Preparation of the highly dispersed powder of titanium carbonitride by SHS azide technology with previous partial nitriding

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Abstract. It is shown that the powder of very hard refractory titanium carbonitride (TiC$_{0.5}$N$_{0.5}$) is the basis of tungsten-free hard alloys which are prospective for application as inexpensive cutting tools. The finer the powder of titanium carbonitride is, the more enhanced properties of hard alloys, sintered from the powder, are. An opportunity to reduce the particle size of the titanium carbonitride powder obtained by energy-saving azide technology of self-propagating high-temperature synthesis at the cost of reducing the particle size of the initial titanium powder was investigated. To ensure the safety of the grinding process of the initial metal titanium powder, it was offered to nitride a Ti powder partially into a TiN$_{0.2}$ compound. Such partial nitriding was performed by the azidetechnology with lack of sodium azide (NaN$_3$) as a nitriding reagent. After intensive grinding in the planetary ball mill, the TiN$_{0.2}$ powder turned into a superfine powder with an ultrafine structure. This powder was capable of nitriding and carburizing in the azide technology with formation of superfine pure powder agglomerates which are composed of ultrafine and nano-particles of TiC$_{0.5}$N$_{0.5}$.

1. Introduction
Hard alloys are widely used in mechanical engineering for manufacture of cutting and punching tools, wear parts, operating in abrasive and corrosive environments [1, 2]. The most common hard alloys are based on tungsten carbide, but due to the shortage of tungsten, its high cost, widening application areas, the problem of the development, production and application of tungsten-free hard alloys becomes more urgent. In this respect, hard alloys, based on refractory compounds of titanium, which is much more common in the earth crust and less expensive than tungsten, are very attractive. First, hard alloys based on titanium carbide were developed, but cutting tools made from these alloys were not widely used because of high brittleness [1, 2]. To reduce the brittleness, the titanium nitride (TiN) was added to the hard alloy composition, and then the titanium carbonitride (TiC$_{1-x}$N$_x$) was used in place of carbide and nitride of titanium [3]. The titanium carbonitride is a solid solution of carbide and nitride of titanium with a wide homogeneity range and combines their best properties: a high melting point, hardness and wear resistance of TiC with the low friction, chemical and oxidation resistance of TiN [4]. Hard alloys based on titanium carbonitride are fine-grained, with a uniform distribution of the binder of Ni-Mo, with low porosity and high values of hardness and bending strength. They are characterized by high scale resistance, heat resistance, a low coefficient of friction on steel, which ensures good cutting properties approaching those of tungsten-containing hard alloys. Hard alloys...
based on titanium carbonitride are applicable for semi-finish and semi-rough turning and milling of steels, cast iron, nonferrous metals, and also for metal forming by pressure without sticking of the formed metal on the forming tool made from these alloys. In connection with the above-mentioned, the hard alloys based on titanium carbonitride are considered as promising for the replacement of tungsten-containing alloys in their application as cutting and forming tools and wear parts [1-5].

There are several methods of producing titanium carbonitride powders which are used for sintering hard alloys and for spraying wear resistant coatings [1, 3, 5, 6]. The powders are produced from the mixture of powders of TiC and TiN due to high temperature diffusion for several hours at 1600-1800°C and under the pressure of 30-300 MPa, followed by prolonged grinding. The high temperature gas nitriding (1700°C, 2 hours) mixture of powders of Ti and TiC leads to the synthesis of the titanium carbonitride, which turns into a powder during less prolonged grinding. Industrial production of titanium carbonitride powders is based on the carbothermal reduction of titanium from cheap titanium oxides, added to the mixture of TiO2-C, lead to the synthesis of titanium carbonitride nano-powders by the carbothermal method [7]. Methods for the synthesis of the titanium carbonitride powders at relatively low temperatures and pressures have been also developed; they include the thermal decomposition of TiCl4 complexes with organic amines (800-1200°C, 1-2 h) [8], the reduction of the solution of TiCl4 in CC14 with magnesium (850-1050°C) in a nitrogen atmosphere [9] or with sodium azide NaN3 [6], the use of exchange reactions at 450°C between reagents of TiCl4, CaC2 and NaN3 [10]. These methods allow producing highly dispersed powders of the titanium carbonitride including nano-powders, but they are complex and involve the use of costly and toxic components. We should also mention a method of synthesis of titanium carbonitride nano-powders during high-energy milling of powders of carbon and titanium in a nitrogen atmosphere [11].

