

Possibilities of production of nanopowders with high power ELV electron accelerator

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Abstract. Electron-beam evaporation of various natural and industrial materials in the atmosphere of different gases at atmospheric pressure can be used for the synthesis of nanosize powders. These powders are characterized by high purity and may exhibit unusual properties. In particular, nanopowders of silicon dioxide and oxide (SiO_2 , SiO), magnesia (MgO), alumina (Al_2O_3), titania (TiO_2), gadolinium oxide (Gd_2O_3), various metals (tantalum, molybdenum, nickel, aluminium, copper, silver), semiconductor (Si), nitrides (AlN, TiN), and some other substances had been produced. The process of nanopowder synthesis is highly effective; in particular, the yield of oxides can exceed ten kilograms per hour.

Keywords. Nanoparticles; electron accelerator; evaporation.

1. Introduction

The synthesis and characterization of fine powders of various substances is an essential trend in modern science and technology. This importance is related, on the one hand, to the practical need for new materials that can sometimes be developed only on the basis of powder components and, on the other hand, to the basics of very small particles (in particular, those with dimensions below 100 nm) within the rapidly developing ‘nanotechnology’ area. Special attention is devoted to the creation of highly effective methods for the synthesis of nanopowders, because the efficiency of most methods especially for production the nanopowders of metals, nitrides and carbides is still very low.

This investigation was aimed at the possibility of nanosize powder production of different substances by means of evaporation of various natural and synthetic (technogenous) materials by electron accelerator in the atmosphere of various gases at atmospheric pressure, followed by cooling of the high-temperature vapour and collection of the deposited particles. Previously, an electron accelerator had been used already (Ramsay and Avery 1974) for the synthesis of fine oxide powders, but the process was carried out at low power (~ 1 kW), pre-

ssure and efficiency. On the whole, the method used in current research can be classified into condensation technologies for fine powder production of refractory substances. To the best of our knowledge, the first use of a CO_2 laser for powder production was reported by Kato (1976) where the process was also performed at low power, pressure and efficiency. The use of plasma generators in the condensation technology of ultradispersed powders dates back to approximately the same period of time (see e.g. Barnes and Barby 1970). In comparison to laser and plasma technologies, the proposed method has the advantage that the energy is released inside the target substance rather than at its surface.

2. Experimental

The experiments were performed on a commercial 100 kW accelerator of the ELV type (figure 1), whose special features are the high electron energy (1.4 MeV) and the possibility of extracting the electron beam directly into atmosphere. Electrons move at relativistic velocities and their mean free path length in air reaches 6 m. The beam power density can be as high as 5 mW/cm^2 , which makes possible both the evaporation of refractory substances under atmospheric conditions and the high-temperature gas-phase synthesis. Other advantages are a high efficiency of the direct conversion of electric energy into thermal energy in the heated material, a high rate of heat-

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ing (above 1000 K/s), and the ‘chemical purity’ of the electron beam. The initial solid material is evaporated inside the reactor, after which the vapour is transported from the zone of heating, diluted and cooled (with air or some other carrier gas). Finally, the solid nanoparticles are collected (in a powder form) inside the corresponding parts of the facility. Evaporation chamber of various types have been designed, in which the synthesis of nanoparticles can be performed in air, argon, nitrogen, helium and xenon. Even with incomplete (below 50%) use of the accelerator power, the nanopowders of some materials were obtained with a yield of several kilograms per hour.

Various nanopowders were synthesized and their properties were studied using transmission and scanning electron microscopy (TEM, SEM), X-ray diffraction (XRD), specific surface measurements, chemical analysis and some other techniques. The XRD measurements were performed for all samples after a comparatively long period of time upon synthesis. The possible fields of application of the obtained nanopowders were evaluated.

In particular, oxide nanopowders have been synthesized. White silicon dioxide (SiO_2) nanopowder with a blue tint was obtained by evaporation of high purity (99.6%) quartz sand (of Tashlinskiy ore mining and processing enterprise, Russia, $\alpha\text{-SiO}_2$, ICPDS card number 46-1045) of sublimation temperature 3000°C. The process was carried out in air at a flow rate of 900 m³/h. The rate of target evaporation reached 6–7 kg/h at a maximum accelerator power of 70 kW. Various SiO_2 powders were obtained, but the product was X-ray-amorphous in all series of the samples. In addition, all samples were characterized by high chemical purity, even when the initial

material had a relatively high content of impurities, their concentration in the final powder was much lower than in the target. This result indicates that the electron-beam evaporation is accompanied by the separation of substances and by the binding of impurities in the melt (probably, with the formation of low-volatile aluminosilicates). In particular, the concentrations of Al, Fe and Ti (recalculated for oxides) in the collected nanopowder were below 0.020, 0.015 and 0.002 wt.%, respectively, which was several times lower than the level of these impurities in the initial material. On the whole, the content of SiO_2 in the final nanopowder was above 99.6%.

