Mill Scale for Synthesis of Fe–Ni and Fe–Ni–Co Alloys through Gaseous Reduction: Reaction Kinetics and Mechanism

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(Received on May 2, 2008; accepted on July 25, 2008)

Nickel and Nickel cobalt ferrite powders were prepared through the ceramic route by calcination of a stoichiometric mixture of nickel oxide, cobalt oxide and mill scale as source for iron oxide. The produced ferrites powders were isothermally reduced in pure hydrogen at 800–1100°C. Based on thermogravimetric analysis, the reduction behavior of the synthesized ferrite and the kinetics reaction mechanism were studied. The initial ferrite powder and the various reduction products were characterized by XRD, SEM and reflected light microscope to reveal the effect of hydrogen reduction on composition, microstructure and reaction kinetics of synthesized ferro-alloys. The activation energy values were calculated from Arrhenius equation. The approved mathematical formulations for the gas solid reaction were applied to confirm the estimated rate controlling reaction mechanism. Complete reduction of home made ferrite powder was achieved with synthesis of nanocrystalline Fe–Ni and Fe–Ni–Co alloys.

KEY WORDS: mill scale; nickel ferrite; nickel cobalt ferrite; H₂-reduction; nanocrystallites; Fe–Ni; Fe–Ni–Co alloy; reduction kinetics.

1. Introduction

Iron and steel-making process is one of the most important industrial manufacturing processes. Actually, day after day many requirements are created for this type of industry. This is owing to the problems that related to the most critical factors of this industry which are resources, energy and environment. The produced CO₂ is the major component of the greenhouse gases, which caused the global warming. So, establishment and development of a new fundamental technology in this industry become an urgent at these moments. The hydrogen reduction route provides an excellent alternative toward the possibility of using green energy for development of economically viable and environmentally friendly processes to meet the growing industrial needs.¹⁾

On the other hand, about 90% of world ferro-alloy production is consumed by the steel industry. These alloys are essential additives in steelmaking used for imparting desired properties to steel and so these alloys act as a means of introducing these alloying elements into the cast or as deoxidizers. Specialized applications for ferro-alloys also exist in fields such as semi-conductors, photovoltaic cells, chemicals manufacture and specialty ceramics.^{2,3)} Namely Fe–Ni and Fe–Ni–Co alloys are of great interest due to their low thermal expansion, remarked magnetic properties, high mechanical and chemical properties.^{4–14)} With this great importance, soon we will face to the depletion of alloying elements such as Cr, Ni, Mo, V and so on. So much attention

should be directed toward these resources deficient. There are several attempts to recover these elements from special steel dust or SUS sludge or slag. Thus, the present research can be carried out as one of the solution for the resource problem of alloying elements using a clean and economic route.

Reduction of ferrites is an important step in developing master alloys in steel production. The mechanism and kinetics of reduction of different ferrites such as ferrites of cobalt, zinc, strontium, barium and magnesium were investigated.^{15–20)} However reduction of Ni_xCo_{1–x}Fe₂O₄ as source for Ferro-alloys was handled very limited through some investigations.^{21–23)}

During the heating of steel slabs before rolling in the steel making process, their upper layer can be oxidized to iron oxide. This oxide called “mill scale”, could be removed from the surface by a shower of water during the rolling of these slabs. This mill scale can be considered as a valuable secondary raw material according to its high iron content, low impurities and stable chemical composition. However, these materials produced in a form of fine powder, where its quantity is increasing rapidly with the current demand of increasing world steel production.

The present investigation handled an economic and clean route for the synthesis of ferro-alloys from a secondary iron oxide resource (mill scale). Ceramic method was used for preparation of NiFe₂O₄ and NiCoFe₂O₄ from a mixed mill scale with analytical grade CoO and NiO. Under the effect

of reaction temperature, the reduction behaviour and kinetics in hydrogen atmosphere with synthesis of Fe–Ni and Fe–Ni–Co alloys was investigated.

