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Investigation of Titanium Carbide – Metal Binder Composite Powders Treated in a Planetary Ball Mill

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Abstract

Metal matrix composite powders based on titanium carbide with titanium and high speed steel as binders were studied by means of X-ray diffractometry, scanning and transmission electron microscopy. The composite powders were obtained by crushing the cakes formed as the products of self-propagating high temperature synthesis (SHS) from titanium, carbon (black carbon) and high speed steel (HSS) powder mixtures, followed by mechanical treatment in a planetary ball mill Aktivator-2S. It was stated that the disintegration rate depends on metal binder content in the SHS product. To obtain the powder suitable for use in additive technologies, SHS powder of titanium carbide was ground preliminarily and then subjected to additional treatment in mixture with Ti powder in the planetary ball mill. As a result, the powder mixture consists of equiaxial granules containing fine TiC particles uniformly distributed in the Ti matrix. Results of the studies of the microstructure of samples obtained by means of selective laser melting (SLM) and electron beam melting (EBM) provide evidence of the advantages of SLM technology over EBM.

Keywords: self-propagating high temperature synthesis, titanium carbide, metal matrix composite, planetary ball mill, additive technology, microstructure

INTRODUCTION

Treatment of powder materials in high-energy planetary mills is widely used to enhance the reactivity both due to an increase in the specific surface of powders and due to an increase in the internal energy accumulated in the powders [1, 2]. In particular, mechanical activation of reactive powder mixtures used to synthesize refractory phases and intermediate compounds in the wave combustion mode and in the mode of thermal explosion promotes a decrease in combustion temperature till the transfer of the reaction proceeding in the presence of the liquid phase into the solid-phase synthesis mode [3, 4]. Another promising application of planetary mills is the preparation of quasi-equilibrium powders suitable for use in additive technologies for the manufacture of products with complicated shapes [5]. However, powders with mainly spherical particle shape are necessary in all additive technologies. For the Direct deposition technology, in which the powder is supplied directly to the fusion zone, the spherical shape of particles provides good friability and uninterrupted powder supply. In the Bed deposition technology, in which the powder layer deposited preliminarily is fused, the spherical shape of particles promotes tight packing in the layer, which is important for achieving decreased porosity after alloying.

Spherical powders of metals and alloys are obtained using two main methods which provide melting of the alloy with target composition and its subsequent crystallization. In the method based on melt spraying, spherical drops are crystallized, which are formed during spraying. In the other method, spheroidization of the powders of arbitrary shapes proceeds during fusion in low-temperature plasma. Both methods require specialized expensive equipment, so the search for simpler and economically more efficient methods of spheroidization of metal powders is urgent.

Spheroidization of the powders with the structure of metal matrix composites (MMC) in which the dispersed particles of refractive compounds are uniformly distributed in the metal matrix (binder) is of special importance. It is well known that the hardness and wear resistance of MMC are several times higher than those of steel and alloys, so they are widely used as the material for wear-resistant coatings deposited onto the vital parts under wear and instruments by means of powder coating or facing. The main method of making spherical powders for deposition and facing of coatings with MMC structure is spray drying of suspensions [6]. The suspensions are composed of a mixture of fine powders of refractory compounds and a metal or an alloy, with an organic liquid that does not interact chemically with the powders. During suspension spraying, the liquid from the drops is evaporated, and granules of the mechanical mixture of refractory powders and a metal binder are formed. In addition to spray drying of suspensions, also the treatment of the mixtures of metal binder powder with ceramic powder in planetary mills is used to form the powders with MMC structure [7].

Composite powders with MMC structure may be prepared using a highly productive and economical method of self-propagating high-temperature synthesis (SHS) from reactive powder mixtures [8–10]. Unlike for powders obtained by spray drying, a strong metallurgical bond is formed in SHS powders between the particles of the strengthening phase and the metal binder as early as at the synthesis stage. In the powders with the same phase composition prepared by spray drying, this bond is formed in the welding bath melt (powder welding), during the fusion of metal binder in granules in plasma (plasma spraying) or during the collisions of granules with the substrate (detonation spraying). In the case of incomplete wetting of the refractory phase with the binder melt, the formation of pores in the coatings is possible.

