Synthesis of submicron titanium carbide in a direct current arc discharge plasma by a vacuumless method

A Y Pak* and A A Gumovskaya

Tomsk Polytechnic University, 30 Lenina Ave, Tomsk, Russia, 634050

*ayapak@tpu.ru

Abstract. This paper studies the possibility of obtaining ultrafine cubic titanium carbide in the direct current arc discharge initiated between graphite electrodes in ambient air. According to X-ray diffraction data, there are 3 crystalline phases in the synthesized powder: graphite, initial titanium and cubic tungsten carbide. Based on transmission electron microscopy data, particles with sizes of 100-300 nm containing titanium and carbon are identified in the synthesis product. These objects are characterized by a structure corresponding to the cubic phase of titanium carbide. The applied vacuumless electrotechnical method is known for its ease of implementation, high productivity, and high energy efficiency in comparison with electrical analogues.

1. Introduction

Titanium carbide is an important superhard refractory material [1], which is characterized by high wear resistance, abrasion resistance, high electrical conductivity, and relatively low density [2, 3]. Titanium carbide is used in various fields of science and technology. Titanium carbide is primarily known as a material for creating refractory ceramics, as well as for the production of abrasive and cutting tools. In the last few years, materials based on titanium carbide are considered as the basis for ultrahigh capacity electric energy storage devices [4], as well as electrochemical storage devices [5]; the use of titanium carbides in photocatalytic and electrocatalytic systems is being studied [6,7]. Interesting developments in the use of titanium carbide for the absorption of carbon dioxide from air [8]. The indicated areas of application of titanium carbide allow us to consider it an important material for existing and promising aerospace technologies.

Titanium carbide is produced using various known approaches, for example, carbothermic reduction of titanium oxide, self-propagating high-temperature synthesis, mechanical synthesis, magnetron sputtering [9-13]. One of the known approaches is the electric discharge [14, 15], including the vacuum-free method, which is implemented in the atmospheric plasma of a direct current arc discharge [16]. The scientific and technical foundations a method for producing carbon nanostructures [17, 18], and carbides of metals and nonmetals [16, 19] need to be further developed in the field of controlling the phase and particle size distribution of the product, and studying the morphology of micron and nanosized synthesized fractions. In this paper the possibility of obtaining ultrafine cubic titanium carbide in the direct current arc discharge under ambient air is shown. According to transmission electron microscopy, the synthesis product contains submicron particles, which identify the crystal structure corresponding to the cubic phase of titanium carbide.
2. Experimental

Experimental studies were conducted on a plasma-chemical transferred atmospheric direct current reactor [16]. The main elements of the device should be considered a direct current power source, a discharge circuit equipped with graphite electrodes, a system for recording electrical parameters. The DC power supply is a reducing transformer with a reversible frequency converter and a pulse-duration modulator. A graphite anode and cathode are connected to the power source by cable lines. The anode is made in the form of a wire, and the cathode is in the form of a vertical crucible, on the bottom of which the initial reagents are placed: a powder mixture of carbon (graphite) and titanium ($\alpha$Ti) in a mass ratio of Ti:C = 2:1 in an amount of 0.6 ± 0.05 g. The mixture of starting reagents is uniformly located along the bottom of the cathode over an area of 3.8 cm$^2$. The arc discharge is ignited by the contact of the anode and cathode, followed by the formation of a discharge gap of 0.5-1.0 mm. In the operating condition of the installation, the current and voltage waveforms are taken using an ohmic voltage divider and an active current sensor.

The multiply of voltage and current calculates the electric power of the discharge, by integrating the power of the discharge over time, the actual amount of energy released in the discharge is calculated. According to the known «titanium-carbon» state diagram, the released energy is enough to the cubic titanium carbide formation. In this case, the discharge burning on graphite electrodes intensively generates a shielding atmosphere consisting of CO and CO$_2$, which makes it possible to achieve the effect of shielding the reaction volume from atmospheric oxygen.

