OPTICAL EMISSION SPECTROSCOPY OF PLASMA OF UNDERWATER ELECTRIC SPARK DISCHARGES BETWEEN METAL GRANULES

T.A. Tmenova¹, A.N. Veklich¹, V.F. Boretskij¹, Y. Cressault², F. Valensi², K.G. Lopatko³, Y.G. Aftandilyants³

¹Taras Shevchenko National University of Kyiv, Kiev, Ukraine;

²Université de Toulouse; UPS, INPT; LAPLACE (Laboratoire Plasma et Conversion d'Energie); 118 route de Narbonne, F-31062 Toulouse Cedex 9, France;

³National University of Life and Environmental Sciences of Ukraine, Kiev, Ukraine

E-mail: tania.tmenova@gmail.com

This paper presents series of experiments carried out with granules of Cu, Fe, Mn and Mo. Optical emission spectroscopy techniques were applied for research of the emission spectra of corresponding elements and improvement of the diagnostics of such plasma. Excitation temperature of plasma of underwater spark discharges between copper granules was determined using Boltzmann plot technique. The electron density of the plasma was estimated from broadening of hydrogen H_{α} line.

PACS: 52.70.Kz, 52.80.-s, 52.80.Wq

INTRODUCTION

Since a few decades, many efforts have been applied to the development of strategies of synthesis nanoparticles of different sizes and morphologies. A large number of scientific contributions are dedicated to the characterization and application of metal nanoparticles. It should be noted, that only few studies have dealt with mechanisms of particle' formation. Therefore, theoretical concepts that describe processes of particle growth are occasional. A few existing models are hardly able to explain the influence of synthesis parameters on the final particles size distribution and their properties. Thus, studies directed to better understanding of these limitations [1] are of high scientific interest.

Nanoparticles are being used for different purposes such as for medical treatments [2, 3] and various branches of industry production, for example, solar and oxide fuel batteries for energy storage [4, 5]. Such particles are also widely used for incorporation into various materials of everyday use such as cosmetics or clothes [6], optical devices [7], catalytic [8, 9], bactericidal and fungicidal [9, 10], electronic [11], sensor technologies [9], biological labelling [9], etc.

In particular, exceptional properties of metal nanoparticles such as antibacterial activity, high resistance to oxidation and high thermal conductivity have attracted attention to their research. Moreover, metal nanoparticles could be used as nutrients within the composition of mineral fertilizers. They accelerate plants' development, enhance their growth and yield increase [12]. Fundamental difference between the colloid and conventional forms of mineral nutrients is that the first are non-toxic, bioavailable and by virtue of the crystalline structure of the dispersed phase are the most suitable for their use in biological objects. Such metal colloids exhibit high efficacy and have already found their application in the cultivation of vegetable

production under conditions of low or disturbed mineral nutrition [13-15].

However, aggregation is the problem associated with nanoparticles in colloidal form. In most of the cases, aggregation leads to loss of properties related to the colloidal transition metal nanoparticles. The stabilization of metallic nanoparticles in colloidal solution and means to preserve their catalytic activity are two important aspects to be considered while synthesizing these colloids [8].

Particular interest is applied to find biologically acceptable carrier form of metal nanoparticles. A critical analysis of the existing methods shows that the electric spark dispersion is one of the most promising methods for obtaining nanoparticles that most closely correspond this target goal [16, 17]. Nanoparticles are synthesized in the form of colloidal solutions by this method. Such form is the most appropriate for biotechnology usage. Nowadays, electric spark technologies of obtaining of nanostructured metals and alloys are very effective. Cheapness of such technologies has made them attractive for solution of different scientific and applied problems. Therefore, the aim of this paper is further development of the given synthesis technique and to study the peculiarities of the underwater spark discharge between metal granules.

1. EXPERIMENT

Colloid solutions of metal particles are obtained by realization of volumetric electric spark destruction of metal granules. This method lies in simultaneous formation of spark channels in contacts between the metal granules immersed in a liquid. A pulsed supply of electric energy was put on from the specially developed generator. The technological unit for performance of experiments consists of a pulse generator 1, control unit 2, oscilloscope 3, Rogowsky coil 4, voltage divider 5; and discharge chamber 6 (Fig. 1). As a result of spark

erosion the part of metal of granules evaporates and, being tempered into a liquid, forms fine dispersion fraction of spark-erosive particles. The experimental values of voltage were up to 300 V, current – up to 600 A and the capacity of the discharge circuit – $1300 \, \mu F$ comparing to [10].