The major disadvantage of composite SHS powders is a non-spherical shape of granules obtained by crushing the porous SHS cakes – synthesis products.

The goal of the present work was to study the possibility of obtaining granules of quasi-equiaxial shape through the treatment of composite SHS powders in a planetary mill and the outlooks for the application of mill-treated powders in additive technologies of growing samples with MMC structure.

EXPERIMENTAL

Materials and methods

Initial materials for the synthesis of composite powders with MMC structure were titanium powder of TPP-8 grade (particle size less than 190 μm; the major component 99.4 mass %, admixtures: Fe – 0.33 mass %; Cl – 0.12 mass %; O – less than 0.1 mass %); soot P-803 (average particle size 0.3 μm) and high speed steel (HSS) PR-10R6M5 (particle size 90 μm). Steel powder contained carbon (1 mass %), doping elements (Cr – 4 mass %, W – 6.5 mass %, Mo – 5 mass %, V – 2 mass %) and admixtures (Si – 0.5 mass %, Mn – 0.55 mass %, Ni – 0.4 mass %). The morphology of initial powders is shown in Fig. 1.

Reaction mixtures were prepared by dry mixing of the weighted portions of initial powders for 4 h. Porous cakes of SHS product with the calculated binder content (titanium TPP-8 or HSS PR-10R6M5) 50 vol. % were obtained by burning the cylindrical pressed blanks 35 mm in diameter prepared from reactive powder mixtures. The synthesis was carried out in a tight reactor in the atmosphere of argon with the excess pressure of about 0.5 atm. Combustion was initiated by heating the igniting tablet with a molybdenum spiral. The surface layer of porous cakes of the SHS product 1–2 mm thick was removed, and the purified cake was crushed and separated into fractions.

The treatment of SHS powders was carried out in Aktivator-2S planetary mill with cylinders 250 mL in volume, the ratio of ball mass to the powder load was 10 : 1. The mass of powder loaded into each cylinder was 30 g, the frequency of cylinder rotation was 960 r.p.m.

Experiments on the growth of voluminous (3D) samples from composite powders by means of selective laser melting (SLM) or electron beam

