PLASMA SYNTHESIS AND TREATMENT OF NANOSIZED CHALCOPYRITE PARTICLES

E. A. Nevar,[a*] **N. A. Savastenko,**[b] **V. Brüser,**[b]
D. A. Lopatik,[b] **F. May,**[a] **A. V. Butsen,**[a]
N. V. Tarasenko,[a] **and V. S. Burakov**[a]

We synthesized chalcopyrite (CuFeS$_2$) nanoparticles by methods involving laser ablation and electrical discharge in water. The nanoparticles obtained were exposed to an oxygen/argon plasma of a microwave discharge. The synthesized material was studied by photometry, x-ray diffraction (XRD), and energy dispersive x-ray elemental analysis (EDX), IR spectroscopy, and atomic force electron microscopy (AFM). We have established that the nanoparticles are morphologically stable relative to exposure to plasma fluxes of power ≤ 1 kW, and can be used as a model system to study processes of interaction between a plasma and minerals.

Keywords: *nanoparticle, chalcopyrite, laser ablation, electrical discharge in a liquid, plasma treatment of minerals, froth flotation.*

Introduction. Plasma methods are quite effective in many modern technologies, including surface treatment of various minerals. A major problem in this technology is our insufficient basic knowledge about the mechanisms of interaction between the plasma and the surface of the minerals. In particular, detailed study of the interaction between the plasma and chalcopyrite (CuFeS$_2$) and pyrite (FeS$_2$) particles is needed for optimization of the technology for separating them, based on the froth flotation method (different wettabilities of the particles). The conventional approach uses an increase in the difference between the wettabilities, with the help of selective surfactants [1–6]. The surface of some particles in the mixture is hydrophobic (water-repellant). The hydrophobic particles, attaching to air bubbles introduced into the aqueous suspension of the mixture of minerals, are transported upward by the bubbles toward the froth layer on the surface of the suspension, thus separating them from the hydrophilic (wettable) particles. The new approach is based on treatment of the surface of the minerals with a non-thermal plasma under conditions leading to a change in wettability without a change in chemical composition. For optimization of the plasma treatment conditions, we need a detailed clarification of the basic mechanisms for interaction between the plasma fluxes and the indicated minerals. Due to the high surface/volume ratio and the reactivity of nanosized particles, they may be ideal model systems for studying processes leading to a change in surface wettability. In this case, laser ablation processes and electrical discharges in liquid media may be effectively used to obtain model CuFeS$_2$ nanoparticles.

In this work, we have obtained nanosized chalcopyrite particles by laser and electrical-discharge spraying of a sample of the original mineral in water. The phase and elemental composition of the particles obtained were studied using x-ray diffraction (XRD) and energy dispersive x-ray elemental analysis (EDX). In order to determine the changes in the morphology of the particles due to plasma treatment, we used Fourier transform IR spectroscopy and atomic force electron microscopy (AFM).

Experimental Section. Pure crystalline chalcopyrite (Alfa Easer, Germany) was used to obtain the nanoparticles.

Synthesis of nanoparticles with pulsed laser ablation in a liquid. The nanoparticles of CuFeS$_2$ were obtained by laser ablation of a chalcopyrite target placed in a cuvet with distilled water. Emission from an Nd:YAG laser was

---

[*]To whom correspondence should be addressed.

