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NICKEL FERRITE FORMATION AT LOW TEMPERATURE

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ABSTRACT

The possibility of obtaining nickel ferrite by a hydrophase method is investigated. The kinetics of the process has been studied. The effect of the main process parameters on the phase composition of the powders obtained is considered. The mechanism of three-stage ferritization is proposed. It is shown that precipitation under suitable conditions makes it possible to obtain nanodispersed nickel ferrite powders.

Keywords: ferrite formation, nickel ferrite, oxidation.

INTRODUCTION

Nanodisperse nickel ferrites are widely used in radio equipment. In order to prepare high quality materials, it necessary to resulting materials that have specific form and size of particles, crystal lattice, chemical purity [1].

In most cases this is defined by the technology of nickel ferrite preparation. Various methods for preparation of nickel ferrite are described in literature. Traditional synthesis technologies are based on solid-state reaction between oxides, hydroxide or salts of corresponding metals and have specific disadvantages [2 - 5].

The liquid-phase method has a number of advantages: low synthesis temperature, high degree of dispersion and monodispersion of powders, good reproducibility of properties [6 - 15].

A ferritization process with preparation of nickel ferrite is investigated in the present work.

EXPERIMENTAL

The concentration of Ni^{2+} ions in the prepared samples has been determined complexometrically. The concentration of iron has been determined using permanganate and bichromate methods. In order to control reaction progress, the reactor has been equipped with electrode system composed of ESL 43-07 electrode for pH measurement, platinum electrode for measuring of oxidation potential and EVL-1M3 reference. The temperature was controlled using thermostat. In order to study the precipitation, the metal ratio was kept Fe^{2+}: Ni^{2+} = 2:1.

All precipitates were washed till negation reaction on sulfate ions. After precipitation the suspension was aged in mother liquor for 48 hours. After ageing the precipitate was separated by means of magnetic separation, after washing and filtering the precipitates were dried at 100°C.

The investigation of nickel ferrite dehydration was made by means of DTA and TG methods using "Derivatograph-Q" in dynamic range of 25 - 1000°C, and heating rate of 10°C/min. The phase composition of the dried powder was studied using X-ray diffraction method (DRON-2.0, Cu-K_α radiation). SEM and X-ray microanalysis were carried using REMMA-102 (SELMI, Ukraine). EDX analysis was conducted using energy-dispersive spectrometer EDX (EDAR).

In order to study the condition of nickel ferrite formation, the experiments regarding the influence of pH and temperature on the phase composition of the formed

products, have been conducted.

The end of the process was determined based on the change of systems' oxidation-reduction potential and the oxidation time required for reaching a constant potential.

The degree of ferritization was calculated using the formula:

$$\alpha = \frac{m_{pr} - m_{npr}}{m_{pr}}$$

where α is the degree of transformation, mpr - the mass of the precipitate, mnpr - the mass of the non-magnetic precipitate.

RESULTS AND DISCUSSION

The phase composition of the formed precipitate depends significantly on the temperature and the initial pH. With variation of synthesis parameters within stated range, the precipitate was composed of oxyhydroxides of iron and nickel, nickel ferrite or a mixture of mentioned phases (Fig.1). With variation of one synthesis parameter at fixed value of another, the following dependencies in change of phase composition are observed. With increasing pH at constant temperature the phase composition changes in order: oxyhydroxides $\rightarrow$ a mixture of oxyhydroxides and nickel ferrite $\rightarrow$ nickel ferrite. With increasing the temperature, the phase formation dependency is analogues to the previous one but it has a different image: oxyhydroxides $\rightarrow$ a mixture of oxyhydroxides and nickel ferrite $\rightarrow$ nickel ferrite.

The ferritization process at different temperatures was investigated too (Fig. 2).

The transformation degree of reaction has been evaluated based on the increasing content of the magnetic phase. It has been established that at temperature range of 20 - 45°C the powder does not demonstrate magnetic properties. At temperature range of 50 - 70°C an oxyhydroxide is formed. The assumption has been confirmed by XRD analysis (Fig. 3).

