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Research Article

Vacuum as a continuum medium forming energy inhomogeneities with a high energy density in the liquid phase

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Abstract

A method for the formation of metal nanoparticles in a localized volume with a high energy density due to the flow of a pulsed electric discharge and the cavitation effect was studied. The mechanism of the formation of energy inhomogeneities providing for the generation of nanoparticles with a high specific energy intensity was considered. Dynamic heterogeneity forms in three stages. There is a breakdown of the inter-electrode gap and the formation of a vacuum volume filled with a vapor-gas medium. When the pressure inside the bubble increases, a pulsed gas discharge is ignited, thus generating metal nanoparticles. This leads to the formation of a localized volume in which the discharge energy reaches values of up to 10^6 K. The increase in energy in the bubble leads to its collapse, after which the metal nanoparticles pass from the high-energy (10^6) medium into water at room temperature, resulting in their hardening. Highly pure nanoparticles of various metals 5–15 nm in size are obtained; these can be grown on a single-crystal silicon surface at room temperature and positioned on the surface of porous materials and products of complex configuration.

Keywords

energy inhomogeneities, metal nanoparticles, nanoparticle generation, electric pulse technology, nanoparticle positioning, carbon matrix

1. Introduction

Nanoparticles of different materials are currently actively used in various fields of science and technology. This is because their dimensional and quantum-dimensional properties are significantly different from those of bulk materials. Their high energy intensity compared to bulk materials, nonlinear optical, electrical and physical characteristics, the ability to obtain materials with a high dielectric constant (10^7–10^9), unique bioactivity, and, in some cases, selectivity of exposure, determine a wide range of scientific and practical use in microelectronics and nanobiotechnology. One of the most intensively developing areas of scientific research is the study of the properties of nanosized particles. This is related to the new promising possibilities of nanomaterial application that have opened in many fields of science and technology, in particular, for obtaining efficient and selective catalysts, creating elements of microelectronic and optical devices, efficient electric energy storage devices, biotechnologies, and the synthesis of new materials with

unique characteristics that cannot be obtained using bulk materials. At present, there are numerous ways to form metal nanoparticles. Most of the methods are based on chemical processes for the formation of metal nanoparticles that require selecting or developing primary components for each material, the constituents of which may be present in the final product and may significantly influence the properties of the resulting materials. In addition, obtaining alloy nanoparticles by chemical methods of synthesis in a liquid medium is a challenging task. Therefore, the development of a unified, physical, electric pulse method for the synthesis of metal nanoparticles in a liquid dielectric medium from initially pure metal, the study of their properties, and the possibility of treating the surface of a solid body with metal nanoparticles, including treatment of the pore volume of materials with a high specific surface (exceeding 1000 m^2/g) is relevant and appropriate.

The objective of this study was to develop a reactor for processes with a high energy saturation.

This objective required solving the following tasks:

1. Form a theoretical groundwork that would allow determining the direction of the search.

2. Study the mechanisms of the system's energy supply and its impact results.

3. Assess the current and prospective feasibility.

2. A theoretical groundwork that allows determining the direction of the search

The theoretical groundwork used to create localized, energy-intensive volumes mainly includes the latest achievements in research on the properties of dynamic inhomogeneities. A dynamic inhomogeneity is a local volume on the surface or inside the medium having properties that are different from its environment; it does not have static inhomogeneities inside and is generated as a result of certain physical and chemical processes. A dynamic inhomogeneity can be localized or can move across the working volume of a continuum medium due to interaction with various physical fields or dynamic inhomogeneities of a similar or different physical nature. This results in the localized volume being pumped with the energy, which significantly exceeds the energy of the environment. An important element of such an energy inhomogeneity is the possibility of its existence in a specific time interval. The continuum medium is the second element of the model. It generally can have any state of aggregation. In this study, distilled water is used as a continuum medium in which a vacuum bubble 100 μm in size is formed at the initial stage of the process. The third element of the model is an energy generator that forms dynamic inhomogeneities in the continuum medium. Consider a situation when the material is exposed to electrical energy and matter and passes into a state far from thermodynamic equilibrium, into the so-called nonlinear regime. In the nonlinear regime, the thermodynamic flows J_a are no longer linear functions of the thermodynamic forces F_a. As a result, states that are far from equilibrium can lose their stability and pass to one of the possible new states [1]. As the basic phenomenon occuring at the nanoscale level is violation of the electrical neutrality, we will be primarily interested in the effect of the electric field on the corresponding continuum medium and the electrical energy dissipation mechanism during their interaction.