---

[a]B. I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, 68 prosp. Nezavisimosti, Minsk, 220072; e-mail: nevar@imaph.bas-net.by; [b]Leibniz Institute for Plasma Science and Technology, Greifswald, Germany; e-mail: savastenko@inp-greifswald.de. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 77, No. 1, pp. 136–141, January–February, 2010. Original article submitted October 27, 2009.
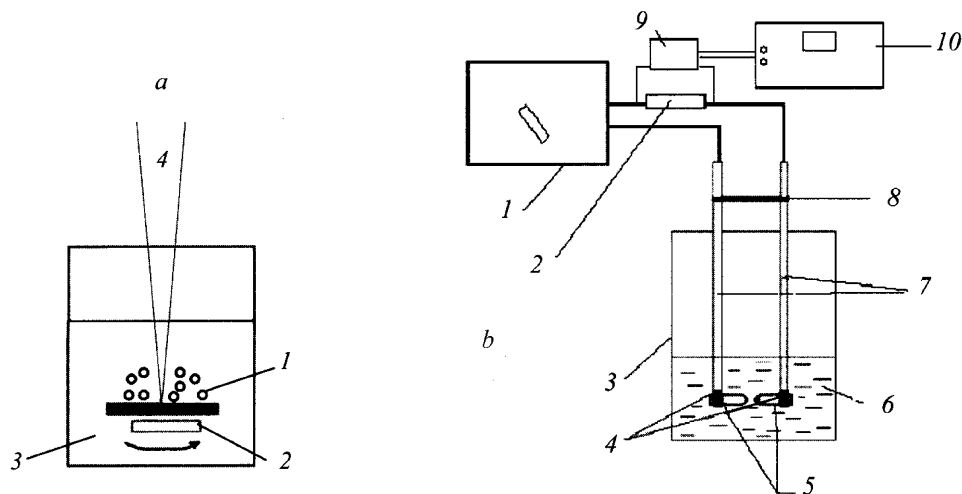
Fig. 1. Schematic drawing of an experimental apparatus for synthesis of nanoparticles by: a) laser ablation [1) nanoparticles, 2) magnetic stirrer, 3) target, 4) laser emission, $\lambda = 1064$ nm]; b) electrical discharge in a liquid [1) power supply, 2) shunt resistor; 3) glass cup; 4) clamp screws; 5) electrodes; 6) liquid; 7) electrode holders; 8) insulator; 9) measurement circuit; 10) oscilloscope).

used ($\lambda = 1064$ nm, pulse energy 60 mJ, pulse repetition frequency 10 Hz, pulse duration 12 nsec). The schematic for the experimental setup is shown in Fig. 1a. With laser ablation of the target, a small plasma plume was formed above the target surface. During particle production, visible coloring of the liquid occurred. The synthesized particles formed a colloidal solution.

Synthesis of nanoparticles with an electrical discharge in water. The $CuFeS_2$ nanoparticles were synthesized in a reactor consisting of a glass discharge chamber filled with water, inside which were placed two chalcopyrite electrodes (Fig. 1b). The experimental setup is described in detail in [7–9]. The main discharge was ignited by a high-frequency discharge with voltage ~3.5 kV. The discharge was powered by an ac source with frequency 100 Hz and pulse duration 50 μsec (spark regime). After initiation of the discharge, in the interelectrode region a gas bubble was formed which first expanded and then collapsed over the course of each discharge cycle, i.e., 100 times per second. The solution took on a dark color even within a few seconds after the beginning of the experiment.

Plasma treatment of the particles. Plasma treatment of the synthesized particles was carried out in a microwave plasma reactor, the schematic of which is shown in Fig. 2. The synthesized particles were deposited on a mica plate and placed on substrate 4. At the beginning of the experiment, the reactor was pumped out to a pressure of 10^{-3} Pa and purged with a mixture of argon and oxygen for 5 min. The gas flow rate was 50 cm^3/min. The power of the plasma generator was 1 kW, the treatment time was 5 min, the pressure inside the reactor was 20 Pa, the gas flow rate Ar:O$_2$ = 25:25 cm^3/min.

Methods for studying the nanoparticles. Atomic force microscopy (AFM) was used to study the topography of the surface for the untreated and plasma-treated nanoparticles. For this purpose, we used a CP-II VEECO apparatus with pyramidal silicon tip having a radius of curvature of 10 nm and doped with *n*-type phosphorus (RTESPA-CP). The images obtained were processed using software supplied with the instrument. The AFM measurements were made under ambient atmospheric conditions at normal temperature and pressure. For the measurements, a drop of the colloidal solution was deposited on the mica plate. The samples were scanned in contactless mode.