The analysis of the kinetic curves has allowed to assume the following mechanism of ferritization process. It is known that the presence of double-charged cations Ni^{2+} and Fe^{2+} in the solution leads to the formation of aqua complexes $[Ni(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$. In this case, polyhydroxocomplexes are formed and polynuclear hydrolysis occurs. With pH increasing, at the first stage of precipitation $Fe(OH)_2$ and $(FeONi)(OH)_2$ are formed. The next step at given selected molar ratio, the formation of an intermediate compound occurs:

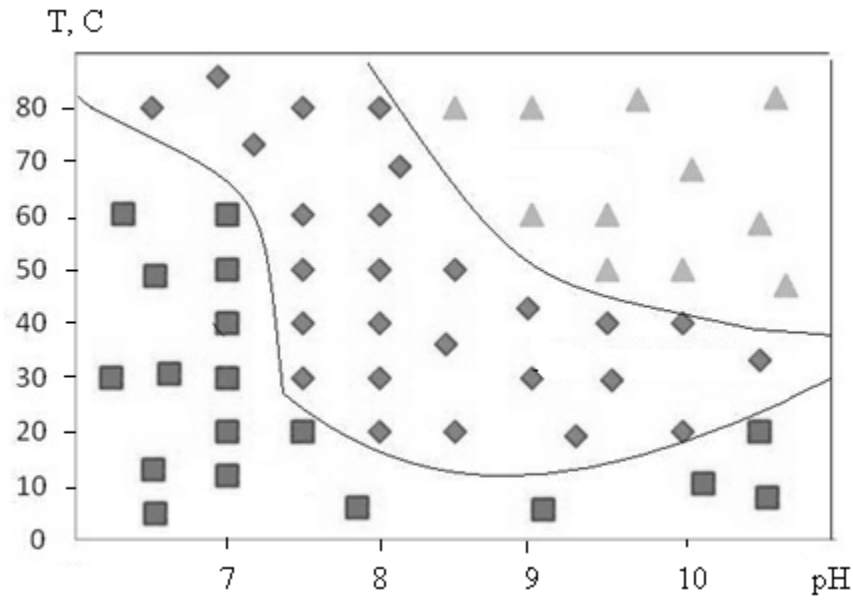


Fig. 1. Dependence of the phase composition of the precipitate obtained in the $FeSO_4$-$NiSO_4$-NaOH-H_2O-O_2 system on the temperature and pH of the solution (■ – MeOOH; -- -$NiFe_2O_4$+MeOOH; ▲- $NiFe_2O_4$).

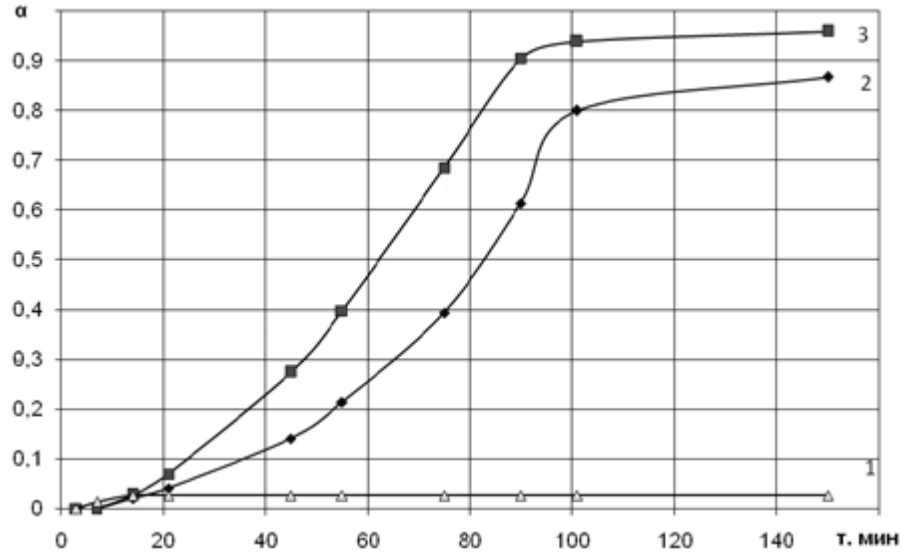


Fig. 2. Kinetic curves of the ferrite process at different temperature: 1- 30°C, 2 - 50°C, 3 - 70°C.