2. Experimental Procedures

Mill scale samples with 74.1% total iron, 0.057% TiO₂, 0.957% MgO, 0.6% SiO₂, 0.18% CaO, 0.357% P₂O₅, 0.873% Al₂O₃, 0.42% MnO, 0.047% S, 0.246% Cr₂O₃ and 0.028% C are obtained from POHANG IRON & STEEL Company (POSCO), South Korea. Mill scale fines (<3 mm) were firstly grinded to a very fine powder and then it is thoroughly mixed in calculated molar ratio with very fine (1 μm) analytical reagent grade (99.9%) nickel oxide and cobalt oxide for synthesis of Ni_xCo_{1-x}Fe₂O₄ (x=1, 0.5) using agate mortar and dry ball milling technique for 6 h. The well mixed oxides powder was dried at 105°C for 24 h. Equal weights of dried powder were compressed into compacts of about 1.5 g weight, 7 mm diameter and 3 mm thickness. The prepared compacts were fired at 1 000°C for 24 h then cooled to room temperature gradually.

The produced Ni_xCo_{1-x}Fe₂O₄ compacts were reduced at 800, 900, 1 000 and 1 100°C in constant flowing hydrogen gas atmosphere. The course of reduction was followed up thermogravimetrically by means of a weight loss method using an automatic sensitive balance equipped with the vertical tube furnace.

The reduction extent is calculated as follow;

$$\% \text{ reduction} = \frac{\text{weight of O}_2 \text{ removed at a given time}}{\text{weight of O}_2 \text{ in Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4} \times 100$$

So the reduction extent was correlated to the total removable oxygen of ferrite powder. A gas purification system was used to obtain 99.99% purity hydrogen gas. The reduction assembly and gas flow system used in this study were previously mentioned.²⁴⁾

In each experiment, after the furnace was heated up to the required temperature the ferrite compact was put inside a basket to be hanged in the balance and adjusted in the middle zone of the tube furnace in flow of purified Ar gas. After settling down for few minutes, the reducing gas was passed while the Ar gas was stopped. The reacted compact was kept in the reducing atmosphere till a constant weight was achieved. For cooling, the reducing gas was replaced by Ar and the reduced sample was pulled up at the upper part of the reaction tube and kept away from the hot zone. After the temperature became below 200°C, the reduced compact was quenched in pure acetone. Preliminary reduction experiments showed that the most suitable hydrogen flow rate required to ensure an adequate supply of gas and overcome the gas boundary layer diffusion resistance, thus avoiding the gas starvation is 1 l/min.

The synthesized Ni_xCo_{1-x}Fe₂O₄ powders and the reduced products were identified and characterized by X-ray phase analysis technique (XRD, High power X-ray Diffractometer System Rigaku D/MAX-2500/PC), High Resolution Field Emission scanning electron microscope (FE-SEM, Hitachi S4800), and optical microscope (Olympus PMG3).

3. Results and Discussion

3.1. Characterization of Synthesized Nickel Ferrite Powder

The ferrite powders (NiFe₂O₄ and Ni_{0.5}Co_{0.5}Fe₂O₄) were successfully synthesized by the ceramic method using the mill scale. **Figures 1(a)** and **1(b)** show the XRD pattern of

Fig. 1. XRD pattern for synthesized (a) NiFe₂O₄ and (b) Ni_{0.5}Co_{0.5}Fe₂O₄ Phase at 1 000°C.

Fig. 2. SEM micrograph of synthesized (a) NiFe₂O₄ (b) Ni_{0.5}Co_{0.5}Fe₂O₄ ferrite.

the synthesized ferrite powders whereas the sharp peaks reflected the good crystallinity of the formed phases. The SEM photos in **Figs. 2(a)** and **2(b)** show the morphological observation of synthesized nickel ferrite (NiFe_2O_4) and nickel cobalt ferrite ($\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$) powder respectively. It was observed that dense grains of ferrites are formed in a well regular crystalline shape as a matrix of small crystals. These grains are homogeneously distributed in the size range of $0.5\text{--}2.0\ \mu\text{m}$ for both of NiFe_2O_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ with presence of macro-pores.

