The Effect of Temperature on Microstructure, Magnetic Properties and Reaction Kinetics of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ Reduction in Hydrogen Atmosphere

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Nickel cobalt ferrite (Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$) powder was prepared through the ceramic route by calcination of a stoichiometric mixture of nickel oxide, cobalt oxide and iron oxide at 1100 and 1200°C. The produced powders of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ were isothermally reduced in pure hydrogen at 800–1100°C. Based on thermogravimetric analysis, the reduction behavior of nickel cobalt ferrite and the kinetics reaction mechanism were studied. The initial ferrite powder and the various reduction products were characterized by XRD, pore size, SEM, VSM and reflected light microscope to reveal the effect of hydrogen reduction on composition, microstructure and magnetic properties of produced Fe-Ni-Co alloy. Microstructure of partially and completely reduced samples was studied and the activation energy values were calculated from Arrhenius equation. The approved mathematical formulations for the gas solid reaction were applied and it was found that the initial reaction stages are controlled by the combined gaseous diffusion and interfacial chemical reaction mechanisms with high contribution to gas diffusion while the final reaction stages is controlled by chemical reaction mechanism. Complete reduction of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ was achieved with synthesis of nanocrystalline (18–20 nm) Fe-Ni-Co alloy. [doi:10.2320/matertrans.MER2007268]

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1. Introduction

Nanostructured materials exhibit superior magnetic properties, such as higher permeability and lower coercivity compared with their polycrystalline counterparts due to a single domain configuration. So there is considerable technological and theoretical interest in magnetic nanoparticles due to the characterized enhancement in its magnetic recording density, recording speed, the noise suppression, and the material lifetime with the decrease in magnetic particle size. Soft, high-magnetization alloy are widely used for recording head poles, thin film inductors or transformers. Fe–Co–Ni alloys have been demonstrated to have a low coercivity and high-saturation magnetization. Also, NiCoFe ternary alloys, rich in Fe, have also been noted for their low thermal expansion property, and commercial applications of these alloys include microwave guides, spacecraft optics, laser housings, and printed wired boards. At the same time, the hardfacing alloys based on Co or Ni are used for their high mechanical and chemical properties especially their wear and corrosion resistance at high temperature. Also Co–Ni–Fe can be used as binder with unique properties. This binder when subjected to plastic deformation, it substantially maintains its face centered cubic (fcc) crystal structure and avoids stress and/or strain induced transformations. Synthesis of Fe-Ni-Co alloy was studied using the electrodeposition technique or with the induction furnace by the semi-levitation method using an inductive cold crucible. Ferrites are important materials with general composition of MFe$_2$O$_4$ where M represents one or several of the divalent transition metals. Reduction of ferrites is an important step in metallurgical processes as applied to M-Fe-O systems and also in developing the different alloys for various applications. In spite of that it is not covered well through the research investigations. The reduction kinetics and mechanism of some ferrites such as ferrites of strontium, barium and magnesium were investigated. NiCoFe$_2$O$_4$ has been synthesized by various methods such as co-precipitation process, sol-gel method, aerosol route, or double sintering ceramic technique. In the present work, double sintering ceramic technique was applied for the synthesis of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$. The reduction behaviour and kinetics of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ in hydrogen atmosphere with synthesis of Fe-Ni-Co alloy nanoparticles was thoroughly investigated.

2. Experimental

Nickel cobalt ferrite powder was prepared through the double sintering ceramic technique. Very fine (1 μm) analytical reagent grade (99.9%) nickel oxide, cobalt oxide and ferric oxide were mixed in calculated molar ratio for synthesis of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ using agate mortar and dry ball milling technique for 6 h. The well mixed oxides powder was dried at 105°C for 24 h and then calcined at 800°C for 12 h. Equal weights of calcined powder were compressed into compacts of about 1.5 g weight, 7 mm diameter and 3 mm thickness. The prepared compacts were fired at 1100 and 1200°C for 24 h then cooled to room temperature gradually. The produced Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts were reduced at 800, 900, 1000 and 1100°C in constant flowing hydrogen gas atmosphere (100% H$_2$). Partial reduction (25 and 80%) was also applied for confirmation of reduction mechanism. 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:

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% reduction = \left\{ \frac{\text{weight of O}_2 \text{ removed at a given time}}{\text{weight of O}_2 \text{ in Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4} \right\} \times 100.

