Synthesis and processing of powder materials in DC arc thermal plasma

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Abstract. The results of work on the implementation of plasma synthesis and spheroidization of powders of metals and their compounds in a thermal plasma generated in a direct current arc plasma torch are presented. The possibility of controlling the properties of the obtained powders is demonstrated.

1. Introduction

Nanosized powders of elements and their inorganic compounds form the basis for the preparation of nanostructured materials, such as nanostructured functional ceramics for various purposes, solid alloys characterized by high wear resistance and toughness, dispersion-hardened and modified structural alloys with improved physical and mechanical properties, nanostructured protective thermo-resistant, corrosion-resistant, and wear-resistant coatings, polymeric composite materials with fillers and modifiers consisting of inorganic nanoparticles, etc. [1–5].

Plasma synthesis is the most versatile method to obtain nanopowders of elements and their various inorganic compounds and compositions in the controlled gaseous atmosphere, including inert, oxidizing, and reducing one [6, 7].

Various types of electric discharge are used to generate thermal plasma, including electric direct current arc (DC), high frequency (HF), microwave (MW), and combined discharges [7]. The power of the modern DC plasma torches is up to 3–5 MW with an operation life up to 103 hours. The use of V-shaped DC plasma torches [8], where tungsten electrodes function in the inert gas (argon) environment, virtually eliminate the presence of electrode material impurities in the thermal plasma flow and enables production of high-purity finished products. Currently, the existing 300–2400 kW plasma torches characterised by the thermal efficiency of 70–85% support the operation of industrial plants, recycling various kinds of waste, and metallurgical furnaces [9].

Currently, the Institute of Metallurgy and Material Science of the Russian Academy of Sciences (IMET RAS) conducts active research into the synthesis of nanopowders in the thermal plasma flow generated in DC plasma torches. The development of plasma-based technologies to produce nanopowder with desired physico-chemical properties determined on the basis of their specific use in the development of new materials is the most important line of the research. For this purpose, the problems of managing dispersion, phase, and chemical composition of the prepared nanopowders are being solved both directly during their preparation in plasma reactors and during subsequent additional thermochemical and thermal vacuum treatment.
In the context of rapid development of additive technologies, the research and development of spheroidization processes for metal and alloy powders with a particle size of 10–100 μm in the thermal plasma flows of DC plasma torches are carried out.

This article provides an overview of the results of the research into the synthesis of nanopowders and spheroidization of powders with a particle size of about $10^1$ μm in the thermal plasma flow generated in DC plasma torches, which were carried out at the IMET RAS.

2. Plasma setup
The developed DC electric arc plasma torches with a nominal power of 30–150 kW and self-adjusting arc length and gas discharge stabilization, as well as plasma torches with an inter-electrode inserts were used to generate the thermal plasma in the laboratory and pilot plants at the IMET RAS. Plasma torches provided stable generation of the thermal plasma flow of reducing, oxidizing, and inert media with an average equilibrium temperature of $(3–10) \times 10^7$ K to conduct nanopowder preparation and spheroidization processes.

Synthesis of nanopowders in the thermal plasma flow generated in the electric arc plasma torch is effectively implemented in the confined jet flow reactor [6, 7]. Plasma jet generated in the electric-discharge thermal plasma generator flows into the space, which is bounded by cooled cylindrical surface with a characteristic dimension ratio $D_r/D_p >> 10$, where $D_r$ – diameter of the reactor, $D_p$ – the diameter of the plasma torch outlet nozzle. Nanoparticles are formed in plasma reactors as a result of condensation of gas phase components, which is accompanied by precipitation of the resulting nanoparticles on the surface, bounding the high-temperature gas-dispersion flow. Deposition of nanoparticles on the directly water-cooled surface prevents their sintering in the formed layer.

The developed structure of the confined jet flow plasma reactor for the synthesis of nanopowders is protected by Russian Federation patent [10]. General view of the plasma reactor based on 30 kW DC plasma torch is shown in figure 1.

![Figure 1. Plasma setup based on reactor with confined plasma jet and 30 kW DC plasma torch.](image)

3. Nanopowders plasma synthesis
Particulate composition is a key characteristic of nanopowders, which determines the possibility of their use, when solving scientific problems and in practical applications.

