Electric arc synthesis of titanium carbide nanoparticles

D V Smovzh

Kutateladze Institute of Thermophysics SB RAS, Lavrentiev ave. 1, Novosibirsk, Russia
Novosibirsk State University, Pirogov str. 1, Novosibirsk, Russia

E-mail: dsmovzh@gmail.com

Abstract. The structure of titanium carbide nanoparticles formed at electric arc spraying of composite Ti-C electrodes is studied. It is shown that the size of titanium carbide particles in condensation products varies in the range of 10–50 nm, crystal lattice of nanoparticles corresponds to TiC carbide. Annealing the material in an oxygen-containing atmosphere leads to carbon burnout and oxidation of titanium carbide nanoparticles. The main part of carbon is oxidized in the temperature range of 250–500°C, oxidation of titanium carbide nanoparticles occurs in the range from 320 to 400°C. When annealed to the temperatures of 1000°C, sintering of oxide TiO$_2$ nanoparticles occurs. The proposed method can be used to obtain particles of titanium carbide with a shape close to the TiC crystal.

1. Introduction

Titanium carbide is currently one of the most popular synthetic materials used both as the additives to modify the structural properties of materials, and in the pure form when creating chemically and wear-resistant products and coatings. One of the relevant trends is the development of technologies of titanium carbide 3D printing. These technologies impose a number of requirements on titanium carbide powder used as a raw material for a 3D printer. First of all, it is the spherical shape of particles, minimization of size and chemical purity of the product. Modern methods of synthesis of titanium carbide nanoparticles include carbothermal reduction of titanium dioxide powder (TiO$_2$) using carbon [1,2], synthesis from polymer precursors based on titanium alkoxides or other organic compounds [3,4], direct reaction of Ti and carbon [5], self-propagating high-temperature synthesis, Mg-thermal reduction [6, 7], and mechanical grinding [8]. Electric arc synthesis can be effectively used for the synthesis of nanoparticles of various elements in the carbon matrix [9] and oxide nanoparticles [10]. The advantages of graphite arc include the one-stage process, chemical purity of products and ability to control the size of nanoparticles by varying the synthesis parameters. The carbon matrix can be removed by annealing the TiC-C composite in an oxygen atmosphere or using the flotation method in the mixture of 50% trichloroethylene and 50% acetone [Binder F, EttmayerP. - Radex-Rundschau, 1981, No. 4, S. 690-696.].

This work is aimed at testing the application of the electric arc method for the synthesis of titanium carbide nanoparticles with a shape as close as possible to a sphere, studying the dynamics of oxidation of materials obtained, and adjustment of the regimes of material enrichment with titanium carbide. Micron titanium carbide powder obtained by the method of self-propagating high-temperature synthesis was used as a source for the synthesis.
2. Experiment
The materials formed in the gas phase at the joint electric arc spraying of titanium-graphite (Ti-G) and TiC-G rods were studied. The synthesis of Ti-C nanostructured material is implemented on a plasma-arc DC setup. The reactor is a vacuum chamber, which is pumped out and then filled with helium to the working pressure. Two electrodes are placed in the reactor with a varying distance between them. The arc discharge of direct current glows between them. The cathode is a graphite tablet with a diameter of 20 mm; the anode is a rod with a diameter of 8 mm and length of 70 mm. A water-cooled removable screen is installed around the electrodes at a distance of 5 cm to collect synthesis products. Under the conditions of these experiments, the interelectrode distance is maintained so that the arc voltage is 20 V and discharge current is 150 A. The anode is a graphite rod with a hole along the axis, which is filled with titanium carbide - graphite powder in a given ratio. The carbon rods are made of carbon with a density of 1.82 g/cm³, purity of 99.99. Titanium carbide powder is used as the titanium additive. The molar fraction of titanium carbide in the sprayed electrode is 20%. The synthesized material is annealed in air at the temperatures of up to 1000°C. The materials are analyzed using transmission (JEM-2010 JEOL) and scanning (JSM-6700F JEOL) electron microscopy and thermogravimetry (Thermoanalyzer STA 409).

3. Results and discussion
Images of the original titanium powder obtained by the scanning electron microscope are shown in Fig.1. It is seen that the structure of the powder particles is far from spherical. The particles ranging in size from several microns to several hundred microns have a porous structure. The composition of material is presented in Table 1, the main components are titanium and carbon with insignificant (at the noise level) impurities. The stoichiometric composition of material corresponds to Ti4C, according to the phase diagram [102], the material consists of a mixture of titanium carbide (TiC) with metallic binder phase (α-Ti) in the 1:3 ratio.