So the reduction extent was correlated to the total removable oxygen of nickel cobalt ferrite.

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. The synthesized nickel cobalt ferrite powder 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), porosity measurements (Pore sizer 9320, Micromeritic), High Resolution Field Emission scanning electron microscope (FE-SEM, Hitachi S4800), optical microscope (Olympus PMG3) and vibrating sample magnetometer (VSM-5-10 TOEI industry co., LTD).

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.

3. Results and Discussion

3.1 Characterization of synthesized nickel cobalt ferrite powder

The nickel cobalt ferrite (Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$) powder was successfully synthesized by the ceramic method at 1100 and 1200 °C. Figure 1 shows the XRD pattern of the synthesized ferrite powder after firing for 24 h at 1200 °C. Only the Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ diffraction peaks are clearly detected as single phase formation which reflects the purity of the synthesized powder. This phase was formed through a solid-state reaction between the mixed materials as follows:

\[
\text{NiO + CoO} + 2 \text{Fe}_2\text{O}_3 = 2 \text{ Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4
\]

The average crystallite size of the synthesized Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ powder at 1100 and 1200 °C was 58.2 and 52.1 nm respectively as calculated from X-ray diffraction peaks using the following Scherer’s formula:\n
\[
t = 0.9 \lambda / B \cos \theta_B
\]

Where \( t \) is the crystallite size, \( \lambda \) the X-ray wave length, \( B \) the angular width of the diffraction peak and \( \theta \) is the diffraction angle.

The pore size measurements show that the synthesized ferrite compacts at 1100 °C have higher total porosity (44.04%) relative to that at 1200 °C (30.98%). The measured pore size distributions are shown in Fig. 2. It can be seen that both samples showed nearly the same pore size distribution ranged from 0.25–4.5 μm but the total pore volume clearly decreased at 1200 °C synthesized samples.

The SEM micrograph of the synthesized nickel cobalt ferrite (Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$) powder at 1100 and 1200 °C is shown in Fig. 3(a) and (b) respectively. It was observed that dense grains of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ are formed in a very well regular crystalline shape. These grains are homogeneously distributed in the size range of 0.5–1.5 μm and 1.5–3 μm for the 1100 and 1200 °C fired samples with presence of large number of micro-pores. Also it can be seen that increasing the firing temperature leads to significant grain growth with clear coalescence.

The magnetic properties of the synthesized ferrite were determined in a vibrating sample magnetometer. The hysteresis loop of fired Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts at 1100 and 1200 °C is shown in Fig. 4. The coercivity (\( H_c \)), saturation magnetization (\( M_s \)) and remnant magnetization (\( M_r \)) were obtained and comparatively seen that the 1100 °C fired...
samples have higher $H_c$ (328.2 Oe) with lower $M_s$ (54.8 emu/g) relative to the $H_c$ (212 Oe) and $M_s$ (151.7 emu/g) values of 1200°C fired samples.

3.2 Reduction behavior and morphological observation

Synthesized Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts were isothermally reduced with pure H$_2$ gas. Reduction was undertaken partially up to completion at different temperatures ranging from 800–1100°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 fired (1100 and 1200°C) Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts are shown in Fig. 5(a) and (b) respectively. 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 total reaction time decreased gradually with increasing the reduction temperatures (20–55 min at 800–1100°C respectively). The correlation between the reduction rate ($dr/dt$) at both initial

![Hysteresis loop of the fired Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts at 1100 and 1200°C.](image)

![SEM micrograph of fired Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts at; (a) 1100°C and (b) 1200°C.](image)
(0–25% reduction extent) and final (60–85% reduction extent) stages and the reduction temperature are shown in Fig. 6(a) and (b). These Figures are clarifying the increasing of the reduction rate with increasing the reduction temperature at both initial and final stages.

