THERMAL BEHAVIOR OF OXIDES AND HYDROXIDES OF IRON AND NICKEL

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ABSTRACT

The intermediate changes that occur when heating oxides and hydroxides of nickel and iron as well as a coprecipitated hydroxide were established using thermal analysis, X-ray diffraction and microscopic examination.

INTRODUCTION

The hydroxides of nickel(II) and iron(III) and the coprecipitated hydroxide(s) are of interest to nickel ferrite production. Intimate mixing can be achieved by coprecipitation which is expected to produce purer ferrite at firing temperatures lower than that required by oxides. In this study, the hydroxides of nickel(II) and iron(III) as well as a coprecipitate were prepared and compared.

PREVIOUS WORK

Nauer et al. [1] prepared α-FeOOH by adding NaOH to a nitrate solution. The crystallized product, a reddish light-brown powder, was reported to completely dehydrate to iron oxide between 250 and 280°C as determined by thermal analysis, although a further loss in weight could be observed in the TG curve. No allotropic transformations were mentioned. Nauer et al. [1] reported that heating the material to 1000°C yielded α-Fe$_2$O$_3$. According to Naono and Fujiwara [2], α-FeOOH occurs as acicular microcrystals.

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Rodriguez et al. [3] prepared nickel hydroxide by adding NaOH to $Ni(NO_3)_2$ solution. The precipitate was composed of plate-like particles [3,4]. Differential scanning calorimetry (DSC) up to $500\,^{\circ}C$ showed that the sample lost physically adsorbed water at $100\,^{\circ}C$ and dehydrated to NiO at approximately $300\,^{\circ}C$.

EXPERIMENTAL TECHNIQUES

Iron(III) hydroxide was prepared in a manner similar to that of Nauer et al. [1]. $Fe(NO_3)_3 \cdot 9H_2O$ (10.1 g) was dissolved in 100 ml of distilled water. NaOH (5.6 g) was dissolved in 50 ml of distilled water and added to the iron nitrate solution. A dark brown solid immediately precipitated. The mixture was stirred vigorously for 5 min. The solid was then filtered out, washed three times with distilled water, and dried for 12 h at $80\,^{\circ}C$.

A technique similar to that of Rodriguez et al. [3] was employed to prepare nickel hydroxide. $Ni(NO_3)_2 \cdot 6H_2O$ (14.6 g) was dissolved in 100 ml of distilled water. NaOH (6.1 g) was dissolved in 50 ml of distilled water and poured into the nitrate solution during stirring. An apple-green solid precipitated immediately. The mixture was stirred vigorously for 5 min. Then the solid was filtered out, washed three times with distilled water, and dried in the same manner as the iron hydroxide.

A coprecipitate of iron and nickel hydroxide was prepared similarly by addition of a strong basic solution to an aqueous solution of nickel nitrate and iron nitrate. $Ni(NO_3)_2 \cdot 6H_2O$ (10.0 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (27.8 g) were dissolved in 200 ml of distilled water. NaOH (11.0 g) was dissolved in 100 ml of distilled water and added to the mixed nitrate solution. A dark brown solid immediately precipitated. The mixture was stirred and then the solid was filtered out, washed and dried in the same manner as mentioned above.

Thermal analysis was carried out on a Netzsch 409 which is capable of performing simultaneous DTA and TG. The reference material in all tests was calcined kaolin. The sample and reference weights were 50.0 mg at the beginning of every test. The heating rate was held constant at either 5 or $10\,^{\circ}C\ min^{-1}$ and is indicated on the curve. The atmosphere was stagnant air at atmospheric pressure unless otherwise indicated.

X-ray analysis was performed with a Seifert-Scintag diffractometer. Cu $K\alpha$ radiation from a Seifert 2000 W tube was used with the X-rays being generated at 40 kV and 30 mA. The angular scanning speed was $4\,^{\circ}C\ min^{-1}$.

A Micromeritics Digisorb 2600 was used for the surface area analysis. Sample holders were made of borosilicate glass and the adsorbate gas was nitrogen.

RESULTS AND DISCUSSION

Iron hydroxide

As expected, the X-ray diffraction pattern for the precipitate is that of pure α-FeOOH. The peaks are broad indicating that fine crystallites are precipitated. Scanning electron microscopy (SEM) photomicrographs reveal that the crystallites are composed of fine needle-like particles.

