Methods of obtaining nanodisperse Ni ferrite, their structure and magnetic properties

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Among ferrites, nickel ferrite, which is a typical soft ferromagnetic material with a completely inverse spinel structure, has a large number of applications. Some applications are determined by the nano-size of the ferrite particles, for example, a gas sensor [1].

The aim of the present work is to study the structure and morphology of nickel ferrite nano-powders by analytical electron microscopy (AEM) methods in dependence on the preparation procedure and to get information on the relation between their structure and magnetic characteristics.

Objects of investigation

Three kinds of nickel ferrite nano-powders have been prepared: 1 - $NiFe_2O_4$ch produced by a chemical method in burning reaction using $NiNO_3$ with citric acid and/or glycine as an inner fuel; 2 – $NiFe_2O_4$ ch_Cu: $NiFe_2O_4$ ch powders with the following copper covering by copper oxides reduction; 3 – $NiFe_2O_4$ pl powders produced by a plasma chemical technique (in radio frequency inductively-coupled nitrogen plasma – ICP).

Methods of investigation

Microstructural characterization was done using a JEM-1230 transmission electron microscope (Hv =100 kV) combined with microdiffraction (MD). For TEM studies, the synthesized nano-powders were dispersed in etylalcohol. The typical time of dispergation was ~ 40 sec. The powders were applied in the form of suspension to a copper grid covered with a thin formvar film. Preliminary, an about 10 nm thick gold layer was attached to a part of the copper grid using the sputtering deposition technique on a VUP-2K sputterer. The gold film serves for ***in-situ*** definition of the constant λL of the instrument, the accurate knowledge of which is important for analysis of diffraction patterns [2].

The phase composition of powders was analyzed by XRD using a diffractometer D8 *Advance, Bruker* Company, model 2005. The samples were filmed in copper filtrated CuK α-radiation (λ = 1.5418 Å).

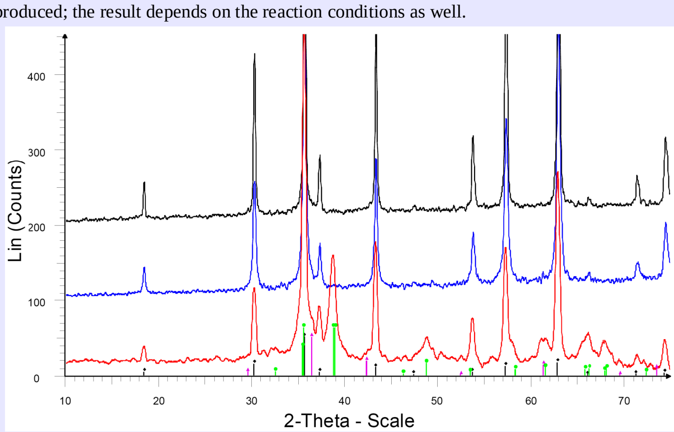
The magnetic properties of the powders were defined employing the vibration sample magnetometer (Lake Shore Model 7404 VSM) at room temperature in a magnetic field varying from –10 to +10 kOe.

Results

Information about the structure and morphology of nano-powders synthesized by wet (chemical) and plasma methods was obtained in a single electron microscopic experiment. Detailed examination of the particles allowed to get information about the relations between the conditions for powders production and their morphology and structure. It has been found that Ni ferrite powders are heterogenous and high disperse. The particles of $NiFe_2O_4$ ch powders have a tendency as to agglomeration of small spherical particles (18-35 nm) as to formation of 3-, 4- and 5-faceted particles (~25 nm) (Fig.1). The particles of $NiFe_2O_4$ ch_Cu powders are more homogeneous if compared with $NiFe_2O_4$ ch powder, but it has a tendency to agglomerate small spherical particles, too (15-25 nm). Plasma powders ($NiFe_2O_4$ pl) consist of semi-transmission six-faceted plates (Fig.3). However, the particle size distribution is wide: the minimum size of crystallites is ~23 nm and the maximum size of separate particles reaches 53.8 nm, but dominates particles with a size of 38.5 nm. The plasma $NiFe_2O_4$ pl powder is more homogeneous regarding as the phase composition as the particles size and form. The inter-planar distance (d_{hkl}) calculated from ring patterns gives d_{hkl} = 2.513, 2.09, 1.697, 1.607, 1.49 Å, which are in good agreement with the table data JCPDS (10-325) for Ni ferrite. Analysis of the electron diffraction patterns for plasma powders proves the existence of the only one crystalline phase (in accord with the XRD result, Table 1) and good enough crystallinity at the electron microdiffraction level (Fig.4-b). Patterns of chemically produced powders indicate the existence at least of two crystalline phases (Fig.4-a); the broadening of the diffraction pattern indicates the grain size of nanometer scale.

The powder X-ray diffraction (XRD) patterns of the samples are presented in Fig.1. Diffraction peaks (can be indexed in a simple cubic lattice of all systems) showed sharp and intensive peaks of cubic inverse spinel structure of $NiFe_2O_4$ (JCPDS *10-325*). The mean size of crystallite particles was calculated from the semi-spheres of the peaks (Table 1).