The complex of processes used to obtain metals and their inorganic compounds implemented in the confined jet flow reactor based on DC plasma torch, having a nominal power of 30 kW. Various individual gases and gas mixtures were used as the plasma-supporting gases. Powders of elements and
their compounds with particle sizes not exceeding 25–40 μm were used as raw materials; liquid reactants were evaporation before feeding to the reactor.

The results of electron microscopic studies show that all prepared nanopowders are polydisperse and consists of equiaxed particles (figure 2); no oriented-growth nano-objects were detected.

Nanoparticle formation under conditions of plasma chemical synthesis is based on “vapor-liquid-crystal” (VLC), “vapor-crystal” (VC), and mixed macro-mechanisms, the latter involves a combination of the mechanisms (VLC-VC). The mechanism of nanoparticle formation in a process may be evaluated based on thermodynamic calculations of temperature dependence of the final product (nanopowder) yield. Assuming that that the substance in question exists in the liquid and solid states, its yield depends on temperature, wherein: \( T^* \) – minimum temperature, which corresponds to the maximum yield of nanoparticle substance; \( T_c \) – maximum temperature, wherein nanoparticle substance exists in a condensed state, \( T_{mp} \) – melting point of the substance. Since the plasma process is carried out at decreasing temperature, which is initially higher than \( T_c \), the temperature conditions of nanoparticle formation through the aforementioned macro-mechanisms can be written as follows:

- **VLC mechanism:** VLC \( T_{mp} < T^* < T_c \), all the particles have a spherical habitus (figure 3a);
- **VC mechanism:** \( T^* < T_c < T_{mp} \), all particles have a faceted habitus (figure 3b);
- **VLC-VC mechanism:** \( T^* < T_{mp} < T_c \), particles have both spherical and faceted habitus (figure 3c).

**Figure 3.** Variants of characteristic temperature ratios during formation of nanoparticles through various macro-mechanisms, A – VLC mechanism \( (T_{mp} < T^* < T_c) \), B – VC mechanism \( (T^* < T_c < T_{mp}) \), C – VLC-VC mechanism \( (T^* < T_{mp} < T_c) \).

VLC mechanism takes place, when under conditions of decreasing temperature of the process, the maximum yield of nanoparticle substance occurs at the temperatures above the melting point (figure 3a). In turn, VC mechanism determines formation of nanoparticles, when nanoparticle substance is formed at the temperatures below the melting point of the nanoparticle substance (figure 3b) or substance does not exist in the liquid state. If the substance crystallizes (solidifies) during formation of nanoparticles
under decreasing temperature condition before maximum yield is achieved, then particle formation mechanism changes from VLC to VC and the final product will contain both spherical and faceted particles (figure 3b).

As can be seen on the photomicrographs of nanopowders (figure 4), formation of nanoparticles in the implemented process can occur through all three mentioned mechanisms, i.e. VLC, VC, and VLC-VC.

Histograms of particle size distribution was plotted based on the photomicrographs of Al₂O₃, TiO₂, W, Cu, TiCN, and TiN nanopowders and W-C compositions, where particle formation occurred through all the above mechanisms, and analysed using statistical methods.

It was found that the log-normal function of particle size distribution

\[
p(d) = \frac{1}{d\sigma(2\pi)^{1/2}} \exp\left(-\frac{1}{2}\left(\ln d - \frac{m}{\sigma}\right)^2\right)
\]

where in \(d\) is particle diameter, \(m\) – distribution median, \(\sigma\) – standard deviation, reliably (with a correlation coefficient higher than 0.95) describes all the studied objects in a wide range of varying disperse composition of the investigated nanopowders. It should be emphasized that correspondence to log-normal particle size distribution was previously confirmed for nanopowders obtained in the processes, where particles are formed through the coagulation mechanism, i.e. VLC [12]. Experimentally determined log-normal particle size distribution in the absence of coagulation growth according to [1] may be due to the log-normal distribution of the residence time of the particles in the growth zone.