Simultaneous thermal analysis curves are shown in Fig. 1. The present results disagree with those published by Nauer et al. [1] mentioned above. The loss of surface-adsorbed H_2O that occurs below 150°C is indicated by the endothermic peak and corresponding weight loss. The large endothermic peak at approximately 230°C and accompanying weight loss can be attributed to partial dehydration and loss of 79% of the H_2O necessary for complete dehydration. The remaining H_2O is lost endothermically with a maximum rate at 650°C. The adjacent endothermic peak immediately following at about 680°C can be attributed to an allotropic transformation of α-Fe$_2$O$_3$. It should be noted that during a study of the thermodynamic properties of Fe$_2$O$_3$, a change in magnetic nature and heat capacity at 677°C was reported by Coughlin et al. [5]. An X-ray diffraction pattern for this material after heating to 1000°C and then cooling to room temperature

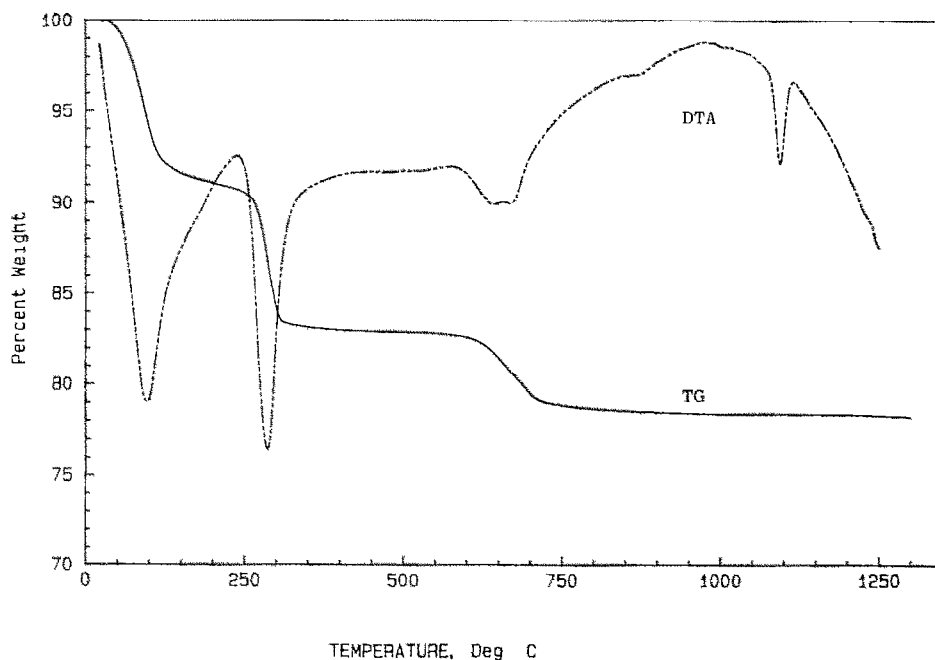Fig. 1. Thermal analysis of iron hydroxide (heating rate, 10°C min^{-1}).

proves that α-Fe_2O_3 is present indicating that the allotropic transformation at 680°C is reversible. The endothermic transition that occurs at 1130°C without a change in weight has not been reported before. X-ray diffraction gives no peaks for the specimen after being heated to 1300°C and then cooled slowly to room temperature. This proves that the transformation at 1130°C is irreversible. Continued heating gives an endothermic peak and weight loss at 1380°C due to the formation of magnetite as will be explained later.
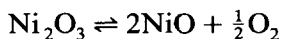
Nickel hydroxide(s)

The X-ray diffraction pattern corresponds to the presence of crystallites of nickel(II) hydroxide and a second unidentified phase.

In polarized light, two different types of crystals are seen; the predominant phase is light green in color and the other is transparent. Between crossed nichols, the transparent phase appears brown, while the green phase does not change. The green crystals have brown discolorations which develop on the cleavage surfaces. The brown phase is generally much finer. The green phase has been reported by Rodriguez et al. [3] to be $Ni(OH)_2$. The brown phase is presumed by us to be $Ni(OH)_3$ since it is difficult to control the equilibrium between the divalent and trivalent nickel and it seems that small particles with high surface area and new cleavage surfaces are active and are oxidized to the trivalent state.

