NiFe$_2$O$_4$ NANOCRYSTALLINE POWDERS PRECIPITATED WITH ADDITION OF SOLUBLE STARCH AS A DISPERSING AGENT

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ABSTRACT

NiFe$_2$O$_4$ nanocrystalline powders were prepared by precipitation method using NiSO$_4$·and Fe(NO$_3$)$_3$ as precursors and Na$_2$CO$_3$ as a precipitating agent, which was added in quantities necessary for reaching values of a degree of substitution (DS) equal to 1 and 3. The applied precipitation process was further adapted by introduction of soluble starch as a dispersing agent. The obtained results of X-Ray diffraction analysis (XRD) of the prepared powders after annealing confirm formation of nanocrystalline NiFe$_2$O$_4$ phase with the same average crystallite size of 21 nm. The results of Fourier transform infrared spectroscopy (FTIR) and ^{57}Fe Mössbauer spectroscopy (MS) further support determined phase composition, whereas the results of scanning electron microscopy (SEM/FE-SEM) demonstrate noticeable differences in morphology and particle size of the studied powders. Values of coercivity and magnetic moment measured at room temperature using Vibrating sample magnetometer (VSM) are consistent with those of soft magnetic material and the recorded hysteresis loops were found to have similar, characteristic „S" shape.
Keywords: nanocrystalline NiFe$_2$O$_4$, precipitation method, microstructure

1. INTRODUCTION

Ni-ferrites represent very important group of functional materials and one of the most commonly used soft magnetic materials. Recent developments in nanotechnology prompted renewed interest in these materials by broadening their already wide range of application and opening investigations for their use in hydrogen production, as catalysts, as photo reactive materials and for gas sensing [1-3]. Due to direct relation between functional properties of Ni-ferrites and their structure, phase composition, crystal and particle sizes, applied synthesis method is very significant. Accordingly, investigation of alternative and innovative processing routes is still a current topic. In the present study, common precipitation method of synthesis of nanosize NiFe$_2$O$_4$ was adapted by introduction of soluble starch as a dispersing agent and sodium carbonate as a precipitating agent instead of usually used sodium hydroxide. The obtained ferrite powders were analyzed and discussed through structural, compositional and magnetic characterization.

2. EXPERIMENTAL

In the applied synthesis method analytical grade $NiSO_4 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were used as precursors for their respective oxides, whereas soluble starch $(C_6H_{10}O_5)n$ was used as a dispersing agent and anhydrous Na_2CO_3 as a precipitating agent. Water solutions of the used inorganic salts were mixed with a water solution of starch and once they have been mixed in, they break up into fine droplets confined within polymer chains. With the subsequent addition of the precipitation agent (anhydrous Na_2CO_3) an insoluble solid phase was formed. Na_2CO_3 and $NiSO_4$ react in the solution to give $NiCO_3$ and/or $Ni(OH)_2$. Thus, $NiCO_3$ precipitation occurs in competition with $Ni(OH)_2$ precipitation and a solid phase is usually a mixed complex of nickel hydroxy-carbonates, which when heated transform to NiO. Moreover, $Fe(NO_3)_3$ reacts with Na_2CO_3 in the solution to give ferric hydroxide or hydrated ferric oxide, which when heated transforms to Fe_2O_3. In order to achieve maximal precipitation during synthesis pH was maintained in range 9 to 11 [4]. Given that the soluble starch reacts with sodium in alkalization reaction [5] certain amount of Na_2CO_3 is lost. The amount of Na_2CO_3 lost due to this secondary reaction can be determined by using a degree of substitution (DS) [5]. The DS is defined as the average number of substituents per anhydro glucose unit (AGU) and can have values between zero and three. In order to make process simpler, two scenarios in which starch reacts with sodium up to level when DS=1 and DS=3 were selected, and the corresponding samples were labeled accordingly. Mixture was continuously stirred and then dried at 80 ^{o}C until solid composite was obtained. As the starch solidifies it entraps the formed crystals in a solid organic matrix [6]. In the final step, the solid composite was combusted and calcinated in muffle furnace at 900°C for 5h in order to remove the organic matrix and transform reaction products to oxides which react and give $NiFe_2O_4$. Microstructure of the obtained $NiFe_2O_4$ powder was analyzed by SEM/FE-SEM technique. FTIR attenuated total reflection spectroscopy analysis was carried out at room temperature using Nicolet 380 spectrophotometer. Phase composition and structure of the prepared powder samples were analyzed by XRD and MS. Room temperature magnetic measurements were carried out by means of a VSM with magnetic field strength of 1000 kAm^{-1}.

