Combustion of ZrO₂ – Ca and TiO₂ – Ca mixtures in nitrogen

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Abstract. Combustion of calcium with zirconium oxide, as well as calcium and calcium nitride with titanium oxide in nitrogen is studied. The products obtained by the combustion of mixtures with titanium and subjected to acid enrichment contain no more than 15% of particles with a size larger than 40 microns, and more than 32% after the combustion of mixtures with zirconium. The use of a calcium and calcium nitride mixture as a reducing agent decreases the combustion temperature. Significant increasing the amount of calcium in the initial mixture decreases the particle size of the product.

1. Introduction

Titanium and zirconium nitrides are used in modern engineering due to high melting temperatures, high hardness, acid resistance, etc. The relatively high corrosion resistance and the use of zirconium nitride as a heat-resistant coating is stimulus to study the possibility of using zirconium nitride as a protective coating exposed to water vapor at 660°C [1]. It was shown that oxidation in water vapor occurred 100 times faster. Due to high melting point, titanium nitride is used as a modifier to reduce grain size. In [2], the effect of the addition of nanosized titanium nitride on the properties of Ti-6Al-4V alloy sintered by the method of spark plasma sintering was studied. The addition of 4 vol.% TiN nano-powder was shown to lead to a change in the shape and size of grains, an increase in hardness and a change in the nature of destruction. Hardness and wear resistance of zirconium nitride are attractive to use it as a coating of cutting tools. In [3], multilayer ZrN/CrN coatings were studied. The highest values of nanohardness (24.58 GPa) were obtained for 732 nm thick coatings with an average grain size of 13.3 nm, and the nitrogen content in the product was 49 at.%. It was concluded that such coatings can be effectively used in the manufacture of industrial cutting tools.

In [4], cermet with a composition of (Ti, W, Mo, Ta, Cr) (C, N) was obtained by the method of carbothermic reduction-nitriding (CRN) from metal oxides. The minimum heating temperature of the reaction mixture was 1600°C. The reaction of titanium oxide was shown to proceed according to the following formula: Anatase-TiO₂ → Rutile-TiO₂ → Ti₄O₇ → Ti₃O₅ → Ti(C,N). The best result was obtained by heating the reaction system at 1800°C for 4 hours. The optimal composition of the product is (Ti₀.₈₈₂W₀.₀₆₈Mo₀.₀₃₀Ta₀.₀₁₃Cr₀.₀₀₅)(C₀.₇₂₄N₀.₂₇₆), where the C/N ratio is close to 7/3, the content of oxygen and free carbon is less than 0.3 wt.%. The authors believe that this material has a high potential for future applications. The possibility of using titanium nitride nanoparticles as a photothermal agent activated in the near-infrared region was studied in [5]. Nanoparticles were obtained by nitriding powders at a temperature of 1000°C. Nanoparticles were shown to have significant absorption for wavelengths above 700 nm. Nanoparticles coated with polystyrene sulfonate and polydiallyldimethylammonium chloride demonstrated well-pronounced spherical morphology with an average size of ~ 50 nm. Their therapeutic efficiency in the destruction of pancreatic cancer cells SW1990 was found. Particles have low toxicity. Titanium nitride nanoparticles are a promising
material for use in the photothermal treatment of cancer. In [6], the possibility of using zirconium nitride as a plasmon nanostructure was studied. Due to the thickness limitations imposed on organic solar cells, their absorption efficiency is limited. Plasmon nanostructures are capable of increasing optical efficiency by increasing the length of the light path inside the active material. Here, refractory plasmonics is a new type of plasmon nanostructures and used in organic solar cells instead of traditional metallic plasmonics. Nanosized particles of cubic zirconium nitride increase the absorption coefficient of light energy and short circuit current. In [7], titanium nitride was used as a component of a hard alloy based on silicon carbide. Addition of titanium nitride up to 40% was found to increase the hardness and strength of the alloy. In [8], wear-resistant TiN/W2N coatings were studied. The addition of W2N increases the hardness of the coating and reduces its friction coefficient and wear at temperatures of 25-500°C. The use of zirconium nitride to increase the ablation resistance of a tungsten-based composite material was studied in [9]. The addition of zirconium nitride significantly reduced the ablation of tungsten. In [10], sintering of ZrN with sialon was studied in order to obtain a composite material with improved mechanical properties. Samples were obtained by sintering ZrN and sialon powders at a temperature of 1700°C for 6 hours in nitrogen. Sintered samples had hardness of 16.16 GPA and high fracture toughness.

