Chemical Dispersion as a Method for Segregation of Ultrafine and Nanosized Powders of SHS Refractory Compounds

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Abstract

Overviewed are some results of our recent works aimed at the synthesis of ultrafine and nanosized refractory powders by self-propagating high-temperature synthesis (SHS) combined with chemical dispersing of combustion products. The possible application of SHS for preparing ultrafine and nanosized powders of refractory compounds is examined. Specific features of SHS afford to affect not only the chemical/phase composition of products but also the morphology and size of synthesized particles. Quenching experiments have shown that the primary product particles formed in the combustion wave may have a size of below 0.1-0.2 μm. By etching a ground SHS cake with appropriate solutions, one can dissolve the defect-rich layers between the crystallites and remove impurities. As a result, the sinter cake breaks into crystalline particles of the same size as the primary crystallites, without compositional changes. This process was termed chemical dispersion. The phase and chemical composition, specific surface and grain size of SHS refractory compounds powders are detected before and after treatment. The influence of the synthesis conditions and the dispersion agent on the morphology and particle size of the resultant powders are ascertained. Successive chemical dispersing of raw products (carbides, nitrides, silicides, borides, oxides of metals and nonmetals) with solutions of different acids, alkalis, and salts leads to an additional grinding of the product, an increase in the specific surface and a decrease in the particle size. So, the possibility to control the SHS processes allows changing the particle size and structure of the synthesized compounds and provides obtaining high-quality products of the preset structure. The following thermochemical treatment of the ground cake by special solutions (chemical dispersion) allows to segregate ultra- and nanosized powders of refractory compounds. Our experience in preparation, separation, and purification of SHS-produced nanopowders can be used as a basis for elaboration of general methodology for pilot-scale production of nanostructured compounds and composites.

Introduction

As compared to conventional coarse-grained materials, finely grained materials are known exhibit higher reactivity, catalytic activity, hardness, as well as new optical, electronic, and magnetic behavior. All this gave impetus to elaboration of new methods (and improvement of existing ones) for synthesis of nanomaterials. One of the most efficient ways of nanomaterial production is application of ultrafine or nanosized powders.

Specific features of SHS – combustion temperature up to 4000 ºC, heating rate 10^3-10^6 deg/s, burning velocity 0.1-10 cm/s, and simultaneous occurrence of chemical reaction and structure formation – afford to affect not only the chemical and phase composition of products, but also the morphology and size of synthesized particles [1, 2].

Quenching experiments [3, 4] have shown that the primary product particles formed in the combustion wave may have a size of below 100-200 nm. The characteristic time of such primary structure formation (10^{-3}-10^{-1} *s*) is close to that of chemical reaction. Behind the combustion wave, the size of primary particles increases in the processes of secondary structurization accompanied by collective recrystallization.

SHS products are cakes or ingots which should be processed for obtaining powders.

One of the promising methods of obtaining nanosized powders is the method microparticle dissolution. Recently, the efficiency of the dissolution processes for converting microparticle size to the nano-level has been confirmed. The method is based on the property of particles to decrease their volume uniformly due to their dissolution in acid and

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alkali media. But simultaneously the structure and the properties of the central part of the substance or phase remain the same [5]. The influence of various solutions on the powder structure, dispersion degree and specific surface area has been already studied for SHS powders of boron nitride and aluminum nitride.

After synthesis, the materials were mechanically disintegrated and subjected to thermochemical treatment in neutral, acid, and alkali media at temperatures ranging from 20 to 100 °C [6]. Such treatment is termed "chemical dispersion" of SHS products.

Chemical dispersion provided for disintegration of the materials, as well as leading to formation of new channels and pores and the appearance of new defects, finally resulting in improved specific surface.

The resultant single crystals may acquire a size of primary crystallites (below 100-200 nm) formed in the combustion wave, without marked changes in their structure and composition. In this article we will overview some results of our recent works aimed at the synthesis and chemical dispersion of ultrafine and nanosized refractory powders.

SHS from the Elements

This wide and best studied class of SHS processes can be exemplified by the following reactions:

$$Si + N_2 + R \rightarrow Si_3N_4 + R' \quad (1)$$

$$B + N_2 + R \rightarrow BN + R' \quad (2)$$

$$Mo + Si + R \rightarrow MoSi_2 + R' \quad (3)$$

where R stands for a modifying agent added to a green mixture.

