Specific Nature of Application of Various Carbon Components for Mechanochemical Synthesis of Titanium Carbide

V P Reva, V U Yagofarov, D A Gulevskii, A E Filatenkov and Yu N Mansurov
Far Eastern Federal University, Vladivostok, Russia

e-mail: festurvp@mail.ru, vyagofarov@gmail.com, psihomail@mail.ru, 3po91@mail.ru, yubarsmans@gmail.com

Abstract. It has been established that structure of carbon modifications, obtained via pyrolysis of vegetable feed, and ash content of natural graphite are crucial factors during mechanochemical synthesis of titanium carbide under vibratory conditions. The possibility of synthesis of titanium carbide with minimal sulfur content has been shown.

1. Introduction
During last years the scope of applications of titanium carbide in production of composite systems of various purposes both in powder technologies and conventional metallurgy has been increased [1]. One of the prospective methods of titanium carbide synthesis is high temperature mechanochemical [2, 3] synthesis [4 – 11], which allows obtaining products with low content of harmful impurities [6, 8].

Chemical composition of synthesized titanium carbide depends mainly on the purity of applied carbon modifications [7, 10– 12]. Searching of effective substituents of traditionally used ash with higher sulfur content is an important issue in mechanochemistry of carbides. Previously the prospects of using carbon modifications from vegetable feed and natural graphite in mechanochemical synthesis of titanium carbide with low sulfur content were shown. Titanium carbide was synthesized in vario-planetary mill Pulverisette-4 (Fritsch, Germany) [6 – 8]. In present study titanium carbide synthesis was carried out in energy-intensive vibratory mill that allowed revealing new aspects of mechanochemical technology.

This work aimed on investigation of crucial factors of mechanochemical synthesis of titanium carbide conducted under vibratory treatment using carbon modifications obtained from pyrolyzed vegetable feed and also from ash and natural graphite.

2. Experimental
As initial materials various types of renewable vegetable feed were used: moss *Sphagnum fuscum* and *Sphagnum magellanicum* and also stems of gumbo (*Abelmoschus esculentus*) of “Green velvet” sort and sprouts of corn of “Catherine SV” sort. Vegetable feed was preliminary sieved in order to remove foreign inclusions, washed with distilled water, then dried at 100-110 ºC and dispersed in disintegrator
DESII-11 (Estonia) down to 100-150 µm. Carbon modifications, which were involved in the synthesis of titanium carbide, with amorphous and crystalline-amorphous structure were fabricated via pyrolytic technology at following temperatures: 950, 11150, 1300 and 1500 ºC. Specific surface area (single-point BET) of carbon modifications synthesized from vegetable feed, ranged within 100-220 m²/g. Ash of PM-15 brand and natural graphite with various ash content were also used as carbon precursors.

Titanium was used as powder of PTES-2 brand with particle size 150-200 µm and purity 99.8%. The stoichiometry TiC₀.₈ was used to calculate amounts of precursors for mechanochemical synthesis of titanium carbide. Activation of precursors and mechanochemical synthesis of titanium carbide were carried out in sealed container (mechanoreactor) of energy intensive vibratory mill, working at 750 min⁻¹ frequency of container oscillations and 90 mm amplitude. As grinding bodies the balls (14 mm diameter) of steel of SCh15 brand were used. Grinding intensity (relation between mass of precursors and mass of grinding balls) was 1:20.

Synthesis completion was identified by abrupt temperature change in mechanoreactor measured on its outer wall by IR laser pyrometer C-20.1. After temperature jump (figure1), vibratory treatment was stopped.

Influence of nature of carbon reagents on synthesis conditions was assessed by the time delay of mechanochemical synthesis – time from the beginning of mechanoactivation of the precursors to the moment of temperature jump.

Figure 1. Thermogramm of mechanochemical synthesis of titanium carbide.

Phase composition of carbon modifications and synthesized carbides was determined by XRD on D8 ADVANCE (Germany) device using Cu-Kα source.

Particle size distribution was obtained on laser analyzer “Analyzezette 22” (Fritsch, Germany).

Morphology of carbon precursors was studied on scanning electron microscope of high resolution Hitachi S5500 (Japan). Investigation of specific surface area was carried out on sorption analyzer Sorptometer-M, CJSC “KATAKON”, (Russia, Novosibirsk), value of specific surface area was determined by thermodesorption of nitrogen.

Sulfur and carbon content in carbon modifications and in carbide powders was measured using sulfur and carbon analyzer CS 600 of “LECO” (USA).

3. Results and Discussion
During the first step, carbon modifications with amorphous and amorphous-crystalline structure were obtained from renewable vegetable feed (agricultural wastes) by pyrolysis at various temperatures: 950, 1150, 1300 and 1500 ºC. Carbon precursor formed during after pyrolysis at 950 ºC has
amorphous structure and doesn’t identified by XRD. As can be seen, morphology of amorphous carbon in all cases is predetermined by original structure of certain type of vegetable feed (figure 2).

At 1150-1500 °C pyrolysis leads to amorphous-crystalline structure of the carbon.

Carbon modifications obtained after pyrolysis of vegetable feed, were used as carbon precursors for mechanochemical synthesis of titanium carbide. Ash of PM-15 brand was used to conduct comparative analysis as recommended in [4].

Mechanochemical synthesis involved abrupt temperature change. Temperature of reactor walls, measured by laser IR pyrometer C-20.1 immediately after mechanochemical synthesis of titanium carbide, was 80-130 °C.

![Figure 2](image_url)

**Figure 2.** SEM image of amorphous carbon after pyrolysis at 950 °C.

a - *Sphagnum fuscum*, b - *Sphagnum magellanicum*, c - gumbo, d - corn of “Catherine SV” sort.