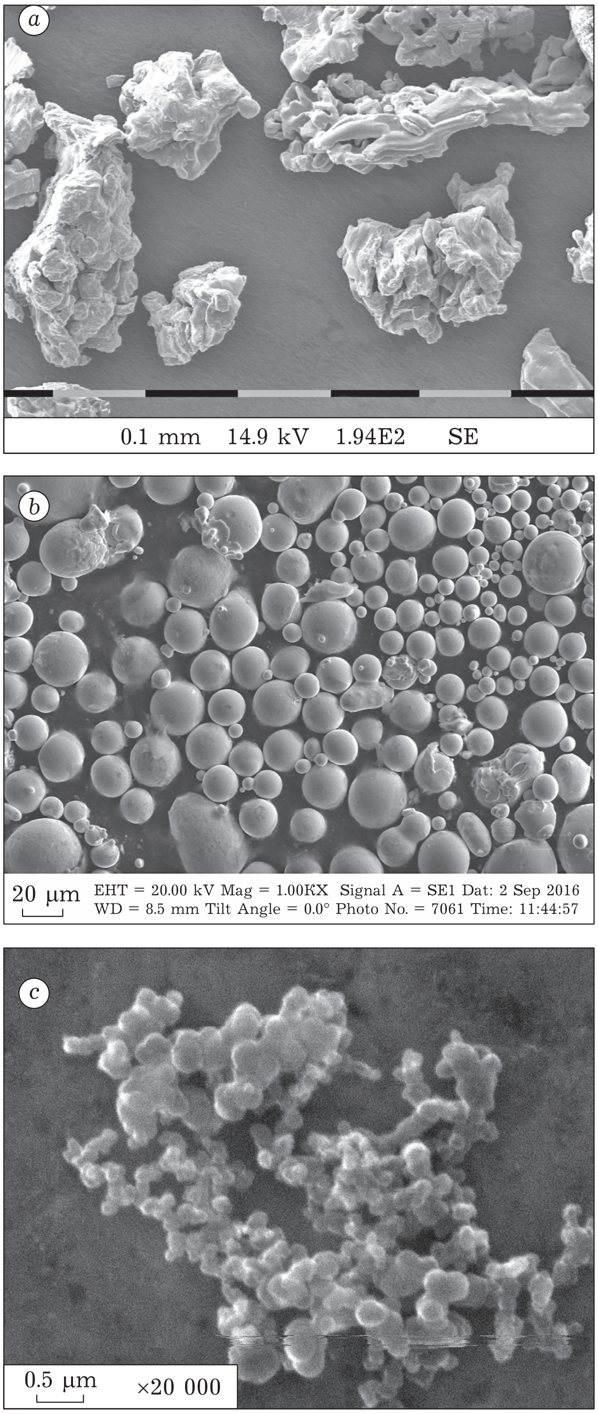

Fig. 1. Morphology of initial powders: *a* – titanium TPP-8; *b* – steel PR-10R6M5; *c* – soot P-803.

melting (EBM) were carried out using the equipment of the research and industrial laboratory Modern Industrial Technologies of the Tomsk Polytechnical University. The main parameters of EBM are: accelerating voltage 40 kV, current strength in the beam 5 mA, the diameter of electron beam during alloying 200 µm. The main parameters of SLM: laser power 200 W, laser beam diameter 250 µm. For all samples, the distance between the passages was 150 mm, the thickness of the powder layer 200 mm, scanning rate 30 mm/s.

Composite powders and samples grown according to additive technologies using these powders were studied with the help of the equipment of the Nanotekh shared centre of the Institute of Strength Physics and Materials Science SB RAS by means of X-ray phase analysis (DRON-7 diffractometer, Burevestnik, Russia), optical metallography (inverted microscope AXIOVERT-200MAT, Zeiss, Germany) and scanning electron microscopy (EVO 50 electron microscope, Zeiss, Germany).

RESULTS AND DISCUSSION

Figures 2 and 3 show the morphology of powders obtained by crushing SHS cakes. The particles of the SHS TiC + PR-10R6M5 powder have splintery, clumpy and mainly equiaxial shape (see Fig. 2, *a*). According to the results of X-ray phase analysis [9], titanium carbide content in the SHS product exceeds 50 %. Titanium carbide is present in the composite structure as dispersed particles with the average size 1.3 µm, which are observed on the surface of granules of the SHS powder (see Fig. 2, *b*) and on the optical photographs of the etched metallographic sections (see Fig. 2, *c*).

Unlike for SHS powders with steel binder, the granules of SHS powders with titanium binder have non-equiaxial splintery shape (see Fig. 3, *a*,*b*), because the actual content of titanium binder in the SHS product is only 6.5 vol. % instead of the calculated value 50 vol. % (assuming the formation of titanium carbide of equiatomic composition). This is in good correlation with the data of the equilibrium titanium – carbon diagram according to which nonstoichiometric titanium carbide TiC_x ($x = 0.5$) is formed during the synthesis under these conditions [8]. The carbide phase is fractured because of the low content of the titanium binder (see Fig. 3, *b*) and is easily splintered. The size of carbide inclusions in SHS granules with titanium binder (see Fig. 3, *c*) is much larger than in SHS granules with the steel binder (see Fig. 2, *b*,*c*), because thermally inert steel binder decreases the combustion temperature [9], which promotes structure refining.

Substantial gap in the content of the metal binder in two studied SHS composites determines different behaviour of SHS powders during the treatment in planetary mill. After the treatment

