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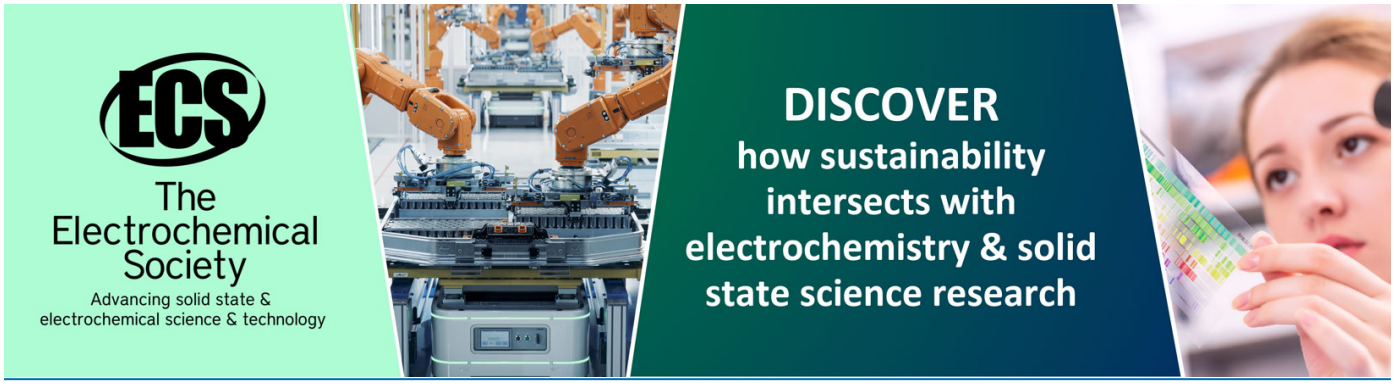

Metal ferrites synthesis by AC plasma torch

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Abstract. The article describes the ac air plasma torch with the supply of a liquid aqueous solution of iron (III) nitrate of (mol/l). When the solution is heated, water evaporates, and the iron nitrate is converted to a solid residue (mainly iron oxide). The obtained samples were collected on a heated filter to prevent condensation of water and nitrogen dioxide. The obtained samples were investigated by the X-ray diffractometer and the scanning election microscope with an elemental analyser. The proposed plasma method can be applied to the synthesis of ferrites of various metals.

1. Introduction

Iron oxide III is used for the production of abrasives (for polishing machine components), dyes, magnetic recording devices, catalysts for dehydrogenation and ammonia production. In industry, two methods of its preparation are used: thermal decomposition of iron salts (sulfate or iron nitrate III), dehydration of FeO(OH) (hydrated iron oxide). However, obtaining nanosized iron oxide is a complex technical task. One of the possible ways of its production can be plasma synthesis. There are several variants of such a synthesis: plasma treatment of iron oxide, oxidation of metallic iron by oxygen, thermal decomposition of iron nitrate III. In the first case, large particles with a size of tens and thousands of microns are formed. For the second method, it is necessary to use pure iron, and the process becomes a fire hazard due to the high activity of metallic iron. The auxiliary methods for their production are hydrothermal [2] and glycine-nitrate synthesis [3]. In addition to these methods, there is information on the production of oxides by the plasma from a mixture of metallic powders [4] and the corresponding oxides [5]. For example, Zajíčková et al. [6] obtained iron oxide nanoparticles by heating the carbonyl iron with a microwave plasma.

The 360 W plasma torch operated on a mixture of $CH_4/H_2/Ar$ (42/430/1540 sccm) and gaseous $Fe(CO)_5$. The nanoparticles were a mixture of various iron oxides (Fe_3O_4 and Fe_2O_3) with an average diameter of 80 nm (in the spherical approximation).

A more productive laboratory setup consisted of a plasma torch with a power of 50 kW (3 MHz) and a plasma reactor connected to a filter [7]. Argon was used as plasma-forming gas, the powder processing gas consisted of a mixture of Ar and H_2. Pure metal powders (nickel and iron) were introduced into the Ar using as the carrier gas. Air was fed into the reaction chamber as an oxygen source to oxidize the

nanoparticles. XRD showed that most metals turned into zinc ferrite. However, the authors recognize that Fe_3O_4 and $NiFe_2O_4$ are almost identical, so they are almost impossible to distinguish. The particle size decreased from 20–30 μm to 20–30 nm.