3. Mechanisms of the system's energy supply and its impact results

Figure 1 shows the operating principle of the setup for metal nanoparticle generation by inducing a voltage with a nanosecond rise time in a discharge gap located in distilled water. This design uses a circuit based on a dedicated uncontrolled air gap P with flat electrodes and an inter-electrode distance $d \approx 1$ mm and a discharge chamber KP with rotating electrodes having an inter-electrode distance of ~100 μm.

The Sh-0105 high-voltage power supply unit provides the 4÷10 kV voltage range required to operate the reactor. When the breakdown voltage set on the high-voltage switch P is reached, a spark discharge is generated through the electrode system placed in the working fluid,

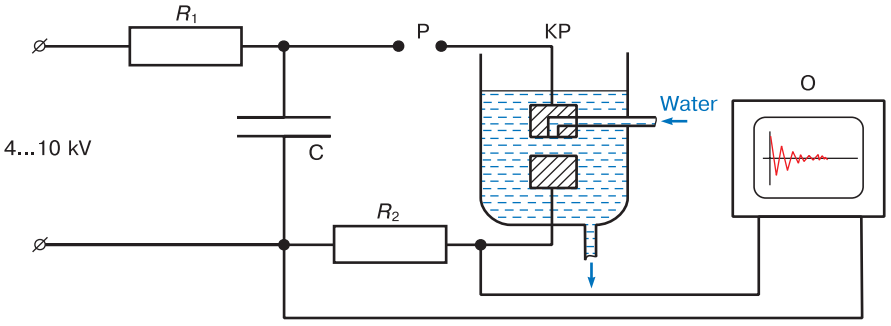

Figure 1. Schematic diagram of the setup for metal nanoparticle generation during a breakdown in distilled water: C is 15 kV high-voltage capacitor; P is air gap (high-voltage switch); O is oscilloscope; KP is discharge chamber; R_2 is measuring resistor; R_1 is ballast resistor

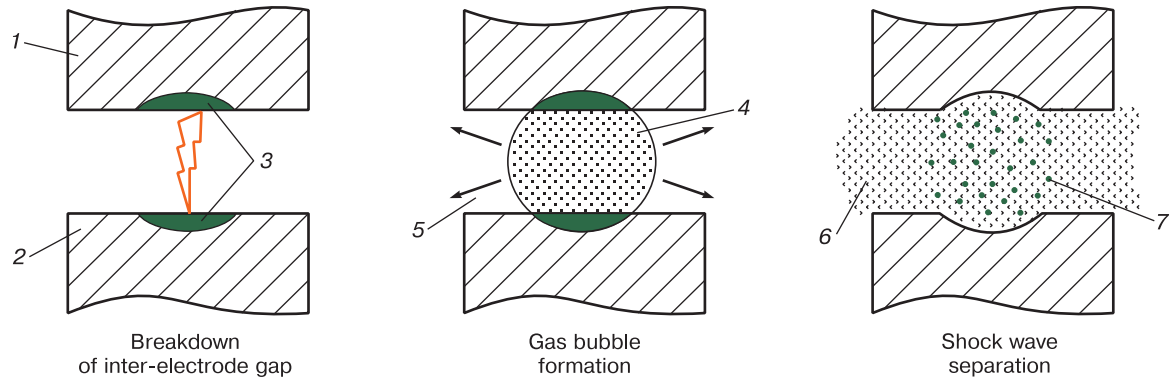

Figure 2. Schematic diagram of the formation of dynamic inhomogeneity: (*1*, *2*) electrodes, (*3*) molten metal of electrodes, (*4*) liquid and metal vapors, (*5*) shock wave propagation direction, (*6*) metal nanoparticles and (*7*) metal microparticles

causing their erosion. The capacitance of the capacitor C is selected depending on the design of the electrodes and the required operation mode of the reactor. The breakdown voltage is determined by the gap between the working electrodes and the settings of the air gap P.

Figure 2 shows a diagram of the formation of a dynamic inhomogeneity in the form of a gas-vapor bubble in which a pulsed discharge is ignited in the inter-electrode gap 1–2.