Comparatively, it was observed that reduction rate of 1100°C fired Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$: Fe-Co-Ni: Fe$_3$O$_4$

Fe-Co-Ni

Fe$_3$O$_4$

Fe-Co-Ni

Fe$_3$O$_4$

For both fired samples, complete reduction was achieved with synthesis of Fe-Ni-Co alloy of average crystallite size about 18–20 nm. Figure 8(a) and (b) shows the X-ray diffraction analyses of the reduced Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ samples

Fe-Co-Ni

Fe$_3$O$_4$

Fe-Co-Ni

Fe$_3$O$_4$

Fig. 8 XRD pattern of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts fired at 1100°C then reduced with hydrogen at (a) 1100 (b) 800°C.
at different temperatures. It was found that at higher reduction temperatures (Fig. 8(a)), the only detected phases were the Fe-Ni-Co alloy which reflected the complete reduction while at lower temperature (Fig. 8(b)) magnetite traces was detected. Also it was observed that the peaks of the synthesized ferro-alloy are strong and sharp revealing the high crystallinity of the nanoparticles.

Morphological observation of reduced nickel cobalt ferrite compacts at different temperatures (900, 1100 °C) using SEM is shown in Fig. 9(a) and (b). It is clearly seen that for both fired samples the reduced Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ at 900 °C have irregular crystalline shape grains of different size with presence of micro-pores (Fig. 9(a)). With increasing the reduction temperature to 1100 °C the Fe-Ni-Co alloy grains were formed in completely deformed dense structure whereas micro-pores decreased drastically and coalescence with sintering effect was obviously detected (Fig. 9(b)).

3.3 Reduction kinetics and mechanisms

Partial reduction of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ 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 illustrate the rate controlling mechanism depending on Arrhenius equation;

$$K_r = K_o e^{-E_a/R_g T}$$

where $K_r$ is the rate constant, $K_o$ is the frequency factor, $R_g$ is the gas constant and $T$ is the absolute temperature. The reaction rate constant ($K_r$) can be derived from a rate equation of the form:

$$dr/dt = K_r P^n$$

where $P^n$ is the pressure of the reducing gas and $n$ is the order of reaction. The relationships between the logarithm of the rate of reduction and the reciprocal of the absolute temperature are plotted at both the initial and latter reaction stages as shown in Fig. 10(a) and (b) for fired Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compacts at 1100 and 1200 °C respectively.

The calculated values of the apparent activation energy obtained from these relationships at the initial and final reaction stages are 24.9 and 63.7 kJ/mole for samples fired at 1100 °C while for the 1200 °C fired one the values are 27.2 and 54.6 respectively. The apparent activation energy values have been calculated by many investigators in order to determine the rate controlling step.\textsuperscript{19} The calculated activa-
tation energy values indicate that for both fired samples (1100 and 1200°C) the initial reduction stages are controlled by the combined gas diffusion and interfacial chemical reaction mechanisms with more contribution 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 Szekely et al.\textsuperscript{20} were applied. The mathematical formulation for gaseous diffusion, interfacial chemical reaction, and mixed control reaction are, respectively

\begin{equation}
\frac{t}{X} = \frac{1}{\tilde{\alpha} X (1 - X)} \ln \left( \frac{1}{1 - X} \right)
\end{equation}

\begin{equation}
\frac{t}{X} = \frac{1}{\tilde{\alpha} X (1 - X)} \ln \left( \frac{1}{1 - X} \right)
\end{equation}

\begin{equation}
\frac{t}{X} = \left( 1 - \frac{1}{2} \right) + \tilde{\alpha}^2 \left[ X + \left( 1 - X \right) \ln \left( 1 - X \right) \right]
\end{equation}

where \( t^* \) is dimensionless time, \( X \) is the fractional reduction degree at a given reduction time, and \( \tilde{\alpha}^2 \) is the shrinking core reduction modulus. The testing of these three mathematical formulations only resulted in a set of straight lines on the application of eq. (6) at the initial and equation (5) at the final reduction stages as shown in Figs. 11 and 12 respectively. This confirmed that the reduction of Ni\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\) compacts with hydrogen gas 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 reaction mechanism.

