

Modification of the Magnetic Properties of α -Fe₂O₃ Powders by Ultrasonic Processing

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Abstract—Hematite (α -Fe₂O₃) powders after ultrasonic treatment (UST) in the regime of cavitation in aqueous suspension and in that with an organic component (albumin protein) have been studied by Mössbauer spectroscopy and ferromagnetic resonance techniques. It is established that the UST in aqueous hematite suspensions with albumin results in the formation of a new magnetic phase with parameters coinciding with those of the α -Fe metallic phase.

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The acoustic and thermal effects of cavitation favor thermolysis of water molecules with the formation of free hydrogen bonds, dispersion, and homogenization of aqueous media with the formation of stable emulsions and synthesis of new compounds [1]. These phenomena provide a promising basis for new technological processes in various fields [2, 3]. The formation of nanoparticles of noble metals (Au, Ag, Pt, Pd) in solutions of their salts as a result of ultrasonic treatment (UST) in the regime of cavitation does not require reducing agents and proceeds at extremely high rates [4]. Reduction of 3d transition metals was reported in [5], where UST in the regime of cavitation led to the formation of monovalent copper oxide in a nanosuspension of divalent copper oxide dissolved in glycerol. Previously [6], we have observed the reduction of metastable ferryhydrite nanoparticles to the metallic state in aqueous suspensions containing albumin subjected to UST in the regime of cavitation. Ferryhydrite (5Fe₂O₃ · 9H₂O) is an iron oxyhydroxide that is characterized by the thermodynamic stability among iron oxides and hydroxides [7] and can only occur in a nanocrystalline state.

The present work was aimed at studying the magnetic properties of hematite powders upon UST of their suspensions in water and in aqueous solution of albumin. Hematite was selected due to its thermodynamic stability and well-known values of magnetic characteristics.

Hematite powders (with average particle size $d = 40$ nm) were subjected to UST in the regime of cavitation in pure water and in aqueous solution (2%) of

bovine serum albumin. The UST was carried out in a Volna UZTA-0.4/22-OM setup (Center of Ultrasonic Technologies Co., Biysk, Russia) at an ultrasound frequency of 22 kHz, an intensity above 10 W/cm², and a treatment duration of 12 min (3 × 4 min).

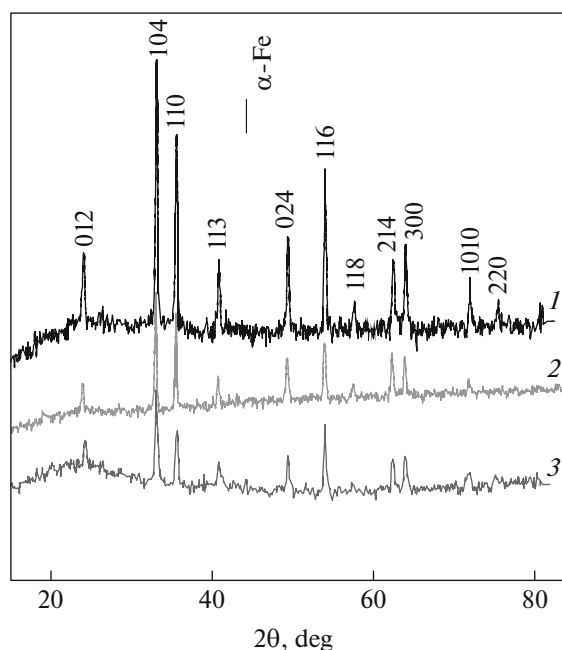


Fig. 1. XRD patterns of hematite powders (1) in the initial state, (2) upon UST in water, and (3) upon UST in aqueous solution of albumin.