It was established [7, 8], that different conditions: the composition and density of the starting mixture, ratio of reactants, their aggregative state in the combustion area, gas pressure, and the nature of adjusting additives,- influenced the size of powder particles.

We improve the extent of conversion and vary the morphology and size of synthesized particles of Si_3N_4 to use in reaction (1) different organic and inorganic compounds acting as modifying agents. Upon etching in potassium hydroxide solution, the product disintegrated into the two fractions – finely crystalline and light flaky ones – that can be separated by floating. Rounded agglomerates below 100 μm in their size (Fig. 1a) are seen to comprise of hollow 4-6 – facet rods 8-15 μm in diameter, 30-50 μm long, at a wall thickness of 0.5-1 μm. Walls of the crystals, covered by melted silicon or silicon nitride, consist inside of nanosized cores (Fig. 1b,c).

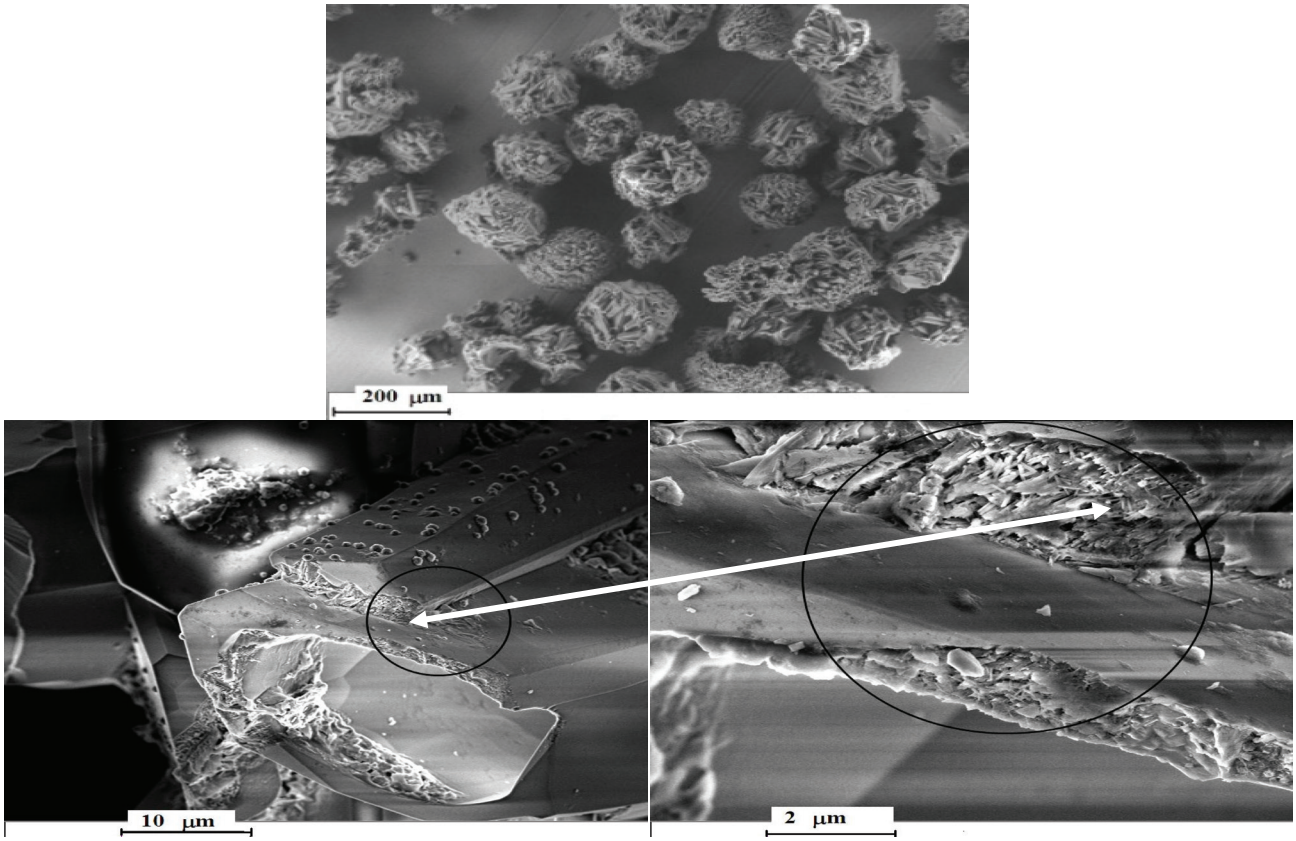

Fig. 1. Finely crystalline fraction of Si_3N_4 powders synthesized in the presence of the inorganic salt additives.

