Plasma chemical technology for processing rare earth elements in the production of nano-powder

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Abstract. The development and application of a plasma chemical method for producing dispersed materials were considered. A laboratory facility was designed to experimentally investigate the plasma chemical method aimed at producing dispersed oxides of several rare earth metals. The basic physical and chemical properties of synthesized titanium, zirconium, cerium and yttrium oxides were studied. Properties of raw materials and final products were investigated by advanced physical and chemical methods. The factors that influence the composition and quality of produced powders were determined. With increasing concentration of a metal nitrate solution in the range of 20-100 g/L, the average particle size of a powder is found to increase from 0.03 to 1 µm.

1. Introduction

Nowadays, rare earth metals (REMs) are actively used in a number of advanced high-tech industries, including electronics and radio equipment, instrumentation, semiconductor materials in the nuclear power industry, as well as composite materials.

The development of new methods for synthesizing advanced materials with specified functional properties is an ongoing challenge, which is associated with a steady trend towards expanding applications of advanced materials for the last 10-15 years.

The essential conditions that determine high performance of functional materials and products based on them include uniformity of chemical and phase compositions, as well as a uniform morphological structure of synthesized products. Much attention is paid to synthesis of fine, especially nanoscale materials and nanostructured films, including those based on REMs.

Functional characteristics of polycrystalline materials are greatly influenced by the presence of impurities that are usually concentrated at grain boundaries. In most cases, it is necessary to use high-cost ultrapure reagents for synthesizing or purify raw materials by special methods. An important requirement for production of functional materials is to use simple equipment, as well as low-cost raw materials and reagents.
2. Description of the laboratory facility and plasma chemical method of synthesizing dispersed materials

Plasma chemical synthesis methods that enable production of highly dispersed and high-purity materials of desired composition with uniform distribution of components have become the most common practice of synthesizing powdered materials based on REMs and their oxides. The plasma chemical process does not require chemical reagents for sedimentation and separation of sediments from mother solutions, as well as such labor-intensive operations as drying and baking. This method reduces a number of process stages, eliminates processing of waste solutions, and minimizes their volume to the level not exceeding initial solutions [1–14]. In addition, waste solutions can be recycled for preparing starting reagents. The plasma chemical method allows materials to be synthesized in the shortest possible time ($10^{-3}–10^{-1}$ sec).

The flow chart of the plasma chemical process used to study processing of aqueous salt solutions is shown in figure 1.

![Flow chart of plasma chemical process](image)

**Figure 1.** The flow chart of processing aqueous REM salt solutions in the plasma chemical facility.

Plasma thermal denitration of aqueous metal salt solutions followed by conversion to oxide powders in a plasma stream carried out in the working space of the plasma chemical facility.

The plasma chemical facility (figure 2) used to synthesize a cerium dioxide powder consists of a high-frequency generator with a power source (1), a plasma torch (2), a compressed air supply system (7, 16, 17), a gas supply system for plasma ignition (8, 19), an aqueous salt solution supply system (3, 9, 18), a battery of cyclones (6), and an exhaust gas purification system (10, 11, 12). A high-frequency induction plasma torch is used in the plasma chemical facility. The plasma torch consists of a water-cooled metal case and a quartz tube that reduces heat loss in the discharge zone, as well as excludes “shorting” of the high-frequency discharge channel to the metal case of the plasma torch, especially at the time of excitation and generation of a high-frequency discharge. A high-frequency discharge is excited using a copper rod introduced into the discharge zone through an opening in a Teflon insulator. The plasma torch is designed with vortex stabilization of plasma for thermal protection of
the chamber walls. For this purpose, the plasma-forming gas supply section with a tangentially oriented ring is secured to the upper part of the quartz tube. At the bottom of the plasma torch, the quartz tube is directed to the nozzle section (solution supply section) made of stainless steel.

**Figure 2.** Schematic diagram of the plasma chemical facility for producing dispersed materials from metal salt solutions.

A gas-droplet mixture is heated to the boiling point in the plasma-chemical reactor (4) by a plasma jet generated in the plasma torch. Water rapidly evaporates, while salt residues are decomposed to oxide according to the pattern:

\[ Me(NO)_x + HNO_3 + H_2O \rightarrow MeO_x + NO + NO_2 + H_2O, \]

where \( Me = Ti, Zr, Ce, Y. \)

The produced powder is separated using the filter and delivered to the product collector (5). The vapor-gas flow is cooled in a refrigerator, released from the liquid, purified in the scrubber and then vented to the atmosphere.

### 3. Experimental part

Aqueous salt solutions of zirconium, titanium, cerium and yttrium were used as raw materials for producing powder oxides. Experimental solutions at the metal concentration of 20, 30, 50, 70, 90, and 100 g/L were prepared. For each experiment, the respective sample was dissolved in one liter of distilled water. The solution was filtered and transferred to a pressure vessel (9) for feeding into the plasma reactor (4).

Morphological characteristics of the structure were analyzed using the SEM 515 scanning electron microscope with an EDX detector. The powders were prepared for electron microscopy studies by depositing them on a coal substrate produced in the VUP-4 vacuum plant. Average particle and grain sizes of the powder were determined by solid geometry methods. Thickness of the diffraction ring was
measured photometrically using the MD-100 densitometer (thickness was taken equal to the width of
the intensity profile at the half-height of the peak).

The electron microscopy studies of produced oxides demonstrate that the basic morphological
components of polycrystalline powders include polycrystalline hollow spheres and their fragments –
transparent polycrystalline films and irregularly shaped particles figure 3. The average size (diameter)
of these spheres is 0.77 µm, while their grains reach 31 nm in diameter. Solid spherical single crystal
structures of metal oxides (opaque irregularly shaped particles) occurred less frequently.

The specific surface area of powders was measured using the ID 188 device by the low-
temperature nitrogen adsorption method. The X-ray phase analysis was performed by the DRON-UM1
unit with filtered copper radiation. Radiographs taken in accordance with were used to determine the
quantitative phase composition, calculate lattice parameters and size of the coherent scattering region.
Furthermore, large variation of particle sizes (from 0.05 to 5 µm) was observed in all experimental
powders, while the size of crystallites in polycrystalline particles does not exceed 20–30 nm.
Depending on the salt concentration in the solution, proportions of powder particles with different
morphology changed. With increasing a salt concentration in the solution, the specific surface area of
particles was continuously increasing. Such changes in the specific surface area could be associated
with both changes in the particle size and changes in quantity of its transparent and opaque particles
depending on a salt concentration in the solution. A higher salt concentration in the solution is
 correlated with a greater number of powder particles in the form of hollow spheres and, therefore,
higher specific surface area.

4. Conclusion
The following conclusions can be made on the basis of the research results:
1) powders of titanium, zirconium, cerium and yttrium oxides produced by the plasma chemical
method are finely dispersed materials;
2) the structure of the synthesized materials contains crystalline and amorphous modifications; the
possibility of generating both hollow and filled with spherical particles has been demonstrated;
3) the average particle size of the powder increases with a salt concentration in the solution.
Based on the completed studies, the process conditions were developed to control dispersity of
materials by changing concentrations of initial metal salt solutions. The strengths and weaknesses of
plasma chemical processes discussed above suggest that plasma is a feasible way to produce and
process a variety of desired products.
Acknowledgments
The results were obtained within the framework of the state task of the Ministry of Education and Science of Russia, project No. 10.3031.2017 / 4.6 and with the support of the TSU Competitiveness Program.

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