Plasma ways to obtain ultrafine oxides

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Abstract. The paper is devoted to a research of the plasma torch application for production of ultrafine materials. The possibility of obtaining a nanosized connection of magnetic ferrite nanoparticles, such as iron oxide Fe₂O₃ is investigated, and also the determination of the experimental parameters of the experimental installation and the experimental conditions. The single-phase low-power alternating current plasma torch was used in the initial stage of the experiments. Plasma torch construction allows the work material to be fed in several points along the plasma flow including directly into the arc chamber. Plasma chemical facility containing the alternating current plasma torch, the feed system of the work material, the plasma chemical reactor and the system of the end product collection is created. Iron(III) nitrate as a precursor is fed into the air plasma jet. The produced iron oxide is investigated by x-ray phase analysis and method of static light diffusion.

1. Introduction
Plasma torch application for production of ultrafine materials has a wide number of advantages. Firstly it is possible to provide high temperature of the chemical processes in a broad range from 1000 to 5500 °C. Secondly the process of the temperature regulation becomes simpler due to the variability of the plasma jet energy content. All those allow using an alternating current plasma torch for obtaining different ultrafine materials. The main part among demanded nanoparticles is made by oxides about 61.3% in 1996, 73.4% in 2000 year. At the same time the amount of the most widely used oxides is 28.5% of SiO₂, 22.1% of Al₂O₃ and 8.8% of TiO₂.

The ratio of the number of atoms in a thin surface layer of 1 nm to their remaining number is significantly higher in comparison with the microparticles for nanoparticles. An increase in the proportion of surface nanoparticle atoms with a decrease in particle size changes the physical and chemical properties of the material, making the use of nanomaterials attractive in many branches of science and technology.

The plasma-chemical method application for nanodispersed materials production [1, 2] can ensure high process efficiency as far as the reaction proceeds in a low-temperature plasma and high non-equilibrium state of temperature parameters is automatically ensured, that being properly organized, allows a high rate of formation of a new phase of the material and prevent conglomeration and enlargement of the particle size.
Ferrites of metals are highly demanded materials in the context of technological applications. They are used in a variety of technological applications: radio electronics, radio engineering, computer technology in chemical catalysis.

Now the main methods of obtaining ferrites are glycine-nitrate combustion, hydrothermal synthesis, sol-gel process, electrochemical method. These methods are quite effective, but they have a common disadvantage such as they allow the process to be carried out periodically and often the process takes quite a long time.

The purpose of the work is, first of all, to obtain a nanosized connection of magnetic ferrite nanoparticles, such as iron oxide $\text{Fe}_2\text{O}_3$, in order to demonstrate the possibility of applying the plasmothermic method to aqueous solutions of precursors, and secondly, to determine the experimental parameters of the experimental installation and the experimental conditions for obtaining particles with small variation in size and shape.

2. Brief review of plasma methods to obtain ultrafine oxides

It is known about the possibility of ferrites production by plasma methods. In [3] the production of ferrites from powders $\text{Fe}_2\text{O}_3$, $\text{ZnO}$, $\text{NiO}$ and $\text{CuO}$ is considered. An electric arc direct current plasma torch with an anode nozzle made of copper and Th–W rod cathode is used. There is a zone for the gas-dust mixture consisting of Ar and oxide powders feeding in the nozzle of the plasma torch outside the arc combustion zone.

The plasma torch is combined with a plasma-chemical reactor in which a substrate for collecting of a sample of ferrites is located. Parameters of the plasma installation: flow rate of plasma-forming gas Ar 20 l/min, flow rate of carrier gas for transporting powders 6 l/min, flow rate of oxide powders 0.5 g/min, plasma torch power is 3 kW.

It is found that this method allows production powders and coatings of ferrites of various metals showing expressed magnetic properties.

A more uniform synthesis of particles of ferrite metals was obtained on the installation comprising a microwave plasma torch [4]. Solutions of zinc and iron nitrates in ethanol were used as a material to be treated. Plate power of plasma torch is from 15 to 25 kW, specific energy consumption from 4.6 to 11.2 kW per 1 mole of Zn–Fe mixture, flow of plasma-forming gas Ar 20 l/min, sheath gas is $\text{O}_2$ 20 l/min and Ar 23 l/min. As a result, reverse zinc spinels are formed in the form of microsized and nanosized particles.

