Obtaining of vanadium nitrides during the combustion of vanadium oxide with calcium and calcium nitride in nitrogen

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Abstract. The paper represents a study of combustion of vanadium oxide with calcium and calcium nitride in nitrogen. The study shows that when 75% of calcium is replaced with its nitride, it is possible to avoid the spread of the reaction mass. When the content of calcium in the green mixture is 1.2 times higher than the stoichiometric ratio and 75% of calcium is added as nitride, the maximum temperatures exceed 2200 °C in the combustion zone. The X-ray study established that single-phase vanadium nitride can be obtained after acid-dissolution of the calcium compounds contained in the product. An increase in the concentration of calcium in the initial mixture leads to the decrease in the size of product particles.

1. Introduction
Vanadium nitride due to its physical and chemical properties can be considered to be a promising material for modern engineering. In the work [1] vanadium nitride was obtained by nitriding the vanadium tape under pure nitrogen at pressures of 150-170 kPa. A compact material with a nitrogen content corresponding to the homogeneous region in vanadium mononitride was obtained. The lattice parameter of the nitrided vanadium tape was equal to the parameter of the vanadium mononitride powder. The temperature of transition to the superconducting state was 6 K. The work [2] reports that vanadium nitride is more effective ligature compared with ferrovanadium. Replacement of ferrovanadium with vanadium nitride decreases consumption of vanadium by 30% during the alloying of steel and provides the same level of hardening of steel, which reduces the cost of steel. Vanadium nitride was obtained from vanadium pentoxide by reducing oxide with carbon (soot) in a resistance furnace under nitrogen for 4 hours. The conditions for the obtaining of vanadium nitride were studied using thermogravimetric analysis. The obtained vanadium nitride contained vanadium carbide. In [3], vanadium nitride was used to obtain supercapacitors. Vanadium nitride was obtained by pyrolysis of xerogel of vanadium pentaoxide with melanin at a temperature of 800°C under nitrogen. The size of the particles of vanadium nitride obtained was about 20 nm. Hybrid nanopowders of vanadium nitride with nanosized carbon particles showed good capacitor properties. The specific capacity was 255 F/g at a voltage of 1.0-1.5 V. In [4] the obtaining of vanadium nitride from vanadium pentaoxide was studied by the carbothermic reduction of oxide under nitrogen at atmospheric pressure for the purpose of using it as a ligature for the manufacture of steel. A green mixture consisting of the powders of vanadium pentaoxide and soot was heated by a microwave heater. The reaction product contained up to 16.1 wt.% nitrogen. In [5], the possibility of using vanadium nitride as a catalyst for propane dehydrogenation (obtaining propylene from propane) was studied. Vanadium nitride was obtained from vanadium pentoxide. The nitriding of oxide deposited on the catalyst support was carried out.
during heating under ammonia. Vanadium nitride catalysts showed high activity in the dehydrogenation reaction of propane. In [6] vanadium nitride was obtained in the combustion mode. Vanadium powder was pressed into cylindrical samples that were placed in a high-pressure unit filled with nitrogen. The self-propagating reaction of vanadium with nitrogen was initiated by the short heating of the upper end of the sample. The rate of reaction and the conversion degree as a function of the pressure of nitrogen were determined. The uniform samples consisting mainly of vanadium mononitride were obtained. The obtaining of metal powders from oxides by the calciumthermal method was studied and introduced by the authors using calcium hydride as a reducing agent [7]. V$_2$O$_5$ oxide cannot be used to obtain vanadium-containing alloys by this method due to high heat release. V$_2$O$_3$ oxide that was obtained by the reduction of V$_2$O$_5$ in hydrogen was used. Calciumthermal reduction of metal oxides is accompanied by high heat release, which leads to the significant heating of a green mixture. The relatively low melting temperature of calcium (838°C) leads to the formation of liquid with high chemical activity, and therefore the choice of the reactor material becomes a serious problem. In [7], the addition of pure-metal powders to a green mixture decreased the temperature of the reduction reaction to a relatively low temperature (1200°C). A self-propagating synthesis mode does not occur at such temperatures. The reaction mass should be heated for several hours, which results in high power costs. When synthesis is conducted in the combustion mode the reaction time decreases from several hours to several minutes. In this paper, we studied the possibility of obtaining vanadium nitride from the most stable oxide (V$_2$O$_5$), reducing it with calcium under nitrogen in the combustion mode.

2. Materials and procedure
The initial materials were vanadium pentoxide (pure, 6-09-4093-88) produced by Vekton company, granulated calcium powder with a granule diameter of 0.5-2 mm produced by Chepetsky Mechanical Plant, and nitrogen of increased purity (GOST 9293-74). The initial powders were mixed in a ceramic mortar and placed in a paper cylindrical crucible with a diameter of 23 mm. The paper crucible was mounted on a graphite stand in a metal crucible with a diameter of 40 mm, coaxially. The temperature was measured with tungsten-rhenium thermocouples WR-5/20 made of wire 0.2 mm in diameter. Thermocouples were embedded through the lateral surface. The combustion rate was determined with two thermocouples. EMF of the thermocouples was digitized using an A/D converter (LA 20 USB) and recorded on a computer. The assembly with the initial mixture was placed in a constant volume bomb that was filled with nitrogen. The ignition was initiated with a molybdenum wire spiral 0.5 mm in diameter, on which a short current pulse was supplied. The first experiments showed that the use of calcium as a reducing agent led to the formation of a large amount of liquid phase due to high heat release during combustion, and the material of the sample flowed and melted the metal crucible. The product could not be separated from the crucible. To reduce the temperature, some amount of calcium in the green mixture was replaced with calcium nitride, as in [8], to avoid spreading the reaction product. The calcium nitride powder was obtained by combustion synthesis in nitrogen at a pressure of 6 MPa (as described in [9]), followed by grinding in a mortar. The composition of the green mixture for the obtaining of nitrided vanadium was calculated by the formula

$$V_2O_5+5n((1-m)Ca+mCa_3N_2/3)$$

where $n$ is the ratio of the Ca content in the green mixture to its stoichiometric ratio, $m$ is the amount of Ca added as Ca$_3$N$_2$.