Dynamic heterogeneity forms in three stages, each of which is accompanied by a phase transition. The first stage involves a breakdown of the inter-electrode gap and the formation of a vacuum volume filled with a vapor-gas medium. The first phase transition occurs. Due to the increase in pressure inside the bubble, a pulsed gas discharge is ignited, thus generating metal nanoparticles. The second phase transition follows. A localized volume forms in which the discharge energy reaches values of up to 10^6 K [2, 3].

The increase in energy in the bubble leads to its collapse, after which the metal nanoparticles pass from the high-energy (10^6) medium into water at room temperature, resulting in their hardening. The collapse of the bubble results in cavitation, which leads to an increase in the kinetic energy of the nanoparticles [4].

A pulsed electric discharge occurs in the single gas bubble that appears in the inter-electrode gap when an electric current passes between the electrodes. The pulsed discharge begins right at the time of formation of the gas bubble and ends upon its collapse. Therefore, millisecond pulses arriving at the discharge gap are split into microsecond pulses with a steep nanosecond front (Fig. 3) [5].

Main characteristics of the electrical impulse Operating voltage 5÷10 kV. Primary pulse repetition frequency 100 Hz, current pulse amplitude 0.5÷5 kA.

4. Study of the properties of nanoparticles and examples of current and future practical implementation

The chemical composition of the obtained colloidal solutions of silver and iron was determined by X-ray spectral analysis using a Zeiss Evo 40 Instrument. The studies showed that the solutions contain insignificant amounts of random impurities (Fig. 4 *b*) [5–7].

The photomicrograph images show the particles having a near-spherical shape. It follows from analyzing the electron diffraction pattern shown in Fig. 5 *a* and 5 *b* and comparing it with the electron diffraction pattern of a bulk sample of crystalline silver that the nanoparticles consist of crystalline silver with an insignificant admixture of salt oxides. Fig. 5 *c* and 5 *d* show photographs of crystals formed on the surface of silicon substrates placed