The extinction spectra of the colloidal solutions were recorded on a CARY 500 spectrophotometer. The phase composition, crystal structure, and lattice parameters of the powder obtained after vaporization of the colloidal solution were analyzed on a D8-Advance diffractometer (Bruker, Germany), based on the angular dependences of the intensities of the diffraction peaks for scattered radiation on the CuKα line ($\lambda = 0.15418$ nm). The elemental composition of
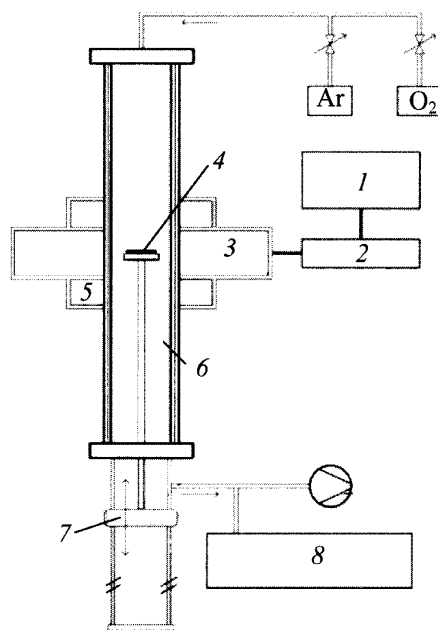
127

Fig. 2. Schematic drawing of the microwave plasma reactor: 1) generator, 2) E-H tuner; 3) cylindrical resonant cavity with annular slits; 4) sample; 5) water cooling loop; 6) quartz glass tube; 7) vertical movable holder; 8) rotary pump.

the powders deposited on a substrate were determined using an x-ray spectrometer included in the SUPRA 55WDS scanning electron microscope (Carl Zeiss, Germany). The Fourier IR spectra of the original chalcopyrite and the synthesized powders were recorded on a Spectrum One FTIR spectrometer (Perkin Elmer).

Results and Discussion. *Absorption spectroscopy.* The optical absorption spectra for freshly prepared colloidal solutions of chalcopyrite are shown in Fig. 3. They have the shape of smoothly decreasing curves with a tendency toward a gradual decrease in total absorption as the wavelength increases.

Determination of the particle parameters. Table 1 gives the elemental composition of the nanosized particles (as determined by EDX) synthesized by pulsed laser ablation in a liquid. We observe that the relative content of the atomic components Fe:Cu:S in the particles obtained, determined from the EDX spectrum, is close to the stoichiometric ratio for the $CuFeS_2$ phase. Despite the fact that the EDX analysis did allow for the presence of oxides, the XRD did not show the presence of oxide phases in the sample. From this we may hypothesize that the samples contained impurity inclusions absorbing the oxygen. They might be carbon atoms, which are invariably present on the surface of the sample.

As follows from the x-ray diffraction patterns (Fig. 4), both of the synthesized powders consist of tetragonal chalcopyrite $CuFeS_2$ (diffraction peaks with $2\theta \approx$ 29.5, 48.7, 49.1, 57.9, and 58.7^o) and CuS (peaks at about 32, 33, and 59.2^o). Note that near the diffraction peaks belonging to CuFeS2, we also detect several small peaks (29.3, 48.6, and 52.7^o) assigned to talnachite $Cu_{18.32}Fe_{15.9}S_{32}$. Thus the formation of metastable copper- and iron-containing compounds is not ruled out. However, no oxide phases were detected either in samples obtained by laser ablation or in samples synthesized in an electrical discharge.

The results of studies of the synthesized particles by Fourier transform IR spectroscopy are shown in Fig. 5. The bands in the interval 1094–1200 cm^{-1} can be assigned to the characteristic bands of chalcopyrite [10, 11]. For the synthesized powders, the positions of the peaks are somewhat different from the positions of the peaks for the bulk material. This may be a consequence of the formation of metastable phases. The characteristic peak at 1021 cm^{-1} appeared at a wavelength of 1065 cm^{-1} for powders synthesized by both laser ablation and electrical discharge. This may indicate the presence of $FeSO_4$ in the studied samples [12]. Since XRD did not reveal the presence of $FeSO_4$,
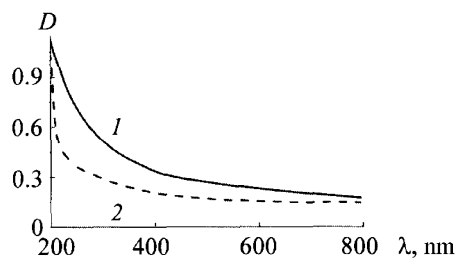
128

