Azide SHS of highly dispersed powder of titanium carbonitride with intermediate partial nitriding or partial carburizing titanium powder

A P Amosov and Yu M Markov
Samara State Technical University, Molodogvardeyskaya 244, Samara, 443100 Russia
E-mail: egundor@yandex.ru

Abstract. It is noted that the powder of titanium carbonitride (TiC$_{0.5}$N$_{0.5}$) is the basis of the TiC$_{1-x}$N$_x$/Ni – Mo system cermets, which are considered as the most promising tool materials for the replacement of classical hard alloys based on tungsten carbide of the WC – Co system. The properties of these cermets are the higher the finer is the titanium carbonitride powder from which they are sintered. First, a simple energy-saving process of self-propagating high-temperature synthesis (SHS) was applied for the intermediate partial nitriding of the initial metal powder of titanium to the composition of TiN$_{0.2}$ or partial carburizing to TiC$_{0.3}$ composition in order to ensure fire safety and efficiency of the grinding process in the planetary ball mill to obtain superfine powders of partially nitried or carburized titanium with ultrafine structure. Further, these powders were used in the azide SHS process for complete nitriding and carburizing to produce titanium carbonitride powder which was composed of superfine agglomerates of ultrafine and nano-particles of TiC$_{0.5}$N$_{0.5}$.

1. Introduction
The powder of titanium carbonitride (TiC$_{0.5}$N$_{0.5}$) is the basis of the TiC$_{1-x}$N$_x$/Ni – Mo system cermets, which are considered as the most promising tool materials for the replacement of classical hard alloys based on tungsten carbide of the WC – Co system [1, 2]. The most complete modern review of cermets based on titanium carbonitride is presented in the article 2018 “Ti(C, N)-Based Cermets: Critical Review of Achievements and Recent Developments” [2]. These cermets are on average twice cheaper and lighter than classical hard alloys, significantly exceeding them in hardness, wear resistance, resistance to oxidation and adhesion to steels, but still noticeably inferior to them in crack resistance and resistance to shock loads. To overcome these shortcomings, various methods are used, mainly, the complexity of the composition of the initial powder mixture, as well as reducing the size of the titanium carbonitride powder, the transition to ultrafine and nanoscale powder. In a number of works it is shown that the properties of these cermets are the higher the finer is the powder of titanium carbonitride from which they are sintered [2–5].

Analysis of existing methods for producing titanium carbonitride powders shows that most of them are energy-intensive, long-term, implemented in complex equipment at high temperatures, which lead to the formation of large particles of the product or strong agglomerates of small particles and the need for subsequent long-term grinding [6]. In this regard, it is of interest to use the method of self-propagating high-temperature synthesis (SHS) or combustion synthesis with low energy consumption, simple equipment, short duration of the synthesis process, high purity of products and great opportunities...
for controlling the particle size of the synthesized powders [7, 8]. Weakly sintered and subsieve powder of titanium carbonitride is obtained by azide SHS (SHS-Az) method in combustion of $(Ti + 0.5C)$ mixtures with sodium azide $Na_3N$ and halide salts [9]. In this case, the combustion temperature is relatively low, a lot of gaseous products are formed, separating the powder particles, and therefore the particle size of the titanium carbonitride powder corresponds to the particle size of the original titanium powder (less than 40 μm), and the content of the base material is 96.5–98.5 wt %. Recently, the authors of this article have investigated the possibility of increasing the dispersion of titanium carbonitride powder $TiC_{0.5}N_{0.5}$, obtained by azide SHS technology, by increasing the dispersion of the original titanium powder [6]. However, if the grinding of pure metal titanium of standard grades is carried out in a planetary ball mill, then it becomes fire-hazardous at high dispersion, especially if it is mixed in the charge with oxidants, when its fire and explosion hazard increases many times. Therefore, in order to improve safety, reduce the activity of highly dispersed pure titanium powder, this powder was passivated by partial nitriding to the composition of $TiN_{0.2}$ before grinding in the planetary ball mill [6]. In addition, the partially nitrided titanium, in contrast to pure titanium, is more brittle and better dispersed in the mill.

Partially nitrided titanium of $TiN_{0.2}$ composition was prepared by SHS-Az method under the conditions of the corresponding limited content of sodium azide according to the equation [6]

$$Ti + 0.066NaN_3 + 0.066NH_4F \rightarrow TiN_{0.2} + 0.066NaF + 0.033N_2 + 0.132H_2$$

To increase the efficiency of the SHS-Az process, the halide salt of ammonium fluoride ($NH_4F$) was added to the charge as it usually done [10]. The process was carried out in the SHS-Az reactor in the gaseous argon medium, not gaseous nitrogen medium, to avoid additional nitriding of titanium with gaseous nitrogen. The synthesis conditions: the diameter of a powdered sample of the original charge of 40 mm; height of 50 mm; bulk density of 0.4, the pressure of argon in the reactor was 4 MPa. The synthesized $TiN_{0.2}$ powder was washed with distilled water to remove the side salt of NaF and then was dried. Grinding with mechanical activation of the synthesized $TiN_{0.2}$ powder was carried out by hard alloy balls for 8 min in the planetary ball mill "Activator-2SL". The scanning electron microscope (SEM) image of the milled particles $TiN_{0.2}$ shown in figure 1a, from which it is seen that the size of the milled $TiN_{0.2}$ particles is in the range from 100 nm to 3 μm, but these particles are combined into agglomerates of a micron size.

