayed constant up to the formation of GR1 upon oxidation of $Ni_xFe_{1-x}(OH)_2$, however, decreased upon further oxidation of GR1, which resulted in decreased Ni(II) content in the final products compared with that in the starting solution. During the transformation of GR1 to γ-FeOOH, Ni(II) content in oxidation product decreased with a release of Ni(II), indicating difficulty in the incorporation of Ni(II) into γ-FeOOH.
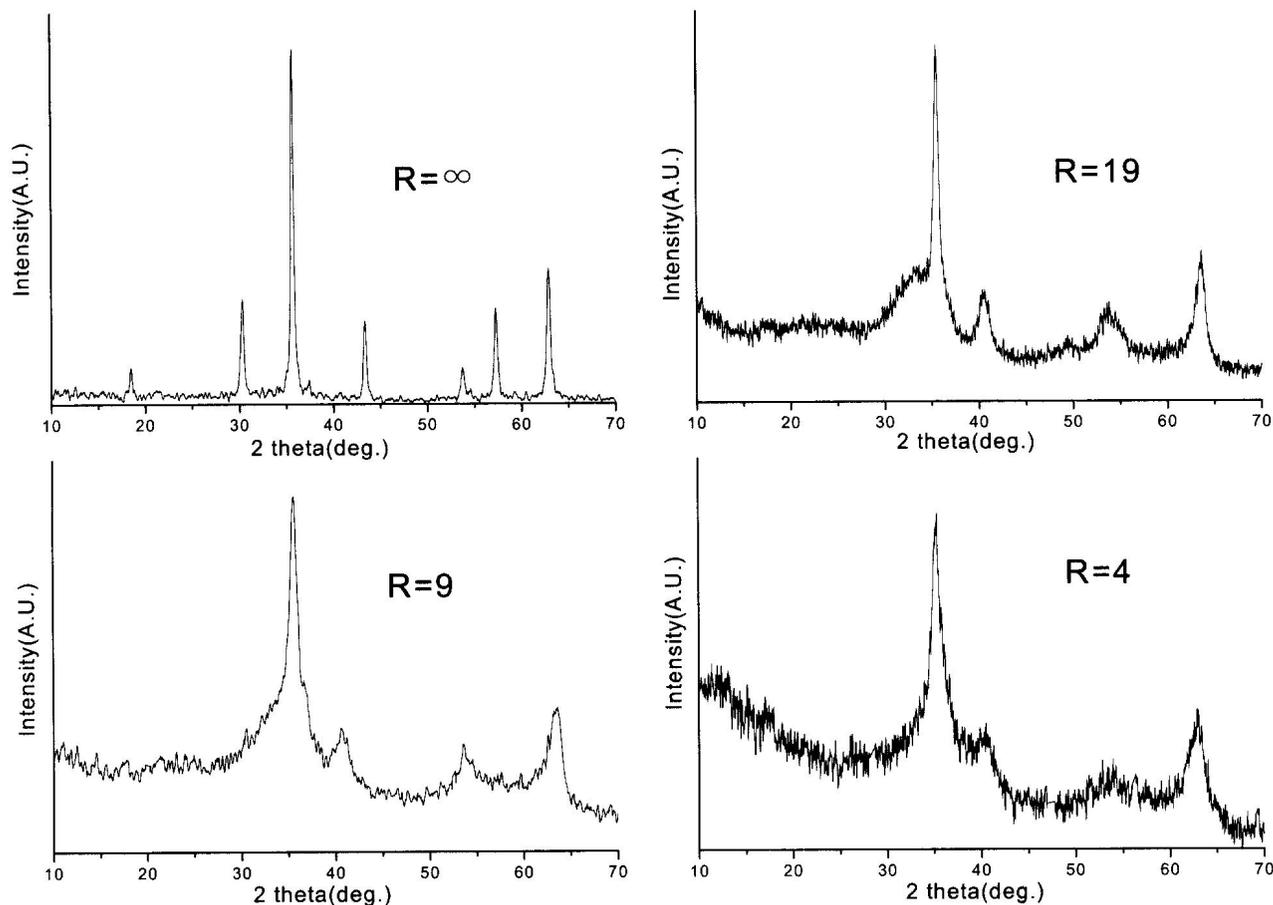
Fig. 2. XRD patterns of final products for different values of R ; oxidation by oxygen under condition Ⅱ.
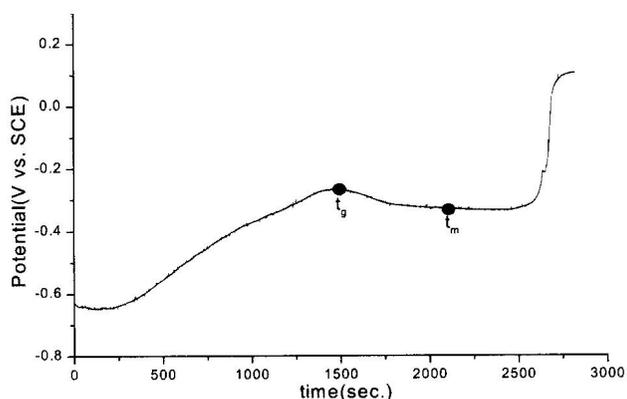