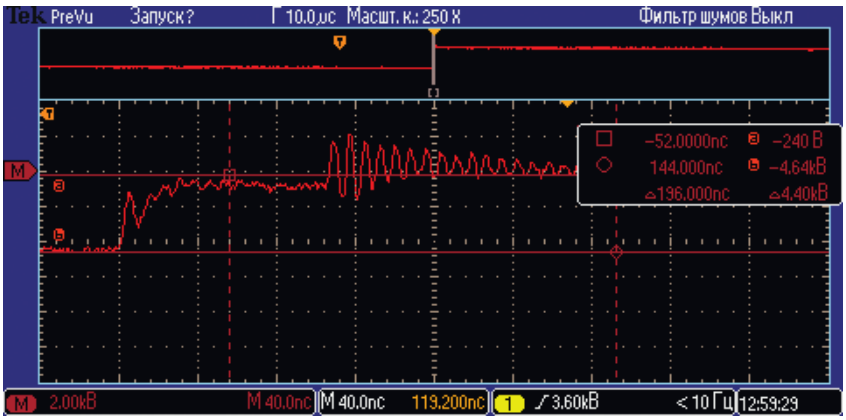

Figure 3. Oscillogram of voltage pulse generated when the air gap is triggered

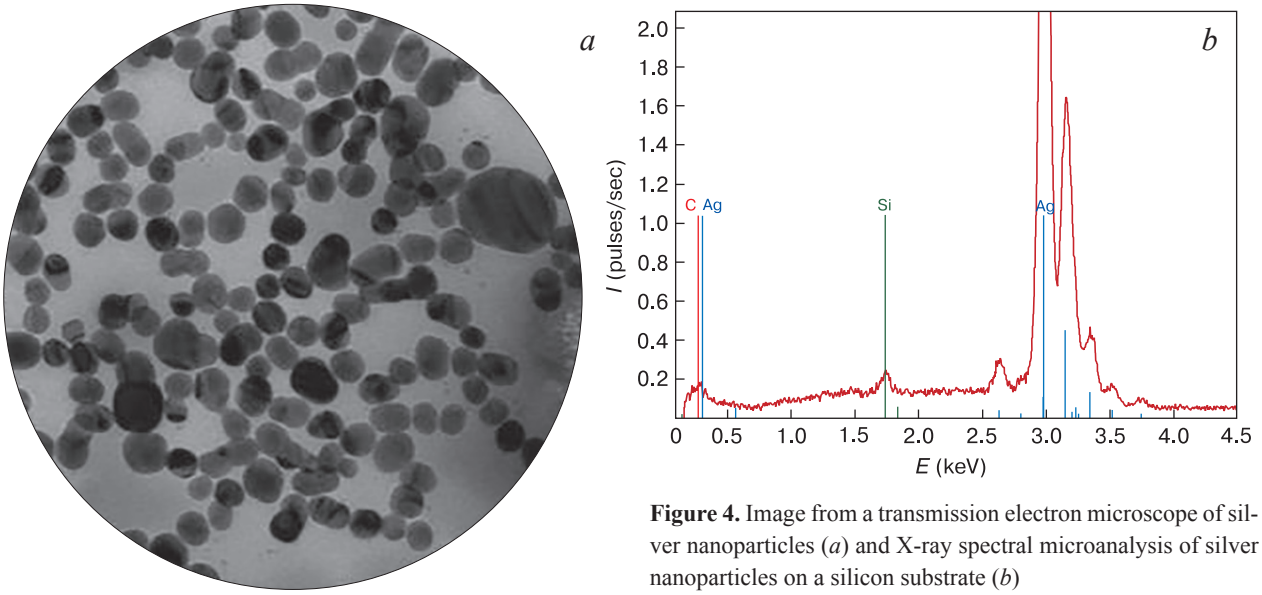

Figure 4. Image from a transmission electron microscope of silver nanoparticles (*a*) and X-ray spectral microanalysis of silver nanoparticles on a silicon substrate (*b*)