During a series of experiments, a current value of 165 A was set at the power source; a series of experiments was carried out with different durations of maintaining the arc discharge; accordingly, the amount of supplied energy changed. The synthesis strategy is to achieve sufficiently high temperatures suitable for the synthesis of crystalline phases of titanium carbide according to the well-known “titanium-carbon” state diagram; the effect of self-shielding of the reaction volume is used to prevent oxidation of the synthesis products and the starting reagents. The resulting product is collected from the interior wall of the graphite cathode, which has been set in the process of burning an arc discharge as a black powder. The material was analyzed by X-ray diffractometry (Shimadzu XRD 7000s, CuK$\alpha$), transmission electron microscopy, Jeol JEM 2100F with an energy dispersion analysis attachment. A quantitative X-ray phase analysis is performed using the PDF4+ database (2019 release), and the Shimadzu XRD PC Suit standard software. The analysis of electron diffraction patterns obtained during transmission electron microscopy was performed using the Gatan Microscopy Suite (GMS) software version 1.8.

3. Results and discussion

Figure 1 shows typical X-ray diffraction patterns of the synthesis product and a powder mixture of the raw initial materials mixture. In a mixture of initial powders hexagonal titanium ($\alpha$Ti) and graphite (gC) are identified; also, several unmarked traces are visible in the diffraction pattern, which may indicate a low titanium hydride content. Three crystalline phases can be identified in the composition of the synthesis product: initial $\alpha$Ti and gC, as well as the synthesized cubic phase of titanium carbide of variable composition with a unit cell parameter range from a = 4.28 Å to a = 4.33 Å, which may correspond to the cubic phase of titanium carbide of variable composition from TiC$_{0.5}$ to TiC. In this case, the error in determining the position of the diffraction maximum was according to the information on the last calibration of the X-ray diffractometer to 20 = 0.04° in the 2θ range from 35° to 43°, which corresponds to possible inaccuracies in determining the corresponding interplanar distances to d=0.003 Å. The average size of the coherent scattering regions calculated by the well-known half-height broadening technique ranged from ~ 20 nm to ~ 35 nm. It was found that the range of unit cell parameters and the average size of the coherent scattering regions do not depend on the amount of supplied energy.
Figure 1. Typical X-ray diffraction patterns: 1 — a powder mixture of the starting gC and αTi regents, and 2 — the synthesis product.

Using an energy dispersive analysis attachment based on a transmission electron microscope, particles were searched and mapped as part of a product containing titanium (Fig. 2). The analysis revealed objects containing titanium. According to the analysis of chemical composition, these particles contain 74.9% (mass) of titanium with a standard deviation of 5.7%; 22.0% (mass) of carbon with a standard deviation of 5.9%, as well as up to 3.2% (mass) of various impurities, including up to 1.8% (mass) of oxygen. Objects are characterized by sizes of the order of ~ 100 nm to ~ 300 nm and are characterized by an inhomogeneous structure: interspersed darker formations with sizes of the order of tens of nanometers are traced in the particle body. In the electron diffraction pattern, reflections from families of planes with the following interplanar distances are identified: 2.53 Å, 2.18 Å, 1.80 Å, 1.32 Å, 1.13 Å. Within the range of possible errors, the identified interplanar spacings of 2.53 Å, 2.18 Å, 1.32 Å can correspond to the cubic phase of titanium carbide, and 1.80 Å and 1.13 Å can correspond to the αTi phase. At this stage, according to the data of transmission electron microscopy, it was not possible to identify individual crystals of the titanium carbide phases and the αTi phase, however, the data obtained suggest that submicron particles containing the titanium carbide phase are present in the product.

4. Conclusion
Based on the data presented, we can conclude that it is possible to obtain submicron particles consisting mainly of carbon and titanium, in the body of which it is possible to identify the structure of cubic titanium carbide and the structure of hexagonal titanium. A feature of this work is the implementation of the synthesis process in atmospheric plasma arc discharge without using vacuum or gas equipment. This approach makes it possible to exclude several nodes from the composition of the laboratory complex: a sealed reactor, vacuum sediment, inert gas cylinders, hoses, pipes, manometers. As a result, the operation of sealing the casing, pumping out air, and injecting inert gases into the reaction zone is not required to obtain titanium carbide. These facts make it possible to simplify the design of the laboratory reactor and increase the productivity and energy efficiency of the system. In the future, it is planned to conduct experimental studies on the production of titanium carbide from its oxide by the
developed vacuumless method, as well as on the search for ways to isolate the desired phase of titanium carbide from the impurities.

![Image of transmission electron microscopy results](image)

**Figure 2.** Results of transmission electron microscopy: a) an image in scanning transmission electron microscopy, b) an appropriate map of the distribution of titanium, c) a typical bright-field image, d) the selected area electron of diffraction pattern.

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