Simultaneous thermal analysis for the precipitate was performed in stagnant air and the curves are shown in Fig. 2. The first endotherm on the DTA trace is accompanied by a weight loss and indicates that physically adsorbed H_2O vaporizes at temperatures of less than 150°C. The large endothermic peak and weight loss at approximately 260°C show the decomposition of nickel(II) hydroxide to nickel(II) oxide. These two changes are in agreement with the results of Rodriguez et al. [3]. (They did not continue differential scanning calorimetry beyond 500°C.) The progressive weight loss at higher temperatures shown in Fig. 2 indicates that further reactions occur.

To study the effect of oxygen partial pressure on these steps, thermal analysis was performed in a reducing atmosphere achieved by passing nitrogen through the reaction chamber. The results are shown in Fig. 3. As expected, the loss of humidity at low temperatures and the dehydration of nickel(II) hydroxide to nickel(II) oxide are not affected. Similar to the results in air, a progressive loss in weight occurs with its maximum rate at 830°C. Further loss in weight takes place at a slower rate until a constant weight is reached at 1180°C corresponding to the formation of stable NiO. It is obvious that the last step is accelerated in the reducing atmosphere indicating that it corresponds to oxygen loss to NiO. Therefore, this step is due to the reaction
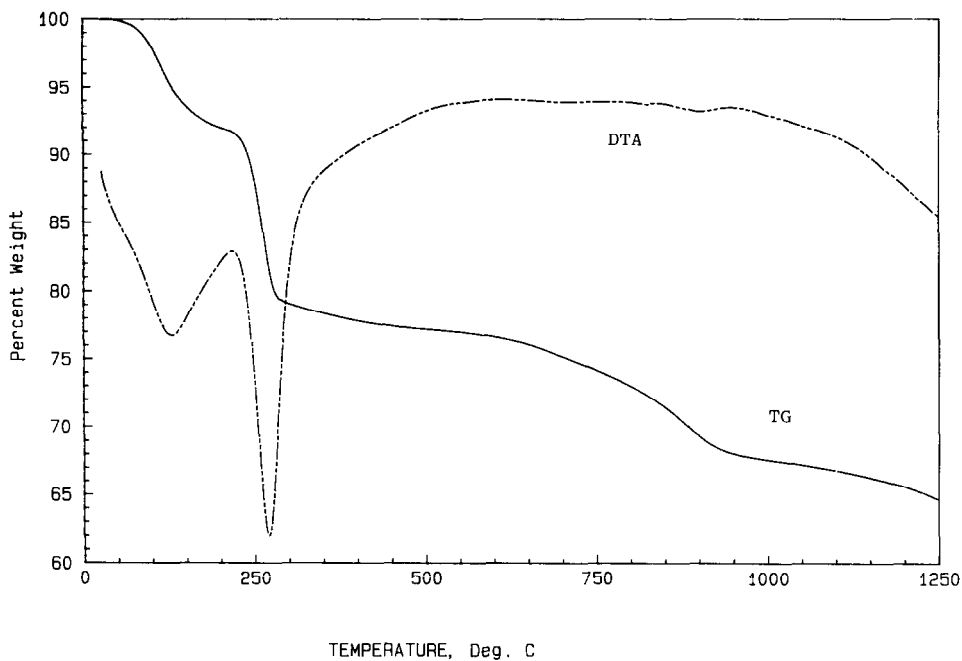
$$Ni_2O_3 \rightleftharpoons 2NiO + \tfrac{1}{2}O_2$$