3. RESULTS AND DISCUSSION

Morphology and structure of the obtained Ni-ferrite powder is illustrated by corresponding SEM and FE-SEM images given in Figure 1.
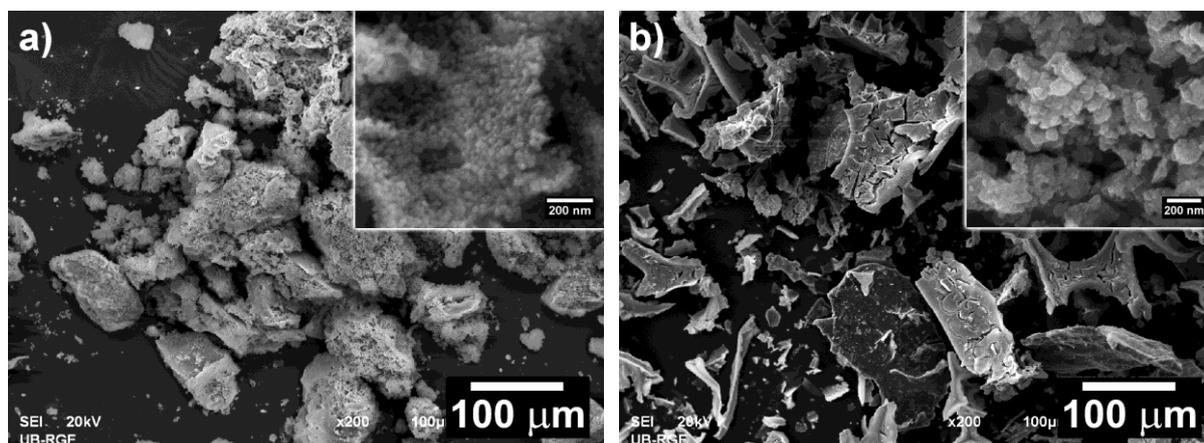

Figure 1. SEM images of morphology of the prepared NiFe₂O₄ powders with insert FE-SEM images: a) DS1 and b) DS3 powder sample

The presented SEM images demonstrate notable differences in morphology of the prepared Ni-ferrite powders. In contrast, the FE-SEM images taken at higher magnification depict similar fine-grained texture of porous network structures with a shape of interstitial space within the starch matrix that was occupied by the solution mixture. From Figure 1, it can be seen that the structure of the DS1 powder sample consists of particles of about 20 nm whereas the DS3 powder sample consist of fairly coarser particles. In order to gain insight into the phase composition of the prepared powders and to confirm that the organic matrix has been completely removed by calcination, FTIR analysis was carried out.