The nonequilibrium structure is as a result formed. The sphere is thermodynamically preferable form of existence for this system. Milling in a planetary mill for several minutes led to disintegration of spherical particles into ultrafine and nanosized ones, which is in-dicative of weak bonding between primarily formed particulates.

Microstructure of the light (flaky) fraction was found to depend on the type of modifying agent (inorganic salts or organic compounds) and combustion parameters. Rounded agglomerates, obtained in case of additive is inorganic salts, are seen to comprise of semi-transparent rods 200-300 nm in diameter and 2-3 μm long or of thin semi-transparent fibers 50-200 nm in diameter and 4-6 μm long (Fig. 2a). Ball-shaped agglomerates obtained in case of organic compounds as additives were found to comprise of nanoparticles below ≤ 100 nm in their size (Fig. 2b). It follows that the type of additives can affect not only the phase composition of combustion products but also the shape and size of product particles.

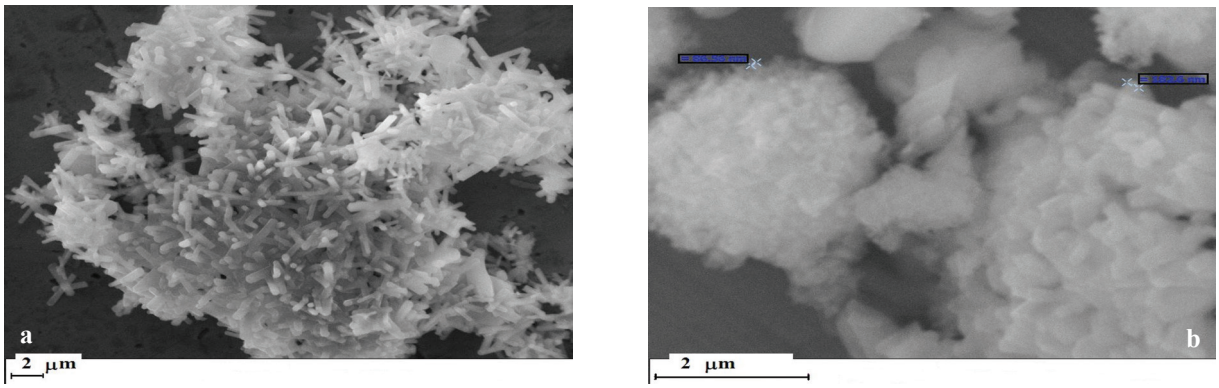

Fig. 2. Light (flaky) fraction of Si_3N_4 powders synthesized in the presence of the inorganic salt additives (a) and organic additives (b).

The particle size of SHS-produced BN powders (equation 2) is found [7] to depend on green composition and burning velocity. So, the addition of B_2O_3 as a diluent to boron was found to result in formation of finer product particles with elevated specific surface. In this case, the reaction can be assumed to proceed by the following scheme:

$$2B + 2B_2O_3 \rightarrow 3B_2O_2$$

$$B_2O_2 + N_2 \rightarrow 2BN + O_2$$

$$2B + 2B_2O_3 + 3N_2 \rightarrow 2BN + 3O_2$$

The presence of gaseous products ensures the formation of a spongy, easily crushed cake.

Washing a crushed BN–B_2O_3 raw product (Fig. 3a) with water was found to yield hollow irregular agglomerates with a size exceeding that of starting particles (Fig. 3b). These agglomerates comprise of acicular particulates below 50 nm in diameter and 2-4 μm long and of transparent platelets several nm thick.