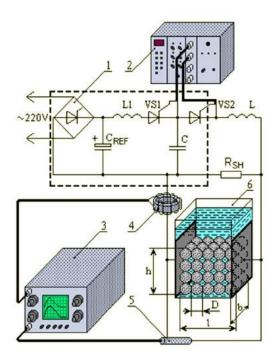


Fig. 1. Experimental setup

2. OPTICAL EMISSION SPECTROSCOPY

Optical emission spectroscopy (OES) methods were used for diagnostics of underwater electric spark discharge plasma between metal granules. Plasma emission was registered by the SDH-IV spectrometer with a 4-position manually switchable diffraction gratings turret. The measurements were performed in all four channels of spectrometer, so the total registered spectral range was 200...1200 nm. Toshiba TCD 1304 AP linear image sensor was used as CCD detector. Spectral sensitivity in every spectral range of the SDH-IV spectrometer was determined. Such measurements were taken into account in all obtained results.

Experiments with granules of Cu, Fe, Mn and Mo were performed. Emission spectra of corresponding elements were obtained in electric spark discharge between granules in water using OES techniques. In this work, authors present an estimation of plasma parameters for case of the copper granules only. This is due to the fact that Cu has been thoroughly studied and Cu I spectral lines and their spectroscopic data that can be recommended for diagnostics of plasma with addition of copper have been previously selected [18].

The emission spectrum of the discharge between copper granules registered with the third channel of spectrometer (440...900 nm) is shown in Fig. 2. One can see that the spectrum contains not only Cu I spectral lines, but also oxygen triplet (λ =777 nm), and hydrogen

Balmer H_{α} and H_{β} lines, which is typical for emission spectrum of electric discharge plasma in water [19].

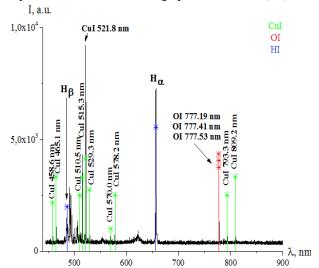


Fig. 2. Emission spectrum of plasma of underwater electric spark discharge between granules of Cu

2.1. EXCITATION TEMPERATURE CALCULATION

The excitation temperature of copper atoms in plasma was determined by Boltzmann plot technique using Cu I spectral lines 456.1, 510.5, 515.3, 521.8, 570.0, 578.2, 793.3 and 809.2 nm under assumption of Boltzmann distribution of population of atom's energy levels. Spectroscopic data for these lines were used from [18].

Fig. 3 shows the Boltzmann plot realized for emission spectrum presented in Fig. 2. The slope of the line in this Boltzmann plot gives the value of an excitation temperature $12,000 \pm 1,700 \text{ K}$.

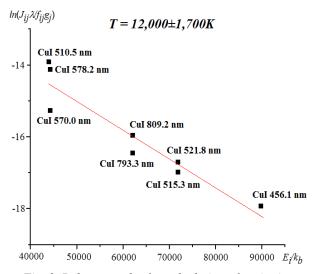


Fig. 3. Boltzmann plot for calculation of excitation temperature of plasma of underwater spark discharge between Cu granules

In the same way, the excitation temperatures for two other registered samples with maximal and minimal intensity of copper emission were determined giving the values of 11.500±2.400 K and 11.200±1.600 K.

2.2. MEASUREMENTS OF ELECTRON DENSITY

Profile of a Balmer H_α line was used for estimation of value of electron density of plasma following the same procedure as presented in [20]. After the application of Voight fitting algorithm to the line profile (Fig. 4), the Stark width $\Delta\lambda_S$ was obtained from the experimental value of FWHM with corrections made for instrumental and Doppler contributions.

Finally, the electron density n_e was calculated by means of $\Delta\lambda_S$ from:

$$n_e = C(n_e, T_e) \times \Delta \lambda_S^{3/2}. \tag{1}$$

The values of coefficients $C(n_e, T_e)$ for Stark broadened hydrogen lines were calculated by interpolation from tables of half-widths presented by Griem [21].