Also, the synthesis of zinc ferrite from the corresponding hydroxide powders was realized using a microwave plasma torch about 27 MHz [5]. The power of the plasma torch was 1–7 kW, flow rate of the plasma-forming gas Ar was 7 l/min, shielding gas flow rate was 19 l/min. However, the formation of spinel was not complete due to the partial heating of the feedstock grains, but the average particle size was varied within 10–30 nm.

In addition, more complex compounds Ni–Mn ferrite-chromite were synthesized using the electric arc. They were formed by erosion of rod electrodes containing 21 wt % Cr, 9 wt % Mn, 4 wt % Ni, 0.4 wt % N and 0.53 wt % C [6].

The electric arc was ignited in a medium of pure oxygen at 100, 200 and 300 A. In this case, uniform particles of about 100-nm size were formed in a spherical shape.

Amorphous hematite was synthesized under the action of a high-voltage discharge in bidistilled water [7]. Since the particles were formed due to the erosion of the electrodes, the products are a mixture of the particles $\text{Fe}_2\text{O}_3$, $\text{Fe}_4\text{O}_4$ and metallic iron.

As already mentioned, this article considers the preparation of nanoparticles by decomposition of a dispersed aqueous solution of iron(III) nitrate using an air high-voltage alternating current plasma torch.

The block diagram of the installation is shown in figure 1.
3. Plasma torches

The aim of the article is to demonstrate the possibility of an application of plasma technology for production of nanoscale ferrites. A single-phase alternating current plasma torch [8] is used for this purpose at the first stage. It helped to demonstrate the principal possibility of the problem solution. After development the method of obtaining and clearing the process main parameters, it is planned to use a more powerful plasma torch with rail electrodes to demonstrate the possibility of industrial application of the developed technique.

The design of a single-phase alternating current plasma torch, which is used in the initial stage of the study, is shown in figure 2. The single-phase alternating current plasma torch consists of the following components: body, bushing insulator, replaceable tips-electrodes, outlet nozzle and feeding device. The body is made of stainless steel and it is water-cooled. Two cylindrical channels converging in the discharge chamber are located in the body. Each channel has tangential gas inlet openings. Work material supply is carried out through the nozzle with the help of the feeding device.

Subsequently it is planned to use a well-proven three-phase alternating current plasma torch with rail electrodes [9] as a basis for creation of a plasma chemical plant [1] for the production of ultradispersed materials [2].

It goes without saying that it is impossible to guarantee an unambiguous transfer of the results to a larger scale, and, as a rule, this requires a considerable improvement. This embodiment can be used as an option demonstrating the plasma process applicability.
The enthalpy of the plasma-forming gas is the confirming criterion. This value is comparable for these types of plasma torches, as well as the mass-average temperatures of the plasma jet for them ranging approximately from 1500 to 3500 K.

A photo of the three-phase single-chamber alternating current plasma torch with rail type electrodes, that is planned to use in the further stages is shown in figure 3. Electric power up to 500 kW, wide temperature range of the plasma jet 1500–5500 K, allows it to be effectively used in a plasma chemical plant for the production of ultradispersed materials. That is why we believe that it is essential to give the expanded characteristic of its operation.

The principle of electrodynamic movement of arcs in the field of their own current, the rail-gun effect is the basis for the operation of plasma torches with rail type electrodes. The rapid movement of the arc attachment point along the electrode under the action of electrodynamic and gas dynamic forces distribute the thermal load along the length of the electrode. This makes it possible to use water-cooled electrodes made of a relatively low-melting material with high thermal conductivity. Arcs move along the divergent electrodes at a speed of 10–30 m/s, depending on the magnitude of the current, the angle of inclination of the electrodes, as well as the flow rate and the method of the working gas supply. The arcs fill most of the discharge chamber, moving in the longitudinal and transverse directions.