The obtained FTIR spectrum of the prepared DS1 ferrite powder is given in Figure 2. Two characteristic peaks can be observed, on the presented FTIR spectrum of the DS1 Ni-ferrite powder. One at 620-550 cm^{-1}, that can be assigned to intrinsic stretching vibrations of metal at the tetrahedral site (Fe $\leftrightarrow$ O) and the other at 450-385 cm^{-1} which corresponds to octahedral-metal stretching vibrations (Ni $\leftrightarrow$ O). The obtained results of XRD analysis are presented in Figure 3.
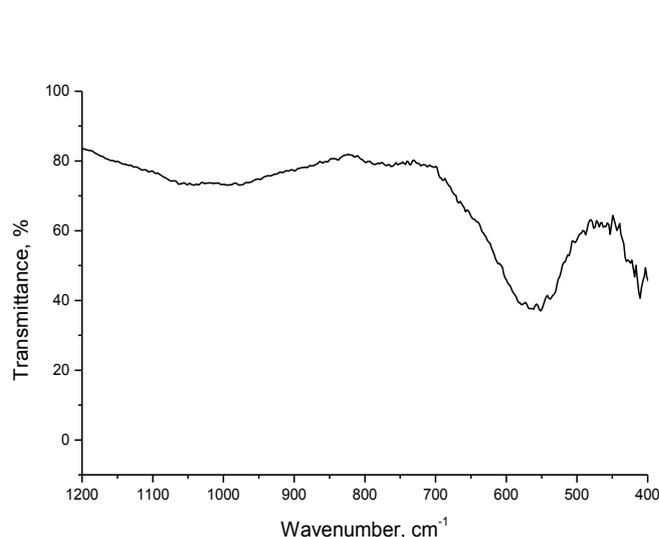

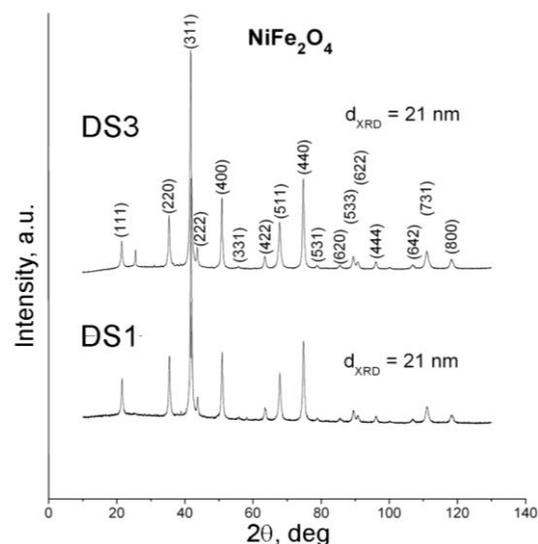*Figure 2. FTIR spectrum of the prepared DS1 Ni-ferrite powder*

Figure 3. X-Ray diffractogram of the prepared Ni-ferrite powders

The obtained results of XRD analysis presented in Fig. 3 confirm the formation of nanocrystalline NiFe$_2$O$_4$ phase (ICSD #158834) in case of the both synthesized powders. The DS1 sample was found to have monophase NiFe$_2$O$_4$ composition with the average crystallite size of about 21 nm, which supports the results of FESEM analysis. Likewise, the DS3 powder sample was also found to consist primarily of NiFe$_2$O$_4$ phase, however, there is an additional single peak at 2θ = 25.5° which most probably belongs toFe$_2$O$_3$ phase. Nonetheless, considering the very small difference in lattice volume of NiFe$_2$O$_4$ and Fe$_2$O$_3$ phases it is very hard to distinguish between those two phases. The determined average crystallite size of about 21 nm suggests that the larger amount of the precipitating agent did not have significant influence on the crystallite size. The prepared nanocrystalline Ni-ferrite powders were further characterized by MS. The obtained spectrums presented on Figure 4 are characteristic of Ni-ferrite material and principally support the results of XRD analysis.
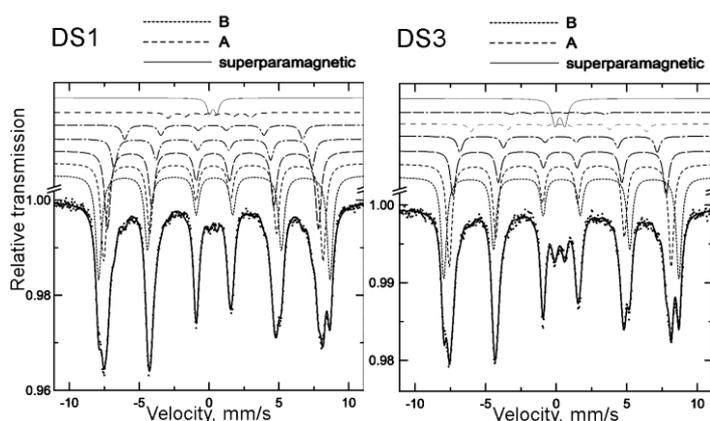