Fig. 3. Curve of E$_{redox}$ vs. time for oxidation of Fe(OH)$_2$; oxidation by oxygen under condition Ⅰ.
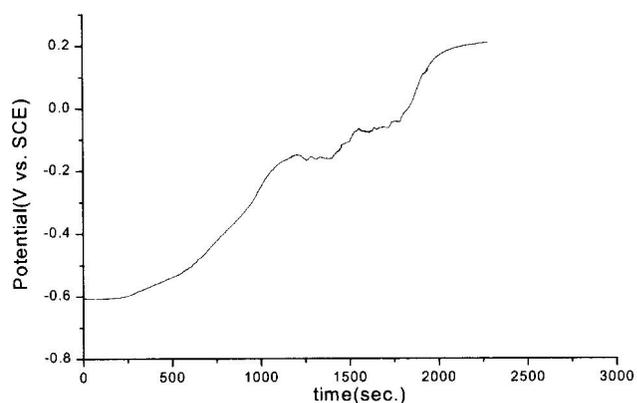
Fig. 4. Curve of E$_{redox}$ vs. time for oxidation of Ni$_x$Fe$_{1-x}$(OH)$_2$ for R=9 ; oxidation by oxygen under condition Ⅱ.

From chemical analysis of the intermediate oxidation products, it could be said that oxidation of GR1 and release of Ni(Ⅱ) in GR1 took place simultaneously. If the release rate of Ni(Ⅱ) into solution is independent of oxidation condition, i.e. oxidation rate, Ni(Ⅱ) content in the oxidation product is a function of time. The longer the time given for the release of Ni(Ⅱ), the higher the amount of Ni(Ⅱ) released. Lower oxidation rate implies slower

Table. 1. Ni(II) content in final products.

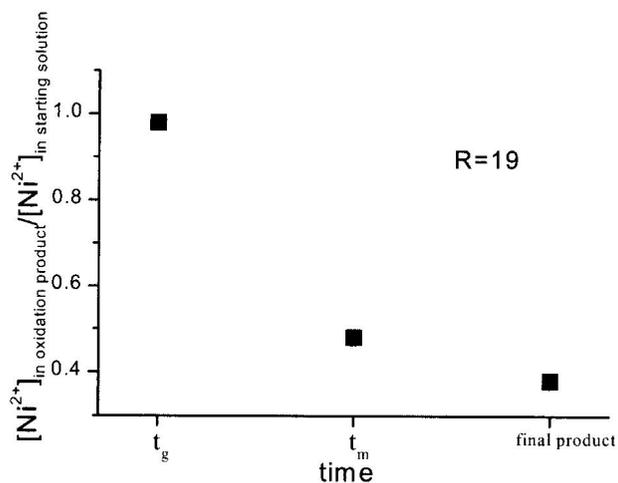| Oxidation Condition	Ni(II) content in the starting solution(Mole%)	Ni(II) content in the Final product(Mole%)
Condition I	5	1.3
	10	3.06
	20	6.13
Condition II	5	3.57
	10	9.1
	20	16.1