An important drawback of powdered $MoSi_2$ and related composites is the agglomeration of particles, which diminishes the mechanical strength of resultant composites (cracking at the interface with coarse grains). The problem can be overcome by using ultrafine and nanosized starting $MoSi_2$ powders.

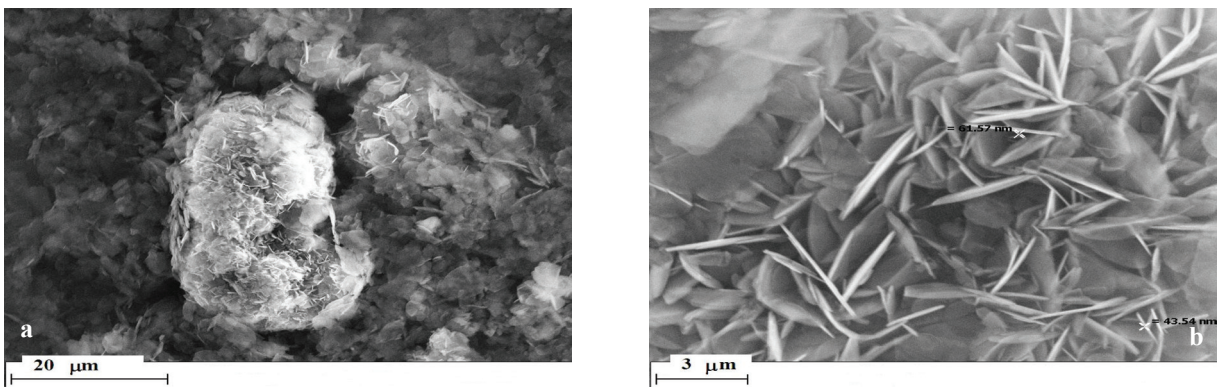

Fig. 3. Microstructure of the BN powder synthesized in reaction (3): a – before chemical dispersion; b – after chemical dispersion.

SHS reaction (3) yielded flocculent layered dark-grey cakes of $MoSi_2$ covered with a layer of unreacted reagents (Fig. 4a). After subsequent processing in the planetary mill the sintered agglomerates destroyed alongside the interfaces. This was accompanied by a 2-fold increase in the HWHM of diffraction peaks, which is indicative of decreasing particle size. Chemically dispersed such powders are seen to contain porous agglomerates formed by ultrafine and nanosized fragments (Fig. 4b).

The amount of pores (several nm in size) was found to increase with increasing processing time in the planetary mill, duration of alkali etching, and concentration of etching solution. The precipitates extracted from etching solutions (upon drying) represented soft agglomerates formed by spherical nanoparticles (< 100 nm) of $MoSi_2$ (Fig. 4c), which was also confirmed by X-ray data.

The process conditions for fabrication of ultrafine and nanosized $MoSi_2$ powders have to be optimized, which will be a subject of one of our forthcoming communications.

