Combustion of titanium and chromium powders in the co-flow of a nitrogen-argon mixture

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Abstract. The combustion of the titanium and chromium powders in the co-current filtration mode was considered. We considered an original equipment that allows us to study the combustion of metal powders in a co-flow gas stream. It was demonstrated that the proportion of argon in a binary gas mixture has a greater influence on the burning temperature of titanium powder than the specific flow rate of the gas mixture. It was found that the actual burning temperature of chromium in the forced filtration mode is higher than the adiabatic temperature and the phenomenon of superadiabatic heating takes place. This method has high energy efficiency and allows you to get nitrides without the use of high pressures. It was found that co-current filtration promotes the formation of Cr$_2$N nitride.

1. Introduction

Metal nitrides have many important properties, due to which they are used in many areas of industry. They are used as protective and decorative coatings, raw materials for nitride ceramics, and master alloys [1-2]. Metal nitrides are obtained by various methods, but not all of them are energy efficient. Self-propagating high-temperature synthesis (SHS) is one of the widespread methods of obtaining such powders. However, this method is not without its drawbacks. One of these disadvantages is the need to use a high-pressure reactor. Along with the natural filtration mode, where the reaction gas is supplied to the combustion zone due to the pressure drop, there is a forced filtration mode. The paper considers one more type of filtration combustion - co-current filtration mode. A distinctive feature of this mode is that the reacting gas is supplied to the combustion zone from the outside and passes through the reaction products [3]. This method has been studied in detail theoretically [4-8] (references to a small part of such publications are provided) and little studied experimentally. Most of the experimental work is devoted to the combustion of titanium and carbon powders in a stream of nitrogen or argon, or their mixture [9-13].

The aim of the study is to reveal the mechanism of combustion of titanium and chromium powders in the co-current filtration mode. The main task is to study the effect of the amount of argon on their burning temperature.

Titanium powder has a high exothermicity compared to chromium, which makes it possible to study the combustion of titanium at a higher concentration of inert argon. Due to the high melting point of
chromium (about 1900 °C) and the low exothermicity of Cr$_2$N nitride (about 1280 °C), the effect of melting is excluded, which favorably affects the study of the filtration combustion process.

Section 2 of this article includes materials and methods, section three includes results and discussion.

2. Materials and methods
As initial chromium powders PH1S (Technical Specifications TU 14-1-1474-75) with a chromium content of 99.5% and a particle size of less than 200 μm were used. As initial titanium powders PTS (TU 14-22-57-92) with a particle size of less than 280 μm were used. Histograms of the distribution of particles of initial powders are illustrated in figure 1.

![Histograms of the distribution of particle sizes of initial powders](image)

Figure 1. Histograms of the distribution of particle sizes of initial powders a) Cr, b) Ti.

Powder granulometry was studied using a laser analyser Analysette 22. The amount of nitrogen was defined on the device TCH600. The phase composition was investigated on a Rigaku diffractometer.

During experimental work, it was found that the initial granulometric composition of powders contains a large proportion of fine particles that make filtration difficult. The supply of gas to the reaction chamber led to the compaction of the powder layer, which significantly impeded the filtration process. As an example, Figure 2 shows a synthesized sample of titanium nitride. The Figure 2 shows that the sample has areas with depleted nitrogen content due to poor gas permeability.

![A sample of the titanium nitride](image)

Figure 2. A sample of the titanium nitride.
The porosity of the powder layer in the case of chromium powder was increased by two methods. In one case, the fine fraction was removed by sifting the powder through a sieve, thus obtaining particles with a size of $\delta = 63 - 80 \, \mu m$. The second method of increasing the porosity of the powder layer was granulation of the initial powder. The size of the granules belonged to the range of 500 – 1000 $\mu m$. As a result of using these methods, 78% porosity was obtained for the sieved powder and 72% for the granule layer. To increase the porosity of the titanium samples, we removed a fine fraction less 50 $\mu m$. The porosity of the sifted titanium powder was ~78.5%.