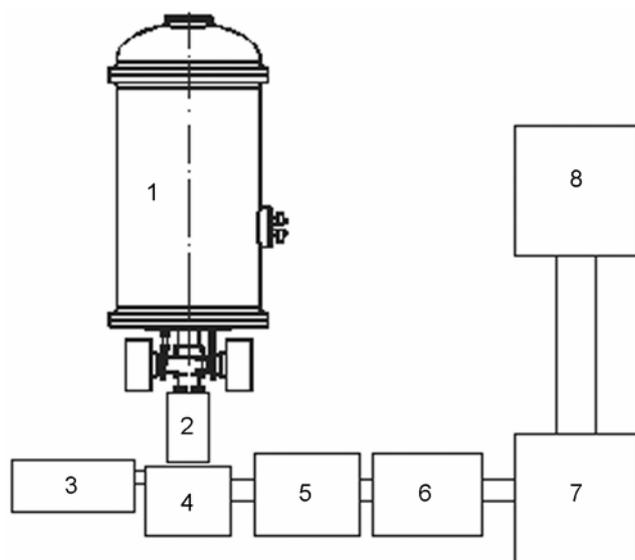


Figure 1. Technology line for the nanopowders production: 1. electron accelerator; 2. focused electron beam extraction device; 3. raw material supplier; 4. high temperature evaporation chamber; 5. large fraction precipitator; 6. cooling line; 7. filter (or cyclone) and 8. fan.

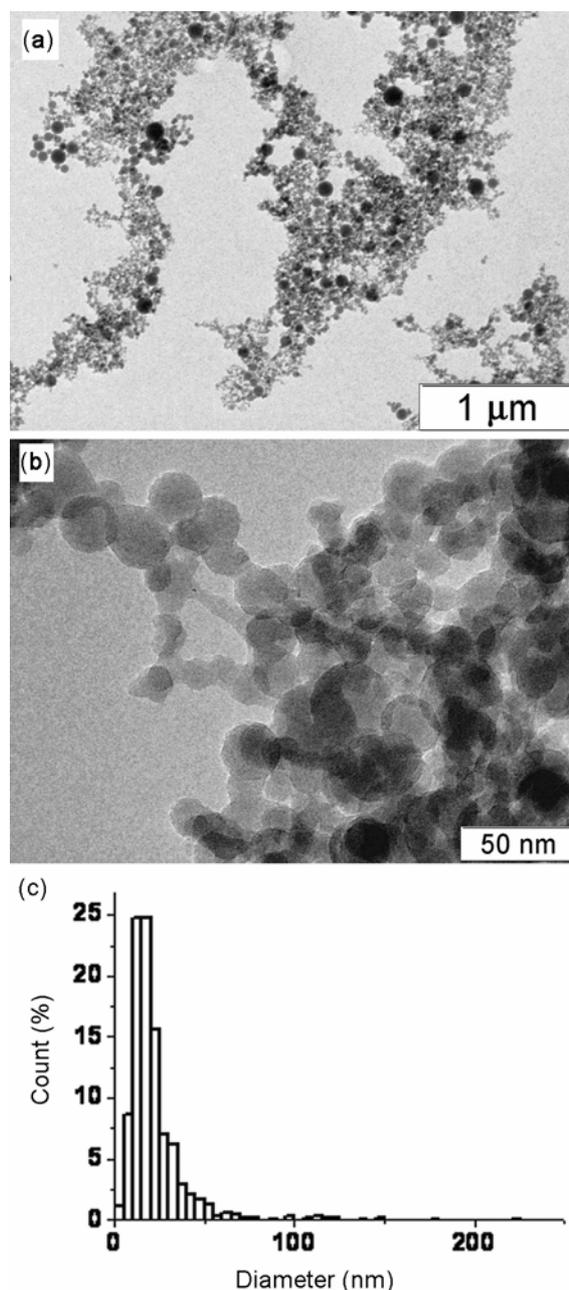


Figure 2. TEM of silica nanopowder: (a) and (b) different magnification, and (c) particle size distribution.