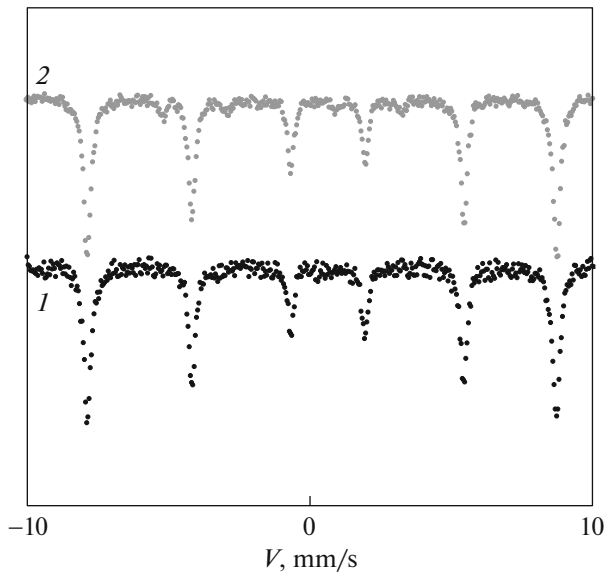


Fig. 2. Mössbauer spectra of hematite powders upon UST (1) in water and (2) in 2% aqueous solution of albumin.

The X-ray-diffraction (XRD) patterns of powders upon drying were measured on a DRON-type diffractometer at a radiation wavelength of $\lambda = 1.54 \text{ \AA}$. The Mössbauer spectra were measured at room temperature on an MS-1104Em spectrometer with a $^{57}\text{Co}(\text{Cr})$ source using powder samples of 5- to 10-mg/cm² mass thickness with natural-iron content. An isomeric chemical shift is indicated relative to $\alpha\text{-Fe}$. The ferromagnetic-resonance (FMR) curves were measured at room temperature on an X-band EPA-2M spectrometer operating at microwave frequency $\nu = 9.2 \text{ GHz}$.

Figure 1 shows XRD patterns of the initial hematite powder and dried suspensions upon UST in water and in aqueous albumin solution. All the observed reflections belong to hematite.

Figure 2 presents the Mössbauer spectra of hematite powders studied, which display characteristic line sextets. Parameters of the Mössbauer spectrum of a powder obtained upon UST in water are identical to those of the initial hematite powder and coincide with published data [8]. The Mössbauer spectrum of

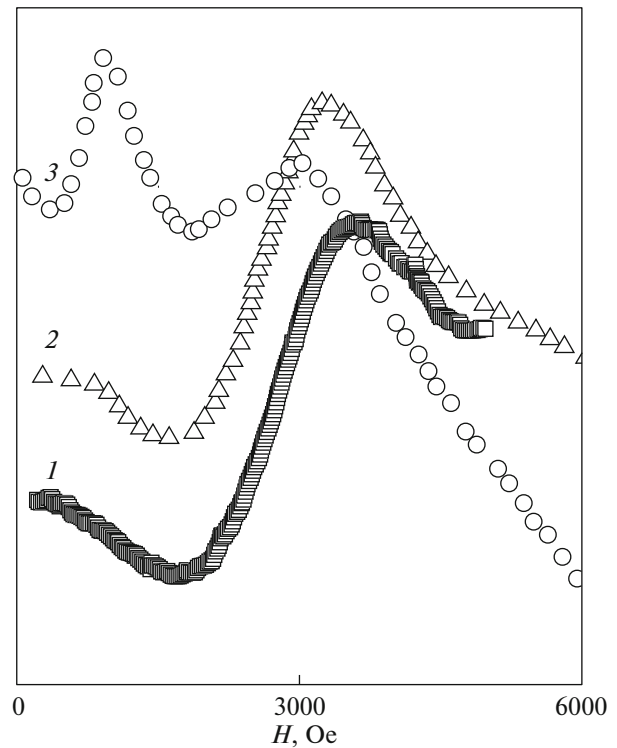


Fig. 3. FMR curves of hematite powders (1) in the initial state, (2) upon UST in water, and (3) upon UST in 2% aqueous solution of albumin.

a powder obtained upon UST in the UST of cavitation in the protein solution exhibited an additional sextet. Interpretation of the spectra (see Table 1) showed that the hyperfine structure parameters of the phase formed due to UST in the albumin solution are characteristic of $\alpha\text{-Fe}$.