There are a number of methods for producing these nitrides: for example, heating of titanium or zirconium powders in the presence of nitrogen or ammonia in furnaces or plasmatrons, and reduction of oxides in nitrogen, where carbon is used as a reducing agent. However, after carbon-thermal reduction products may contain an increased content of carbon [11]. In [12], titanium nitride powder containing 18.4–21.9 wt.% N with a particle size from 50 to 500 nm was obtained by the combustion of titanium powder with a gasifying additive in nitrogen. Calcium is an effective reducing agent for metal oxides. In [13], the technology is described for producing titanium nitrides by the reduction of oxides with calcium hydride, followed by nitriding in a furnace. The patent [14] describes a method for producing titanium and zirconium nitrides by the reduction of oxides of these metals with calcium in nitrogen in a self-propagating mode with further removal of calcium oxides by the method of acid enrichment. However, that process and the formation of products have not been studied enough, which was stimulus to carry out this work.

2. Materials and procedure

Granulated calcium with a grain diameter of 0.5-2 mm produced by Chepetsk Mechanical Plant, pigment TiO2 (anatase) zirconium oxide powder (TU 6-09-2486-77), and gaseous higher-purity nitrogen (GOST 9293-74) were used as initial reagents. The composition of initial mixtures was calculated in accordance with the stoichiometric ratio: MeO2 + n2Ca, where: Me – Ti or Zr; n is the ratio of the real calcium content to its stoichiometric content in the mixture, i.e. (n-1) characterizes excess calcium.

The partial replacement of calcium with calcium nitride in the reaction mixture reduces the combustion temperature; therefore, for the samples containing titanium, combustion with partial replacement of calcium with calcium nitride was studied. Mixtures with titanium and calcium nitride were prepared as follows TiO2+2n((1-m)Ca+(2/3)mCa3N2), where m is the proportion of Ca added as Ca3N2. The mixtures were placed in cylindrical paper cups with a diameter of 23-24 mm and burned in a constant pressure bomb in nitrogen using a known method [15]. The combustion temperature was measured with thermocouples W-5%Re/W-20%Re. The combustion products were subjected to acid enrichment in a solution of hydrochloric acid to remove CaO, Ca3N2 and residual calcium. Studying the kinetic of chemical enrichment of products showed that this process was divided into two characteristic stages. It was found that the speed of the process was determined by the concentration of acid at the first stage, and at the second stage, it is limited by the delivery of acid through the micropores of the “calcium-containing phases - titanium or zirconium nitride” composition. The effect of the concentration of hydrochloric acid (0.5 ÷ 5 wt.%) on the acid enrichment was studied. The transition rate of calcium into the solution increases with an increase in the concentration of hydrochloric acid and reaches maximum values in 2–5% solutions. However, with increasing the acid concentration, the content of titanium and zirconium in the solution increases. Therefore, HCl solution
was used for the removal of calcium oxides 2%. The degree of acid enrichment and the nature of dependence indicate that the complete removal of calcium in this case takes a long time (1-2 hours).

The phase composition of the products was studied with a DRON UM X-ray diffractometer, and the size and shape of the particles were determined by a Philips SEM 515 electron microscope. The content of nitrogen and oxygen was analyzed using a LECO ONH 836 analyzer. Sieve analysis was performed using a RETCH AS 200 sieve analyzer.