These phases were formed through a solid-state reaction between the mixed materials as follows:

The average crystallite size of the synthesized NiFe_2O_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ powder was 37 and 54.4 nm respectively as calculated from X-ray diffraction peaks using the following Scherer's formula,²⁵⁾

$$t = 0.9\lambda / B \cos \theta_B \dots \dots \dots (1)$$

Where t is the crystallite size, λ the X-ray wave length, B the angular width of the diffraction peak and θ is the diffraction angle.

3.2. Reduction Behavior and Morphological Observation

Synthesized NiFe_2O_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compacts were isothermally reduced with pure H_2 gas. Reduction was undertaken partially up to completion at different tempera-

tures ranging from $800\text{--}1100^\circ\text{C}$. The influence of reduction temperature on the structural characteristics of the products was extensively studied in order to get clear comprehension of reduction process. It was found that the temperature at which the reduction occurs has an effect on the reduction rate. The reduction curves for the prepared NiFe_2O_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compacts are given in **Figs. 3(a)** and **3(b)**. It can be seen that for each reduction curves, the rate of reduction was highest at early stage and gradually decreased with time till the end of experiment. The reduction rate increased as the reduction temperature increased either in the initial or final reaction stages and so the reaction time decreased gradually with increasing the reduction temperatures. Comparative reduction curves for NiFe_2O_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compacts at 900 and 1100°C are given in **Fig. 4**. It is observed that the reducibility of NiFe_2O_4 compacts is slightly faster than $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$

Fig. 3. Reduction curves of (a) NiFe_2O_4 and (b) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compacts reduced at $800\text{--}1100^\circ\text{C}$ with pure hydrogen gas.

Fig. 4. Comparative reduction curves of NiFe_2O_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compacts at 900 and 1100°C .

Fig. 5. XRD pattern of Synthesized (a) Fe-Ni and (b) Fe-Ni-Co alloys after reduction of fired compacts with hydrogen at 1100°C .

Fig. 6. System Fe–Ni–O at 1100°C. W=wustite (“FeO”–NiO solid solutions); N=nickel oxide (NiO–“FeO” solid solutions); S=spinel (Fe₃O₄–NiFe₂O₄ solid solution); F= nickel ferrite (NiFe₂O₄); H=hematite; A=alloy (Fe–Ni solid solutions); M=magnetite (Fe₃O₄).

compacts either at higher or lower reduction temperatures.

For both fired samples, complete reduction was achieved with synthesis of Fe–Ni and Fe–Ni–Co alloys as shown in **Figs. 5(a)** and **5(b)** for the XRD pattern of reduction products.

Fe–Ni–O phase diagram in **Fig. 6**²⁶⁾ is showing the reaction path of ferrite reduction into alloy.

The average crystallites size of synthesized nanocrystalline Fe–Ni and Fe–Ni–Co alloys as depicted from XRD data are about 22 and 28 nm respectively. Also it was observed that the peaks of the synthesized ferro-alloy are strong and sharp revealing the high crystallinity of the particles.

Morphological observation of reduced nickel ferrite and nickel cobalt ferrite compacts using SEM is shown in **Figs. 7(a)** and **7(b)**. It is clearly seen that the Fe–Ni alloy were formed in two different shape structures that are homogeneously distributed all over the sample. One is dense grains with irregular crystalline shape structure and the other is filament shape form of 50 nm thickness (**Fig. 7(a)**). The coalescence and sintering effect due to high reaction temperature was observed with presence of macro-pores. On the other hand, the synthesized Fe–Ni–Co alloy was formed with irregular crystalline shape grains in very dense structure whereas severe coalescence with sintering effect was obviously detected (**Fig. 7(b)**).

