

Self-purification effect in the synthesis of titanium carbonitride in a combustion regime

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A self-purification effect was found in the combustion synthesis of carbonitrides from a powder mixture of titanium and carbon black under forced nitrogen filtration.

The aim of this work was to demonstrate a self-purification effect of the condensed products synthesized from a powder titanium and carbon mixture by combustion in a nitrogen flow. The condensed reaction product can be the titanium carbonitride $\text{TiC}_{0.5}\text{N}_{0.5}$. Titanium carbonitrides are widely used in the production of tungsten-free hard alloys and the protective coatings.¹ The mass fraction of additives in the condensed reaction products is lower than that in the components used. The chemical analysis of the reaction gas phase showed that hydrogen and carbon monoxide are released during the combustion process.

The combustion of the test mixture was carried out using an experimental setup schematically shown in Figure 1.[†] The setup allowed us to measure gas consumption and pressure and to record the combustion process using a video camera. The gas supply was performed from the top face using a three-positional switch (12) under a pressure of 2 atm. For the sampling of the released gas, a special metal cylinder was used. Prior to every test, the cylinder was pumped out and then, using an adapter with cock, connected to the gas manifold (after the consumption and pressure sensors). During the sample combustion process, the cock was opened and the combustion products filled the cylinder. After the reaction, the cylinder was disconnected from the gas manifold and the gas samples were analyzed on a TOF-SIMS-5-100 mass spectrometer, an AAS-30 spectrophotometer and a Crystallux-4000M chromatograph. The obtained titanium carbonitride samples were studied by electron microscopy and chemical and X-ray phase analysis.

The results showed that the combustion of the Ti + 0.5C mixture [Figure 2(a)], which was previously blown-through by argon

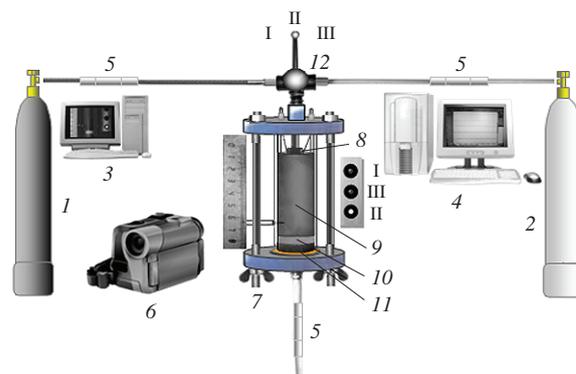


Figure 1 Experimental setup: (1) gas container with nitrogen; (2) gas container with argon; (3) computer for video signal recording; (4) computer for sensors signal recording through ADT; (5) consumption and pressure sensors; (6) digital video camera; (7) tungsten/rhenium 5/20 thermocouple; (8) electric coil; (9) green mixture; (10) mineral wool layer; (11) metallic gauze; (12) three-positional switch (position I, nitrogen; position II, argon; and position III, cut off a gas feeding into the reaction chamber).

at the closed top face (the switch in position III), was accompanied by noticeable gas release. The analysis of the gas samples from the system revealed that the H_2 content was > 99.0 wt%. The chemical analysis of the initial components demonstrated that the main source of hydrogen is titanium, containing about 0.08 wt% hydrogen. This result is in excellent agreement with the well-known fact that hydrogen dissolution in titanium is a reversible reaction; thus, the hydrogen content in titanium decreases with temperature. The calculated adiabatic temperature for the Ti + 0.5C mixture combustion (at an external pressure of 1 atm) is 1840°C , which exceeds the melting temperature of titanium,² and it means that the necessary and sufficient conditions are fulfilled for a convective-conductive combustion mode.³

The combustion temperature calculations were carried out using the Thermo computer program. The analysis of the gas consumption dependence on time [Figure 2(b)] shows that the gas amount released during the burning of a heated up layer (formed at the initiation stage) is more than that during the combustion front propagation. These amounts correspond to a peak on the consumption curve and to the level of its horizontal section. This dependence is explained by the fact that the temperature achieved in the heated up layer is higher and thus it corresponds to the more intense release of highly volatile and gas-like additives. The gas release process in the system coincides with the moment when the combustion front reaches the sample bottom face [Figure 2(b)].

During the combustion of a Ti + 0.5C (soot) mixture in a nitrogen flow (the switch in position I in Figure 1), besides

[†] The experiments were carried out by the following procedure: a powder mixture (9) was charged into a vertically placed transparent quartz tube (external diameter of 16 mm; height of 90 mm; and wall thickness of 1 mm). The tube was placed on Al_2O_3 mineral wool substrate (10) with 15 mm height and the steel gauze ring (11) with 10 mm height. Using an ADC (analog to digital converter) L-154 (L-card firm production), the signals from sensors (5), thermocouple (7) and photodiodes, showing the switch (12) positions, in real time arrive at computer (4). The combustion process was initiated from the tube top (*i.e.*, charging) face by an electric pulse passed to coil (8). By a digital Sony DCR-HC96E video camera (6), the combustion process was recorded directly into computer (3) memory.

The green mixture samples were prepared from the powders of PTS titanium and P804-T soot at a component ratio that gave titanium carbonitride containing 10.1 wt% carbon and 10.2 wt% nitrogen (CAS # 12627-33-7) upon combustion in nitrogen. To increase the nitrogen fraction in the condensed products, a solid nitrification agent (titanium nitride) was introduced into the initial mixture and the combustion was carried out in a nitrogen flow. The powders were mixed for 30 min in a 'drunk barrel' type mixer. The green mixture sample weight was 14.00 ± 0.01 g in all experiments.

