A new approach to the high-yield synthesis of nanoparticles by spark discharge

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Abstract. A new approach to the high-yield synthesis of nanoparticles in the multi-gap (up to 12) spark discharge generator operating at a repetition rate as high as 2.5 kHz is discussed. This approach allows to increase the production rate by a factor of up to 100 as compared to the conventional approach utilizing single gap generator operating in the self-breakdown mode. In the case of spark erosion of aluminum electrodes in the air atmosphere, the production rate of 300 mg/h has been achieved. From the analysis of transmission electron microscopy images it was found that primary particles of the synthesized material are nearly spherical in shape and their size is 11 nm; these primary particles are united into larger objects (~80 nm) with fractal structure. The fraction of amorphous phase is 54% and the rest 46% is of cubic $\gamma$-Al$_2$O$_3$ phase with the mean crystallite size of 12 nm as determined from X-ray diffraction analysis. The specific surface area of the nanoparticles determined by BET method is equal 180 m$^2$/g.

1. Introduction
The synthesis of nanoparticles using spark discharge is a promising method for low-cost industrial-scale nanofabrication of advanced materials [1]. The distinctive features of this method are: a) the possibility of the synthesis of very small primary nanoparticles with a diameter of less than 10 nm from metals, oxides, semiconductors and carbon materials; b) high chemical purity of the synthesized nanoparticles with a low content of impurities; c) the relative simplicity of the implementation of the method. However, low production rate of about 10 mg/h [2] has been a limiting factor for a wide application of nanoparticles produced by spark discharge. In this regard, researchers are developing approaches that will increase the production rate of the synthesis of nanoparticles by spark discharge. The most successful approaches are associated with an increased frequency of discharge impulses [3] or an increased number of consecutive inter-electrode gaps [4].

In this paper, we propose combining two approaches in one setup and investigate the properties of the nanoparticles produced by spark discharge at the maximum production rate. Specifically, the paper presents new results of the synthesis of nanoparticles at high repetition rate of discharge pulses (2.5 kHz) and a large number of series-connected inter-electrode gaps (up to 12) implemented in one setup.

2. Experimental
The multi-spark discharge generator consisted of 12 pairs of aluminium electrodes was used in the experiments (figure 1). The voltage between the electrodes was applied by a 12 nF capacitor. The
capacitor is charged from a source of up to 4.5 kV voltage. Initiation of the gas discharge was carried out using the principle of switching multi-spark dischargers by supplying a trigger voltage pulse [5]. The frequency of the discharges of up to 2.5 kHZ was regulated by a generator of pulsed currents. The space between the electrodes was constantly purged by the flow of clean air at velocity of 15 m/s. The nanoparticles were deposited onto an aerosol filter made of porous stainless steel.

The particle size distribution, morphological and structural features of the obtained nanoparticles were investigated by a transmission electron microscope (TEM) JEM-2100 (JEOL). The structure and phase composition of the collected nanoparticles were studied by a powder X-ray diffractometer (XRD) D8 DISCOVER (Bruker). Qualitative and quantitative elemental composition of the nanoparticles was determined using a mass spectrometer with inductively coupled plasma (ICP-MS) iCAP Qc (Thermo Scientific). Real-time measurements of size of the nanoparticles in the aerosol flow were performed by an aerosol spectrometer DAS 2702 (AeroNanoTech). The specific surface area of the nanoparticles was analyzed using a gas adsorption analyzer TriStar 3000 (Micromeritics).

3. Results and discussions

The photos of the filter with precipitated particles are shown in figure 2. The area of the filter with precipitated nanoparticles becomes white, which is characteristic of alumina powder.