3. Results and discussion

The results of the specific surface (S) measurements based on the nitrogen adsorption showed that, depending on the regime of synthesis, this value ranged from 20 to 200 m^2/g , which implies that the average particle radius in the obtained nanopowders varied from 14 to 140 nm. The sample of the TEM micrograph for $S = 180 \text{ m}^2/\text{g}$ illustrating silica nanoparticles is presented in figures 2a and b, which shows that nanoparticles form relatively large agglomerates. The particle size distribution is pretty narrow (figure 2c). It should be noted that SiO_2 powders did not change their specific surface and remained X-ray amorphous upon prolonged storage in air under uncontrolled humidity conditions. The results of tests showed that SiO_2 nanopowders synthesized using the proposed method can be successfully applied, at least in several fields traditional for the use of highly dispersed silica.

The clean commercially available magnesia powder (MgO) was first melted before the evaporation in air. The nanopowders produced after melt evaporation of this substance had average particle size of ~ 80 nm and a minimum size of about 20 nm estimated from X-ray analysis and supported by electron microscopy (figure 3). One can see agglomerates again, but in contrast to the case of silicon dioxide, magnesium oxide particles possessed a crystalline structure (periclase; ICPDS card 45-496) with standard values of the crystal lattice parameters, and cubic shape nanoparticles, pointed by arrows, are clearly seen. Bulk density measured after some period of time was about 130 g/l. It should be noted that immediately after the experiment it was approximately three times less. The interaction of magnesia with H_2O and CO_2 of air after some time can be a reason. The magnesia nanopowder could also be obtained with rather high efficiency.

In addition to the above two oxides, the alumina (Al_2O_3), silicon monoxide (SiO), titania (TiO_2) and gadolinium oxide (Gd_2O_3) nanopowders were obtained in

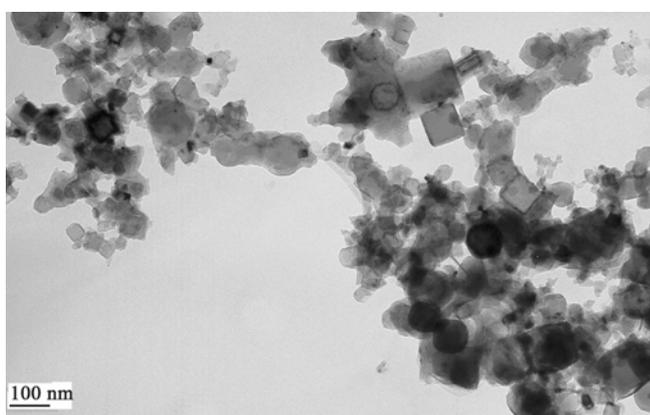


Figure 3. TEM of magnesia nanopowder. Arrows show the examples of cubic shape nanoparticles.

much smaller amounts compared to the yield of, for example, SiO_2 , which was mostly related to a lower beam power and vapour pressure. In particular, the rare-earth Gd_2O_3 oxide at this stage mostly had been tested with the objective to estimate the yield, which was about few grams for 40 kW. Figure 4 illustrates that nanoparticles of Gd_2O_3 have the size less than 100 nm and form the chain-like agglomerates.

The possibility of metal nanopowder production was mostly studied during their evaporation in argon at a pressure slightly above atmospheric. In order to determine limitations of the proposed technology, we tried to evaporate compact tantalum (of sublimation temperature about 5500°C). The product, which was obtained at a significant yield, represented a black conducting powder with a cubic metallic phase (ICPDS card 4-7883) and an orthorhombic Ta_2O_5 phase (ICPDS card 25-922). The powder had a specific surface of 7–10 m^2/g , which corresponded to an average particle size of about 50 nm (but TEM micrographs of some samples showed the presence of some coarse particles with dimensions reaching 500 nm).

Generally, the same results were obtained for molybdenum (of sublimation temperature about 4800°C). This powder had a black colour with blue tint and consisted of nanodimensional particles. The smallest particles were about 20 nm in size but had variable shapes. The X-ray data showed that the powder consisted predominantly of pure molybdenum (42-1120) with admixtures of the monoclinic MoO_3 (47-1320), orthorhombic MoO_3 (32-671) and MoO_2 (32-671) phases; the total impurity content was below 20%. (The possible reason of oxides appearance is the existence of oxygen inside and at the surface of evaporated compact metal, due to the consequent oxidation in air.) A joint analysis of these results with allowance for the TEM data suggested that particles of various shapes have different phase compositions. Being evapo-