Figure 4. Mössbauer spectrums of the prepared Ni-ferrite powders
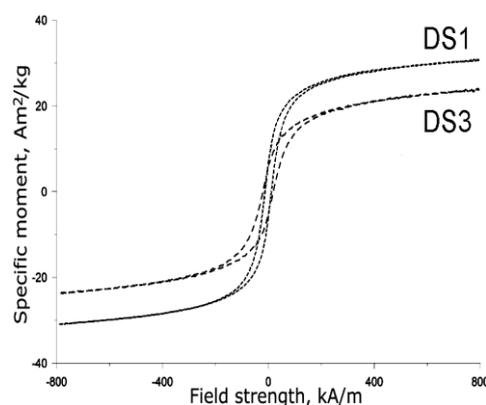
Figure 5. Room temperature hysteresis loops of the prepared Ni-ferrite powders

Determined Mössbauer parameters (isomer shift, hyperfine field) correspond to those of $NiFe_2O_4$ phase, so characteristic spectral components were assigned to tetrahedral (A) and octahedral (B) Fe^{3+} atom sites. The diminishing intensity of the magnetically split sextets implies a distribution of crystallite sizes of $NiFe_2O_4$ phase, whereas presence of small doublets can be related to existence of superparamagnetic fraction of $NiFe_2O_4$ phase, having crystallite size in range 10-13 nm. With the decrease of particle size surface area increases and the portion and influence of surface and interface atoms and/or atoms at irregular positions increases. In light of this, it can be assumed that the observed decrease of intensity of the sextets and the small superparamagnetic component are related to nanocrystalline structure of the prepared powders. Even so, the somewhat stronger influence of nanocrystalline component i.e. surface layer atoms can be observed on the spectrum of the DS3 sample. Magnetic properties of nanocrystalline Ni-ferrites are strongly related to their microstructure and the changes in magnetic behavior are usually consequence of changes in exchange interactions between tetrahedral and octahedral sublattices, magnetocrystalline and shape anisotropy of crystal, structure and size of domains and presence of defects. In order to investigate magnetic properties of the prepared nanocrystalline Ni-ferrites room temperature hysteresis loops were recorded using VSM. Even so, on Figure 5, only minor differences between the presented hysteresis loops can be observed. Such result is not surprising when subtle differences in structure and phase composition of the studied powders are considered. However, it can be said that the DS1 sample exhibits a bit higher mass magnetization, although not so significant that any serious discussion can be made. Nevertheless, the both hysteresis loops have typical "S" shape characteristic of soft magnetic materials.

4. CONCLUSION

Nanocrystalline Ni-ferrite powders were successfully prepared using the modified precipitation method. The powders prepared according to the two adopted scenarios have almost the same composition consisting of practically pure Ni-ferrite phase. Both materials were found to have very similar fine-grained structure with the same crystallite size ~ 21 nm. The measured magnetic properties of the both powder samples are within the expected range for this type of material and differ only slightly. Hence, it can be concluded that the added amount of precipitation agent predominantly had effect on morphology of the powders and their particle size. The observed differences in morphology and particle size could be very significant for other surface dependent functional properties e.g. gas sensing and catalytic efficiency and in that sense, more apparent differences in performance of the prepared powders can be expected.

5. ACKNOWLEDGEMENT

6. REFERENCES

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