Fig. 2. Thermal analysis of nickel hydroxide in air (heating rate, $10\,°C\ min^{-1}$).
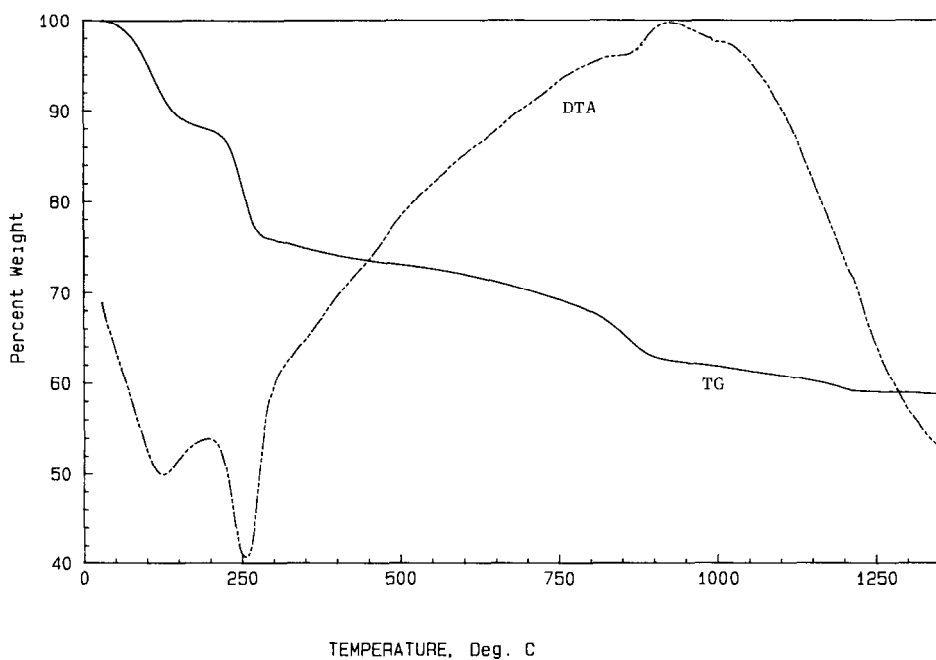

Fig. 3. Thermal analysis of nickel hydroxide in nitrogen (heating rate, $10\,°C\ min^{-1}$).

Accordingly, it is concluded that the preceding loss in weight is due to the dehydration of $Ni(OH)_3$.

This confirms the hypothesis that $Ni(OH)_3$ is present and that the unidentified X-ray peaks correspond to this phase. No reference was found regarding the X-ray pattern for this compound in the literature, possibly due to the difficulty of separating it as a pure phase. The difference in the relative weight losses corresponding to dehydration that occur during the two thermal analyses (Figs. 2 and 3) is due to a gain in moisture and to further oxidation of the aged sample (the one that was tested in the reducing atmosphere).

Coprecipitation

Although the coprecipitate is expected to be a mechanical mixture of crystalline hydroxides, X-ray diffraction shows it to be non-crystalline. Examination with an optical microscope reveals that the sample is isotropic. SEM reveals a lack of acicular α-FeOOH.

Thermal analysis curves, shown in Fig. 4, are not superpositions of those for the pure hydroxides. The weight loss and endothermic peak which occur below $200\,^{\circ}C$ can be attributed to the loss of physically adsorbed H_2O, as seen for the pure hydroxides. After the sharp change in enthalpy and the

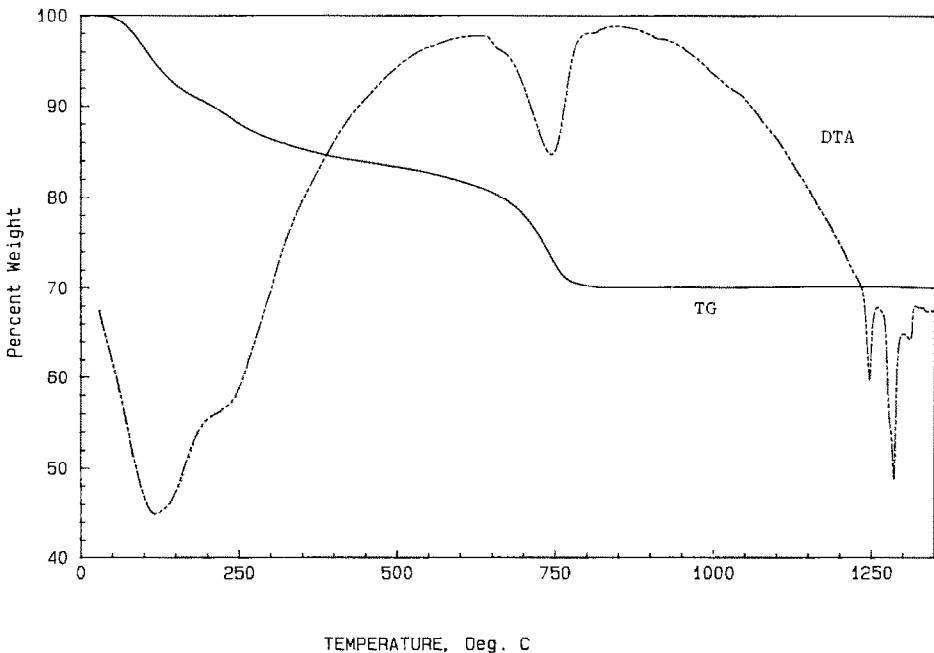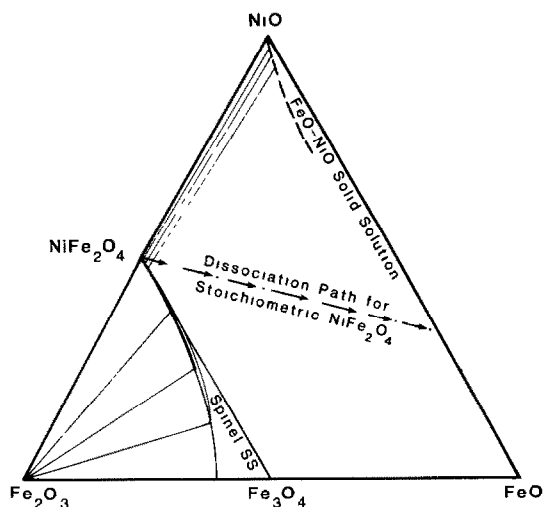Fig. 4. Thermal analysis of coprecipitate ($10\,^{\circ}C$ min^{-1}).