Fig. 3. Absorption spectra of colloidal solutions prepared by laser ablation (1) and electrical discharge (2) in distilled water.
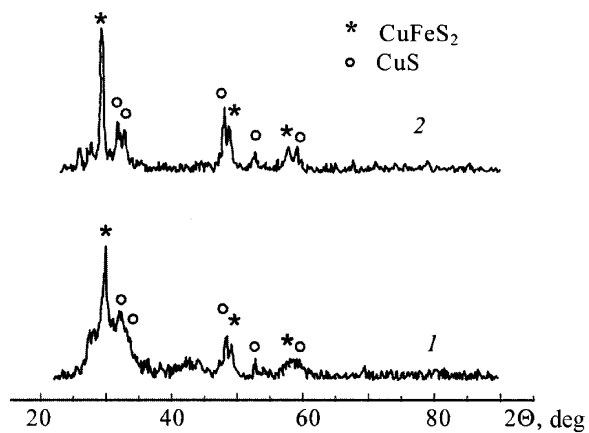

Fig. 4. X-ray diffraction patterns of samples prepared by laser ablation (1) and electrical discharge (2) in water.
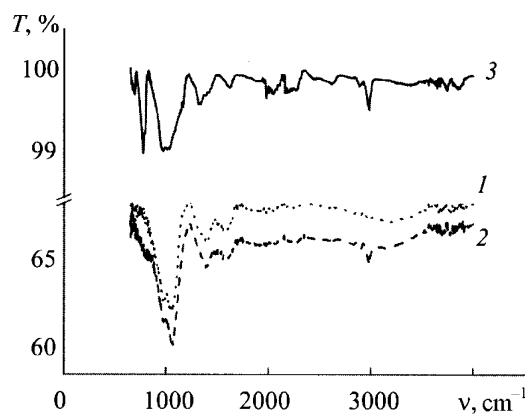

Fig. 5. Fourier transform IR spectra of samples obtained by laser ablation (1) and electrical discharge (2); 3) spectrum of bulk chalcopyrite.
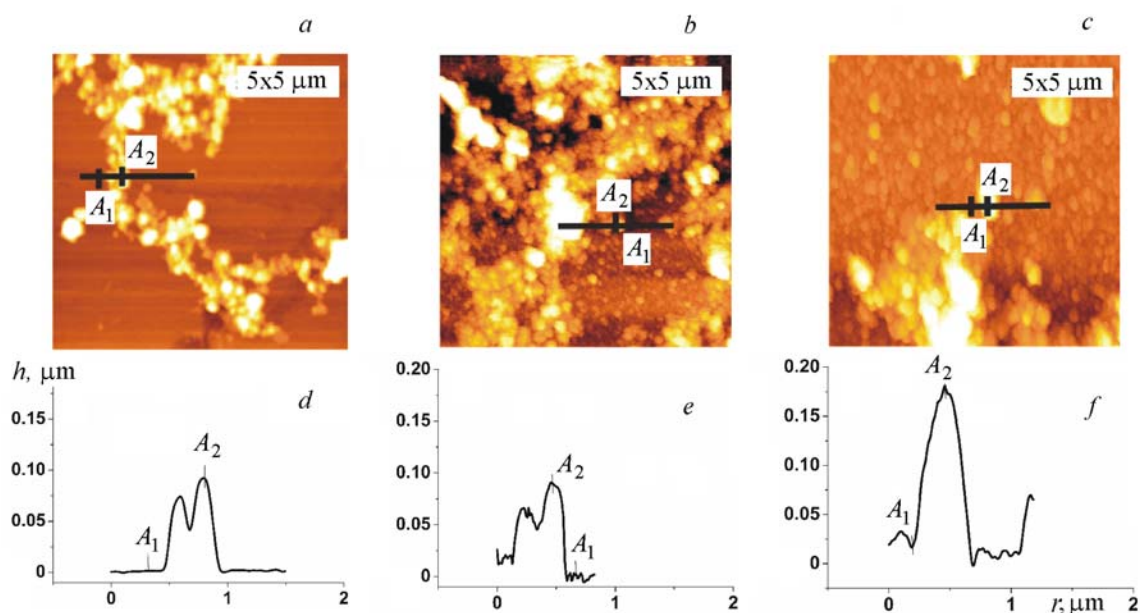
Fig. 6. AFM image (a–c) and selected scanning profiles (d–f) of the original
(a, b) and plasma-treated (c) nanoparticles, synthesized by laser ablation (a, d)
and electrical discharge (b, c, e, f).