Fig. 5. Change in Ni(II) content in oxidation product with time ; oxidation by oxygen under condition I .

transformation of GR1 to the final oxidation products and subsequently longer time allowed for release of Ni(II). To investigate the effect of oxidation rate of Fe(II) on the behavior of $Ni_xFe_{1-x}(OH)_2$, oxidation of $Ni_xFe_{1-x}(OH)_2$ was conducted using air as an oxidant and phase and chemical analysis of their final products was made by X-ray diffraction.

Fig. 6 shows the XRD patterns of the final products formed under condition I using air as an oxidant. All XRD patterns show strong peaks typical of γ-FeOOH. When the oxidation rate of Fe(II) was decreased using air as an oxidant instead of oxygen, γ-FeOOH became the main phase of the final product even for R=4 where β-FeOOH was main phase of the final product formed using air as an oxidant. An decrease in oxidation rate of Fe(II) by use of air as an oxidant led to the preferred formation of γ-FeOOH over β-FeOOH. This indicates that the oxidation rate of Fe(II) as well as Ni(II) content initially present in GR1 are important factors in determining the main phase of the final product.

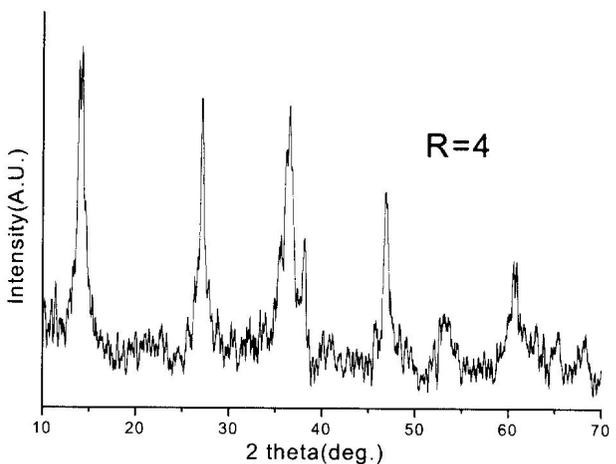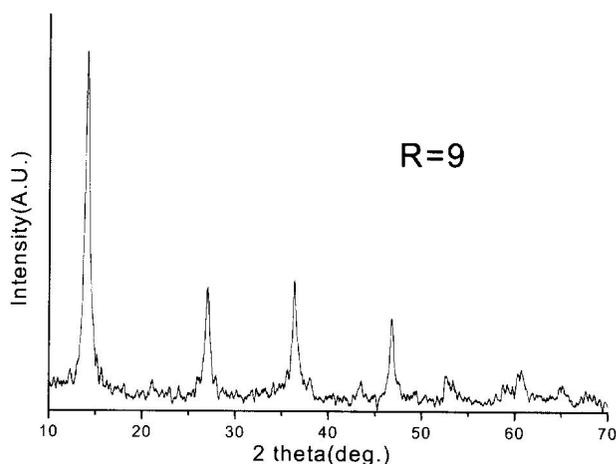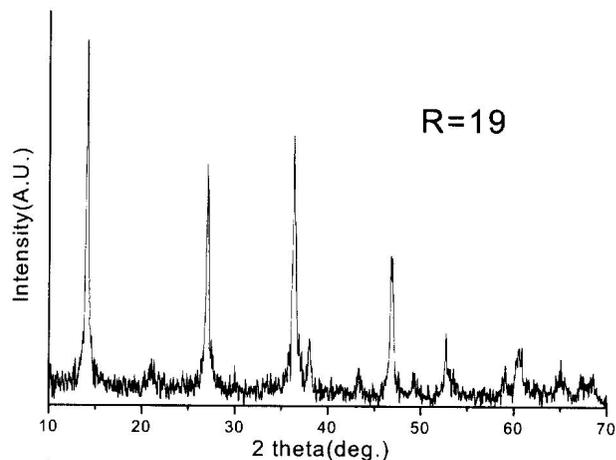Fig. 6. XRD patterns of final products for different values of R ; oxidation by air under condition I .