Fig. 5. Tentative diagram for the system NiO–FeO–Fe$_2$O$_3$.

corresponding weight loss, no weight change is observed above 790°C which indicates that oxidic phase(s) are formed. Accordingly, the endothermic loss in weight below 790°C can be attributed to dehydration.

Three endothermic peaks are present above 1200°C. The product after heating to 1300°C is a black, ferromagnetic powder. X-ray diffraction shows that the main phase has a tetragonally distorted spinel structure. Referring to Fig. 5 which was constructed by us in view of Paladino's results [6] and similar Fe$_2$O$_3$–FeO–MO systems, it is evident that after forming stoichiometric NiFe$_2$O$_4$, a ferritic spinel phase poorer in nickel with a composition (Ni,Fe)Fe$_2$O$_4$ is formed plus a small amount of (Ni,Fe)O with a slight loss of oxygen. Accordingly, the three endothermic peaks above 1200°C in Fig. 4 can be explained. The endothermic peak at 1230°C may be attributed to crystallization of the oxidic phase(s) and the endothermic peak at 1285°C is attributed to the formation of NiFe$_2$O$_4$. The peak at 1310°C thus corresponds to the partial dissociation of ferrite, which is accompanied by a weight loss of 0.2% as revealed by computer analysis of the TG data.

