

SYNTHESIS OF MAGNETIC CLUSTER NANOPARTICLES

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INTRODUCTION: The existing chemical and physical methods [1-4] of producing nanoparticles do not allow synthesizing nanoparticles in the size range of about 1 nm with high degree of certainty. The nanoparticles must possess pre-designed physical and chemical properties, such as: size, composition, charge, magnetic momentum, etc, which are necessary in a number of technological applications.

The presented article describes synthesis of nanoparticles in the air performed due to the heterogeneous condensation of iron atoms on ions. The size range is about 1nm.

METHODS: The general concept of the proposed method for the controlled synthesis of cluster nanoparticles (CNP) having pre-designed physical and chemical properties is as follows:

realization of the exclusively heterogeneous condensation, which occurs on ions; creation of the premeditated required correlations of the condensed molecules' concentrations (N_m) to the amount of condensation nuclei – ions, (N_i) : N_m / N_i . The control of transferring atoms and ions, participating in the CNP synthesis is carried out by the external electromagnetic fields.

To accomplish this objective, a well-known phenomenon – facilitation and stabilization of heterogeneous condensation of substance molecules on ions was employed [5,6]. Investigators mentioned that stabilization and termination of the particles' growth (their size is about 1 nm) were observed in the course of condensation [7].

The effect of the charge of a condensation nucleus on the process of trapping the surrounding molecules (i.e., condensation) can be explained in terms of polarization of the neighboring substance molecules by the Coulomb field of the condensation nucleus (ion). The induced dipoles of these molecules are attracted by the heterogeneous electric field of the condensation nucleus. It continues till $W \gg kT$. Here W stands for the energy of attraction of

the polarized molecules by the Coulomb field of the condensation nucleus and kT defines the thermal energy of molecules. It should also be noted that the Coulomb field of an ion effects the chemical and physical properties of the nanoparticle being synthesized. Hence, when moving in the heterogeneous electric field of an ion, an electric axis of the polarized molecule (dipole) will orient by the normal onto the ion's surface. It implies a certain geometric configuration of the synthesized nanoparticle during the condensation process. The simultaneous superimposing of the external magnetic fields onto the condensation process, results in the configuration of the magnetic moments of the condensed molecules. The combination of the above-mentioned processes advances the controlling physical and chemical properties of the nanoparticles being synthesized.

To verify the above stated ideas, an experimental investigation aimed at synthesizing CNP with the pre-designed physical and chemical properties, i.e. size, charge, magnetic momentum, etc, was carried out. This process was performed in the air according to the following technological sequence on a setup consisting of: – ion generators; – Ohmic furnaces; – measuring dish; – differential mobility analyzer (DMA); – electrostatic precipitator (ESP); – rotation meters; – electrometers; – power supply units with high and low voltage; – gas aspiration units.

The air supplied by the compressor (through the system of highly and roughly purifying filters and through a receiver) passes into the ion generator. The generators operate using the corona discharge and may generate a definite concentration of ions ($N \sim 10^6 - 10^7 \text{ cm}^{-3}$) with a pre-designed polarity. Having passed through the ion generators, the air goes to the furnaces having spirals made of iron wire with the diameter 0.1 cm and could achieve temperatures up to $T \sim 1200^\circ \text{ C}$. Afterwards the air is advanced into a metal dish ($2r = 6 \text{ cm}$ and $h = 50 \text{ cm}$). To control the parameters of the generated media, DMA or ESP were introduced into this dish.

Upon high temperatures of the spirals, there occurs the active realization of the phase transfer “solid body – vapor” of iron atoms, which later condense onto the artificially generated condensation nuclei – ions (created by the ion generators) and further form nanoparticles. The condensation occurs in the external fields: the Coulomb field of an ion; the magnetic field, created by the current from the spirals and achieving the values of $H \approx 4 \cdot 10^4 A/m$. We also controlled the transfer of the electricity carriers, which participated in the nanoparticles’ synthesis. It was realized with the help of the external electrical field, which was generated between the spiral and the walls of the furnace. The parameters (concentration, charge, mobility, sizes of the generated ions and of the synthesized nanoparticles) were registered by a differential mobility analyzer. The size of the synthesized nanoparticles was analyzed at an AFM. The trapping of the synthesized nanoparticles was carried out in the electrostatic precipitator [8]. To detect the magnetic properties of the synthesized CNP we carried out photo registering of their velocity in water under the effect of the external heterogeneous magnetic field and by employing the phenomenon of opalescence [9].

RESULTS: Measuring of the particles’ spectra (the dependency of the sizes of particles on their concentration) was carried out on the DMA At first, a single-mode spectrum with particles’ sizes characteristic of insignificantly clusterized O_2^- ions in the air has been obtained. During this process only the generator of ions was functioning. A two-mode spectrum for the negatively charged particles and the three-mode spectrum for the positively charged particles have been obtained in the course of the subsequent measurement of the spectra when both generators and the furnaces were working and iron atoms were being generated. It caused the increase of the particles’ sizes, which confirms their condensation growth, i.e., the clusterization of condensation nuclei – ions. The first mode showed the presence of mildly clusterized particles with the sizes ~ 0.5 nm. The particles’ sizes for the second mode were ~ 1 nm and for the third ~ 1.7 nm. While measuring the size spectrum of the particles, only the positively charged particles were registered, whereas ion

generators were not functioning and only furnaces were working ($T \sim 900^\circ C$). It resulted in obtaining a three-mode size spectrum. The range of particles’ sizes was repeated for each of modes under various operating regimes of the setup. The only factors being slightly changed were the width of the modes and the concentration of the particles. When the external electric field was superimposed on the synthesis process and when the potential on the spirals was positive, the form of the size spectrum of the synthesized particles changed and, starting with the 60 V potential, the spectrum became one-mode and the particles’ size was about 1 nm. Further increase of the potential (90 V) at first increased the concentration of particles and then (at ~ 100 V) caused the widening of the mode. The ions’ generators were not working and only positive charges of these particles were registered.

