NANO- AND MICRO-PARTICLES OF Fe_3O_4 OBTAINED BY SPRAY PYROLYSIS FOR MAGNETORHEOLOGICAL APPLICATIONS

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Ultrasonic spray pyrolysis approach was used to prepare Fe_3O_4 powders with sizes of ~40 nm and ~1,5 mkm as potential additives to magnetorheological suspensions. The magnetization of magnetite was shown to depend on the particles size (58 and 65 $A \cdot m^2 \cdot kg^{-1}$ for nano- and micro-sized Fe_3O_4, respectively). The difference in the grain size, magnetic features and specific surface is expected to produce different effects on the magnetorheological behavior of suspensions on their base. The measured growth in shear stress (τ/τ_0) of the suspensions has reached 4 units for micro-sized Fe_3O_4 under applied magnetic field.

1. Introduction

Ferrimagnetic oxides, including γ-Fe_2O_3, Fe_3O_4 and metal ferrites, have been a subject of interest due to their attractive electronic, magnetic and rheological properties [1-4]. Semiactive control devices for various applications have received a significant attention in recent years since they offer an adaptability of active control devices without requiring the associated large power sources. Magnetorheological (MR) dampers are semiactive control devices that use MR fluids to produce controllable dampers. When magnetic field is applied to the MR fluids, particle chains form, and the fluid becomes a semisolid and exhibits viscoplastic behavior. They potentially offer highly reliable operation and can be viewed as fail-safe in that they become passive dampers in case of the control hardware or software malfunctions [3].

A wide range of additives is used with MR fluids to enhance their stability, MR response, seal life etc. Powdered magnetic materials are promising additives to MR fluids since they combine several functions. In particular, they enhance the sedimentation stability and increase the MR response of the suspensions. A synergizing effect of magnetic field on the MR response of the fluids could be achieved. However, there is no strict background for the compositions of the fluids to control their behavior. The grain size and magnetic properties are important parameters affecting the rheological features of the materials [1, 3, 4].

Herein, we represent a study on the preparation of Fe_3O_4 powders with a grain size ranging from nanometers to micrometers as potential modifying additives for MR suspensions of carbonyl iron in mineral oil.

2. Experimental

Water solutions of $Fe(NO_3)_3$ and citric acid (CA) were taken in various proportions to synthesize magnetite (Fe_3O_4) by spray pyrolysis approach. CA played a role of reducing agent. The solution was transformed into aerosol state with an ultrasonic atomizer and directed to the reaction zone with a flow of nitrogen. The reaction zone was placed in a furnace heated to 500–650 °C. In order to prepare nano-sized particles, an inert component (NaCl) was additionally introduced to the reactant mixture. The resulting powder was washed with distilled water to remove NaCl.

Powdered samples were characterized by scanning electronic microscopy (SEM), X-ray diffraction (XRD) and infrared spectroscopy (IR). Grain size and morphology were estimated on a LEO 1420 microscope. The XRD analysis was carried out on a DRON-2 diffractometer using Co-$K\alpha$ radiation. IR spectra were recorded from powdered samples on an AVATAR FTIR-330 spectrometer.

Magnetization measurements were performed with a Cryogen Free Measurement System (CFMS) Cryogenic Ltd (T = 7–300 K, B_{max} = 18 T).

Rheological parameters of suspensions of the prepared powders in mineral oil (15 wt. %) were measured on a Rheotest RN-4.1 rheometer (T = 20 °C, shear rate is 200 s^{-1}). In order to estimate the effect of magnetic field, a toroidal ferrite magnet with B = 0.5 T was used. The MR response was measured here as τ/τ_0, where τ and τ_0 are shear stress with and without magnetic field, respectively.

3. Results and Discussion

In order to obtain powders with spinel-type Fe_3O_4 structure, different conditions of the synthesis were applied. Proportions of the iron salt and CA, as well as the pyrolysis temperature were varied. Examples of the XRD patterns of the products are given in Fig. 1. As seen, a single-phased powder based on Fe_3O_4 that does not contain admixtures of paramagnetic α-Fe_2O_3 phase has been achieved in case of sample 3. In spite of a high temperature of the synthesis, the diffraction lines are broad, which reflects poorly crystallized structure of the sample. This is evidently caused by a short-time exposure of the reactant mixture to heat. Note that the presence of an inert additive (NaCl) does not influence noticeably the shape of the XRD patterns. IR-spectroscopy examination of the samples confirms the results of XRD analysis.

SEM picture of the powder synthesized without NaCl is given in Fig. 2-*a*. The sample consists of spherical particles with a size ranging from 1 to 2 mkm. The described morphology results from drying the droplets of initial solution dispersed with ultrasonic atomizer.