THERMAL ANALYSIS OF Fe$_2$O$_3$ AND NiO

Thermal analysis was performed on Fe$_2$O$_3$, NiO and a mixture of the oxides in the ratio to form stoichiometric nickel ferrite. No reactions or weight losses were observed for NiO up to 1500°C. Figure 6 shows the curve for pure Fe$_2$O$_3$ and the mixture. No reaction is observed for iron oxide until 1375°C where an endothermic peak is accompanied by a loss in weight. This corresponds to the formation of magnetite from hematite.
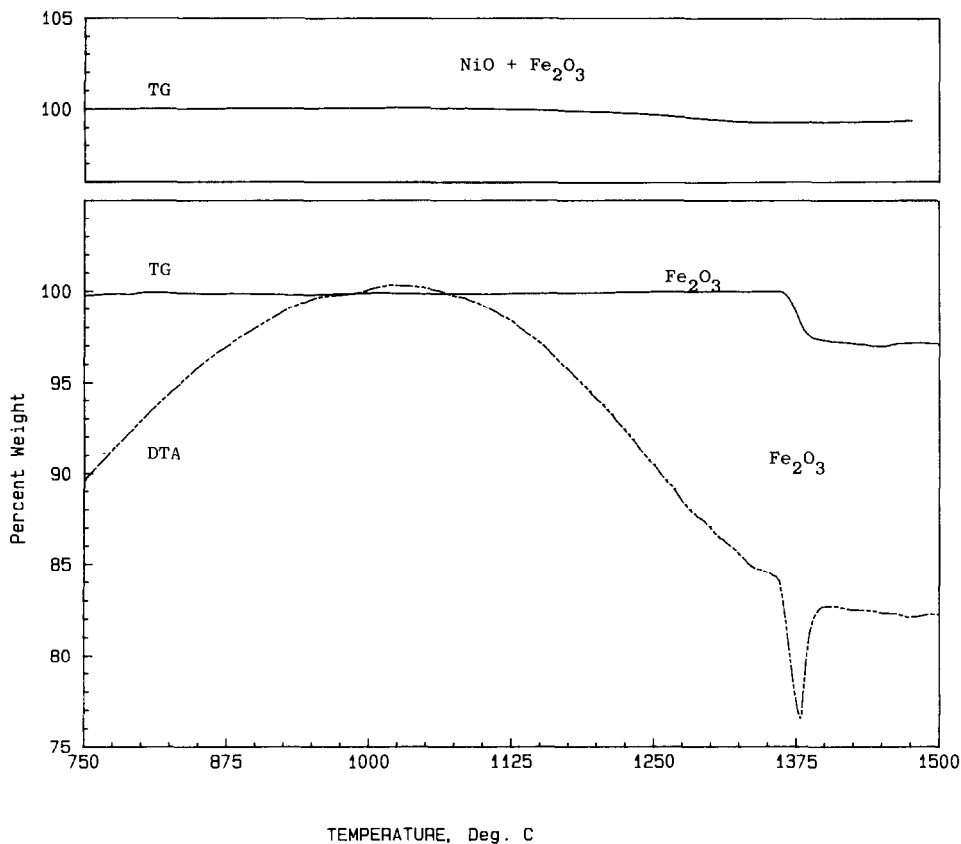
Fig. 6. Thermal analysis of Fe_2O_3 and mixed oxides (heating rate, $5°C$ min^{-1}).

Fine powders of Fe_2O_3 and NiO were then well mixed in an agate mortar and thermal analysis was performed on the mixture. No peaks were detected on the DTA curve but the TG curve in Fig. 6 shows that a gradual weight loss begins at approximately $1150°C$. No abrupt loss occurs at $1380°C$ indicating that Fe_2O_3 is not present due to the formation of nickel ferrite. Indeed, the final product is a black, ferromagnetic powder. These results are in agreement with the tentative phase diagram shown in Fig. 5 which shows that $NiFe_2O_4$ dissociates to a spinel solid solution rich in iron and a cubic oxide solution rich in NiO.

CONCLUSIONS

(1) α-FeOOH dehydrates in two steps. The first step is characterized by an endothermic reaction and weight loss beginning at $230°C$ and the second step involves an endothermic reaction and weight loss beginning at $630°C$. The dehydration product, pure α-Fe_2O_3, undergoes an allotropic transfor-

mation at 680°C that is accompanied by a change in magnetic nature. This transformation is endothermic and is reversible since X-ray diffraction proves that α-Fe_2O_3 is retained on cooling. The product undergoes an irreversible transformation at 1130°C. Continued heating gives an endothermic peak and weight loss at about 1380°C due to the formation of magnetite.

(2) In the precipitation of nickel hydroxide from an aqueous nickel nitrate solution, both divalent and trivalent nickel hydroxide precipitate. While the divalent species appears as green crystals, the trivalent species appears as brown crystals. (Thermal analysis in different atmospheres allowed differentiation between the dehydration and redox steps).

(3) Coprecipitation from an aqueous solution of nickel nitrate and iron nitrate by addition of strong base can be performed so as to give a non-crystalline binary hydroxide that has not been reported in the literature. Firing of this material at 1280°C at a rate of 10°C min^{-1} yields nickel ferrite.

(4) Heating finely divided powders of Fe_2O_3 and NiO, mixed in the ratio to form stoichiometric nickel ferrite, at a heating rate of 5°C min^{-1} results in a gradual weight loss beginning at approximately 1150°C corresponding to the formation of nickel ferrite and the partial dissociation of nickel ferrite to a spinel solid solution (Fe_3O_4–$NiFe_2O_4$) and a cubic solid solution (FeO–NiO) accompanied by a slight oxygen loss.

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