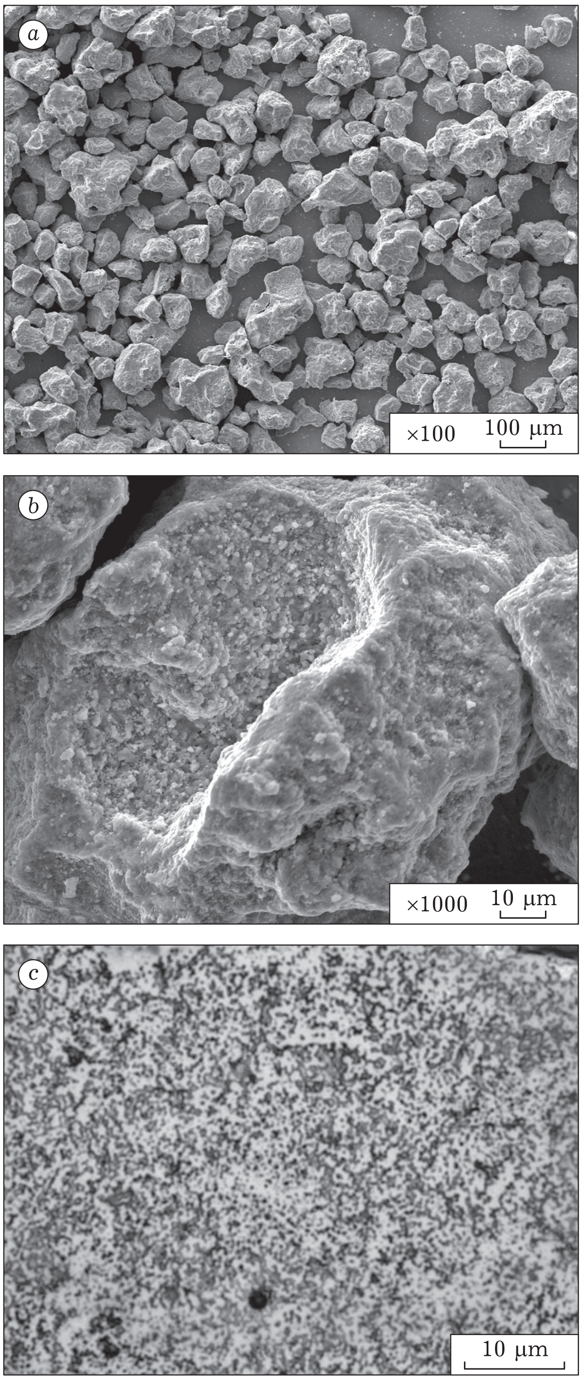

Fig. 2. Morphology (*a*, *b*) and microstructure (*c*) of composite powders TiC + PR-10P6M5 obtained by crushing SHS cake.