It was established that structure of carbon modifications, obtained under different conditions of pyrolysis of vegetable feed, influence on time delay of mechanochemical synthesis of titanium carbide (figure 3).

Thus, the higher temperature at which vegetable feed is annealed the faster mechanochemical synthesis is. However, one should note that the higher temperature of pyrolysis, the lower temperature jump $\Delta t$ is ($\Delta t = t_2 - t_1$ – the difference between the temperature of the reactor walls after and before temperature jump).
Figure 3. Influence of pyrolysis temperature of sphagnum moss on time delay of mechanochemical synthesis of titanium carbide.

So, if pyrolysis temperature was 950 °C the temperature jump was 40-50 °C, in the case of 1500 °C pyrolysis temperature the jump value was just 7-10 °C (figure 4).

Figure 4. Influence of sphagnum moss pyrolysis temperature on temperature jump during mechanochemical synthesis of titanium carbide.

During visual assessment of the products, obtained using carbon components and under temperatures from 1150 °C and higher, the presence of agglomerates (figure 5a) 3-8 mm in diameter has been revealed.

If carbon material that was obtained by pyrolysis at 950 °C is used, then titanium carbide is formed in the bulk of reacting mixture without formation of agglomerates (figure 5b).

Figure 5. Products of mechanochemical synthesis of titanium carbide. Pyrolysis temperature of sphagnum moss: a – 1150 °C, b – 950 °C.
According to XRD analysis, mechanochemical synthesis with carbon components obtained after 950 °C pyrolysis results in only titanium carbide. If pyrolysis is increased to 1150 °C, the powder product contains titanium, and agglomerates are a cake of titanium and titanium carbide (figure 6).

Thus, to conduct mechanochemical synthesis of titanium carbide under vibratory conditions one must not use carbon components that have amorphous-crystalline and crystalline structure. Usage of carbon precursor with amorphous structure is the most promising.

Modifications of amorphous carbon from various vegetable feed obtained by pyrolysis at 950 °C were used to conduct mechanochemical synthesis of titanium carbide. The influence of the type of vegetable feed on the time delay of synthesis of titanium carbide is presented (figure 7).

![XRD spectra](image)

**Figure 6.** XRD spectra of the products of mechanochemical synthesis of titanium carbide. Pyrolysis temperature: a – 950 °C; b, c – 1150 °C (b – powder, c - agglomerate).

As one can see, the type of vegetable feed influence significantly on the time delay of mechanochemical synthesis if titanium carbide.
Figure 7. Time delay of mechanochemical synthesis of titanium carbide depending on the type of vegetable feed: 1 – ash PM-15; 2 – magellanicum; 3 – corn of “Catherine SV” sort; 4 – gumbo; 5 – brown sphagnum.

Laser analysis showed that maximal dispersity corresponds to the powder of titanium carbide synthesized using carbon obtained by annealing sphagnum moss, while particle size of titanium carbide is 1-25 µm and 70 % of the particles have size lower than 10 µm.

In order to reveal the influence of the type of vegetable feed, using to obtain carbon precursor, on the chemical composition of synthesized product, the investigations of sulfur and free carbon content in titanium carbide were carried out (table).

| Titanium carbide, synthesized using carbon modification | Chemical compositions, % |
|-------------------------------------------------------|--------------------------|
|                                                       | C<sub>free</sub>, % | S, % |
| from moss magellanicum                                | 0.29                    | 0.012 |
| from sphagnum moss                                    | 0.39                    | 0.014 |
| from corn                                              | 0.49                    | 0.085 |
| from gumbo                                             | 0.59                    | 0.095 |
| Ash PM-15                                             | 0.50                    | 0.19 |

Temperature of pyrolysis of vegetable feed - 950 °C

Sulfur content in titanium carbide synthesized using carbon modifications obtained by pyrolysis of vegetable feed is lower than that in titanium carbide synthesized using ash PM-15, from 2 to 17 times. The best result is observed for carbon modifications formed from magellanicum moss. Free carbon content in titanium carbide synthesized using investigated carbon modifications is also lower than that using ash PM-15.

The possibility of conducting mechanochemical synthesis of titanium carbide under vibratory conditions using natural graphite as carbon component.

Graphite with ash content from 1 to 5.2% was used. Graphite and ash PM-15 were used to make carbon composites with graphite content varied from 10 to 90 wt. %. Graphite and ash PM-15 were preliminary dried at 150 °C for 3 hours after what the carbon composites with carious graphite content were fabricated.

The influence of ash content of graphite and its concentration in carbon composite on time delay of mechanochemical synthesis of titanium carbide is presented (figure 8).
Figure 8. Influence of ash content of graphite and its content in the composite on time delay of synthesis. Ash content of graphite: a – 5.2%; b – 4.8%; c – 1.0%.

Chemical composition of titanium carbide obtained by mechanochemical synthesis using as carbon precursor the composite “ash + graphite” showed, that sulfur content in all of the synthesized products from 2 to 3 times lower than in titanium carbide obtained using ash.

Thus, application of graphite with low ash content as carbon component for conducting mechanochemical synthesis of titanium carbide allows decreasing applied energy while increasing quality of obtained product.

4. Conclusions
The structure of carbon components is the crucial factor in implementation of mechanochemical synthesis of titanium carbide under vibratory treatment conditions. Titanium carbide synthesized using carbon modifications obtained from vegetable feed possess chemical composition with low sulfur and free carbon content that is preferably for implementation in production of dispersion strengthened steel, fireproof materials and also in powder metallurgy. The crucial factor in conducting mechanochemical synthesis of titanium carbide in the presence of graphite is ash content of graphite.

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