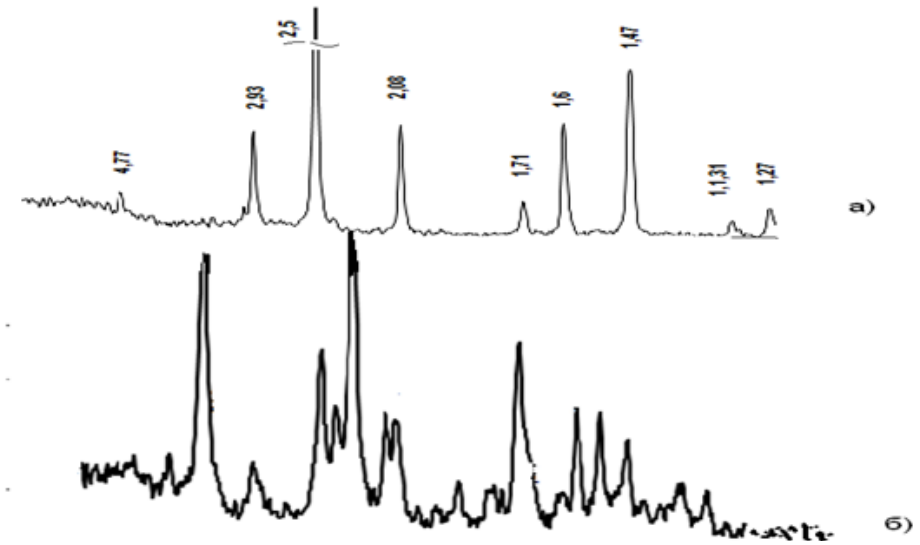
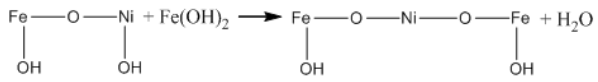
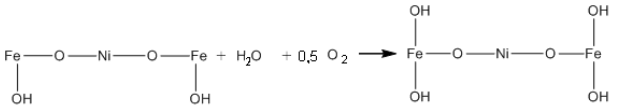


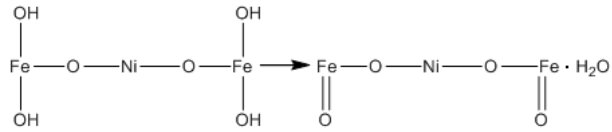
Fig. 3. X-ray diffraction patterns of sediments obtained by coprecipitation: a) nickel ferrite obtained at 70°C, b) oxyhydroxides obtained at 40°C.



As the iron in the intermediate compound is in the form of Fe^{2+}, the next step is the oxidation of Fe^{2+} to Fe^{3+} by the reaction:



The third stage is the formation of nickel ferrite due to intramolecular dehydration:



For clearing the mechanism of nickel ferrite formation, the thermogravimetry was used to determine the structure of the coprecipitated compounds.

The curves of mass loss (TG), differential mass loss (DTG), differential thermal analysis (DTA) and

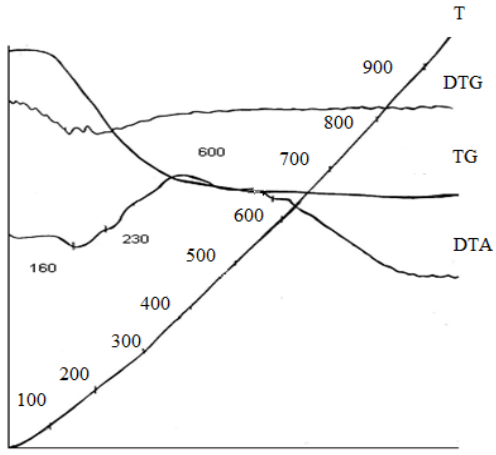


Fig. 4. Derivatogram of nickel ferrite powder obtained by coprecipitation.