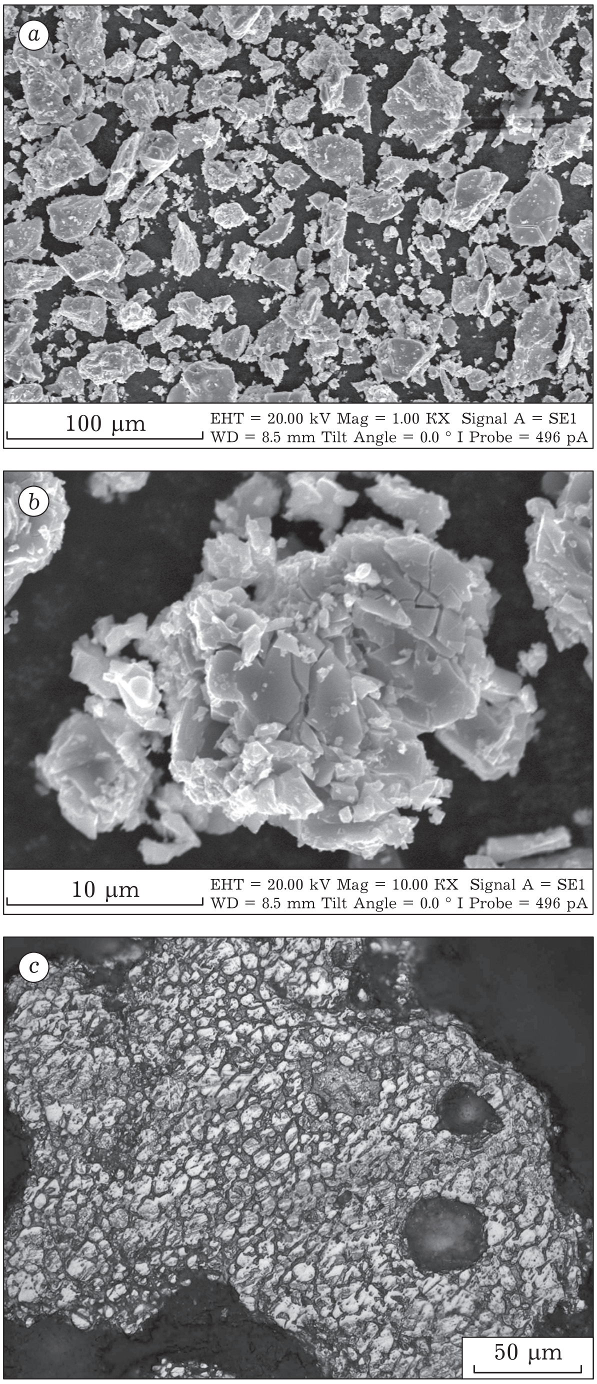

Fig. 3. Morphology (*a*, *b*) and microstructure (*c*) of composite powders TiC + Ti obtained by crushing SHS cake.

of SHS powders with titanium binder for only 2 min, particles with a size less than 1 μm are formed; however, larger sharp-cornered particles prevail (Fig. 4, *a*). With an increase in treatment time up to 10 min, the fraction of sharp-cornered particles decreases substantially, while the size of equiaxial particles varies from the submicron size to several micrometres (see Fig. 4, *b*). After long-term treatment (180 min) larger (up to 5 μm) particles are still conserved and get the shape close to spherical. It is most probable that these are rounded inclusions of the titanium binder, while the particles with the size 1 μm and smaller are titanium carbide; it is known that its inclusions in MMC are usually characterized by equiaxial rounded shape.

During the treatment of SHS powders with steel binder, the changes in the morphology and

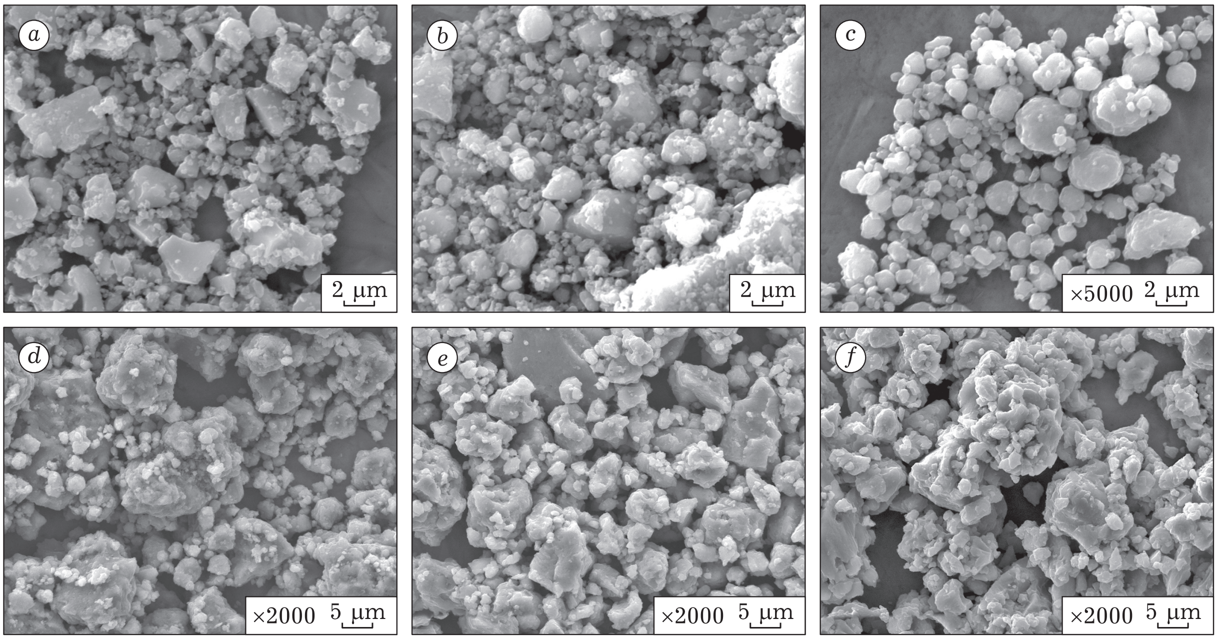

Fig. 4. Morphology of composite SHS powders TiC + Ti (*a*–*c*) and TiC + PR-10R6M5 (*d*–*f*) after treatment in the planetary mill for different time, min: 2 (*a*), 10 (*b*), 180 (*c*), 30 (*d*), 60 (*e*), 180 (*f*).