The investigation of the magnetic properties of the produced ferrite powders showed that the samples had a significant magnetic coercivity (Table 2, Fig.6); it might be connected with the particle size. Furthermore, both the coercivity and the magnetization depend on the method of powder production. So the magnetization for powders produced by the plasma method is larger than that of chemically produced; the result depends on the reaction conditions as well.



↑ *Fig. 5.* XRD patterns of powders synthesized by different methods: 1 – plasma (black on XRD); 2 – chemical (blue on XRD); 3 - chemical with CuO reduction $NiFe_2O_4$ch_Cu (red on XRD).

Table 1. Characteristics of the produced powders

Preparation procedure	SSA (m^2/g)	X-Ray data: phase composition	X-Ray data: Particle size (nm)	AEM: TEM + MDK: Phase composition	AEM: TEM + MDK: Particle size (nm)
Chemical process $NiFe_2O_4$ ch	24	Trevorite $NiFe_2O_4$	29	Trevorite $NiFe_2O_4$	18-35
Combined chemical: $NiFe_2O_4$ ch +CuO reduction $NiFe_2O_4$ ch _Cu	25	Trevorite $NiFe_2O_4$, 50%; Tenorite, syn.CuO-30%; Cuprite,synt.Cu_2O-20%	22	Trevorite $NiFe_2O_4$, Tenorite, syn.CuO	15-25
Plasma process $NiFe_2O_4$ pl	28	Trevorite $NiFe_2O_4$	40-45	Trevorite $NiFe_2O_4$	23; 38,5; 53

SSA – specific surface areas

Table 2. Magnetic characteristic of $NiFe_2O_4$ nano-powders

Sample	Coercivity (Oe)	Magnetization at 10 kOe (emu/g)	Spontaneous M (emu/g)
$NiFe_2O_4$ ch (chemical)	136	35.6	30.6
$NiFe_2O_4$ ch _Cu ($NiFe_2O_4$ ch +CuO reduction)	120	20.4	18.1
$NiFe_2O_4$ pl (Plasma)	74	43.5	41.3

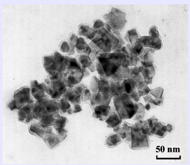
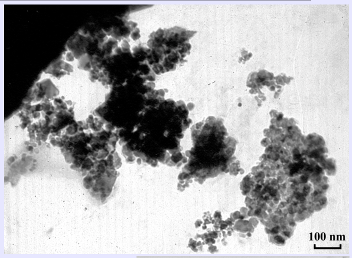


Fig.1. TEM image of nano-powders produced by a chemical method ($NiFe_2O_4$ ch) ←



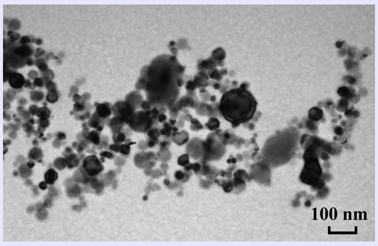
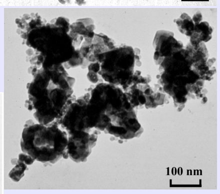


Fig.3. Micrographs of the nano-powders ↑ produced by a plasma technique ($NiFe_2O_4$ pl)

Fig.2. Micrographs ↑ of $NiFe_2O_4$ch_Cu nano-powders →



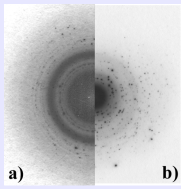


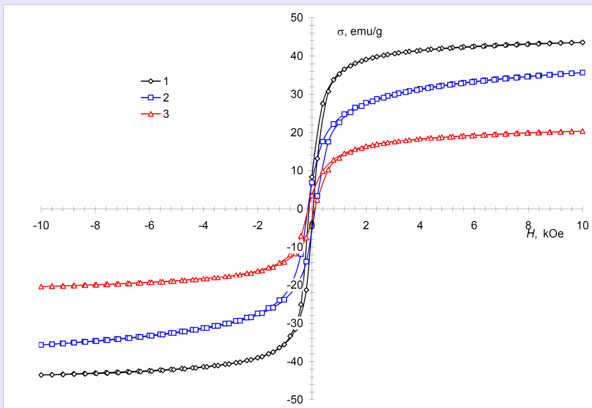
Fig. 4. Microdiffraction ← patterns:
(a) - chemical powders
(b) - plasma powders

Conclusion

Detailed examination of the particles allows to get information on the dependence of morphology and structure of powders on the conditions of their production.

The study of the magnetic properties of the produced Ni ferrite powders shows that the samples have a significant magnetic coercivity, which might be connected with the particle size. Furthermore, both the coercivity and the magnetization depend on the method of powder production. Therefore, the magnetization for the powders produced by the plasma method is larger than that of chemically produced.

Fig.6. Room-temperature hysteresis loops for Ni ferrites produced by different methods:
1 – plasma; 2 – chemical; 3 - chemical with CuO reduction (Fe_2O_4ch_Cu). →



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