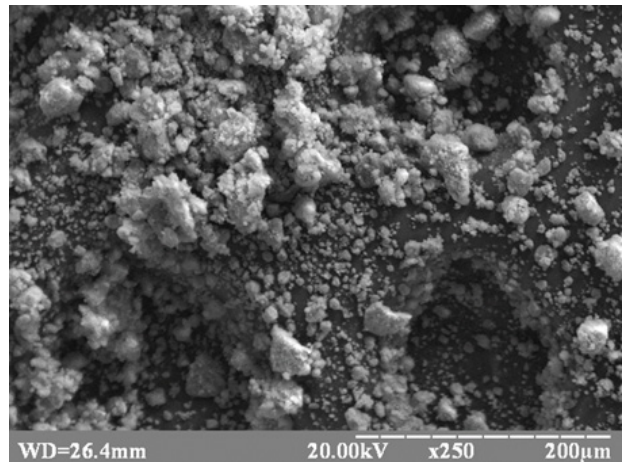


Fig. 5. SEM micrographs of nickel ferrite powder.

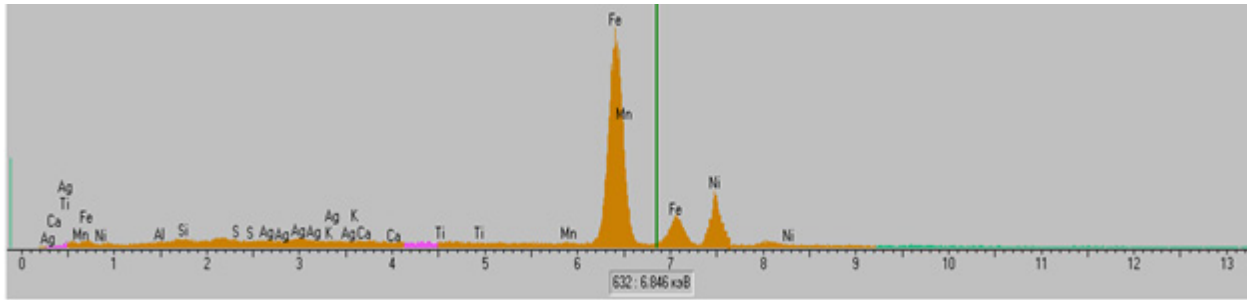


Fig. 6. Elemental analysis using energy-dispersive spectrometer EDX (EDAR) of ferrite samples.

temperature (T) are presented on Fig. 4. The DTA curve shows four features in form of poorly-defined alternating endo- and exothermic events, peaks at 160 - 170°C, 290 - 300°C and 790 - 800°C. An intensive mass loss starts at temperature above 100°C, with maximum mass loss on DTG curve situated at 160°C, 230°C. The temperature of 550 - 600°C corresponds to transformation of non-magnetic oxides. Exothermic event at 640 - 650°C reflects the transition of the samples from amorphous to crystalline state and could not be observed on TG curves. The conducted analysis has proven the possibility of preparing of nanodisperse nickel ferrite powders (Fig. 5).

The results from the elemental analysis of ferrite samples confirm the majority of iron atoms (more than 75 %) and a small amount of impurities.

CONCLUSIONS

The liquid-phase ferritization method is proposed for synthesis of nickel ferrite, which allows preparation on nickel ferrite for application in various field of industry. The influence of such factors as temperature and pH of the medium on the ferritization process has been established. The optimal conditions for preparation of nickel ferrite are pH = 1, temperature 70°C. Multistage mechanism of ferritization has been proposed. Based on XRD, derivatography and SEM analyses, the phase and disperse composition of formed precipitate and its dependency on synthesis conditions have been established.

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