Iron oxide nanoparticles were obtained using a DC plasma torch [8]. The plasma torch operated with the highest rated current of 250 A and helium was added to the main argon stream to achieve a power of 6.7-7.0 kW. The results showed that higher power and mass flow rate of helium leads to the production of particles with superparamagnetic properties. Gaseous ferrocene $(C_5H_5)_2Fe$) with a saturated vapor pressure of 1.165 Pa and oxygen were introduced into the inert gas plasma. In this case, magnetite (Fe_3O_4) was formed with a small admixture of maghemite (γ-Fe_2O_3), as well as hematite (α-Fe_2O_3). The produced material consisted of individual crystallites (8-9 nm) and of small agglomerates with a maximum size of ~ 30 nm.

2. Experimental part

The experimental setup consists of a single-phase AC plasma torch, the plasma reactor, the precursor feed system, and the power supply system.

The plasma torch is connected to a high-voltage three-phase power source, shown in Figure 1. It is assembled from standard electrical components: reactive power compensator, current-conducting inductance (LL), step-up transformer (T) (380/6000V, 50 Hz), measuring transformers (TI and TU) and current sensors (DI) and voltage sensors (DU). The power source is described in more detail in previous studies [9].

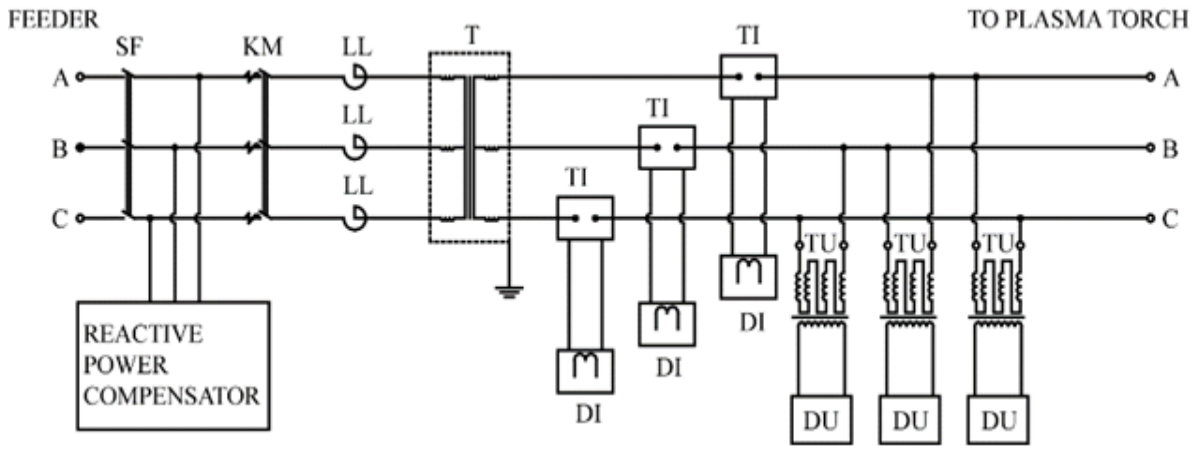

Figure 1. Plasma torch power source.

Air was chosen as the plasma-forming gas, its flow rate was varied from 1 to 1.5 g/s. The electric power of the plasma torch was maintained constant throughout the experiment and was 6 kW. The plasma-chemical reactor is made of stainless steel pipe with an internal diameter of 50 mm. The nozzle for the supply of precursors was located perpendicular to flow of the air plasma. Iron III nitrate (99.5% wt of the basic substance) was chosen as the precursor. The concentration of the aqueous solution of the precursor was 0.1 M, the mass flow rate of the precursor solution was 0.01 g/s. The basis for the synthesis of iron oxide nanoparticles is the thermal decomposition of metal nitrates with the formation of oxides:

$$4Fe(NO_3)_3=2Fe_2O_3+12NO_2+3O_2 \quad (1)$$

When relatively small particles of aqueous solutions are formed in the plasma stream, corresponding particles of iron oxide should be formed. At the same time, much smaller particles can be obtained in comparison with the plasma treatment of solid powders. The iron oxide particles were collected on a

metal target at a temperature above the condensation temperature of water and nitric acid, which can form when water interacts with nitrogen dioxide (121° C for 70% HNO_3).

3. Experimental part

During the test, the mass-average temperature of the mixture of plasma and precursor aqueous solution did not exceed 1600 °C. Thus, the formed particles of iron oxide did not turn into a liquid phase. This ensured the formation of particles only due to the evaporation of water and the reaction (1). Two samples of oxide particles were collected on the metal target. Their composition and properties were determined using an X-ray diffractometer and an electron scanning microscope.

Figure 2 shows the diffraction pattern taken on a SHIMADZU XRD-7000 X-ray diffractometer (Cu Kα (λ = 1.5046 Å)).