3. Results and discussion

The combustion temperatures of the test compositions were higher than the melting points of calcium, calcium nitride, titanium, and zirconium. Therefore, combustion proceeds with the formation of a liquid phase. The samples after the dissolving of calcium compounds were obtained in the form of powders of different dispersity. The particle size of products is determined by the size of initial oxide powders, as well as by the agglomeration rate that depends on the combustion temperature, the diffusion rate of components in liquid, and the time spent by components in the liquid phase.

Figure 1 shows that after the combustion of the composition with TiO$_2$ at $n = 1.7$ most of the product obtained is a powder with a dispersion of less than 40 microns, and the proportion of the fine powder increases with increasing pressure. Figure 2 shows that after the combustion of the composition with ZrO$_2$ at $n = 1.7$ the portion of coarse particles (more than 40 microns) is more than 0.32 and increases with increasing pressure. With an increase in excess calcium in the initial mixture with TiO$_2$ (Figure 3), the concentration of nitrogen in the product increases and the concentration of oxygen decreases. For the compositions with ZrO$_2$ (Figure 4), by increasing $n$, the content of nitrogen in the products decreases and the content of oxygen increases, dissimilarly to the compositions with TiO$_2$. The dissimilarity might be explained by the distinction of melting points of TiO$_2$ and ZrO$_2$.

![Figure 1](image1.png)

**Figure 1.** Ratio of the mass of coarse TiN particles to the total mass of TiN particles in the products obtained by the combustion of mixtures with TiO$_2$ as a function of pressure; $m_1$ is the mass of the powder with a size larger than 40 microns, $m_2$ is the total mass of the powder. $n = 1.7$.

![Figure 2](image2.png)

**Figure 2.** Ratio of the mass of coarse ZrN particles to the total mass of ZrN particles in the products obtained by the combustion of mixtures with ZrO$_2$ as a function of pressure; $m_1$ is the mass of the powder with a size larger than 40 microns, $m_2$ is the total mass of the powder. $n = 1.7$.

By increasing nitrogen pressure, the content of nitrogen in the product increases and the content of oxygen decreases (Figure 5), which is explained by an increase in the nitriding rate with increasing pressure.

Also, with increasing pressure, the content of nitrogen increases and the content of oxygen in products with ZrO$_2$ decreases (Figure 6).
Figure 3. Content of nitrogen (1) and oxygen (2) in the product as a function of the parameter $n$ for compositions with TiO$_2$, $P_{N_2} = 6$ MPa; powder size less than 40 microns.

Figure 4. Content of nitrogen (1) and oxygen (2) in the product as a function of excess calcium for compositions with ZrO$_2$, $P_{N_2} = 6$ MPa; powder size less than 40 microns.

Figure 5. Content of nitrogen (1) and oxygen (2) in the product as a function of nitrogen pressure after acid enrichment for compositions with TiO$_2$; $n = 1.7$; powder size less than 40 microns.

Figure 6. Content of nitrogen (1) and oxygen (2) in the product as a function of nitrogen pressure after acid enrichment for compositions with ZrO$_2$, $n = 1.7$; powder size less than 40 microns.

X-ray diffraction analysis shows that the products obtained by the combustion of compositions with TiO$_2$ at pressures more than 3 MPa consist of a single phase, titanium nitride (Figure 7). At lower pressures, phases Ti, TiN$_{0.3}$, and CaTiO$_3$ are detected in the products. The products obtained by the combustion of compositions with ZrO$_2$ contain ZrN and CaZrO$_3$ phases (Figure 8).

The images in figures 9, 10 show that the particles of the obtained titanium and zirconium nitrides are mainly round-shaped, which ensures good flowability. The size of the powder particles is greater than 1 micron.

Partial replacement of calcium in the reaction mixture with calcium nitride reduces the combustion temperature.