In such a way, the values of electron density were calculated in correspondence to the previously obtained values of plasma excitation temperatures (Table).

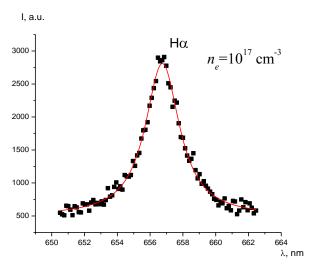


Fig. 4. Voight fit of the Balmer H_a line's profile

Parameters of plasma of underwater electric spark discharge between Cu granules

Intensity of	Electron	Excitation
copper	number	temperature, K
emission	density,	-
	10^{17}cm^{-3}	
Low	1	11.500±2.400
Medium	4.3	12.000±1.700
High	7.7	11.200±1.600

CONCLUSIONS

Studies of plasma of underwater electric spark with granules of Cu, Fe, Mn and Mo were carried out.

Detailed research of such plasma with copper granules was performed. The emission spectra of such plasma were obtained using OES techniques. Estimations of plasma excitation temperature were also

fulfilled. The value of electron density was received from broadening of profile of H_{α} line.

The obtained results (see Table 1) show that values of the excitation temperatures, calculated for three different registered samples of plasma irradiation lie within the range (11.000...12.000) K. The values of electron density $(1...7.7)\times10^{17}$ cm⁻³ show strong correlation with copper irradiation.

In future, authors plan to calculate the composition of plasma of underwater discharge between Cu granules using the values of experimentally obtained temperature and electron density, and intensity relations of Cu I to O I lines and Cu I to H I lines.

REFERENCES

- 1. J. Polte. Fundamental growth principles of colloidal metal nanoparticles a new perspective // *CrystEngComm*. 2015, v. 36, № 17, p. 6809-6830.
- 2. A. Agarwal. Optical Properties and Application of Metallic Nanoparticles and their Assembled Superstructures // A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Engineering). University of Michigan, Ann Arbor, USA. 2010.
- 3. I. Brigger, C. Dubernet, P. Couvreur. Nanoparticles in cancer therapy and diagnosis // Advanced Drug Delivery Reviews. 2012, v. 64, p. 24-36.
- 4. V.K. Sethi, M. Pandey, P. Shukla. Use of Nanotechnology in Solar PV Cell // International Journal of Chemical Engineering and Applications. 2011, v. 2, № 2, p. 77-80.
- 5. Z. Zhang, S. Han, C. Wang, et al. Walled Carbon Nanohorns for Energy Applications // Nanomaterials. 2015, No. 5, p. 1732-1755.
- 6. L. Yildirimer, N. Thanh, M. Loizidou, et al. Toxicological considerations of clinically applicable nanoparticles // Nano Today. 2011, № 6, p. 585-607.
- 7. R.A. Ismail. Preparation of Colloidal Lead Sulfide Nanoparticles by Laser Ablation in Water for Optoelectronic Devices Applications // High Energy Chemistry. 2015, v. 49, № 1, p. 58-63.
- 8. K. Gude. Synthesis Characterization and Applications of Colloidal Supported Metal Nanoparticles // A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry). University of Rhode Island, Kingston, USA. 2013.
- 9. A. Schröfel, G. Kratošová, I. Šafarík, et al. Applications of biosynthesized metallic nanoparticles A review // Acta Biomaterialia. 2014, v. 10, № 10, p. 4023-4042.
- 10. K.G. Lopatko, Y.G. Aftandiliants, A.N. Veklich, et al. Enrichment of colloidal solutions by nanoparticles in underwater spark discharge // Problems of Atomic Science and Technology. 2015, v. 95, № 1, p. 267-270.
- 11. S.A. Makhloufa, Z.H. Bakra, H.Al. Attara, et al. Structural, morphological and electrical properties of Cr₂O₃ nanoparticles // Materials Science and Engineering: B. 2013, v. 178, № 6, p. 337-343.
- 12. K.G. Lopatko, M.D. Melnychuk, Y.G. Aftandiliants. Application of Colloidal Forms of Trace Elements in the