Due to this, a relatively high thermal efficiency of the plasma torch can be obtained, the efficiency depends on the operating conditions and can reach 85%. In the near-wall zone, where the cold gas is fed creating the insulating layer, the concentration of charged particles sharply decreases and the arc extinguishes. The process described above is continuously repeated, as a result of which a jet of low-temperature thermal plasma with a mass-average temperature of about of 1500–5500 K is formed at the outlet of the plasma torch nozzle.

The initiation of arcs in the zone of the minimum distance occurs due to the plasma injector. The ac plasma torch is used as a plasma injector. Its power is 5–10 kW, plasma forming working gas flow rate is 2–5 g/s. When the injector is operating in the zone of the minimum distance between the main electrodes of the plasma torch, a plasma flow with an electron concentration
\[ n_e = 10^{14}–10^{16} \text{ cm}^{-3}, \]
sufficient for ignition of the main arcs, is established.

There are several points of tangential gas injection into the electric arc chamber of the plasma torch, which can also be used for feeding the material to be treated.

Nevertheless the paper deals with the principal possibility of conducting a technological process for production of ultrafine ferrites in plasma with certain parameters. Impossibility of immediate construction of a large-scale installation for economic reasons dictates the need for using of single-phase low-power alternating current plasma torches.
Installations for the destruction of chloro-fluorobibinil, medical waste, pyrolysis of organic materials, etc were developed according to a similar scheme. Everywhere at the initial stage of the study the single-phase low-power alternating current plasma torches were used.

4. Experimental results
Aqueous solution of iron(III) nitrate was chosen as the model substance for preliminary experiments. The purpose of the experiment was to show the possibility of using a plasma-thermal method for production of ultradispersed and nanosize materials and determine the initial parameters for the design of an experimental installation based on the alternating current plasma torch.

To this day, searching experiments have been conducted, the purpose of which was to demonstrate the possibility of obtaining by this method of ultradisperse oxide powders by the example of iron(III) oxide. When using the solution of iron(III) nitrate as the precursor, the
Figure 5. Distribution of sizes of $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles produced by plasma chemical method.

The following parameters for the operation of an ac plasma torch have been established, contributing to the formation of a $\text{Fe}_2\text{O}_3$ nanopowder: power of 6 kW, operating voltage of 1000 V, total flow rate of plasma-forming gas of 1 g/s, precursor consumption of 0.5 to 1.5 g/s.

A fine powder of brown color was obtained as a result of plasmoc hemical synthesis under the specified conditions. This powder, according to the results of x-ray phase analysis, is practically a single-phase $\alpha$-$\text{Fe}_2\text{O}_3$ in figure 4.

As a result of the performed experiments, it was shown that it is possible to organize a continuous process of ferrite production using a plasma-chemical reactor based on a high-voltage alternating current plasma torch.

The following particle size distribution has been obtained, it is shown in figure 5.

Based on the broadening of x-ray diffraction lines, Scherrer’s formula estimated the mean crystallite size, which was $57 \pm 6$ nm. The estimation of the size of $\alpha$-$\text{Fe}_2\text{O}_3$ nanocrystals thus obtained correlation with the results obtained by the method of light-dynamic scattering in figure 5.

According to these data, the obtained iron(III) oxide nanoparticles have a submicron size ranging from a few tens to several hundred nanometers. This indicates that the products of plasma-chemical synthesis are both $\alpha$-$\text{Fe}_2\text{O}_3$ nanocrystals and their agglomerates from a relatively small number of particles. Thus, the presented method looks promising from the point of view of slightly agglomerated oxide nanocrystalline powders production.

5. Conclusion

The possibility of $\alpha$-$\text{Fe}_2\text{O}_3$ nanopowder production under conditions of the plasma-chemical synthesis using a continuous reactor based on an alternating current plasma torch was shown. The produced nanocrystals of iron oxide have an average size of $57 \pm 6$ nm and are slightly agglomerated with each other, which makes it possible to consider this synthesis method as promising for the synthesis of oxide nanopowders from aqueous solutions of their salts.
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