(a)  (b)

Figure 1. SEM images of powders: (a) TiN$_{0.2}$ and (b) TiC$_{0.5}$N$_{0.5}$ [6].
Then this TiN$_{0.2}$ powder was used for the synthesis of powder of titanium carbonitride by the SHS-Az process according to the stoichiometric equation:

$$\text{TiN}_{0.2} + 0.5\text{C} + 0.1(\text{NaN}_3 + \text{NH}_4\text{F}) \rightarrow \text{TiC}_{0.5}\text{N}_{0.5} + 0.1\text{NaF} + 1.08\text{N}_2 + 1.3\text{H}_2$$

In order to prevent the target product from sintering during the synthesis process and to be obtained as an ultrafine powder, an excess of oxidants NaN$_3$ and NH$_4$F was introduced into the initial charge compared to 0.1(NaN$_3$ + NH$_4$F). They give a large volume of gaseous products and thereby separate the titanium carbonitride particles, preventing them from merging and becoming larger. In addition, the presence of excess of oxidants reduces the combustion temperature of powder mixtures, thereby reducing the size of the synthesized product particles [8]. The excess of oxidants is 100% in the case of 0.2(NaN$_3$ + NH$_4$F), 200% at 0.3 (NaN$_3$ + NH$_4$F), and so on. The SEM image of powder TiC$_{0.5}$N$_{0.5}$ synthesized under 300% excess of oxidants is shown in figure 1b. This powder was obtained by hand grinding the loose combustion product in a porcelain mortar. Particle sizes of the target powder TiC$_{0.5}$N$_{0.5}$ were from 40 to 400 nm, but these particles were combined into agglomerates of micron sizes. The X-ray diffraction (XRD) phase analysis of washed titanium carbonitride powder, synthesized in SHS-Az mode using partially nitrided titanium (TiN$_{0.2}$) ground in a planetary mill, confirmed the presence in the combustion product of titanium carbonitride only [6].

This work is a continuation of the work [6]. Its purpose is also to study the possibility of increasing the dispersion of titanium carbonitride powder TiC$_{0.5}$N$_{0.5}$, obtained by the azide SHS technology, by increasing the dispersion of the starting titanium powder, but using the intermediate partial carburizing of the starting titanium powder instead of its intermediate partial nitriding.

2. Materials and methods of investigations

In the process of experimental study, the following powders were used: the titanium powder of PTM brand (purity ≥ 98.9 wt %, particle size < 45 µm), carbon black of P804T brand (99.5%, < 0.2 µm), sodium azide NaN$_3$ (98.7%), ammonium fluoride NH$_4$F (98.5%), ground table salt NaCl of Extra brand (99.7%, < 80 µm), polytetrafluoroethylene (-C$_2$F$_4$-)$_n$ of Ftoroplast-4 brand or Teflon (100–180 µm). The planetary ball mill "Activator-2SL" with centrifugal acceleration of 30 g was used for intensive grinding with mechanical activation of powders. 375 grams of grinding hard alloy balls with a diameter of 7–11 mm and 37.5 g of the powder to be ground were loaded in each of the two drums with a volume of 250 ml. [6].

Powders of initial components were weighed on electronic scales, mixed in a porcelain mortar, filled up (bulk relative density of charge 0.4) in a calc cartridge with a diameter of 30 mm and a height of 45 mm, which was placed in a laboratory reactor SHS-Az of constant pressure with a working volume of 4.5 l. The arrangement of this reactor and the method of work on it with the measurement of linear velocities and the maximum combustion temperature by the thermocouple method using tungsten-rhenium thermocouples TR 5/20 with a diameter of 100 µm are described in detail in [11]. The temperature and velocity of combustion were recorded using an analog-to-digital converter connected to a computer. The reactor was filled with argon in the case of the preparation of partially carburized titanium or with nitrogen in the case of preparation of titanium carbonitride to the required operating pressure. The initial powder mixture (the charge) was ignited by a hot tungsten spiral from an electric DC source. After the end of combustion and short exposure for 10–15 min, the cooled sample was removed from the reactor. In the case of partially carburized titanium, the combustion product was ground in the planetary ball mill "Activator-2SL", and in the case of titanium carbonitride, the combustion product was easily destroyed manually to a loose powder state in a porcelain mortar. The resulting powder was washed from the residue of by-product NaF with distilled water at room temperature for 5–10 min, filtered on a vacuum funnel and dried in a vacuum drying cabinet to a constant weight.