The above-listed methods of producing the titanium carbonitride powders are energy consuming, long-term, and are implemented on the basis of complex equipment at high temperatures, which lead to the formation of large particles or strong agglomerates of fine particles and the subsequent need for prolonged grinding. The powders often contain impurities of oxygen, free carbon and a material of grinding bodies [6, 9]. In this connection, it is of interest to use the method of self-propagating high-temperature synthesis (SHS) with low energy consumption, simple equipment, a short duration of the synthesis process, high purity products and great possibilities to control the particle size of the synthesized powders [12].

Direct synthesis of the titanium carbonitride of a different composition is possible when burning a mixture of powders of Ti and C in the nitrogen atmosphere only when this mixture is diluted with the TiN powder and at increased pressure of nitrogen (0.6-1.65 MPa) [13, 14]. A finer and less sintered powder can be obtained by the method of azide SHS (SHS-Az) when burning mixtures of Ti and C with sodium azide (NaN3) and halide salts [15]. In this case, the combustion temperature is relatively low, a lot of gaseous products, which separate the powder particles, are generated; the particle size of the titanium carbonitride powder corresponds to the size of the particles of the initial titanium powder (less than 40 µm), and the content of the basic substance is 96.5-98.5 wt. %. Recently, the SHS method was used to prepare a fine powder of titanium carbonitride, when the titanium reacted with the zinc dicyanide, 4Ti + Zn(CN)2 → 4TiC0.5N0.5 + Zn, followed by removal of the zinc by dilute hydrochloric acid [6]. The temperature of proceeding of this reaction was approximately 2600°C and the titanium carbonitride powder was synthesized in the form of particles of a rounded shape with a size of about 1 µm which were not agglomerated. When three moles of zinc were added to the original mixture, the reaction temperature decreased to about 1000°C, the particles became of a submicron size, but the final product contained the impurity in the amount of 0.86 wt. % Zn.

Increased dispersion of the titanium carbonitride powder, that is a reduced size of its particles, is an important task, as the smaller and purer the powder is, the stronger the hard alloys, sintered from it, are [9]. Along with this, to expand the use of the titanium carbonitride powder, it is necessary to reduce its
The aim of this work was to study the possibility of increasing the dispersion of the TiC₀.₅N₀.₅ powder prepared by the SHS azide technology due to the increase of dispersity of the initial titanium powder.

2. Materials and methods of investigations

The following initial powders were used in the experimental study: the titanium powder of the PTM (small powder of titanium) brand (purity ≥ 98.9 wt. %, particle size < 45 μm), carbon black of the P804T brand (99.5%, 0.2 μm), sodium azide NaN₃ (98.7%) and ammonium fluoride NH₄F (98.5%). All the powders were sifted through a sieve with a cell of 80 μm on a shaking machine of the WS-2 type. Intense grinding with mechanical activation of powders was performed in a planetary mill ‘Activator 28L’ with a centrifugal acceleration of 30 g. Two drums with a volume of 250 ml contained (each) 375 g of cemented carbide grinding balls with a diameter of 7-11 mm and 37.5 grams of the powder to be milled. Experimental investigations were conducted in the SHS-Az reactor of constant pressure with a volume of 4.5 l. The arrangement of this reactor and methods of work with the measurements of the linear velocity and the maximum combustion temperature by thermocouple method using tungsten-rhenium thermocouples TR 5/20 were described in detail in [16]. The cylindrical samples (40 mm diameter, 50 mm height) of the initial powders mixture of bulk density were burned. The phase composition of the powdery combustion product was determined on an automated X-ray ARL X TRA diffractometer ‘ThermoScientific’. Shooting X-ray spectra was performed using Cu-radiation with continuous scanning in the range of angles 2θ = 20°÷80° at a speed of 2 deg./min. The obtained spectra were processed using a special software package ‘WinXRD’. The study of the morphology and the size of powder particles was performed on the scanning electron JSM-6390A microscope ‘Jeol’.