Figure 3 presents the differential FMR curves of the initial powder in comparison to those of dried powders upon UST. For the initial powder and a sample prepared upon UST in water, resonance field H_p coincides with internal field $H_0 = 2\pi\nu/\gamma = 3 \text{ Oe}$ (where γ is the gyromagnetic ratio and ν is the microwave frequency), which is indicative of the validity of a relationship between anisotropy field $H_a(\alpha\text{-Fe}_2\text{O}_3)$ of

Table 1. Mössbauer parameters of hematite nanoparticles (IS, isomeric shift relative to bcc $\alpha\text{-Fe}$; QS, quadrupole splitting; W , absorption line width; H , hyperfine splitting field on Fe nucleus; A , fractional occupancy)

| | IS, mm/s (± 0.005) | H , kOe (± 3) | QS, mm/s (± 0.02) | W , mm/s (± 0.02) | A (± 0.03) | Position |
|----------------------------|-----------------------------|--------------------------|----------------------------|------------------------------|-----------------------|--------------------------------|
| UST in water | 0.377 | 516.8 | -0.426 | 0.272 | 1.000 | $\alpha\text{-Fe}_2\text{O}_3$ |
| UST in albumin solution | 0.380 | 517 | -0.41 | 0.27 | 0.929 | $\alpha\text{-Fe}_2\text{O}_3$ |
| | 0 | 333 | 0 | 0.21 | 0.071 | $\alpha\text{-Fe}$ |

powdered hematite and frequency-dependent internal field H_0 : $H_a(\alpha\text{-Fe}_2\text{O}_3) \ll H_0$ [9]. As can be seen from Fig. 3, the FMR curve of a powder obtained upon UST in albumin solution is characterized by additional absorption in small fields at $H_p \approx 1$ kOe. The shift of a resonance field in the magnetic phase formed as a result of UST in the regime of cavitation is related to anisotropy field H_a of this phase.

According to previous results [10–12], the relation between H_p and H_a for powders consisting of spherical particles can be expressed as $H_p = H_0(1 - (H_a/H_0)^{1.25})^{0.44}$. Then, the anisotropy field in the magnetic phase formed as a result of UST is ~ 2.8 kOe, which agrees with the anisotropy field in nanocrystalline $\alpha\text{-Fe}$.

In concluding, the formation of $\alpha\text{-Fe}$ phase in hematite nanopowder upon UST in the regime of cavitation in aqueous suspensions containing 2% protein (albumin) has been detected by magnetic methods. The volume fraction of this metallic phase amounts to 7%.

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REFERENCES

1. M. A. Margulis, *Ultrasonics* **23**, 157 (1985).
2. N. A. Bulychev, M. A. Kazaryan, V. N. Nikiforov, S. N. Shevchenko, V. G. Yakunin, V. Yu. Timoshenko, A. B. Bychenko, and V. G. Sredin, *Tech. Phys. Lett.* **42**, 495 (2016).
3. R. K. Savkina and A. B. Smirnov, *Tech. Phys. Lett.* **41**, 164 (2015).
4. J. H. Bang and K. S. Suslick, *Adv. Mater.* **22**, 1039 (2010).
5. R. N. Galiakhmetov, A. G. Mustafin, and R. R. Garafutdinov, *Pis'ma Mater.* **1** (3), 176 (2011).
6. S. V. Stolyar, O. A. Bayukov, V. P. Ladygina, R. S. Iskhakov, and R. N. Yaroslavtsev, *Bull. Russ. Acad. Sci.: Phys.* **81**, 608 (2017).
7. J. Majzlan, A. Navrotsky, and U. Schwertmann, *Geochim. Cosmochim. Acta* **68**, 1049 (2004).
8. I. S. Lyubutin, C. R. Lin, Yu. V. Korzhetskiy, et al., *J. Appl. Phys.* **106**, 034311 (2009).
9. S. G. Ovchinnikov and V. V. Rudenko, *Phys. Usp.* **57**, 1180 (2014).
10. A. Sukhov, K. D. Usadel, and U. Nowak, *J. Magn. Magn. Mater.* **320**, 31 (2008).
11. C. Antoniak, J. Lindner, and M. Farle, *Europhys. Lett.* **70**, 250 (2005).
12. U. Wiedwald, J. Lindner, M. Spasova, et al., *MRS Proc.* **818**, M1.5.1 (2004).

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