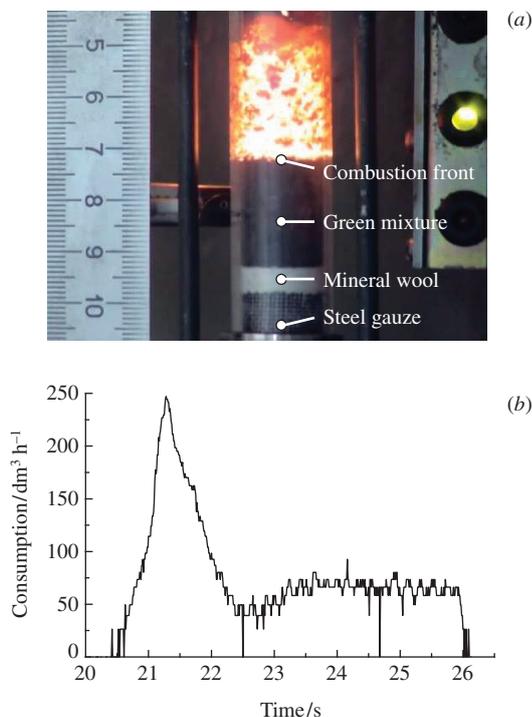


Figure 2 (a) Photograph of the Ti + 0.5C–N system combustion process at closed top face and (b) the corresponding gas consumption curve.

a carbidization front, a nitridation front can be formed for which the propagation velocity depends on the nitrogen consumption. In our experiments (with the pressure of 2 atm at the tube top face), the nitridation front propagation velocity is lower than that for the carbidization front; therefore, we observed the two successive fronts during the combustion process. The chemical, X-ray phase and microstructure analysis of the reaction products showed that, in the second front, the nitridation depth did not achieve 100%, though, according to the filtration combustion theory,⁴ conversion must be complete in the active gas cocurrent flow (coflow). It may be supposed that such a discrepancy is connected with some peculiarities of the interaction between titanium and nitrogen. For example, titanium, which does not react with carbon, can interact with nitrogen to form a surface titanium nitride layer inhibiting the total nitridation because the nitrogen diffusion coefficient in titanium nitride is low.

To increase the nitrogen fraction of the condensed products in several experiments, a titanium nitride powder was introduced into the initial mixture [Figure 3(a)]. The experiments with gas sampling revealed that the main gaseous component released under combustion is hydrogen, similarly to experiments with Ti + 0.5C mixture combustion at closed top face (without any blow-through). The chemical analysis of the initial components and reaction products (Table 1) indicates that the mass fraction of additives

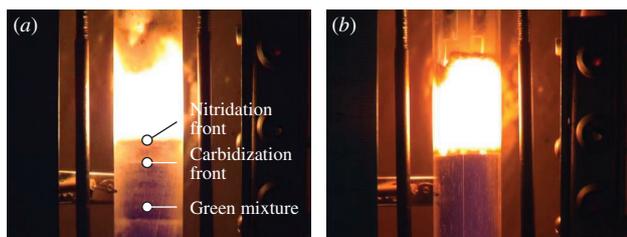


Figure 3 Photograph of the mixture (with titanium nitride addition) combustion process in the nitrogen flow: (a) dried mixture and (b) the mixture with 1 wt% water.

Table 1 Results of chemical analysis of the substrate and reaction products.

Initial components	Content in the substance (wt%)	Reaction products			
		Condensed products	Content in the products (wt%)	Gaseous products	Content in the gaseous mixture (wt%)
Ti	98.1	Ti	79.9	H ₂	99.69
C	99.5	C	10.1	CO	0.31
TiN	95.0	N	10.2		
N	99.29				

in the condensed reaction products decreases as compared with the components used, *i.e.*, there is a self-purification effect. Note that, according to chemical analysis, the content of oxygen in the bottle was 0.71 wt%, whereas it was not detected in a gaseous phase after synthesis (only in the CO form, Table 1).

Special experiments showed that the presence of 1 wt% water in the same mixture leads to the decrease of the self-purification effect. The required water content of the mixture can be achieved by placing the initial mixture into a desiccator containing moisture. The moisture mass fraction was controlled by the mixture weight growth, and after the necessary increase was achieved the samples were removed from the desiccator and used in the combustion experiments. The presence of 1 wt% water in the mixture leads to a decrease in the first front velocity to the second front velocity after which the fronts naturally become non-distinguishable [see Figure 3(b)]. In this case, instead of the gas release from the system, the gas absorption from the atmosphere occurred, which was recorded by a pressure sensor placed in the gas tapping line (about a 30% decrease at 1 atm). According to chemical analysis, the presence of 1 wt% water in the system results in composition changes in both the gaseous mixture and condensed products. As compared with the initial values, the carbon content of the condensed products decreased from 10.1 to 9.6 wt%, but the nitrogen content increased from 10.2 to 10.4 wt% (Table 1).

Thus, it has been demonstrated that single-phase titanium carbonitride TiC_{0.5}N_{0.5} can be synthesized at nitrogen pressures below 2 atm. This involves a sequence of titanium conversions in the combustion wave, namely, carbidization (the first front) and nitridation (the second front). Based on the experimental results, we found that the combustion of the Ti–C–N system was accompanied by noticeable gas release and a self-purification effect.

The mass fraction of additives in the condensed reaction products decreased, as compared with that in the initial components. The presence of 1 wt% water in the system affected the composition of the gaseous and condensed products and diminished the described self-purification effect.

The addition of titanium nitride powder to the initial mixture results in an increase in the nitrogen content of the condensed reaction products.

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