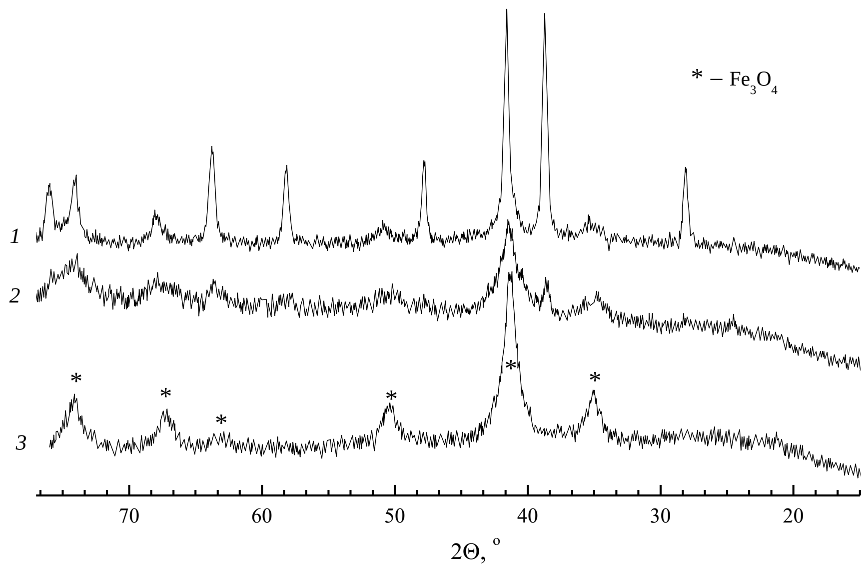

Figure 1. XRD patterns the pyrolysis products at different conditions: *1* – 15 g of $Fe(NO_3)_3$, 5 g of CA, 650 °C; 2 – 15 g of $Fe(NO_3)_3$, 10 g of CA, 500 °C; 3 – 15 g of $Fe(NO_3)_3$, 10 g of CA, 650 °C.

When NaCl is added to the initial reactant mixture, the resulting powder has the same size and shape. However, the spheres consist of Fe_3O_4 nanoparticles distributed over NaCl matrix. The inert component could be washed out with distilled water to separate the oxide nanoparticles. A typical SEM image of the powder is given in Fig. 2-*b*.

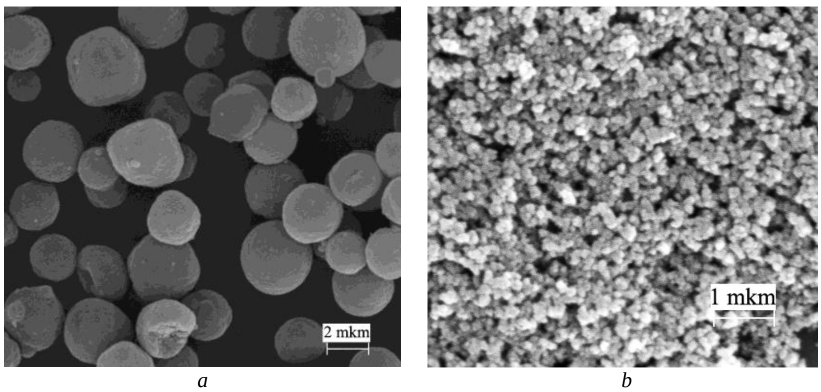

Figure 2 SEM images of the pyrolysis products without (*a*) and with (*b*) NaCl as an inert additive.

Note that the diameter of the grains could be controlled by varying the amount of the inert component. Under the conditions used in the paper, Fe_3O_4 grains have an average diameter of ~40 nm.

The magnetic measurements have revealed a difference between the nano- and micro-sized Fe_3O_4 samples. Thus, the oxide with a size of 1.5 mkm is characterized by enhanced specific magnetization and coercivity.

Rheological tests have shown that in case of the powder with the greater grain size, the magnetic field has more pronounced influence on the viscosity (τ/τ_0) of the suspension. However, the smaller particles could possess a stronger stabilizing effect when used as a modifier of MR fluids based on carbonyl iron. The structural and functional features of the obtained materials are summarized in Table 1.

Table 1. The characteristics of the synthesized powders and MR fluids on their base

Phase composition	Grain size	M_{sat}, $A \cdot m^2 \cdot kg^{-1}$	H_c, $kA\ m^{-1}$	Calculated S, $m^2 \cdot g^{-1}$	τ/τ_0, r.u.
Fe_3O_4	~40 nm	58±1	4.5±0.1	~20	~2.5
Fe_3O_4	~1,5 mkm	65±1	6.5±0.1	~0.5	~4

4. Conclusion

Spray pyrolysis method has been employed to prepare Fe_3O_4 powders from inorganic iron precursor (iron nitrate) and organic reducing agent (citric acid). The conditions of the synthesis that allow preparing both nano- and micro-sized particles have been chosen. The effect of grain size on the magnetic properties of the powders and magnetorheological behavior of the suspensions on their base has been revealed. The synthesized material will be used as modifying and stabilizing additives to carbonyl iron in mineral oil MR fluids for semiactive dumping devices.

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