It was experimentally found that increase in the concentration of precursor used in the primary gaseous components results in higher average size of the obtained nanopowder particles for the implemented nanopowder preparation processes through various macro-mechanisms [14–21]. The influence of the plasma process parameters and characteristic reactor size was studied in [16] for preparation of tungsten and nickel nanopowders by reduction of their oxides WO₃ and NiO in the hydrogen-nitrogen and propane-air plasma. It was shown that, in addition to the aforementioned precursor concentration, the average particles size of the produced metal powders can be influenced by the characteristic dimensions of the plasma apparatus, i.e. the reactor diameter and plasma torch nozzle diameter, determining the size of the high temperature zone, where particles are formed. The patterns of formation and growth of the particles may be affected by chemical processes, occurring on their surface. The research into the preparation of various nanopowders in the plasma reactor shows that the effect of process parameters on the average size of produced particles is a multifactorial problem, which is significantly affected by physical and chemical characteristics of the process.

The results showed that the average particle size depends on the synthesis parameters, including initial concentration of the precursor, enthalpy, and plasma jet outflow velocity, wherein the influence
of the above parameters is determined by the individual characteristics of the process. Preparation of extremely small particles in the confined jet flow reactor can be achieved only with a significant decrease in the initial concentration of vapors or increase in jet outflow velocity. Decrease in the initial concentration results in reduced synthesis productivity, while increase in speed have substantial physical and engineering restrictions.

In the case of particle formation through the VLC mechanism in the thermal plasma flow, particle size can be controlled by altering the time of coagulation particle growth, i.e., forced termination of the process after vapor-liquid phase transition stage, for example, by cold gas injection. In [17], such a process scheme was used in the synthesis of aluminium oxide nanopowder by metal powder oxidation in the air plasma flow. Multipoint radial injection of the quench gas on the periphery of the high-temperature flow was organized in the confined jet flow reactor. Quenching was carried out at a different distance from the reactor inlet, which enabled varying the time of particles residence in the coagulation growth zone. Varying injection intensity and injection point of the quenching gas enabled varying the average particle size within the range of 35–75 nm.

The results show that the confined jet flow reactor based on DC plasma torch enables obtaining a wide range of nanopowders of elements, their inorganic compounds, and composites.

4. Spheroidization of metal powders

Spherical powders with a particle size of about $10^1 \mu m$ are the starting materials to prepare products of metals and alloys using additive techniques. Processing of powders having irregularly shaped particles in the thermal plasma results in their melting and formation of spherical particles.

When processing titanium powder prepared through the hydrogenation-dehydrogenation process in the stream of argon thermal plasma, spherical titanium powder fractions sized 40–70 $\mu m$ and below $40 \mu m$ were produced, whose spheroidization level reaches 96% and the average circularity coefficient of the particles is 1.01 (figure 5).

Experimental studies have shown the possibility of preparing nonporous spherical powders of multicomponent metal alloys starting from ultrafine powder alloy components, having a particle size of less than 1 $\mu m$. A model high alloy Fe-Ni-Cr was used to exemplify the possibility of preparing spherical alloy powders with a particle size of 25 to 50 $\mu m$ through the process comprising the following steps: microgranulation of the ultrafine powder, heat treatment of microgranules (drying at 100°C, removal of organic binder at 300°C, thermochemical treatment in the atmosphere of H2 at 1000°C, vacuum treatment at 1200°C), classification of the heat-treated microgranules with separation of microgranule fractions sized 25 to 50 $\mu m$, spheroidization of the separated fraction of microgranules in the thermal plasma flow, classification and separation of micron and submicron size fractions. Photomicrographs of the microgranules of alloy components and plasma spheroidized particles are shown in figure 6.

The experimental results showed the possibility of obtaining spherical powders of metals and alloys starting from various powder materials in the confined jet flow plasma apparatus based of the electric arc plasma torch.

![Figure 5. SEM photomicrographs of spheroidized titanium powder.](image-url)
Figure 6. SEM Photomicrographs of granules of alloy components (1) and plasma spheroidized particles (2).

5. Conclusions
The results of research and development demonstrated broad possibilities of plasma processes and apparatuses for producing nanopowders of metals and their various inorganic compounds with desired properties. Nanopowders obtained in plasma systems were used in a large number of research and development to prepare novel materials with special and improved properties.

Apart from obtaining nanopowders, confined jet flow plasma reactors enable spheroidization of metal and alloy powders to be used in additive technologies.

Accumulated experience forms the basis for the development of efficient industrial production of powders using plasma reactors on the basis of electric arc plasma torch.

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