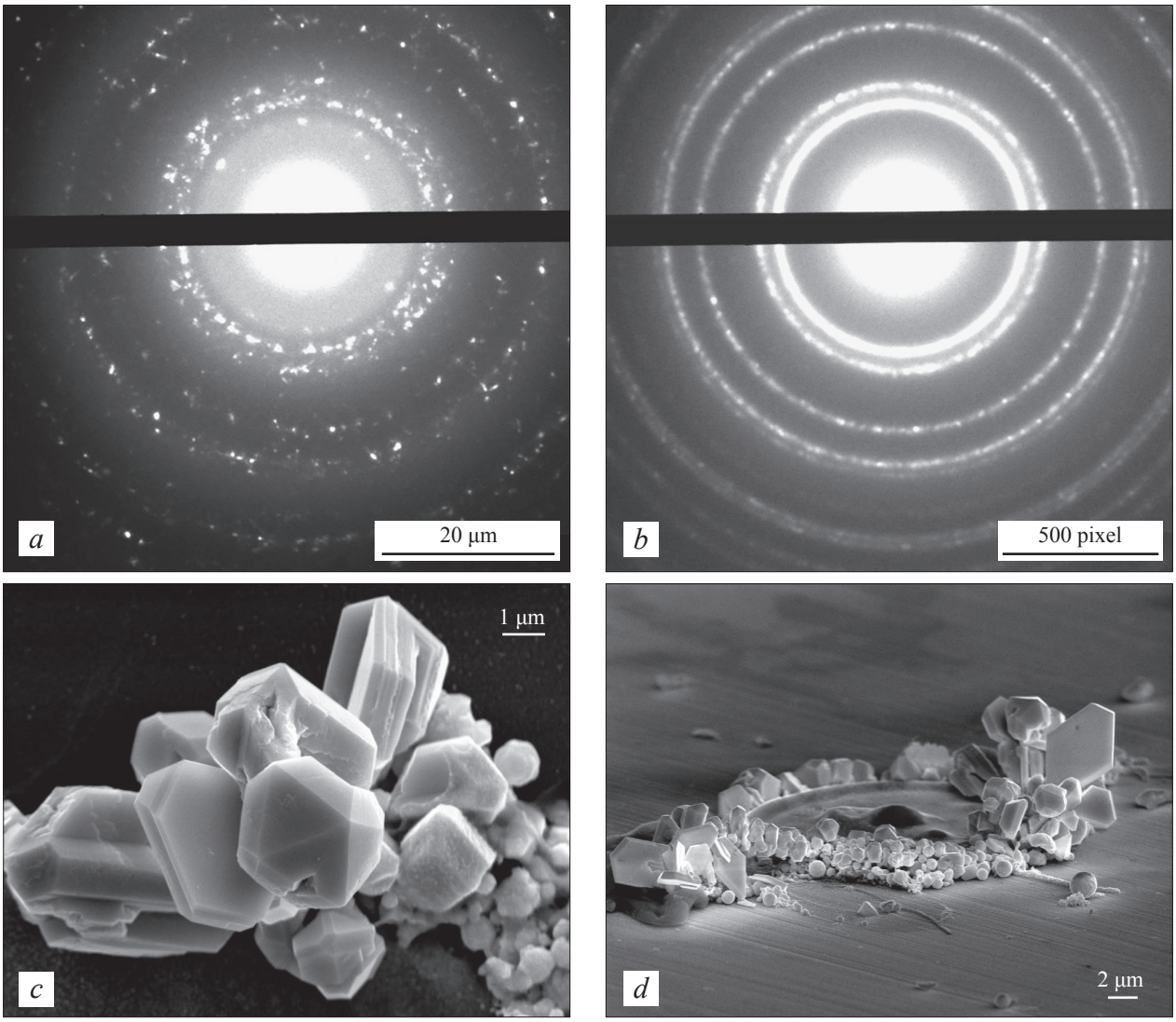

Figure 5. Electron diffraction pattern of initial silver nanoparticles (*a*) and electron diffraction pattern of a bulk sample of crystalline silver (*b*); (*c*, *d*) electron microscope image of silver mono-crystals grown on mono-crystal silicon at an interface with a copper film

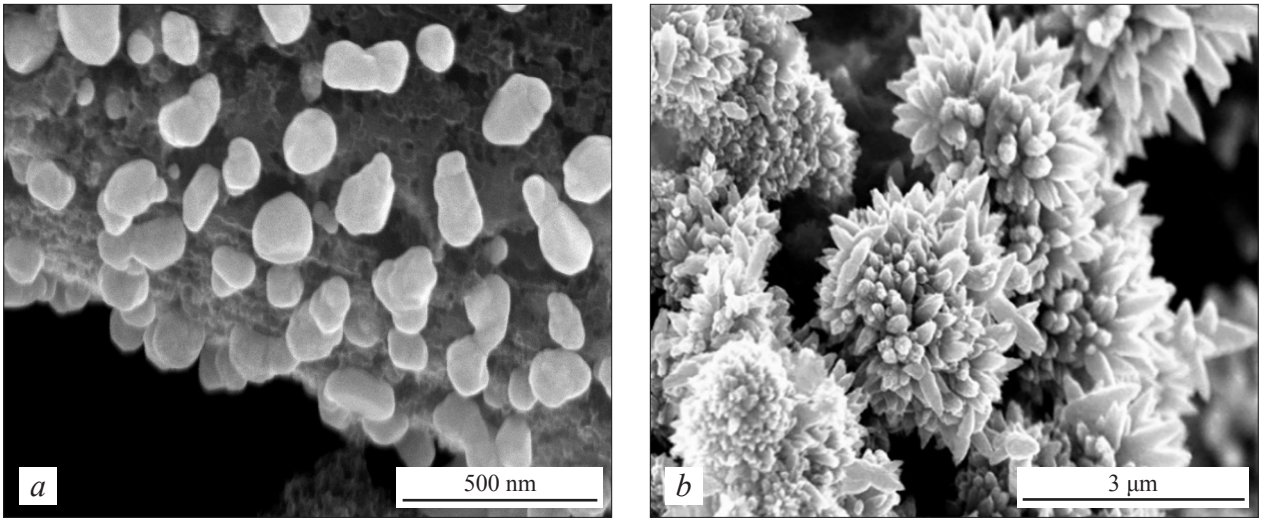

Figure 6. Coating of silver (*a*) and zinc (*b*) nanoparticles on a carbon matrix surface

in a silver hydrosol, including crystals nucleating at the silicon-metal interface. For this, the samples presented below were kept in a silver solution for 10 h, after which they were submitted for X-ray photoelectron spectroscopy and elemental analysis (see Fig. 5) [5, 6].

The results presented provide a basis to speak about the fundamental possibility of silver monocrystal formation on a silicon monocrystal at room temperature, something that can find wide application in nanoelectronics and photonics technology.