The microstructure observation for partially reduced (25%) samples at 1000°C is shown in Fig. 13(a) and (b) for 1100 and 1200°C fired samples respectively. Similar microstructure is observed for both samples whereas homogenous porous structure with presence of large size dense metallic grains is formed which slightly hindered the gas diffusion and confirmed that the controlling mechanism in the initial reduction stage is the combined gas diffusion and interfacial chemical reaction mechanisms with more contribution for the gas diffusion. However after 80% reduction extent, the reduction developed with Fe-Ni-Co alloy formation in quite
porous and homogeneous structure of metallic alloying element that facilitate the reducing gas access and successful progressing of the reduction process as shown in Fig. 14(a) and (b) for 1100 and 1200°C fired samples respectively. This observation confirmed that the rate controlling mechanism at the final reduction stages of Ni₀.₅Co₀.₅Fe₂O₄ is the interfacial chemical reaction mechanisms.

3.4 Magnetic properties

The magnetic properties of reduced samples including coercivity (Hc) and saturation magnetization (Ms) were determined from the hysteresis loops measured by the vibrating sample magnetometer at room temperature under a maximum applied field of about 15 kOe. Hysteresis loops of fired (1100 and 1200°C) Ni₀.₅Co₀.₅Fe₂O₄ and after reduction at 900 and 1100°C are shown in Fig. 15(a) and (b).

The magnetic measurements indicated a significant decrease in coercivity (Hc) with increasing the reduction temperature while reversely the saturation magnetization
(Bs) shows sharp increase with increasing reduction temperature as shown in Fig. 16(a) and (b). Namely for the fired samples at 1100°C, the Hc values decreased from 328.2, 95 to 52.5 Oe while the Ms values increased from 54.8, 241.7 to 277.2 emu/g for fired, 900 and 1100°C reduced samples respectively. Also for the fired samples at 1200°C, the Hc values decreased from 221, 100.8 to 52.5 Oe while the Ms values increased from 151.7, 212.4 to 216.1 emu/g for fired, 900 and 1100°C reduced samples respectively. Comparatively the reduced product of 1100°C sintered samples has more saturation magnetization relative to the 1200°C sintered one.

The significant decrease in coercivity (Hc) is correlated to grain growth and sintering effect with increasing the reduction temperature (SEM photos Fig. 9) that leads to a great continuity of grain domains. However the sharp increases in saturation magnetization (Ms) are explained by the formation of metallic alloying elements Fe, Ni, Co as products of reduction process whereas Fe–Co–Ni alloys have been demonstrated to have a low coercivity and high-saturation magnetization. So the micro-structural development of the synthesized Fe/Ni/Co alloy with the increase of reduction temperature could be responsible for the promotion in its magnetic behavior.

4. Conclusion

(1) Nanocrystalline (58.2, 52.1 nm) nickel cobalt ferrite (Ni_{0.5}Co_{0.5}Fe_{2}O_{4}) powder was synthesized through the classic ceramic route at 1100, 1200°C.

(2) Fired compacts were reduced in hydrogen atmosphere at 800–1100°C. Complete reduction was achieved with synthesis of Fe-Ni-Co alloy of average crystallite size about 18–20 nm.

(3) The calculated activation energy values from Arrhenius equation indicate that the initial reaction stages are 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. The concluded mechanisms were confirmed by applying different mathematical models for heterogeneous gas–solid reactions and microstructure observation.

(4) The magnetic measurements indicated significant de-
crease in coercivity ($H_c$) and reversely sharp increase in the saturation magnetization ($B_s$) with increasing reduction temperature to have Fe-Ni-Co alloy with low coercivity and high-saturation magnetization. The micro-structural development of the synthesized Fe-Ni-Co alloy with the increase of reduction temperature could be responsible for the promotion in its magnetic behavior.

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