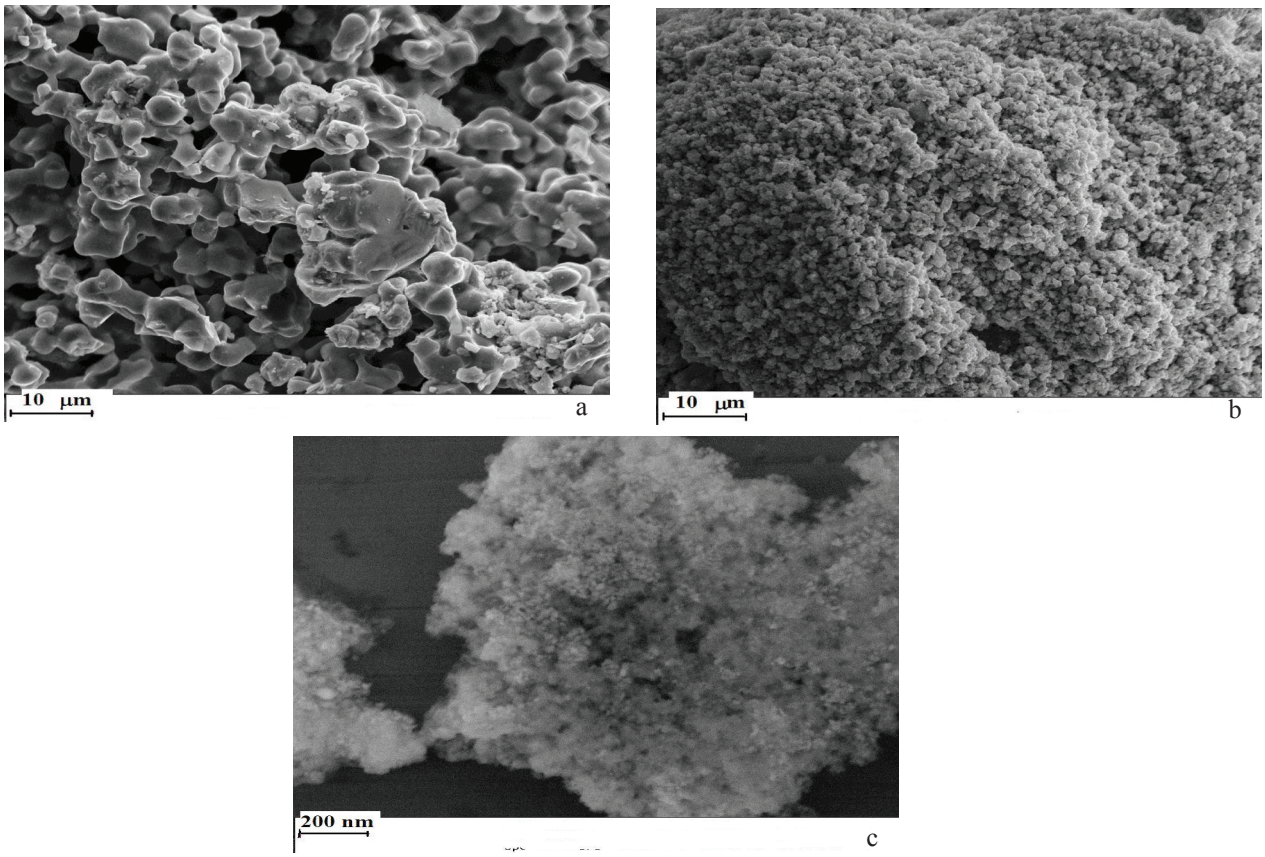

Fig. 4. SEM images of $MoSi_2$ powders: a – after diminution in the planetary mill; b – after chemical dispersion of powders in KOH solution; c – $MoSi_2$ nanoparticles extracted from etching solution.

SHS with a Redaction Stage

This class of SHS processes can be exemplified by the following reactions (for example):

$$MoO_3 + Si + Mg + R \rightarrow MoSi_2\text{-}MgO + R' \quad (1)$$

$$TiO_2 + C + Mg + R \rightarrow TiC–MgO–Mg + R' \quad (2)$$

$$TiO_2 + WO_3 + C + Mg + R \rightarrow TiC\text{-}WC\text{-}MgO\text{-}Mg + R' \quad (3)$$

It was found [8] that the particle size of synthesized powders depends on green composition, combustion characteristics, pressure of ambient inert gas, and the type of modifying additives R too.

Powders were synthesized in the conditions found to be optimal to form ultrafine and nanosized particles.

A microstructural analysis (Fig. 5) showed that the sintered products consisted of ultrafine $MoSi_2$ (a), TiC (b) or TiC-WC (c) crystallites embedded in magnesium oxide melt. In addition to magnesium oxide formed in the oxidation–reduction reaction, X-ray diffraction revealed some amount of unreacted magnesium or silicium in the intermediate product and also intermediate compounds (magnesium carbides, for example) formed in the synthesis.

