Microwave-induced phase transformations of iron oxide particles

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Abstract. The article presents results of study of $\alpha$-$\text{Fe}_2\text{O}_3$ response on microwave treatment. Microwave influence on iron oxides constituting nature occurring kaolinite clay were studied by a complex of methods. The original sample S0 was made from fine-dispersed $\text{Fe}_2\text{O}_3$ iron oxide particles. Sample S1 was produce d via treatment with 2.45 GHz microwave field. Microwave treatment induced structure changes in iron oxides which manifest themselves through polymorphic changes. X-ray phase analysis shown that a deformation polymorphic transformation $\alpha$-$\text{Fe}_2\text{O}_3 \rightarrow \gamma$-$\text{Fe}_2\text{O}_3$ takes place and two-phase hematite-maghemite state is formed. Problem of faint and overlapping diffraction peaks resolution is solved with wavelet transformation skeleton technique. Crystal particles of S0 sample are $\alpha$-$\text{Fe}_2\text{O}_3$ hematite particles with rhombohedral lattice. After microwave treatment sample S1 developed new diffraction peaks corresponding to cubic $\gamma$-$\text{Fe}_2\text{O}_3$ maghemite crystal system. Polymorphic transition is accompanied with morphological changes. After the treatment surfaces of large particles are covered with smaller particles which are proved by the increase of samples fractal dimension from 2.83 to 2.85. Powder color changes from red-orange to dark brown which results in changes of all color parameters; the red component experience the biggest suppression and it is suppressed by the factor 2.

1. Introduction

Creation of materials with unique physicochemical characteristics is one of the relevant branches of studies. During the last decade researcher’s attention was attracted to studies of microwave influence on oxide materials. Traditional baking technology is based on thermal conductivity and convective heat transfer from surface layers to the bulk of material, which results in non-uniform structure formation; microwave treatment, on the contrary, provides uniform heating in the whole volume and results in uniform samples heating. Because the heating rate is no longer constraint by the standard thermal conductivity, in principle, it is possible to create uniform structures with desired features. Multiple research [1-3] comparing traditional and microwave baking methods, for instance, alumo-silicate ceramics, show significant increase of baking efficiency and decrease of power consumption, which shows efficiency of microwave material treatment and its capability to enhance oxide material features.

Interaction between a baking material and the microwave field is not well-understood up to this moment. Existing studies were very selective and were lacking direct justification. Authors of [4], in particular, established that in oxides occurring in clay minerals microwave treatment induces phase transitions: in iron oxides instead $\text{Fe}_2\text{O}_3$ hematite $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ magnetite is formed; in aluminum oxides polymorphic changes take place and a part of alumina is transformed to $\alpha$-corundum. Of the four
silicon dioxide modifications found in nature occurring clay only two remain after microwave treatment in air environment, namely, \( \beta \)-quartz and \( \beta \)-cristobalite, while in a humid medium only \( \beta \)-quartz remains.

In paper [5] it was established, that microwave treatment in air environment results in cell water loss in clay materials, which is accompanied with clay particles agglomeration and polymorphic transformations of the constituting oxides.

Microwave treatment of a dispersal system as a whole causes multiple local interactions in the bulk of the system, which produce a microscopic effect. Physicochemical features of oxide particles structure formation are significantly affected by their chemical composition, morphology, cell structure, cell defects, ion exchange processes, and many other factors. Generalization of structure change laws driving microwave treatment induced transformations of oxides constituting kaolin clay can be done with detailed study of physicochemical processes taking place in the basic clay components.

Iron oxides enter the most part of nature occurring clays of various genesis. High-dispersion iron oxides \( \gamma \)-Fe\(_2\)O\(_3\) (maghemite) and Fe\(_3\)O\(_4\) (magnetite) manifest a wide array of magnetic features. These features are defined by size and shape of constituting particles which, in term, are affected by external treatment conditions. Some publications propose various methods of maghemite and magnetite nanoparticles production with heat treatment, chemical condensation, aerosol pyrolysis, and precursor method particle synthesis [6-10].