The work of the corona discharge generators and the supply of the negative potential onto the heating spiral also resulted in changing the form of the size spectrum of the particles. Therefore, when the potential on the spiral was negative (-112 V), we registered a clear two-mode spectrum, containing charges of only negative particles. When the potential value of the spiral was still negative and changed into (-90 V), we observed one-mode size spectra of both positively and negatively charged particles with the size of about 1 nm .

DISCUSSION & CONCLUSIONS: The obtained results of the measurements can be interpreted in terms of the analyzed elementary processes occurring on the phase interface “hot metal – air”. Heating the metal starting from certain temperature will cause thermal emission of electrons from the metal surface as well as thermal emission of positive ions of metal atoms and a more active sublimation of metal atoms. The particles, which escaped from this metal, move into the kinetic zone without any interactions. The particles started to interact with air molecules and with one another on the kinetic zone boundary, where $l \approx 6 \cdot 10^{-8} m$ (the mean value of an ion and an electron path). Thus, electrons, which interact with oxygen, create ions O_2^- , and if they interact with iron atoms, they produce negative ions of iron. Eventually, as the time, characteristic for such reactions is

$t \sim 10^{-8}$ sec, there exist three ions O_2^- , Fe^- and Fe^+ , which are real nuclei of condensation for the neutral atoms of Fe. The presence of these nuclei may explain the three modes appearing during the synthesis of CNP. The fact that only positive particles are present, is interpreted in terms of a possible thermal emission from the negatively charged particles, sited close to the hot surface, i.e. at $T \sim 900^\circ C$. Superimposing of the external electric fields causes the selection of the condensation nuclei – ions – depending on the potential sign on the spirals. Hence, when the potential is positive, the electric field collect negative ions and gathers them onto the spiral, thus causing the appearance of a one-mode size spectrum of the synthesized particles. When the potential on the spiral is negative, the generated electric field attracts positive charges (ions) to the surface of the spiral and repels the negative ones. Thus, the synthesis of nanoparticles occurs on two condensation nuclei – ions of O_2^- and of Fe^- , which causes a two-mode size spectrum of nanoparticles. The possibility to generate exclusively negative charges is explained by the attraction of the positive particles produced close to the spiral. It is also possible to generate exclusively negative nanoparticles on the negative ions, which were pushed out by the electric field into the “cold” zone of the gas. The thermal emission from the nanoparticles surface is not realized in this “cold” zone.

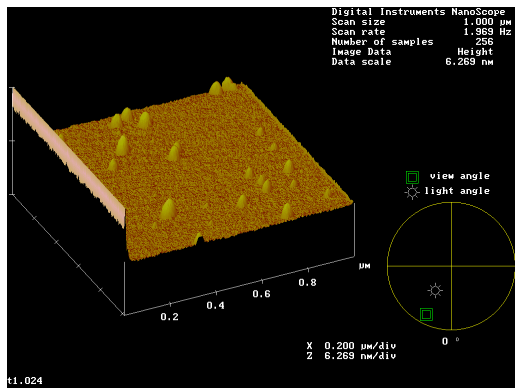


Fig. 1: AFM view of cluster nanoparticles.

The investigation has also shown an active movement of the synthesized CNP in the heterogeneous magnetic fields. This fact confirms the existence of the non-compensated magnetic momentum in CNP. Estimations based on measurements (diffusion coefficient) and

calculations of the number of the clusterizing molecules in the synthesized nanoparticle, showed that the density of the particles is the same for Fe_3O_4 particles. The characteristic look of the synthesized particles is given in Figure 1.

In conclusion we would like to state that the above-analyzed approach to synthesizing CNP in the air, enables to synthesize nanoparticles in the size range of ~ 1 nm. with a great degree of certainty. The produced particles will possess various physical and chemical properties. Controlling the synthesis by electric fields enables to change the sizes of nanoparticles, the signs of their charges, and the value of their magnetic parameters.

REFERENCES ¹. H. Gleiter ” Structure and Properties of Nanometer-Sized Materials”, *Phase Transitions*, 1990, v.24-26, pp.15-34 . ² M.Magnusson, et. al. “Gold Nanoparticles: Production, Reshaping and Thermal Charging”, *J. of Nanoparticle Research* 1:243-251 (1999). ³ K. Yagi, M. Tokuda, T. Kobayashi and T. Kishita 1999 *International Symposium on Micromechatronics and Human Science*, pp.157-162 (1999). ⁴ M.H.Nayfeh (2000), *J. Applied Physics Letters*, (U.S. patent pending). ⁵ L.Kip. et. al. *J. Chem. Phys.* **6**, 264 (1938). ⁶ C.T.R. Wilson. *Phil. Trans. Poy.Soc.*, 193, 289 (1899). ⁷ A.G. Amelin *Theoretical Basis of the Fog Formation During Vapor Condensation*. Moscow, 1972, p.304. (In Russian). ⁸ J. Dixkens and H. Fissan *Development of an Electrostatic Precipitator for Off-Line Particle Analysis*, *Aerosol Science and Technology* 30: 438-453 (1999). ⁹ D. Fridregsberg *Curs Colloidnoy chemistry*, Leningrad, 1974, p. 350 (In Russian).