![SEM image, initial powder is TiC, obtained by the SHS method.](image)

After arc spraying, the resulting Ti-C composite consists of titanium carbide nanoparticles of 10-50 nm with a cubic lattice of Fm-3m symmetry group surrounded by a carbon matrix, Fig. 2(a-c). Titanium carbide nanoparticles have a crystalline faceting, with similar characteristic sizes along different crystallographic directions. After annealing the TiC material, the particles have a much larger size. The crystal lattice of particles most closely corresponds to the Ti₄C₇ triclinic syngony of the A-1 (-1) symmetry group and TiO₂ orthorhombic syngony of the Pbca symmetry group, Fig. 2d.
Thermogravimetric analysis was carried out at a heating rate of 5°C per minute with an exposure for 1 hour at the points indicated in the diagram. After material annealing at 1000°C, all carbon forms are completely burned out and titanium carbide nanoparticles are oxidized (Fig. 2d, Fig. 3). As a result, 18.5% of the initial mass remains, which corresponds to the content of titanium in the initial mixture of about 12% by weight.

**Figure 2.** TEM images of material obtained after electric arc spraying (a – c) and annealing at the temperature of 1000°C (d).

**Figure 3.** The mass loss vs. temperature of Ti-C composite annealing and carbon content in the material as a percentage of the initial mass of sample.
To study the dynamics of material oxidation, the materials after exposure at various annealing temperatures, marked in the diagram in Fig. 3, were examined by the method of transmission microscopy. At the temperature of 150–200°C, oxidation of amorphous carbon material begins, then nanocrystalline carbon burns out; graphite fragments with a small number of defects in the crystal structure have the highest oxidation resistance and are able to withstand the temperatures of up to 1000°C. According to the literature, oxidation of titanium carbide occurs at the temperatures above 800°C, TEM analysis showed that the crystal lattice of nanoparticles in carbon soot changes from the carbide, observed during annealing at up to 320°C, to the oxide one after annealing at 400°C, Fig. 4.

![Figure 4. Crystalline structure of nanoparticles after annealing at 320°C (on the left) and 400°C (on the right).](image)

According to data presented, it can be concluded that the electric arc method can be applied to the synthesis of titanium carbide nanoparticles with TiC stoichiometry; the shape of nanoparticles corresponds to the crystallographic structure of titanium carbide. High carbon content in the synthesized composite can be considered as a disadvantage of technology. In the sprayed material, the carbide content is determined by concentration of titanium in the sprayed electrode, however, at high concentrations, there can be a significant change in the discharge parameters, including formation of melts and drops during spraying. Excess carbon can be removed by annealing the synthesized material in an oxygen-containing atmosphere. Under our conditions, when the initial concentration of carbide in the sprayed material is 15%, after annealing at 320°C, concentration of carbide increases to 26%; when annealing at 400°C, 42% of carbon remains in the material. At that, at 400°C, titanium carbide nanoparticles are oxidized; the lower oxidation temperature in comparison with the bulk material is a characteristic feature of nanoparticles and it is caused by the high contribution of surface to the internal energy of a particle. Thus, the estimated maximum degree of material enrichment with titanium carbide by the method of calcination before oxidation of carbide particles is not more than 54%.

**Conclusions**
It is shown that a material consisting of carbide nanoparticles of 10-50 nm encapsulated in a carbon matrix is formed during arc spraying of composite titanium carbide - carbon electrodes using titanium carbide powder with a size fraction of 10-100 microns and complex particle morphology. The shape of nanoparticles corresponds to the shape of TiC crystals. The maximum enrichment of material with titanium carbide to 54% can be achieved by the method of calcination. At a temperature of 400°C, the nanoparticles are completely oxidized to TiO₂, while subsequent calcination of material to 1000°C, carbon is burned out completely and TiO₂ nanoparticles sinter. The proposed method can be used to synthesize titanium carbide nanoparticles with a shape close to the spherical one.
Acknowledgement
The study of initial powder was carried out under state contract with IT SB RAS, the study of material obtained after electric arc spraying was financially supported by Russian Science Foundation Grant No. 18-19-00213.

References
[1] Toth L E 1971 Academic Press. 13 279
[2] Koc R and Folmer J S 1997 J. Mater. Sci. 32 12
[3] Preiss H, Berger L M and Schultze D 1999 J. Eur. Ceram. Soc. 19 2
[4] Jiang Z and Rhine W E 1991 Chem. Mater. 3 6
[5] Miracle D B and Lipsitt H A 1983 J. Am. Ceram. Soc. 66 8
[6] Nersisyan H H, Lee J H and Won C W 2002 J. Mater. Res. 17 11
[7] Lee D W and Kim B K 2003 Scr. Mater. 48 11
[8] Cui X L, Cui L S, Wang L and Qi M 2002 Petrol. Sci. Technol. 20 9
[9] Gulyaev R V, Slavinskaya E M, Novopashin S A, Smovzh D V, Zaikovskii A V, Osadchii D, Bulavchenko O A, Korenev S V and Boronin A I 2014 Applied Catalysis B: Environmental 147 132
[10] Smovzh D V, Sakhapov S Z, Zaikovskii A V, Chernova S A, Novopashin S A 2019 Ceramics International 45 6