To establish a law driving external treatment influence on morphology and magnetic features of iron oxide it is required to perform systematic experimental study. This allows one to establish laws of iron oxide structure-phase transitions at the nano-scale and to control their phase composition.

It is sensible to study structure changes in dispersion system induced by microwave treatment at various hierarchical levels. Alongside the optical microscopy providing an image of dispersion samples one should use modern framework of digital images procession based on implementation of colorimetric gradation, multifractal and wavelet analysis methods [5].

The main aim of research presented is to study structure response of iron oxide constituting nature occurring kaolin clay which is induced by microwave treatment with a complex of optic and mathematical methods.

2. Experimental

The original sample S0 was a batch of iron oxide Fe\(_2\)O\(_3\) powder (chemically pure), sample S1 was produced from it via treatment of 2.45 GHz microwave field.

Phase analysis of S0 and S1 samples were performed with X-ray powdered diffraction in automated diffractometer DRON-4 with Bragg-Brentano method geometry in the range of diffraction angles from 15° to 100° with the usage of Co K\(_{\alpha}\)-radiation according to methodology presented in [4]. Diffractograms were interpreted with LookPDF software and International Centre for Diffraction Data (ICDD) database.

X-ray phase analysis is based on study of position, intensity, and form of diffraction peaks, which requires a special treatment of empirical data, spectrum smoothing, and choice of selective peaks. Faint peaks can be treated either as a diffusion background or measurement errors and thereby excluded. Such an approach may lead of a partial information loss and result in interpretation ambiguity. If the X-ray signal is treated as a random signal — dependence of the reflected signal intensity from the diffraction angle — then it can be analyzed with contemporary mathematical methods, namely, wavelet analysis [5, 11]. Implementation of wavelet transform for diffractogram decoding solves problems of selection of faint and overlapping peaks search of faint peaks, and estimation of true peak parameters [12].

Recently the number of papers devoted to fractal analysis increased as it is viewed as a tool for study of various structures and processes taking place during structure formation. It allows one not only to study surface morphology of a sample, but also morphology changing processes induced by an
external treatment. Fractal analysis of dispersion samples morphology was performed in accordance with technology presented in paper [13] in great details.

Another perspective approach is RGB-analysis, which allows one to detect color difference in the bulk of a sample, to estimate their anisotropy and non-uniformity of structural characteristics [14]. There are a few color models used in contemporary colorimetry for various purposes [15]. For the analysis of structure, the RGB color space system was selected. Images in this system are described by three components — red R, green G, and blue B. The combination of these colors forms coloration of the substance. The RGB-system allows one to precisely identify the color based on the values of the color coordinates and determine the contribution of each component of the colorimetric system within the composition of the considered color. The sum of the three main components at maximum saturation gives white light and is taken as unity. The colorimetric gradation method was applied to the analysis of ceramic made up of Orenburg montmorillonite [14]. A digital microscope with a high definition camera was used for imaging where a 1 mm image is equivalent to 60 pixels. A color profile was constructed in advance for this device by ICM (ICC). The profile was obtained by the following scheme: a standard image containing colored parallelograms with color coordinates determined in advance was digitized, and in the obtained file the ratio of data points obtained by the device was determined and correlated to known color coordinate values.

3. Results and discussion
Structure changes in iron oxides induced by microwave treatment manifest themselves through polymorphic changes. Microwave field energy consumption results in particles heating and induce phase transition of hematite either to magnetite or to maghemite (figure 1).

![Figure 1. Diffractograms of iron oxide in the initial state (a) and after the microwave treatment (b).](image)

Maghemite $\gamma$-Fe$_2$O$_3$ is isostructural to magnetite and forms a continuous series of solid solutions with it. This feature makes it difficult to differentiate between them via standard X-ray analysis; to avoid this complication wavelet analysis method was used to identify samples phase composition.
Namely, wavelet analysis was used to resolve diffraction peaks and to define their positions in the primary diffractogram with the use of Spectra Analyzer software.

Graphic interpretation of wavelet-transformations were based on local extremum lines – skeletons, which shown the internal structure of the studied sample and its features. Gravity centers of the true peaks match with the skeleton lines (figure 2) [4].