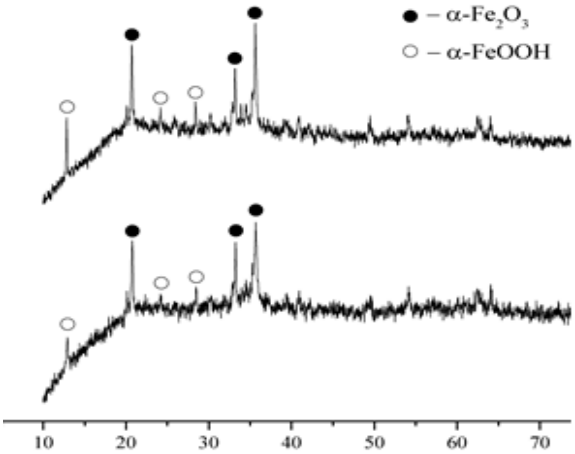

Figure 2. Diffraction pattern.

From figure 2 it can be seen that α-iron oxide and limonite dominate in the crystalline phase. Most of limonite was formed as a result of the interaction of iron oxide particles with moist atmospheric air.

To determine the elemental composition of the samples, elemental analysis was performed (energy dispersive X-ray spectral analysis) using a attachment (EDAX FP 2012/12) of Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM). The error in determining the content of elements by this method varies depending on the atomic number of the element and an average data is ± 0.3 % mass. Figure 3 shows micrographs of samples at different magnifications, from which it can be seen that the formed particles have a complex shape and are agglomerates of smaller particles.

The basic composition of the powder is as follows: O - 59.65% mol., Fe - 34.58% mol., Ni - 0.35% mol., Cu - 0.86% mol., Cr - 0.89% mol., other metals - 2.61% mol. The presence of metal impurities is explained by the interaction of the electric arc with the plasma torch case (stainless steel) and electrodes (copper).

The results show that the formation of several oxides is possible with the plasma-thermal treatment of several metal nitrates. At the same time ferrites of metals (including rare earth metals) used in microelectronics can be formed. For this, it is necessary to ensure minimum crystallite sizes, since relatively large particles rapidly decompose into two corresponding oxide phases. This is due to the high surface tension of the corresponding pure oxides.

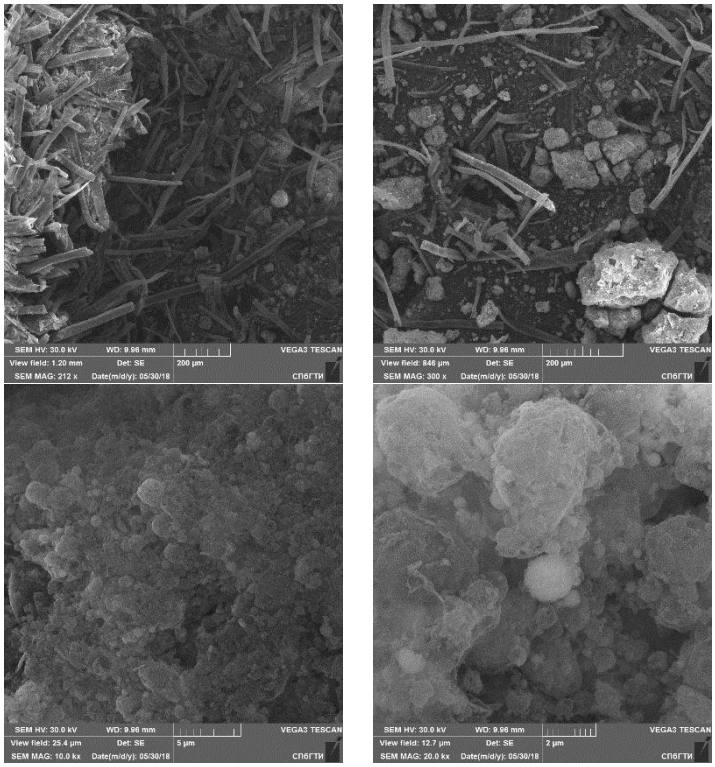

Figure 3. Micrographs of iron oxide samples.

4. Conclusions

During the experimental study of the method of plasma-thermal decomposition of metal nitrates, it was established that this method can be applied to the synthesis of nanoparticles of the corresponding oxides. The use of aqueous solutions leads to the formation of oxide particles of irregular shape. An increase in the mass-average temperature will certainly lead to the spheroidization of these particles, but their sizes will be difficult to control (most of them will be distributed over the Gaussian distribution). Since the solubility of most nitrates is very high, complex oxide systems can be synthesized, including rare-earth ferrites. The formation of such oxide systems is a complex technical task that can be implemented in the presented single-stage plasma synthesis.

5. Acknowledgments

This work was supported by Programs of Fundamental Research of the Presidium of the Russian Academy of Sciences No. 31 and by the Russian Science Foundation (project No. 16-13-10252).

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