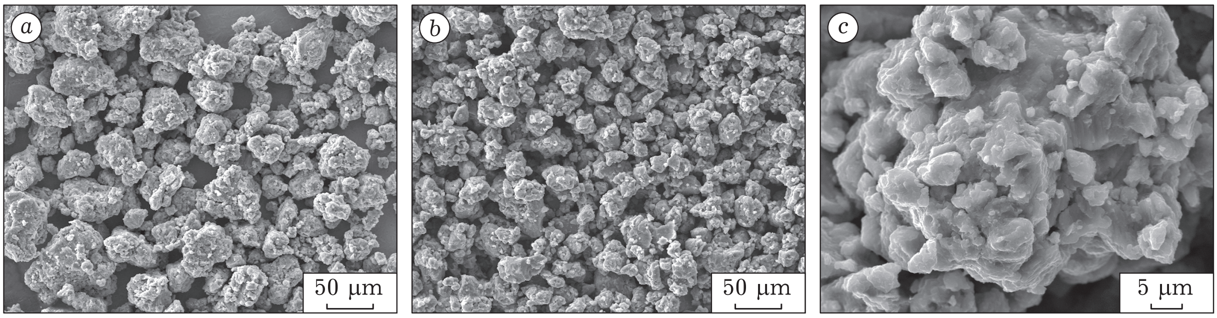

Fig. 5. Morphology of granules obtained by additional treatment in the planetary mill of a mixture of preliminarily ground SHS TiC + Ti powder with titanium TPP-8 powder for 10 (*a*) and 40 min (*b*, *c*).

dispersity of initial powders are less substantial (see Fig. 4, *d*–*f*). Independently of treatment time, the powder contains small (1–2 μm) and coarse (10 m and larger) particles. Relying on the comparison between the sizes of inclusions on the surface (see Fig. 2, *b*) and on the sections (see Fig. 2, *c*) of the granules of SHS powder after crushing and the sizes of small powder particles after treatment in the planetary mill (see Fig. 4, *d*–*f*), we may state that thee are carbide particles formed during the synthesis. Large particles are granules which are not destroyed even during long-term grinding because of the large (50 vol. %) content of relatively plastic binder in them. They play the role of a damper preventing the destruction of free carbide particles under the impacts of balls. During long-term grinding, the major part of the free carbide particles get driven into the surface layer of the granules without changing their size (see Fig. 4, *f*).

SHS TiC + Ti powders contain only 6.5 vol. % titanium binder, so they are unsuitable for use in additive technologies based on complete or partial melting of the filler powder. For the purpose of increasing titanium content in faced powders, titanium powder was added to SHS powders ground preliminarily, then the mixture was subjected to additional treatment in the planetary mill. The morphology of the granules obtained as a result of additional treatment is shown in Fig. 5. One can see that the majority of granules are quasi-equiaxial in their shape. Under the action of ball impacts, large titanium particles with the characteristic branched shape of spongy titanium (see Fig. 1, *a)* are ground, and some small particles combine. As a result, the fraction composition of initial polydisperse powder gets narrower to the size necessary for additive technologies: 30–50 μm. At the same time, solid carbide particles get inserted into plastic titanium, and the granules attain the MMC structure, which is confirmed by the studies of their fine structure by means of transmission electron microscopy (Fig. 6).

In the dark-field image of the peripheral region of granules (see Fig. 6, *a*), one can see submicron particles of titanium carbide (see Fig. 6, *b*) distributed uniformly in the titanium binder.

The granules of the composite TiC + Ti powder obtained as a result of the additional treatment were used to manufacture 3D samples by means of SLM or EBM. The microstructure of the resulting voluminous samples is presented in Fig. 7.