The next technology is based on the effect of cavitation, which occurs in the nanoparticle formation zone during gas-vapor bubble collapse [8]. This generates a powerful electro-hydraulic impulse that induces a directed movement of nanoparticles, which guarantees the development of technology for obtaining nanoparticles and positioning them on a solid body surface in a single process cycle. The acoustic waves cause the nanoparticles contained in the solution to penetrate into the material, where they attach due to the shock-wave nature of cavitation. Figure 6 *a* shows the result of depositing silver island films on a carbon fabric with a high specific surface area (exceeding 1,000 m^2/g). In addition to silver island films and thin, smooth nickel coatings, this technology allows obtaining coatings with a high specific surface area from zinc nanoparticles as shown in Fig. 6 *b*.

Analysis of the composition of the deposited coatings allows concluding that no foreign impurities appear during the formation of the coating (Fig. 7).

The advantage of this method is the possibility of obtaining high- purity nanoparticles of various metals and positioning them on the surface of porous materials and products of complex configuration, as well as a sharp reduction in material losses, speeding up of the process, and its automation. The principal advantage of the studied methods for applying thin layers is the possibility of implementing them on an industrial scale as roll-to-roll processing technologies.

It is important to note that the reactor for generating the nanoparticles appears during the process, after which

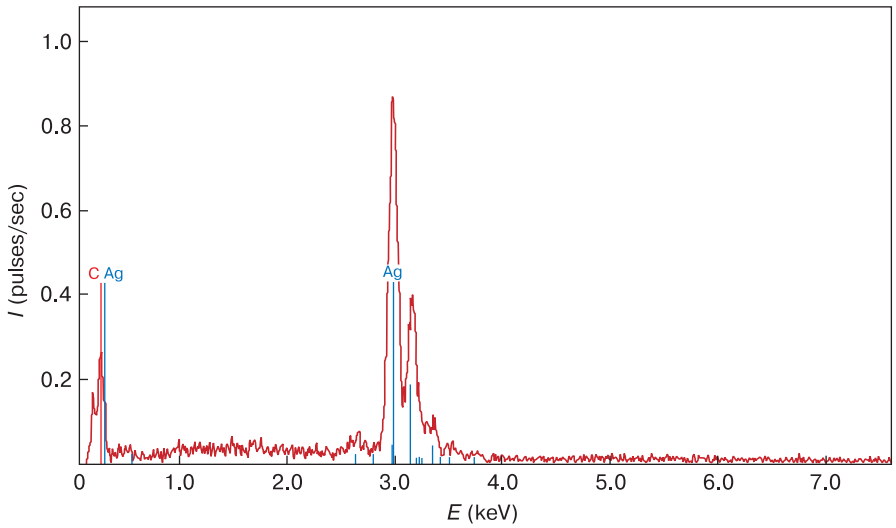

Figure 7. X-ray spectral microanalysis of a carbon fiber modified with silver nanoparticles of a Busofit-type material

a new reactor is formed. This means that the process does not have any issues with the reliability and stability of the reaction volume characteristics. The results of a preliminary estimate of the temperature inside the bubble allows making an assumption about the considerable energy saturation of the bubble in comparison with the environment. The temperature inside the bubble at the initial time reaches 10^7 K; during long-term operation lasting more than 5 min, it begins to decrease noticeably. This phenomenon was attributed to the fact that the electrical resistance of water decreases as a result of its saturation with metal ions and nanoparticles. This hypothesis was confirmed experimentally. Therefore, to further increase the energy intensity of the localized energy inhomogeneity, the equipment needs to be improved to obtain a primary electrical impulse with higher characteristics.

5. Conclusion

This study provided fundamental results on the process of the formation of metal nanoparticles in a liquid dielectric phase and their deposition on a solid body surface. It was shown that silver monocrystals from nanoparticles 5–15 nm in size can be grown on a monocrystal silicon surface at room temperature by precipitating their solution. The formation mechanism was not clearly established. However, it can be assumed that it is largely due to the high internal energy of nanoparticles obtained at temperatures above 10^6 K that instantly enter the liquid at room temperature.

Two methods for positioning metal nanoparticles on the surface of a carbon matrix with a specific surface area of 1,000–1,200 m^2/g were studied. The fundamental possibility of forming coatings on porous materials that can simultaneously significantly increase the surface of the initial material was shown. The principal advantage of the studied methods is the possibility of implementing them on an industrial scale as roll-to-roll processing technologies.

The prospects for the development of electric pulse technology for carrying out high-energy processes in localized micro-volumes were adequately shown.

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