Phase composition of the powdery combustion product was determined on an automated X-ray diffractometer ARL XTRA “ThermoScientific”. Shooting X-ray spectra was performed using Cu-
radiation with continuous scanning in the range of angles $2\theta = 20° \div 80°$ at a speed of 2 deg/min. The obtained spectra were processed using a special software package WinXRD. The study of the morphology and size of powder particles was performed on the scanning electron microscope JSM-6390A “Jeol”.

3. Results and discussion

Our attempts to obtain non-stoichiometric titanium carbide of TiC$_{0.1}$ or TiC$_{0.2}$ compositions in combustion of the charge of (Ti + 0.1C) or (Ti + 0.2C) respectively in the atmosphere of argon at a pressure of 4 MPa, as in the bulk density of the charge, and in an compacted form, have not led to success, as the charge was not ignited by the incandescent tungsten spiral filament. The charge of (Ti + 0.3C) was already ignited, but its combustion was unstable and incomplete. It turned out that the combustion of this charge (Ti + 0.3C) becomes stable with the addition of powdered Teflon. It is known that the addition of Teflon activates the combustion reaction of the charge (Ti + 0.3C) and promotes the synthesis of smaller particles of the combustion product [12]. Our studies have shown that the minimum amount of Teflon, which should be added for sustainable combustion and synthesis of non-stoichiometric titanium carbide TiC$_{0.3}$, is 5 wt % from the mixture of (Ti + 0.3C). The dependence of the combustion parameters (combustion temperature and combustion velocity) of the charge (Ti +xC) at different ratios of titanium and carbon with the addition of 5% Teflon, leading to the synthesis of non-stoichiometric titanium carbide of different composition of TiC$_x$, was investigated. The results are shown in figure 2a.

Figure 2. Combustion parameters at SHS of TiC$_x$ from Ti (a) and TiC$_{0.5}$N$_{0.5}$ from TiC$_{0.3}$ (b).

Figure 3 shows the results of XRD phase analysis of the product of such synthesis that is non-stoichiometric titanium carbide of TiC$_{0.3}$ composition. According to these results, the product contains phase TiC$_{0.3}$ only.

Figure 3. The XRD pattern of the sample of non-stoichiometric titanium carbide.
Synthesis of non-stoichiometric titanium carbide of composition TiC$_{0.3}$ was carried out also with another additive, which was the salt of sodium chloride NaCl, according to the equation Ti + 0.3C $\rightarrow$ TiC$_{0.3}$ with the bulk density of the charge. The NaCl can melt and evaporate during combustion, loosening and reducing the target product TiC$_{0.3}$ in size. The maximum content of NaCl, in which combustion was possible, was 13 wt % from a mixture of (Ti + 0.3C). As can be seen from figure 4a, the particle size of TiC$_{0.3}$, synthesized at 13% NaCl and milled in the planetary ball mill for 15 min, was in the range from 90 to 400 nm.

![SEM images of powders: (a) TiC$_{0.3}$ and (b) TiC$_{0.3}$N$_{0.5}$](image)

But the combustion of the charge (Ti + 0.3C) with the addition of 13% NaCl in argon was unstable, so the preparation of non-stoichiometric titanium carbide TiC$_{0.3}$ was carried out at 10% NaCl.

Powder of non-stoichiometric titanium carbide TiC$_{0.3}$, prepared from the charge as with the addition of NaCl, and with the addition of Teflon, has been used to produce the titanium carbonitride of TiC$_{0.5}$N$_{0.5}$ composition by the SHS-Az method in the atmosphere of nitrogen according to the reaction equation:

$$TiC_{0.3} + 0.2C + 0.16NaN_3 + 0.16NH_4F \rightarrow TiC_{0.5}N_{0.5} + 0.16NaF + 0.08N_2 + 0.32H_2$$

The dependences of temperature and velocity of combustion of this system from the nitrogen pressure in the reactor are shown in figure 2b.

The combustion product was a loose cake, which was easily ground by hand in a porcelain mortar into a very fine powder. The morphology and size of synthesized at nitrogen pressure 4 MPa powder of titanium carbonitride TiC$_{0.5}$N$_{0.5}$ is presented in figure 4b, which shows that the final product TiC$_{0.5}$N$_{0.5}$ has the same particle size as the ground non-stoichiometric titanium carbide TiC$_{0.3}$ used for synthesis of TiC$_{0.5}$N$_{0.5}$. Figure 5 shows the results of the XRD phase analysis of the titanium carbonitride synthesized from TiC$_{0.3}$. It is seen that the final product is TiC$_{0.5}$N$_{0.5}$ which does not contain impurities.
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Figure 5. The XRD pattern of the sample of titanium carbonitride synthesized from TiC_{0.3}.

4. Conclusion

Thus, the SHS process can be applied for intermediate partial nitriding of the starting metal powder of titanium to the composition of TiN_{0.2} or partial carburizing to the composition of TiC_{0.3} to ensure fire safety and the efficiency of the grinding process in a planetary ball mill for preparation of superfine powders of partially nitried or carburized titanium with ultrafine structure. It is shown that such powders can be used further in the process of azide SHS to produce the titanium carbonitride powder which was composed of superfine agglomerates of ultrafine- and nano-particles of TiC_{0.5}N_{0.5}.

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