In spite of the close energy contributions, the structures of samples obtained using different methods differ from each other. Carbide particles in the samples obtained by means of SLM (see Fig. 7, *b*) possess smaller and disordered structure, while in the EBM samples carbides form dendrite structure with the axes up to the third order (see Fig. 7, *c*). The observed differences are connected with more rapid crystallization proceeding during SLM. In the EBM technology, preliminary heating of the working area for sample growth up to the temperature of 700–800 °C is necessary. This heating involves additional caking of the powder in the deposited layer, which prevents its separation under the action of electrostatic forces.

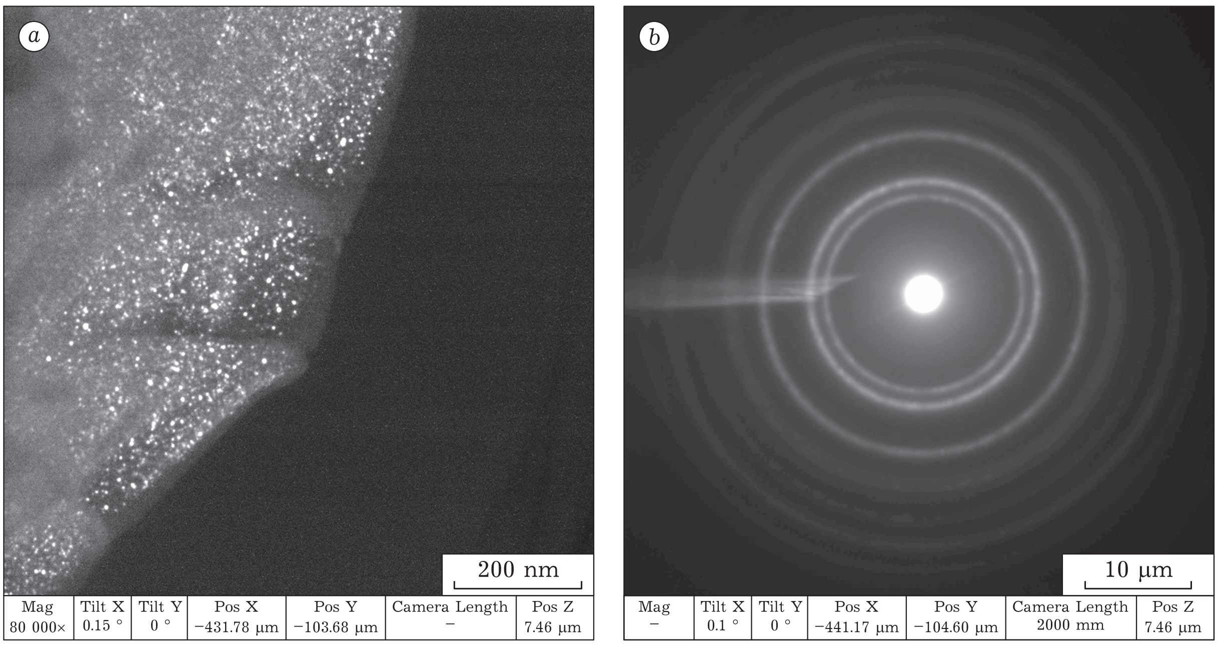

Fig. 6. Transmission electron microscopy of the granules after additional treatment of a mixture of prelimnarily ground SHS TiC + Ti powder with titanium TPP-8 powder in the planetary mill: *a* – dark-field image of the peripheral part of granules; *b* – electron diffraction.