Crystal particles of S0 samples are constituted by $\alpha$-Fe$_2$O$_3$ hematite particles with rhombohedral lattice (space group $R\overline{3}c$) [16]. Skeletons obtained via wavelet-transformation of the S0 sample diffractogram correspond to $\alpha$-Fe$_2$O$_3$ rhombohedral diffractogram which contains diffraction peaks corresponding to interplanar distance $d$ presented in Table 1. After microwave treatment S1 sample developed new peaks corresponding to cubic system $\gamma$-Fe$_2$O$_3$ maghemite. The other peaks correspond to interplanar values of rhombohedral cell of $\alpha$-Fe$_2$O$_3$ hematite.

Microwave treatment results in decrease of the number of hematite crystal phases but the total number of crystal component remains almost the same due to creation of a new modification — $\gamma$-Fe$_2$O$_3$ maghemite. Therefore a new two-phase hematite maghemite state is formed (Table 1).

**Table 1.** Phase compositions of iron oxide before and after microwave treatment

|       | S0          |       | S1          |       |
|-------|-------------|-------|-------------|-------|
| $D$, nm | $HKL$      | phase | $d$, nm     | $HKL$  | phase |
| 0,269  | 104        | hematite | 0,269      | 104    | hematite |
|        |            |        | 0,253      | 311    | maghemite |
| 0,252  | 110        | hematite | 0,252      | 110    | hematite |
| 0,221  | 113        | hematite | 0,221      | 113    | hematite |
|        |            |        | 0,208      | 400    | maghemite |
| 0,185  | 024        | hematite | 0,184      | 024    | hematite |
| 0,170  | 116        | hematite | 0,170      | 116    | hematite |
|        |            |        | 0,152      | 440    | maghemite |
| 0,149  | 214        | hematite | 0,145      | 300    | hematite |
| 0,146  | 300        | hematite | 0,145      | 300    | hematite |
The size of particle almost unaffected by microwave treatment: more than 90% of particles have linear size from 1 to 30 µm, less than 10% are large particles with linear size from 90 to 120 µm. In both samples batches particles have globular shape, however, after the treatment large particles are covered with smaller ones. These changes are independently supported with fractal analysis data: fractal dimension of the samples increased from 2.83 to 2.85, i.e. particles surface appeared to become more sophisticated.

Colorimetric characteristics of samples depend mainly on the color and coloring ability of iron compounds and their relative amounts. The R component was considered the main color parameter, changes in the value of which are related to structural transformations in iron oxide. Transition of α-Fe₂O₃ to γ-Fe₂O₃ is accompanied with the change of powder color from red-orange to dark brown. Color values of Red, Green, and Blue are significantly reduced after microwave treatment, but the red component is reduced the most — by the factor of 2 (Table 2).

| Colour parameter, % | S0 | S1 |
|---------------------|----|----|
| Red                 | 39.3 | 17.9 |
| Green               | 18.5 | 10.5 |
| Blue                | 19.8 | 11.9 |
| Reflection coefficient | 25.8 | 13.9 |

The redistribution of ions in the maghemite lattice under microwave action, associated with the ordering of vacancies and Fe³⁺ ions, leads to the appearance of magnetic properties. Thus, a second-order magnetic phase transition between magnetically ordered states is observed. Magnetic transitions of the order-order type (antiferromagnetism–ferrimagnetism) in finely dispersed systems can occur under microwave irradiation spontaneously at temperatures below the critical ones characteristic of massive samples.

4. Conclusions
Microwave treatment of fine-dispersion samples a part of α-Fe₂O₃ hematite particle experience polymorph transformation to γ-Fe₂O₃ maghemite. Wavelet analysis with skeletons of wavelet transformation technique allowed us to perform reliable analysis of diffraction peaks positions in the original diffractograms and to establish phase composition before and after microwave treatment.

It is advisable to develop α-Fe₂O₃ particles microwave treatment technique that would be capable to produce maghemite particles. This technique would not require usage of any chemical reagents and further additional purification of the sample.

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