As mention above, release of Ni(II) from oxidation product into solution took place simultaneously with oxidation of GR1. This means that oxidation time needed for oxidizing GR1 to final product might be an important

factor in determining the Ni(II) content in the final product when the release rate of Ni(II) released into solution is assumed to be constant. It is thought that the Ni(II) content in the oxidation product during further oxidation of GR1 could be determined by the two competing steps: release of Ni(II) into solution and oxidation of GR1. If the oxidation rate of GR1 is low, i.e., longer time is allowed for oxidation, the formation of γ-FeOOH from GR1 would take place even though a large amount of Ni (II) is present in GR1. On the other hand, if oxidation rate of GR1 is high, i.e., short time is allowed for oxidation, the transformation of GR1 to γ-FeOOH would be suppressed by Ni(II) remaining in oxidation product since γ-FeOOH can not accommodate Ni(II) into its structure. And the formation of other iron oxides which can contain Ni(II), possibly over-chlorinated GR1, is facilitated. Subsequently, the further oxidation of over-chlorinated GR1 results in the formation of β-FeOOH. Even in the presence of Ni(II) in over-chlorinated GR1, the transformation of over-chlorinated GR1 to β-FeOOH can take place unlike the transformation of GR1 to γ-FeOOH since β-FeOOH can contain Ni(II) unlike γ-FeOOH. On the basis of this hypothesis, the oxidation rate of GR1 as well as Ni(II) content in GR1 would have great influence on Ni(II) content in oxidation products during oxidation of GR1 and subsequently the oxidation behavior of GR1. The oxidation rate of Fe(II) is a function of Fe(II) concentration, dissolved oxygen and pH; specifically first order with respect to dissolved oxygen and second order with respect to pH.[19] For a given value of Ni(II) content in the GR1, the formation of γ-FeOOH was facilitated and the formation of β-FeOOH was suppressed using air instead of oxygen as an oxidant irrespective of oxidation conditions. Namely, a decrease in oxidation rate of Fe(II) using air as an oxidant favored the formation of β-FeOOH over γ-FeOOH for a given value of Ni(II) content in GR1. In addition, the main phase of the final product was closely related with oxidation condition, which might be attributed to pH-dependence of oxidation rates of Fe(II). Oxidation of Ni$_x$Fe$_{1-x}$(OH)$_2$ under condition I was accompanied with a decrease in solution pH to near 7.2 during further oxidation of GR1, while oxidation of Ni$_x$Fe$_{1-x}$(OH)$_2$ under condition II was conducted at pH 8. An increase in pH from 7.2 to 8 indicated an increased oxidation rate of Fe (II) and the increased oxidation rate of Fe(II) favored the formation of β-FeOOH over γ-FeOOH for a given value of Ni(II) content in GR1. An increase in oxidation rate of Fe(II) by an increase in solution pH or oxygen partial pressure induced the preferred formation of β-FeOOH over γ-FeOOH for a given value of Ni(II) content in GR1.

4. Conclusions

This study reports the oxidation behavior of Ni$_x$Fe$_{1-x}$(OH)$_2$ in Cl$^-$-containing solution at two different pH regions(condition I under which the solution pH is allowed to decrease and condition II under which solution pH is maintained at 8) where γ-FeOOH and Fe$_3$O$_4$ are predominantly formed respectively upon oxidation of Fe(OH)$_2$.