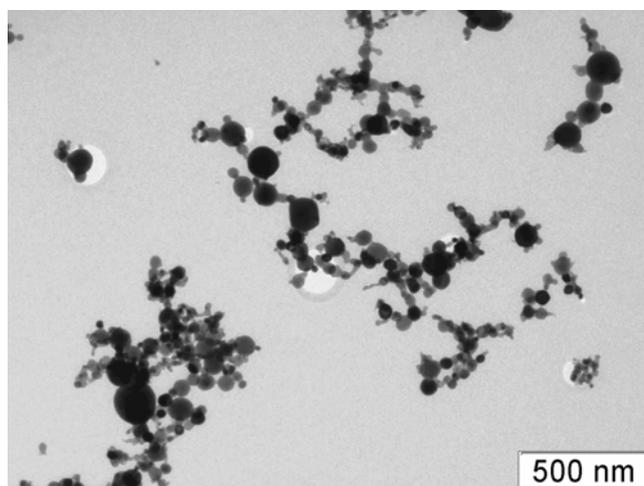


Figure 4. TEM of gadolinium oxide nanopowder.

rated in argon and rapidly extracted from the experimental set up, nickel (possessing a relatively low sublimation temperature 2900°C) had the form of a grayish-black powder. The product volume rapidly decreased, and its specific surface changed from the initial value of 3.2 m²/g (that corresponded to an average particle size of approximately 200 nm) to about half of this value. Nevertheless, the obtained particles represented to within experimental accuracy pure nickel (4-850) with equilibrium crystal lattice parameters.

The evaporation of an aluminum target in nitrogen under certain conditions led to the formation of an aluminum powder with a small (~1 wt%) content of aluminum nitride. In contrast to what was expected in view of the well-known pyrophoric properties of fine metal powders, this aluminum powder (as well as the nickel powder described above) did not exhibit self-ignition in air. In contrast, the powders of aluminum and nickel obtained using an electric-wire explosion technology usually require a long period of controlled oxidation prior to being transferred into the atmosphere. Such a behaviour was typical of most metal powders synthesized during this research in argon, nitrogen and helium, although these powders (except for silver), burned at different rates in an open flame, applied in the following tests. This is probably related to the more equilibrium conditions of synthesis as compared to those for the electric-wire explosion technology, or it can be due to certain features of the formation of particles in the presence of electrons and gamma radiation. It should also be noted that the powders of tantalum, nickel, aluminum and silver obtained in an argon atmosphere retained electric conductivity for a more or less prolonged period of time.

Nevertheless, at least for some of the synthesized powders, it was established that the nanoparticles were formed under substantially nonequilibrium conditions. This circumstance was manifested in both the structure and properties of the material. In particular, a silicon nanopowder obtained using the electron-beam evaporation in argon possessed, albeit representing pure silicon (27-1402), a distorted lattice with the parameter $a = 0.5437$ nm (instead of 0.5430 nm). In response to the UV irradiation, this powder exhibited photoluminescence in the blue visible spectral range (Efremov *et al* 2004). The different silicon nanopowders were produced including wire-like silicon nanostructures (figure 5). Silver nanoparticles (of the maximum and minimum size of about 1000 nm and 50 nm obtained by the evaporation in argon) contained a significant number of defects and other structural features and exhibited high catalytic activity (Korchagin *et al* 2005).

A nanopowder containing 60–70 wt% of hexagonal aluminum nitride (25-1133) (and the phase of metallic aluminium Al (4-787)) and possessing a specific surface of 7 m²/g was obtained by evaporation of aluminum in nitrogen under certain conditions. The XRD spectrum is

presented in figure 6. The powder consisted of various particles with a rather complicated morphology. Some particles had a relatively large size (several microns), an approximately spherical shape and a developed flaky surface containing a large number of smaller particles with dimensions below 100 nm. In addition, the powder contained unusual extended and mushroom-shaped structures with transverse dimensions below 200 nm. This powder reacted with water, which was accompanied by the origination of gaseous ammonia. This behaviour resembled the phenomenon reported by Il'in and Gromov (2002) for a superfine aluminium nitride obtained by means of electric-wire explosion. Apparently, aluminum nitride nanoparticles obtained in present research were also highly reactive. Indeed, being tested in ceramic technology, this nanopowder exhibited an almost complete conversion of the metal aluminum into aluminum nitride comprising a mixture of cubic (34-679, about 70%) and hexagonal (25-1133, about 20%) phases.