The products were treated with a solution of HCl to remove oxide and calcium nitride formed during combustion and then washed in distilled water. The content of N and O in the washed samples was determined using a LECO ONH 836 device (Tomsk Shared Research Facilities SB RAS). The phase content was studied using a DRON-2.0 X-ray diffractometer and the PDF2 database. The Philips SEM 515 electron microscope was used to study the powders of the products. The adiabatic combustion temperatures were preliminarily calculated using the TERRA numerical code [10].
3. Results and discussion
The calculated values of the adiabatic reaction temperatures for different compositions and pressures are shown in figure 1.

![Figure 1](image1.png)

**Figure 1.** Adiabatic combustion temperature of the stoichiometric composition «V$_2$O$_5$ – Ca – Ca$_3$N$_2$ – nitrogen», depending on the proportion of Ca$_3$N$_2$ replacing metallic calcium. Nitrogen pressure: (1) 1; (2) 3; (3) 6 MPa.

The combustion temperatures measured were lower than the calculated ones, which can be explained by heat dissipation to the environment. The samples after combustion is found to retain their shape, that is, they do not spread when at least 75% calcium ($m>0.75$) is added as nitride. Figure 2 shows the products obtained during the combustion of the compositions, the contain of calcium in which was 1.2 times more compared to the stoichiometric ratio ($n=1.2$) for the case when 75% calcium was added as calcium nitride. At nitrogen pressure of more than 1 MPa, the samples retain their original shape (a), and at a pressure of 0.2 MPa, the samples are broken, probably, by the evolved gases (b).

![Figure 2](image2.png)

**Figure 2.** Combustion products of the samples for $n$=1.2 and $m$=0.75 at the nitrogen pressure of (a) 8 MPa; (b) 0.2 MPa.

The combustion temperatures exceed the melting points of almost all possible compounds that can be formed in the combustion zone [11], except for calcium oxide. The substance in the reaction zone is
suspension that contains the solid particles of calcium oxide and has a high viscosity, which does not allow it to spread during the existence of the liquid phase. The time for the existence of the liquid phase can be estimated from the combustion thermograms. The thermogram in figure 3 shows that the temperature exceeding the melting point of calcium is maintained for 20 seconds. The dependence in figure 4 shows a slight decrease in the maximum combustion temperature with increasing pressure.

**Figure 3.** Thermogram of combustion of a sample for $n=1.2$, $m=0.75$ at nitrogen pressure of 8 MPa.

**Figure 4.** Maximum combustion temperature as a function of nitrogen pressure ($n=1.2$, $m=0.75$).

This fact may be explained as follows. The real Ca-V$_2$O$_5$-N$_2$ system is not isolated. Excess calcium evaporates and leaves the system without reaching the temperature of maximum adiabatic heating. The total heat capacity of the remaining products becomes lower. But the heat release from chemical conversions maintains at the same level. The combustion temperature, which can be considered to be the ratio of the released heat to the average heat capacity of the products, in this case increases.

**Figure 5.** X-ray diffraction pattern of the product obtained at a pressure of 4 MPa.
Moreover, the increase will be the greater, the lower the temperature of calcium removed from the combustion zone and the more calcium leaves the zone of chemical conversions. The increase in pressure leads to the decrease in the amount of calcium removed and to the decrease in the maximum combustion temperature. The increase in the evolution of the gaseous phase with decreasing pressure also explains the damage of the samples at a pressure of 0.2 MPa (figure 2b).

The combustion rate was 15.7 mm/s at a pressure of 8 MPa and 10.9 mm/s at 4 MPa. The nitrogen content in the obtained products varied from 13.5 wt.% to 17.6 wt.%. Homogeneous vanadium mononitride is 16-21.6 wt.% nitrogen [12]. Therefore, it is possible to obtain single-phase vanadium nitride. The X-ray diffraction pattern of such a sample is shown in figure 5.

Vanadium nitride particles are formed in liquid containing vanadium, calcium, and nitrogen. Reducing the concentration of vanadium should lead to the decrease in the growth of vanadium nitride crystals and, consequently, to the decrease in the size of the product particles.

![Figure 6](image1.png)

**Figure 6.** Images of particles of products obtained by combustion in nitrogen for the compositions: (a) excess calcium is 20% \((n=1.2), (m=0.75)\); (b) excess calcium is 50% \((n=5), (m=0.75)\).

The images shown in figure 6 show that when the content of calcium in the green mixture is 5 times greater than the stoichiometric ratio \((n=5)\), the particle size of the product is noticeably smaller than that when the calcium is 1.2 of the stoichiometric ratio \((n=1.2)\). The further increase in the excess calcium will reduce the particle size of the product.

4. Conclusion
1. The samples obtained by the combustion of \(\text{V}_2\text{O}_5\), Ca and \(\text{Ca}_3\text{N}_2\) powder mixtures retain their initial form when more than 75% of calcium is added as calcium nitride.
2. When the excess calcium is 20% \((n=1.2)\) and \(m=0.75\), the maximum combustion temperatures exceed 2200 °C and decrease with increasing pressure.
3. The single-phase vanadium nitride can be obtained during the combustion of the mixtures of vanadium oxide with calcium and calcium nitride in nitrogen.
4. The increase in the excess calcium in the mixture leads to the decrease in the size of the product particles.
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