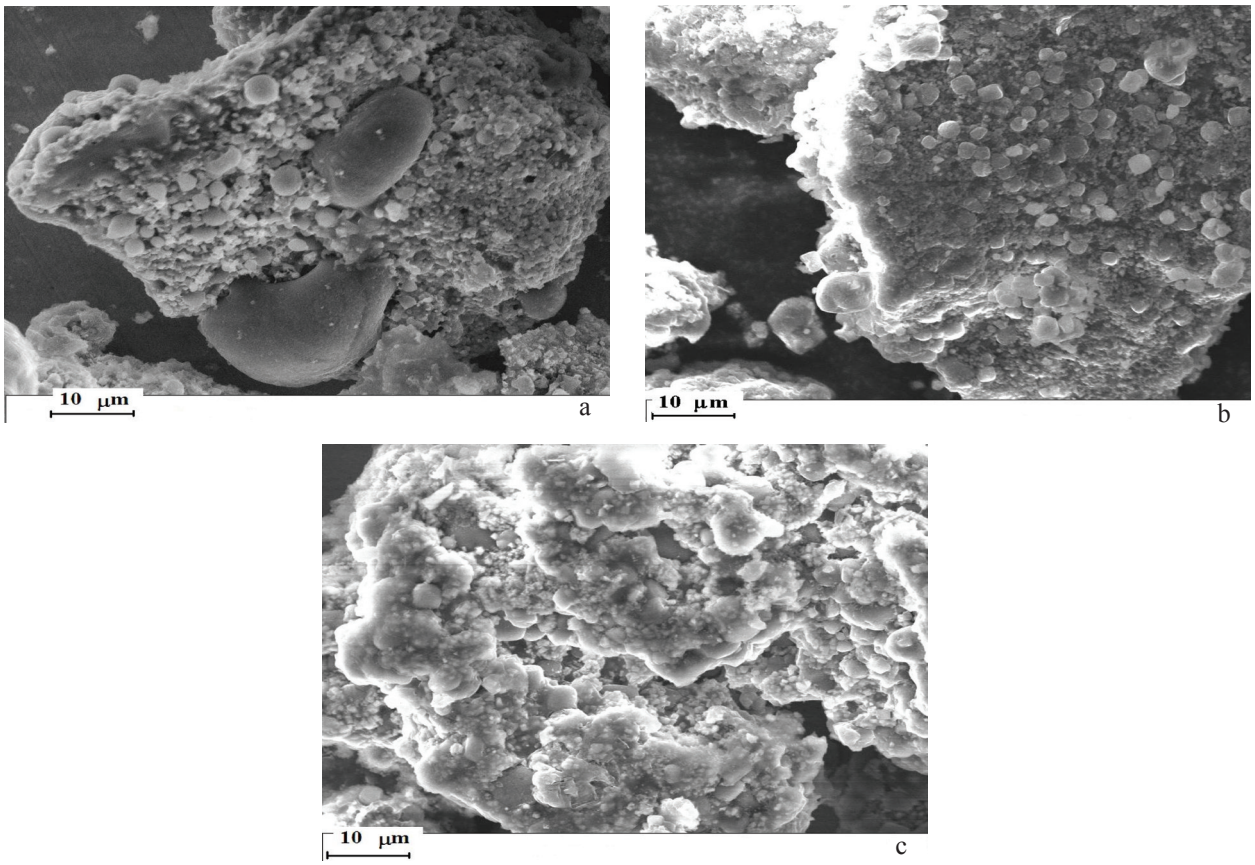

Fig. 5. Microstructure of raw products: a – $MoSi_2$-MgO, b – TiC-MgO and c – TiC-WC-MgO.

Powders were recovered from the synthesized products by dissolving magnesium, magnesium oxide, and intermediate compounds in different acid solutions. This process was called "acid enrichment". Powders resulting from acid enrichment represented large accumulations of fine particles of the main product and unreacted (free) carbon in carbides or silicium in silicides. After carbide powders had been refined with chromium mixture, the content of free carbon decreased from 1.0-5.0 to 0.02-0.2%, while the content of oxygen increased since the surface of carbide particles oxidized to form relevant oxides. These oxides and unreacted Si in silicides ($MoSi_2$) are easily dissolved in diluted alkaline solutions.

Successive chemical dispersing of raw products with solutions of different acids, alkalis, and salts have shown that this process was associated with the destruction of agglomerates caused by dissolution and wash-out of the impurities and intermediate products present in raw products. Prevailing particles were no larger than 300 nm (Fig. 6).

Based on the research, an SHS process has been developed to produce ultrafine and nanosized powders using chemical dispersion to recover, treat, and additionally refine the target product.

The data obtained in these studies of the effect of chemical dispersion on the physical parameters (specific surface, grain size) of powdered refractory compounds point to the feasibility of powder macrostructuring not only during synthesis but also by using a gentler thermochemical treatment, which from our point of view represents significant academic interest and opens new potentials for practical application.