![Figure 2. The photo of the filter before and after the deposition of airborne particles produced by spark erosion of aluminium electrodes in the air.](image)

The mass of the filter was increased by 52 mg within 10 minutes of the generator operation. Thus, the production rate of ~300 mg/h was achieved. This production rate is 100 times higher than the rate
of conventional spark discharge generators with single gap [2,6]. The comparison of the production rate of the multi-spark and conventional discharge generators is presented in table 1.

| Type of generator                      | Production rate (mg/h) | Number of pairs of electrodes | Frequency of the discharges (Hz) | Voltage (kV) | Flow rate (l/min) | Reference |
|----------------------------------------|------------------------|-------------------------------|----------------------------------|--------------|-------------------|-----------|
| Multi-spark discharge generator        | 300                    | 12                            | 2500                             | 4.5          | 160               | This study |
| Conventional spark discharge generator | 0.5                    | 1                             | 30-300                           | -            | 0-20              | Other [6] |

In table 1 the production rate for the conventional spark discharge generator was determined by multiplication of the mass concentration of particles and flow rate [6]. In this study high-yield synthesis of nanoparticles is due to two factors. The first factor is related to the increase in the number of interelectrode discharge impulses by increasing their density in time (i.e. by increasing the repetition rate discharges up to 2.5 kHz). The second factor is the twelve-fold increase in the number of evaporated electrodes, which in turn increases the amount of discharge pulses in space.

A typical TEM-image of the nanoparticles is shown in figure 3a. The sample consists of large agglomerates of spherical primary particles. It is found that the size of the primary nanoparticles remains small despite high production rate. Indeed, the size of the primary particles is in the range of 3 to 30 nm with the mean size of 11±4 nm (figure 3b). The particle size distribution is well described by the log-normal function with the following parameters: median = 10.9 nm and sigma = 0.336.

![Figure 3](image_url)

**Figure 3.** TEM image of nanoparticles and corresponding electron diffraction pattern (inset) (a); Particle size distribution calculated from TEM data (b).

The mean size of the agglomerates is about ~80 nm by TEM-analysis; which is consistent with the data measured by the aerosol spectrometer (figure 4). The large size of the agglomerates is due to the high production rate.
Figure 4. Size distribution of number concentration of as-synthesized airborne nanoparticles measured by diffusional aerosol spectrometer.

Additionally, it is found that the nanoparticles are aluminum oxide with a fraction of amorphous particles of about 54 wt.% and the crystalline fraction of about 46 wt.% with the phase $\gamma$-$\text{Al}_2\text{O}_3$ according to the results of X-ray diffraction analysis (figure 5). The formation of alumina is due to the fact that erosion of the aluminum electrodes was in the oxygen-containing atmosphere: $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$.

Figure 5. XRD spectrum of nanoparticles produced by spark erosion of aluminum electrodes in the air.

A detailed result of X-ray diffraction analysis of the nanopowder, including lattice parameters and mean size of the crystallite is shown in table 2.

| Composition                  | Parameters of the lattice ($\AA$) | Mean crystallite size (nm) |
|------------------------------|----------------------------------|---------------------------|
| $\text{Al}_2\text{O}_3$ amorphous (54 wt. %) | -                                | -                         |
| $\gamma$-$\text{Al}_2\text{O}_3$ cubic (46 wt. %) | $a = 7.94\pm0.02$               | 12                        |

It was found that the synthesized nanoparticles contained about 36 wt% of Al according to the results of elemental analysis by ICP-MS. The measured concentration was greater than theoretically-
calculated concentration of Al in Al₂O₃ (53 wt. %). This result indicates that the sample is not pure alumina. The specific surface area of the nanoparticles was determined equal to 180 m²/g. In terms of size this is equivalent to particles with a diameter of 8 nm. Thus, the result of measurement of the specific surface of the particles is in good agreement with TEM-data.

4. Conclusion
New combined approach in the spark discharge allows to increase the production rate of nanoparticles by a factor of up to 100 compared to the conventional approach utilizing single gap generator operating in the self-breakdown mode. The combined approach consists of increasing the repetition rate of discharges up to 2.5 kHz and the number of discharge gaps up to 12, combined in one setup. It was shown to generate nanoparticles of Al₂O₃ at high production rate more than 300 mg/h. The synthesized primary nanoparticles have an mean size of 11 nm, which fractal form agglomerates with size of about 80 nm. The developed method is promising for the application in industrial-scale nanofabrication of advanced materials.

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