TABLE 1. Elemental Analysis Results for Chalcopyrite Nanoparticles Obtained by Laser Ablation

Element	Content	
	wt.%	at.%
O	0.64	33.34
S	0.60	21.97
Cu	1.09	16.17
C	0.81	13.34
Fe	1.99	13.09
Si	0.21	2.08
Total		100.00

we may hypothesize that if iron sulfate is present in the sample, it is present only in an insignificant amount. The characteristic peak for $CuSO_4$ at 1144 cm^{-1} was not observed [13]. It is not possible to confirm formation of CuS using IR spectroscopy, since this compound is not IR-active [13, 14].

Atomic force micrographs of the chalcopyrite nanoparticles deposited on mica substrates are shown in Fig. 6. We see that for both laser ablation and in an electrical discharge, agglomerates of nanoparticles are formed, although for the sample obtained with an electrical discharge, we also observed unagglomerated particles. The original particles had practically identical dimensions: from 50 nm to 100 nm (in depth). As we observed, treatment of the synthesized nanoparticles in a microwave discharge plasma does not lead to an appreciable change in their morphology (Fig. 6c), which indicates stability of the chalcopyrite particles relative to exposure to plasma fluxes of power up to 1 kW.

Conclusion. Our experiments showed that pulsed laser ablation and electrical discharge in a liquid are methods resulting in formation of nanoparticles of chalcopyrite $CuFeS_2$. We have established that the chalcopyrite nanoparticles are morphologically stable relative to exposure to plasma fluxes of power up to 1 kW, and can be used as convenient model systems for detailed studies of the interaction between a plasma and the surface of nanosized parti-

cles. Information obtained in the experiments will make it possible to optimize the technology for separation of the minerals chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) based on the froth flotation method.

REFERENCES

1. D. A. Beattie, L. Huynh, A. Mierczynska-Vasilev, M. Myllynen, and J. Flatt, *Can. Metall. Quart.*, **46**, 349–358 (2007).
2. R. Crawford and J. Ralston, *Int. J. Miner. Process.*, **23**, 1–24 (1988).
3. W. Forsling and Z. X. Sun, *Int. J. Miner. Process*, **51**, 81–95 (1997).
4. M. Miettinen, P. Sten, S. Backman, J. Leppinen, and J. Aaltonen, *Miner. Eng.*, **13**, 245–254 (2000).
5. W. Tolley, D. Kotlyar, and R. Van Wagoner, *Miner. Eng.*, **9**, 603–637 (1996).
6. J. von Steiger and O. Bayramgil, *Helv. Chim. Acta*, **26**, 112–116 (1943).
7. V. S. Burakov, A. V. Butsen, V. Bruser, F. Harnisch, P. Y. Misakov, E. A. Nevar, M. Rosenbaum, N. A. Savastenko, and N. V. Tarasenko, *J. Nanopart. Res.*, **10**, 881–886 (2008).
8. V. S. Burakov, N. A. Savastenko, N. V. Tarasenko, and E. A. Nevar, *Zh. Prikl. Spektrosk.*, **75**, No. 3, 372–378 (2008).
9. V. S. Burakov, N. A. Savastenko, N. V. Tarasenko, and E. A. Nevar, *Zh. Prikl. Spektrosk.*, **75**, No. 1, 111–120 (2008).
10. R. K. Rath, S. Subramanian, V. Sivanandam, and T. Pradeep, *Can. Metall. Quart.*, **40**, 1–11 (2001).
11. K. Sasaki, Y. Nakamuta, T. Hirajima, and O. H. Tuovinen, *Hydrometallurgy*, **95**, 153–158 (2009).
12. J. G. Dunn, W. Gong, and D. Shi, *Thermochim. Acta*, **215**, 247–254 (1993).
13. J. G. Dunn and C. Muzenda, *Thermochim. Acta*, **369**, 117–123 (2001).
14. H. T. Boey, W. L. Tan, N. H. H. Abu Bakar, M. Abu Bakar, and J. Ismail, *J. Phys. Sci.*, **18**, 87–101 (2007).