3.3. Reduction Kinetics and Mechanisms

Partial reduction of NiFe₂O₄ and Ni_{0.5}Co_{0.5}Fe₂O₄ compacts was carried out to 25 and 80% reduction extent to clarify the reduction progressing and mechanism investigating. The apparent activation energy (E_a) of reduction was calculated at both the initial and the final reaction stages to

Fig. 7. SEM photos of Synthesized (a) Fe–Ni and (b) Fe–Ni–Co alloys after reduction of fired compacts with hydrogen at 1100°C.

illustrate the rate controlling mechanism depending on Arrhenius equation;

$$K_r = K_0 e^{-E_a/R_g T} \dots \dots \dots (2)$$

where K_r is the rate constant, K_0 is the frequency factor, R_g is the gas constant and T is the absolute temperature.

The relationships between the logarithm of the rate of reduction for nanocrystallites NiFe₂O₄ and Ni_{0.5}Co_{0.5}Fe₂O₄ compacts and the reciprocal of the absolute temperature are plotted at both the initial and latter stages as shown in **Figs. 8(a)** and **8(b)**. The calculated values of the apparent activation energy obtained from these relationships at the initial and final stages are 33 and 51.5 kJ/mol for NiFe₂O₄ respectively. For Ni_{0.5}Co_{0.5}Fe₂O₄ the calculated E_a values at the initial and final reaction stages are 27.5 and 56.7 kJ/mol respectively. The apparent activation energy values have been calculated by many investigators in order to determine the rate controlling step.²⁷⁾ The calculated activation energy values indicate that the NiFe₂O₄ reduction at the initial and final reaction stages is controlled by the combined gas diffusion and interfacial chemical reaction mechanisms with high contribution for the interfacial chemical mechanism at the latter stages. Comparatively in the previous investigation for the authors²³⁾ the E_a value at the final stage of the reduction of NiFe₂O₄ using chemical reagent is lower. In spite of the change in E_a value but they are belonging to the same reaction controlling mechanism. So this change might be owing to the presence of minor impurities in the mill scale that effect on the microstructure at the final reaction stages to facilitate the gas diffusion compared to the interfacial chemical reaction and so the E_a value is increased.

In case of Ni_{0.5}Co_{0.5}Fe₂O₄ reduction the initial reduction stage is controlled by the combined gas diffusion and interfacial chemical reaction mechanisms with more contribu-

Fig. 8. Arrhenius plots for initial and final reduction stages of (a) NiFe_2O_4 and (b) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compacts at 800–1100°C with pure hydrogen gas.

tion for the gas diffusion mechanism while the final reduction stages are controlled by the interfacial chemical reaction mechanism.

To confirm the reduction mechanism concluded from apparent activation energy values, different mathematical models for heterogeneous gas–solid reactions derived by Szekeely *et al.*²⁸⁾ were applied. The mathematical formulation for gaseous diffusion, interfacial chemical reaction, and mixed control reaction are, respectively

$$t^* = X + (1 - X) \ln(1 - X) \dots\dots\dots(3)$$

$$t^* = 1 - (1 - X)^{1/2} \dots\dots\dots(4)$$

$$t^* = [1 - (1 - X)^{1/2}] + \sigma^2 [X + (1 - X) \ln(1 - X)] \dots\dots\dots(5)$$

where t^* is dimensionless time, X is the fractional reduction degree at a given reduction time, and σ^2 is shrinking core reduction modulus. The testing of these three mathematical formulations only resulted in a set of straight lines on the application of Eq. (5) at both of the initial and final stages of NiFe_2O_4 reduction as shown in Figs. 9(a) and 9(b) respectively. This confirmed that the reaction is controlled by the combined gas diffusion and interfacial chemical reaction mechanisms at both of the initial and final reaction stages. On the other hand, testing of these mathematical formulations for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ reduction resulted in a set of straight lines on the application of Eq. (5) at the initial and Eq. (4) at the final reduction stages as shown in Figs. 9(c) and 9(d). This confirmed that the reduction is controlled by the combined gas diffusion and interfacial chemical reaction mechanisms at the initial reaction stages while the final stages are controlled by the interfacial chemical re-

Fig. 9. Applying the mathematical formulation for (a, b) mixed control at the initial and final reduction stages of NiFe_2O_4 , (c) mixed control at the initial reduction stages of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ and (d) interfacial chemical reaction at the final reduction stages of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$.