The aerial oxidation of Fe(OH)$_2$ yields γ-FeOOH and Fe$_3$O$_4$ under condition I and under condition II, respectively. However, γ-FeOOH and/or β-FeOOH was formed in the presence of Ni(II) in the starting solution. No Fe$_3$O$_4$ was formed in the presence of Ni(II) under condition II, indicating that Ni(II) has Fe$_3$O$_4$-suppressing effect.

In the presence of Ni(II), β-FeOOH was formed along with γ-FeOOH upon the oxidation of Ni$_x$Fe$_{1-x}$(OH)$_2$ even in a solution with Cl$^-$ content as low as 0.2 moll^{-1} and the ratio of [Fe(II)+Ni(II)]/[OH$^-$] = 4/7. The proportion of γ-FeOOH and β-FeOOH in the final products varied strongly depending on various factors such as Ni(II) content in starting solution and oxidation condition. The formation of β-FeOOH was favored over γ-FeOOH with increasing Ni(II) content in the starting solution. Furthermore, the formation of β-FeOOH was facilitated over γ-FeOOH by an increase in solution pH or oxygen partial pressure for a given value of Ni(II) content in the starting solution.

References

1. H. Kihira, S. Ito, and T. Murata, *Corros. Sci.* **31**, 383 (1990).
2. H. E. Townsend, T. C. Simpson, and G. L. Johson, *Corrosion* **50**, 546 (1994).
3. A. Nishikata, Y. Yanashita, H. Katayama, T. Tsuru, A. Usami, K. Tanabe, and H. Mabuchi, *Corros. Sci.* **37**, 2059 (1995).
4. T. Nishimura, H. Katayama, K. Noda, and T. Kodama, *Corros. Sci.* **42**, 1611 (2000).
5. H. Okada, Y. Hosoi, K. Yukawa, and H. Naito, *J. Iron Steel Inst. Japan* **55**, 355 (1969).
6. K. Inouye, S. Ishii, K. Kaneko, and T. Ishiwasa, *Z. anllg. Chem.* **391**, 86 (1972).
7. T. Misawa, T. Kyuno, W. Suetaka, and S. Shimodaira, *Corros. Sci.* **11**, 35 (1971).
8. M. Yamashita, H. Miyuki, U. Matsuda, H. Nagano, and T. Misawa, *Corros. Sci.* **36**, 283 (1994).
9. Sei J. Oh, D. C. Cook, and H.E. Townsend, *Corros. Sci* **41**, 1687 (1999).
10. P. Refait and J. M. R. Genin, *Corros. Sci.* **34**, 2059 (1993).
11. P. Refait and J. M. R. Genin, *Clay Min.* **32**, 597 (1997).
12. R. M. Cornell, R. Giovanoli and W. Schneider, *J. Chem.*

Tech. Biotechnol. **53**, 73 (1992).

13. T. Misawa, K. Hashimoto, and S. Shimodira, *Corros. Sci.* **14**, 131 (1974).

14. J. M. R. Genin, D. Rezei, Ph. Bauer, A. Olowe, and A. Beral, Electrochem. Meth. in Corr. Res., *Mater. Sci. For.* **8**, 477 (1986).

15. P. Refait and J. M. R. Genin, *Corros. Sci.* **34**, 797 (1993).

16. P. Refait and J. M. R. Genin, *Corros. Sci.* **39**, 539 (1997).

17. V. F. Buchwald and R. S. Clarke Jr., *Am. Min.* **74**, 656 (1989).

18. J. E. Post and V. F. Buchwald, *Am. Min.* **76**, 272 (1991).

19. W. Stumm and G. F. Lee, *Ind. Engin. Chem.* **53**, 143 (1961).