3. Results and discussion

Our experience shows that a high dispersity of the initial titanium powder can be achieved by intensive grinding in the planetary mill ‘Activator 28L’, which allows reducing the particle size from 45 μm to a submicron size. The use of this finely ground powder instead of the standard titanium powder of the PTM brand inspires the hope that it is possible to prepare titanium carbonitride powder by SHS-Az process of the same small size as the milled titanium. However, we must keep in mind that if we make a grinding pure metallic titanium in a planetary mill, it may present a fire hazard at high dispersity, especially if it is mixed with oxidants, when its fire and explosion hazard increases many times. To reduce the activity of the highly dispersed powder of titanium is possible if the powder is passivated by paraffin during milling in the planetary mill. Our research in this direction has shown that effective passivation of the submicron powder is achieved at a large amount of paraffin ranging from 5 to 10 wt. %. This paraffin decomposes to carbon and hydrogen in the combustion wave and participates as a carbon reactant in the synthesis of titanium carbonitride. However, paraffin reduces the temperature and velocity of combustion at the expense of losing a part of the combustion heat for the decomposition of paraffin, and also due to the fact that the major portion of carbon is emitted when the combustion wave passes and free carbon remains in the target product. Because of this, using paraffin, it is difficult to achieve the desired ratio of carbon and nitrogen in the carbonitride and to prepare a pure product without free carbon. In this connection, to reduce the activity of titanium and to enhance the safety of grinding, prior partial nitriding of Ti and transformation into TiN₀.₂ compound were used in this study instead of passivation by paraffin. Titanium nitride of such composition of TiN₀.₂ should maintain its ability to participate in the reactions of carburizing and nitriding in the SHS-Az process and to ensure fire safety of grinding and preparation of powder mixtures. In addition, the partially nitrided titanium, in contrast to pure titanium, is more brittle and is dispersed in the mill better.

TiN₀.₂ was obtained by the SHS-Az method with the limited content of sodium azide according to the following equation:

\[ \text{Ti} + 0.066\text{NaN}_3 + 0.066\text{NH}_4\text{F} \rightarrow \text{TiN}_0.2 + 0.066\text{NaF} + 0.033\text{N}_2 + 0.132\text{H}_2. \]  \quad (1)
To increase the efficiency of the SHS-Az process, a halide salt of ammonium fluoride NH₄F was added to the mixture as it is usually done [15, 16]. The process was carried out in the reactor in argon atmosphere at a pressure of 4 MPa instead of nitrogen atmosphere to avoid additional nitriding of titanium with gaseous nitrogen. Synthesized powder TiN₀.₂ was washed with distilled water for removal of byproduct salt of NaF and then was dried.

Synthesized powder TiN₀.₂ was intensively ground with mechanical activation in the planetary mill ‘Activator 28L’ within 8 min. An SEM image with different magnifications of the ground TiN₀.₂ is presented in figure 1.

![SEM images of ground TiN₀.₂](image)

*Figure 1. SEM magnifications of the ground TiN₀.₂: (a) x 5000; (b) x 20000.*

As can be seen from this figure, the size of the ground particles of the TiN₀.₂ is in the range from 100 nm to 3 µm, but these particles are combined into agglomerates of a micron size. This powder can be qualified as a superfine powder with an ultrafine structure.