Fig. 10. Microstructure photos of fired compacts partially reduced at 900°C with pure hydrogen gas. (a) 25%, NiFe₂O₄ ($\times 100$), (b) 80%, NiFe₂O₄ ($\times 1000$), (c) 25%, Ni_{0.5}Co_{0.5}Fe₂O₄ ($\times 100$), (d) 80%, Ni_{0.5}Co_{0.5}Fe₂O₄ ($\times 1000$).

action mechanism.

The microstructure observation for partially reduced (25 and 80%) samples at 900°C is shown in **Fig. 10**. It is observed that in case of NiFe₂O₄, after 25% reduction extent, lower oxides such as Fe₃O₄ and NiO (gray and dark gray) with metallic grains (bright) are formed in a relatively reasonable porous (black) structure with successful progressing of the reduction (Fig. 10(a)). Also Fig. 10(b) showed that after 80% reduction extent, the reduction developed with Fe-Ni alloy (bright and gray) formation in a relatively porous (black) structure. These observations confirmed that the rate controlling mechanism either at the initial or final reduction stages of NiFe₂O₄ is the combined gas diffusion and interfacial chemical reaction mechanisms. On the other hand, in case of Ni_{0.5}Co_{0.5}Fe₂O₄, after 25% reduction extent porous structure in homogeneous distribution is observed as shown in Fig. 10(c). However after 80% reduction extent, the reaction developed with Fe-Ni-Co alloy formation in quite porous (black) and homogeneous structure of metallic alloying element (bright and gray) that facilitate the reducing gas access and successful progressing of the reduction process (Fig. 10(d)). These observations supported that the controlling mechanism in the initial reduction stage is the combined gas diffusion and interfacial chemical reaction mechanisms while the rate controlling mechanism at the final reduction stages of Ni_{0.5}Co_{0.5}Fe₂O₄ is the interfacial chemical reaction mechanisms.

4. Conclusions

This work demonstrated an economic route for synthesis of Fe-Ni and Fe-Ni-Co alloys from secondary iron oxide resources (mill scale). Reduction behaviour and kinetics of prepared nickel ferrite and nickel cobalt ferrite in hydrogen atmosphere were investigated.

(1) Using mill scale, nanocrystalline NiFe₂O₄ (37 nm) and Ni_{0.5}Co_{0.5}Fe₂O₄ (54.4 nm) powders were synthesized through the classic ceramic route at 1 000°C.

(2) The prepared ferrites were reduced in hydrogen atmosphere at 800–1 100°C. Complete reduction was achieved with synthesis of nanocrystalline (22 nm) Fe-Ni and (28 nm) Fe-Ni-Co alloys.

(3) The reduction rate increased with increasing the reduction temperature in both of the initial and final reduction stages. The apparent activation energy was calculated using Arrhenius equation and indicated that the NiFe₂O₄ reduction rate was controlled by combined interfacial chemical reaction and gas diffusion mechanisms. In case of Ni_{0.5}Co_{0.5}Fe₂O₄ reduction the initial reaction stage is controlled by the combined gas diffusion and interfacial chemical reaction mechanisms with more contribution for the gas diffusion mechanism while the final reaction stages are controlled by the interfacial chemical reaction mechanism.

(4) The concluded mechanisms were confirmed by applying different mathematical models for heterogeneous gas-solid reactions and microstructure observation.

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