Figure 11 shows that the maximum temperature in the combustion zone decreases with increasing excess calcium and the fraction of calcium replaced with calcium nitride. By varying these parameters of the initial mixture, as well as the pressure of nitrogen, the combustion temperature changes in the range from 1700 to 2600°C. The dependence of the nitrogen and oxygen content in the combustion
products after acid enrichment (Figure 12) is non-monotonic. It may be due to the fact that at relatively low pressure, the absorption rate of nitrogen is not high enough, and with significant increasing the pressure, the rate of oxygen removal from the sample slows down worsening gas filtration conditions. Similar dependences were observed for other compositions (with different values of “n” and “m”).

![Figure 7](image1.png)  ![Figure 8](image2.png)

**Figure 7.** X-ray diffraction pattern of the sample with TiO$_2$ burned at a pressure of 6 MPa after acid enrichment.

**Figure 8.** X-ray diffraction pattern of the sample with ZrO$_2$ burned at a pressure of 6 MPa after acid enrichment.

![Figure 9](image3.png)  ![Figure 10](image4.png)

**Figure 9.** Product obtained by the combustion of the composition TiO$_2$ - Ca at $P_{N2} = 6$ MPa after acid enrichment.

**Figure 10.** Product obtained by the combustion of the composition ZrO$_2$ – Ca at $P_{N2} = 6$ MPa after acid enrichment.

The sizes of nitride particles after acid enrichment are determined by nucleation and growth in the reaction zone. The combustion temperatures are higher than the melting point of calcium (842°C), calcium nitride (1195°C) and titanium oxide (1843°C), but much below the melting point of titanium nitride (2930°C). The concentration of nitride nuclei and their growth rate are determined by the concentration of titanium atoms in the initial mixture. A decrease in the concentration of titanium atoms leads to a slower growth of nitride grains. The concentration of titanium oxide in mixtures with calcium and calcium nitrides can be reduced to almost any value by increasing the value of “n”, since calcium and its mixture with nitride can burn in nitrogen without oxide, and oxides and calcium nitrides are removed by acid enrichment. Thus, very fine particles of titanium nitride or oxynitride can be obtained and, possibly, those of the compound CaTiO$_3$ with the selection of appropriate conditions.
Figure 11. Combustion temperature as a function of pressure for compositions 1- (n = 2.85, m = 0.57); 2 - (n = 2.027, m = 0.33); 3- (n = 1.7, m = 0.1); 4- (n = 1.3, m = 0.23).

Figure 12. Content of nitrogen (1) and oxygen (2) in the product as a function of nitrogen pressure after acid enrichment for compositions with TiO$_2$ and Ca$_3$N$_2$ - (n = 1.3, m = 0.23).

Figure 13. Thermograms of the composition - (n=5,0, m= 0.5). (TiO$_2$), pressure - 2 MPa

Figure 14. Product obtained by combustion of the composition TiO$_2$ – Ca$_3$N$_2$ - with a fivefold excess of reducing agent at $P_{N_2} = 6$ MPa, after acid enrichment.

Figure 13 shows the thermograms of the combustion of a mixture with a fivefold excess of reducing agent. The reaction front propagation velocity was 0.755 mm/s. Figure 14 shows the image of titanium nitride particles after acid enrichment. It is seen that the product consists of particles, many of which are less than 200 nm in diameter. Particles are much smaller than those shown in Figure 9.

4. Conclusions
Combustion of calcium with TiO$_2$ and ZrO$_2$ oxides in nitrogen, followed by acid enrichment can be used to obtain nitride powders containing up to 0.9 of the stoichiometric concentration of nitrogen in TiN and up to 0.86 in ZrN. These values exceed those for nitrides obtained by the combustion of pure metal powders in nitrogen.

After acid enrichment, the content of particles with a size of more than 40 μm in combustion products with TiO$_2$ is not more than 15% and this content decreases with increasing pressure. In
combustion products with ZrO$_2$, the content of particles with a size of more than 40 $\mu$m exceeds 32% and varies slightly with pressure.

Increasing the excess calcium in initial compositions reduces the size of particles.

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