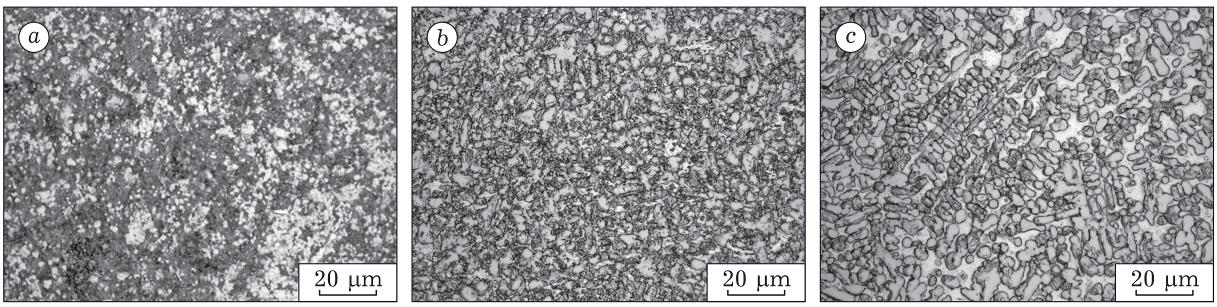

Fig. 7. Microstructure of initial granules (*a*) obtained by additional treatment in the planetary mill of a mixture of preliminarily ground SHS TiC + Ti powder with titanium TPP-8 powder, and 3D samples deposited by means of additive technologies SLM (*b*) and EBM (*c*) using these granules.

It follows from the comparison of the microstructure of granules of the faced powder (see Fig. 7, *a* and 6, *a)* and the samples grown by means of additive technologies (Fig. 7, *b*, *c*) that complete recrystallization of the carbide phase occurred during the use of TiC + Ti composite powders in EBM and SLM additive technologies. Dispersity and morphology of carbides crystallized from the melt-solution of titanium and carbon is completely determined by the rate of cooling the welding bath.

CONCLUSIONS

1. Composite powders of titanium carbide with titanium (TPP-8 grade) or HSS (PR-10R6M5) binder were obtained by the combination of SHS and mechanical treatment in the planetary ball mill.

2. Composite powders have quasi-equiaxial shape and are suitable for use in additive technologies of obtaining materials and coatings which greatly exceed HSS, titanium and its alloys in wear resistance.

3. The method of obtaining 3D samples from composite powders based on the use of the laser beam (SLM) exceeds the electron beam melting (EBM) in technological effectiveness, structure and properties of the material.

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REFERENCES

1 Avvakumov E. G., Mechanical Methods of the Activation of Chemical Processes, Novosibirsk: Nauka, 1986, 306 p. (in Russ.).
2 Grigoryeva T. F., Barinova A. P., Lyakhov N. Z., Mechanochemcial Synthesis in Metal Systems, Novosibirsk: Parallel, 2008, 311 p. (in Russ.).
3 Korchagin M. A., Lyakhov N. Z., *Khimicheskaya Fizika*, 2008, Vol. 27, No. 1, P. 73–78. (in Russ.).
4 Korchagin M. A., *Fizika Goreniya I Vzryva*, 2015, Vol. 51, No. 5, P. 77–86. (in Russ.).
5 Shishkovskiy I. V., Laser Synthesis of Functionally Gradient Meso-Structures and Voluminous Products, Moscow: Fizmatlit, 2009, 424 p. (in Russ.).
6 Pawlowski L., Finely grained nanometric and submicrometric coatings by thermal spraying: A review, *Surface & Coatings Technology*, 2008, Vol. 202, P. 4318–4328.
7 Panin V. E., Stepanova I. V., Panin S. V., Korchagin M. A., Pochivalov Yu. I., Durakov V. G., Dudina D. V., *Fizicheskaya Mezomekhanika*, 2005, Vol. 7, Special issue, P. 125–128. (in Russ.).
8 Pribytkov G. A., Krinitsyn M. G., Korzhova V. V., *Perspektivnye Materialy*, 2016, Vol. 5, P. 59–68. (in Russ.).
9 Pribytkov G. A., Korzhova V. V., Baranovskij A. V., Krinicyn M. G., *Izvestiya Vuzov. Poroshkovaya Metallurgiya i Funktsionalnye Pokrytiya*, 2017, No. 2, P. 64–71. (in Russ.).
10 Pribytkov G. A., Firsina I. A., Korzhova V. V., Krinicyn M. G., Polyanskaya A. A., *Izvestiya Vuzov. Poroshkovaya Metallurgiya i Funktsionalnye Pokrytiya*, 2018, No. 2, P. 43–53. (in Russ.).