A nanopowder with a specific surface of 28 m²/g was obtained by evaporation of a titanium nitride target in a nitrogen atmosphere. The product appeared as a black powder with blue tint and contained a pure cubic titanium nitride phase (38-1420). Particles of the corresponding

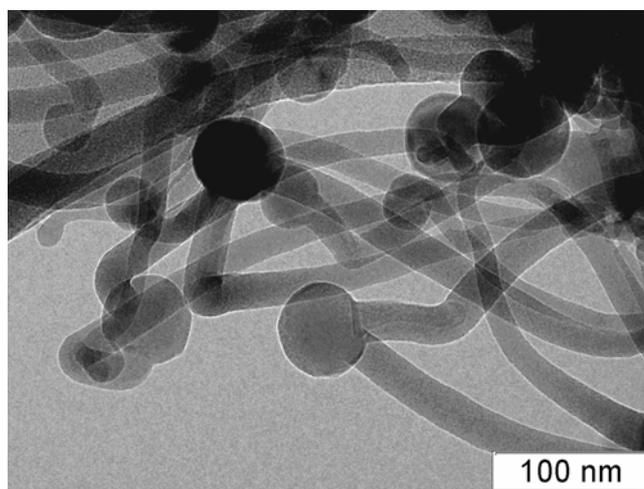


Figure 5. TEM of silicon nanostructures.

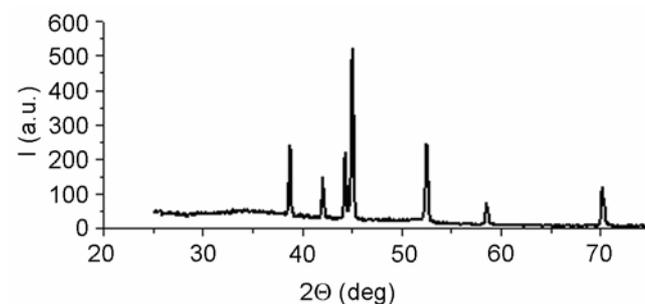


Figure 6. XRD spectrum of AlN nanopowder.

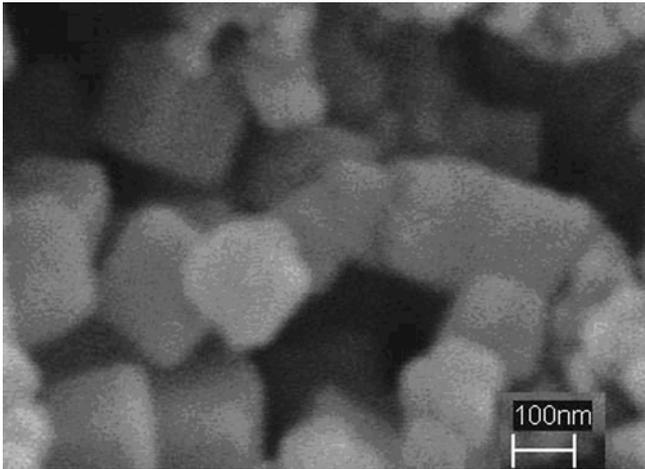


Figure 7. SEM of titanium nitride nanopowder.

shape are clearly distinguished on TEM micrographs (figure 7). However, this powder also contained a large fraction of straight filaments with lengths of up to several microns and a transverse size within 100–500 nm. The surface of these filaments was, in turn, covered by smaller particles with dimensions below 100 nm. Being pressed into pellets, this material exhibited electric conductivity.

4. Conclusions

The results show that electron-beam evaporation of various natural and industrial materials in an electron accelerator in the atmosphere of various gases at atmospheric pressure can be used for the synthesis of nanopowders. These powders are characterized by high purity, exhibit unusual properties, and can be used in different applications (electronics, catalysis, ceramics, composites, etc.).

In particular, the following nanopowders had been produced: silica and silicon oxide (SiO_2 , SiO), magnesia (MgO), alumina (Al_2O_3), titania (TiO_2), gadolinium oxide (Gd_2O_3), various metals (tantalum, molybdenum, nickel, aluminum, copper, silver, and other), nitrides (AlN , TiN), semiconductor (Si) and some other compounds. An important feature of the proposed technology is that the main device of the technological set up (commercial electron accelerator) is capable of generating high power electron beam, which ensures the high temperatures necessary for the evaporation of any refractory material. The process of nanopowder synthesis is highly effective; in particular, the yield of oxides can exceed 10 kg/h.

Acknowledgements

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