- Disturb Mineral Nutrition of Plants // Earth Bioresources and Quality of Life. 2013, № 4, p. 85-92. 13. N.Y. Taran, O.M. Gonchar, K.G. Lopatko, et al. The effect of colloidal solution of molybdenum nanoparticles on the microbial composition in rhizosphere of Cicer arietinum L. // Nanoscale Res Lett. 2014, v. 9, p. 289.
- 14. Nanobiotechnology can boost crop production and quality: first evidence from increased plant biomass, fruit yield and phytomedicine content in bitter melon (*Momordica charantia*) // *BMC Biotechnology*. 2013, v. 13, p. 37.
- 15. D.W. Ehrhardt, W.B. Frommer. New Technologies for 21st Century Plant Science // *The Plant Cell*. 2012, v. 24, № 2, p. 374-394.
- 16. K.G. Lopatko, M.D. Melnychuk, Y.G. Aftandiliants, et al. Obtaining of metallic nanoparticles by plasmaerosion electrical discharges in liquid mediums for biological application // Agriculture (Agricultural and Forest Engineering). 2013, № 61, p. 105-115.
- 17. Y. Cressault, Ph. Teulet, A. Gleizes, et al. Peculiarities of metal nanoparticles generation by underwater discharges for biological applications //

- XXXI International Conference on Phenomena in Ionized Gases. Granada, Spain, 2013, E-book of abstracts. (http://icpig2013.net/papers/550_1.pdf).
- 18. I.L. Babich, V.F. Boretskij, A.N. Veklich, R.V. Semenyshyn. Spectroscopic data and Stark broadening of Cu I and Ag I spectral lines: Selection and analysis // Advances in Space Research. 2014, v. 54, p. 1254-1263.
- 19. H.L. Li, J. Kang, K. Urashima, et al. Comparison between the Mechanism of Liquid Plasma Discharge Process in Water and Organic Solution // J. Inst. Electrostat. Jpn. 2013, v. 37, № 1, p. 22-27.
- 20. D.A. Batistoni, R.N. Garavaglia, R.E. Rodríguez. Evaluation of hydrogen line emission and argon plasma electron concentrations resulting from the gaseous sample injection involved in hydride generation-ICP-atomic emission spectrometric analysis // Fresenius' Journal of Analytical Chemistry. 2000, v. 366, №3, p. 221-227.
- 21. H.R. Griem. *Plasma Spectroscopy*. Moscow: "Atomizdat", 1969 (in Russian).

Article received 30.12.2016

ОПТИЧЕСКАЯ ЭМИСИОННАЯ СПЕКТРОСКОПИЯ ПЛАЗМЫ ПОДВОДНЫХ ЭЛЕКТРОИСКРОВЫХ РАЗРЯДОВ МЕЖДУ ГРАНУЛАМИ МЕТАЛЛОВ

Т.А. Тменова, А.Н. Веклич, В.Ф. Борецкий, Я. Крессо, Ф. Валенси, К.Г. Лопатько, Е.Г. Афтандилянц

Представлены серии экспериментов, проведенных с использованием гранул Cu, Fe, Mn и Mo. Спектры излучения соответствующих элементов были получены методами оптической эмиссионной спектроскопии. С их же помощью проводилась диагностика такой плазмы. Используя метод диаграмм Больцмана была получена температура возбуждения электронных уровней плазмы подводного электроискрового разряда между гранулами меди. Уширение линии водорода H_{α} было использовано для оценки величины электронной концентрации плазмы.

ОПТИЧНА ЕМІСІЙНА СПЕКТРОСКОПІЯ ПЛАЗМИ ПІДВОДНИХ ЕЛЕКТРОІСКРОВИХ РОЗРЯДІВ МІЖ ГРАНУЛАМИ МЕТАЛІВ

Т.А. Тменова, А.М. Веклич, В.Ф. Борецький, Я. Крессо, Ф. Валенсі, К.Г. Лопатько, Є.Г. Афтанділянц

Представлені серії експериментів, проведених з використанням гранул Сu, Fe, Mn і Mo. Спектри випромінювання відповідних елементів були отримані методами оптичної емісійної спектроскопії. Із залученням цих же спектрів виконувалась діагностика такої плазми. Температура збудження електронних рівнів плазми підводного електроіскрового розряду між гранулами міді порахована методом діаграм Больцмана. Уширення лінії водню H_{α} було використане для оцінки величини електронної концентрації плазми.