This TiN₀.₂ powder has been used for the synthesis of the powder of titanium carbonitride by the SHS-Az process with the application as reagents powders of carbon, sodium azide and ammonium halide according to the stoichiometric equation:

$$\text{TiN₀.₂} + 0.5\text{C} + 0.1(\text{NaN₃} + \text{NH₄F}) \rightarrow \text{TiC₀.₅N₀.₅} + 0.1\text{NaF} + 1.08\text{N}_₂ + 1.3\text{H}_₂.$$  (2)

To reduce sintering of the target product during the synthesis process and to obtain a very fine powder, the oxidizing agents of NaN₃ and NH₄F were introduced into the initial charge in excess as compared with 0.1(NaN₃ + NH₄F). They yield a large amount of gaseous products and thereby divide the particles of carbonitride without letting them merge and become stronger. In addition, the presence of an excess of oxidants reduces the temperature of combustion of powder mixtures, thereby also reducing the size of the synthesized product particles [12]. An excess of oxidizing agents is equal to 100% for 0.2(NaN₃ + NH₄F), 200% for 0.3(NaN₃ + NH₄F), and so on. To determine the optimal excess of oxidizing agents, the dependence of combustion temperature $T_c$, °C, and combustion velocity $U_c$, mm/s, on the value of the excess of oxidants has been investigated. The results of these studies are as follows: 1400 °C and 6.2 mm/s at 100% excess of oxidants, 1350 °C and 4.1 mm/s — at 200%, 1200 °C and 3.2 mm/s — at 300%, 900 °C and 2.3 mm/s — at 400%, and no combustion — at 500%. Thus, with an excess of the oxidants over 400 %, the combustion is impossible. The optimum excess can be considered as 300%, when the temperature is sufficient for the synthesis of titanium carbonitride, but its sintering is prevented.
Figure 2 shows a XRD pattern of combustion products of the mixture with a 300% excess of sodium azide and ammonium fluoride. As can be seen, X-ray analysis of the washed powder confirmed the presence of titanium carbonitride only in the SHS-Az product.

![Figure 2](image1)

**Figure 2.** The XRD pattern of the combustion product of the mixture with a 300% excess of oxidants.

Figure 3. SEM magnifications of the combustion product of the mixture with a 300% excess of oxidants:
(a) x 20000; (b) x 80000.

![Figure 3](image2)

Micrographs of the synthesized powder of TiC$_{0.5}$N$_{0.5}$ are presented in figure 3 with different magnifications. These pictures show that the particle sizes of the target powder of TiC$_{0.5}$N$_{0.5}$ range from 40 to 400 nm, but these particles are combined into agglomerates of a micron size. Thus, synthesis of titanium carbonitride, using partially nitrided titanium of composition TiN$_{0.2}$ activated in a planetary mill, confirmed that the use of the initial mixture of TiN$_{0.2}$ + 0.5C + 0.4(NaN$_3$ + NH$_4$F) with a 300% excess of oxidizing agents made it possible to store and even slightly reduce the initial particle size of TiN$_{0.2}$ when turning it into carbonitride. Therefore, using a superfine partially nitrided titanium powder
with an ultrafine structure, it is possible to obtain superfine pure titanium carbonitride agglomerates which are composed of ultrafine- and nano-particles of TiC$_{0.5}$N$_{0.5}$ in a safe way.

4. Conclusion
A method of passivation of a pure metallic titanium powder is proposed by partially nitriding it by the SHS azide technology into TiN$_{0.2}$ to ensure fire safety and effectiveness of grinding in a planetary ball mill till obtainment of a superfine powder with an ultrafine structure. It is shown that the partially nitrided and milled superfine powder of TiN$_{0.2}$ can be then used in the simple energy-saving azide SHS technology to produce the superfine agglomerated powders with size less than 3 µm which are composed of TiC$_{0.5}$N$_{0.5}$ ultrafine- and nano-particles of size from 40 to 400 nm instead of a much larger powder of titanium carbonitride with a particle size of 40 µm [15].

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