Conclusions

The possibility to control the SHS processes allows changing the particle size and structure of the synthesized compounds and provides obtaining high-quality products of the preset structure. The following thermochemical treatment of the ground cake by special solutions (chemical dispersion) allows to segregate ultra- and nanosized powders of refractory compounds.

Our experience in preparation, separation, and purification of SHS-produced nanopowders can be used as a basis for elaboration of general methodology for pilot-scale production of nanostructured compounds and composites.

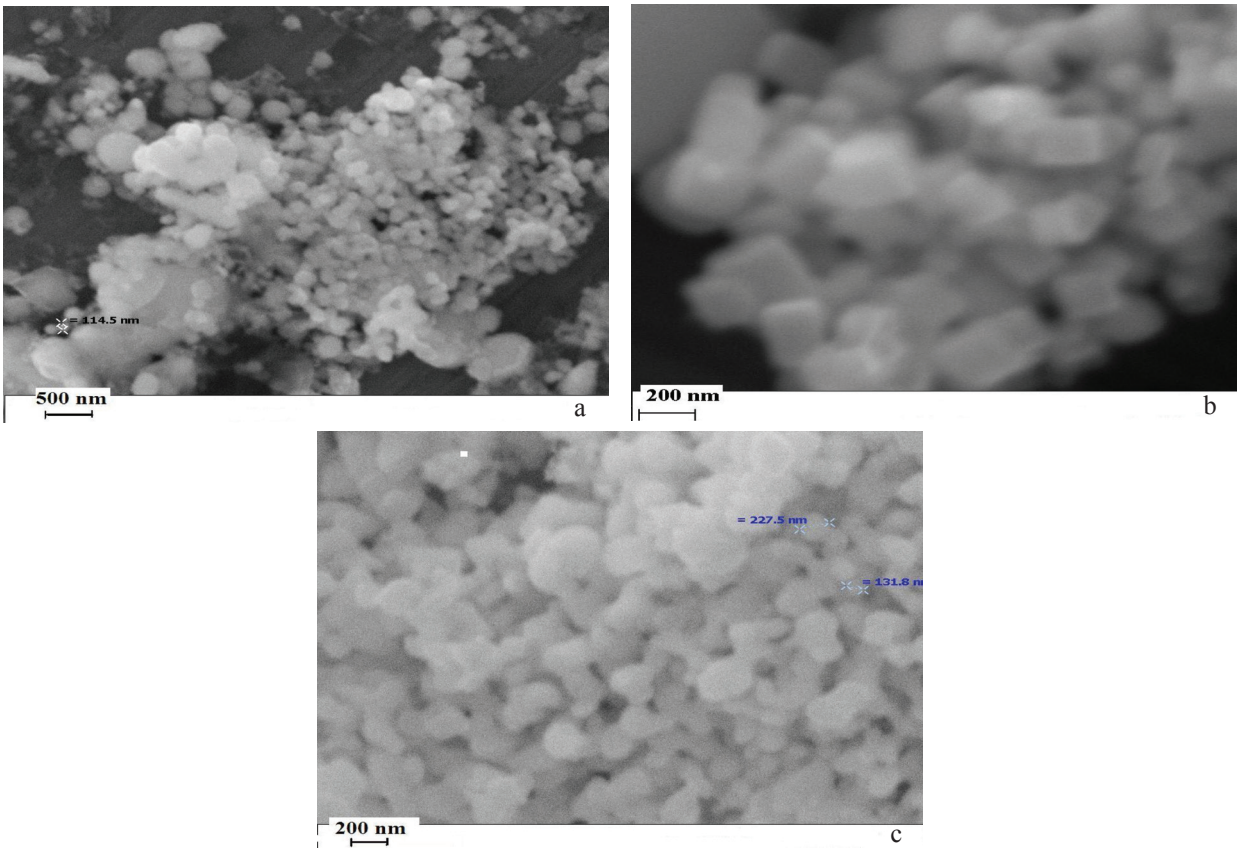

Fig. 6. Microstructure of chemically dispersed powders: a – $MoSi_2$, b – TiC , and c – TiC-WC.

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