Particle sizes of the initial and sieved powders are shown in Table 1.

### Table 1. Particle size of the initial powders.

| Volume, % | Initial powders | | Sieved powders | |
|-----------|-----------------|-----------------|-----------------|-----------------|
|           | Cr | Ti | Cr | Ti | |
| 10        | < $\mu m$ | < $\mu m$ | < $\mu m$ | < $\mu m$ | |
| 50        | 27  | 27.4 | 58.4 | 73.0 | |
| 90        | 107.3 | 212.2 | 87.3 | 185.0 | |

The granulation process of chromium powder was carried out as follows. The chromium powder was mixed with a 3% solution of polyvinyl alcohol, until a consistency in which a homogeneous plastic mass is formed. Then, the obtained mixture was sieved (sieve classification of ~ 18 mesh) and sintered in a vacuum furnace at a temperature of 1100 °C. A holding time was 1 hour. The obtained product was subsequently sieved two times (sieve classification of ~ 18 mesh and ~ 32 mesh). Thus, granules were obtained, the size of which was in the range of 0.5÷1 mm.

The process of filtration combustion under forced filtration was carried out on the original equipment - laboratory SHS reactor, the scheme of which is shown in Figure 3. The laboratory co-flow reactor is made of complex devices consisting of a reactor (a), a gas supply unit (b) and a unit for registering and processing data (c).

![Figure 3. Laboratory co-flow reactor scheme.](image-url)
During the preparation of the experimental work, a number of actions were performed. The bottom layer in the reaction tube is a powder of aluminum oxide or silicon. This layer is necessary for faster gas cooling at the outlet of the reaction chamber. The initial powder is poured into a quartz tube (1). Powder layer parameters: \(d = 0.016 \, \text{m}, \, h = 0.05 \, \text{m}\). The electric spiral (2) is brought into contact with the powder layer. Using a reducer (3), the reaction gas is fed into the quartz tube from a gas cylinder (4) containing a mixture of gases of a given composition. By applying an electrical impulse to the spiral in the surface layer, an exothermic reaction is initiated. Burning front is formed, which begins to spread along the sample. Pressure control is carried out according to a manometer (5) and a pressure detector (6). Gas flow at the reactor inlet and outlet is carried out by electronic micro flowmeters of the thermoanemometric type. The reaction temperature is measured by a W/Re thermocouple WR5/20 (7), the signal of which is fed through an amplifier to a recording device. Process parameters are recorded by a multi-channel meter.

3. Results and discussion
The temperature profiles recorded during the combustion of chromium granules (Figure 4 a, b, c) and chromium particles (Figure 4 d) at a different mass concentrations of argon in the binary mixture are shown in Figure 4. The specific flow rate of the mixture was \(12 \, \text{cm}^3 / (\text{s cm}^2)\).

![Figure 4](image)

**Figure 4.** Effect of argon concentration on the structure of temperature profiles: \(q=12 \, \text{sm}^3/(\text{s sm}^2)\); a) \([\text{N}_2]=100 \%\); b) \([\text{Ar}]=12.8 \%\); c) \([\text{Ar}]=24 \%\); d) 1 – \([\text{N}_2]=100 \%\); 2 – \([\text{Ar}]=7 \%\).
It was revealed that the gas composition strongly affects the combustion process, while the temperature profiles are qualitatively different. In the case of combustion of chromium in nitrogen, a small heating region is observed, in which the temperature rises rapidly to the maximum mark. This is followed by a small area (in the form of a small flat area), where the temperature reaches its highest values. With the addition of 12.8% argon to nitrogen, the first region changes slightly; at the same time, an increase in the region with the maximum temperature is observed. An increase in the argon concentration to 24% leads to an increase in the heating region and a narrowing of the region with a peak temperature. Figure 4d presents the temperature profiles at the combustion of chromium powder when [Ar] = 0 % (curve 1) and [Ar] = 7 % (curve 2). It was found that an increase of argon in the nitrogen-argon mixture can lead to the formation of an inverse combustion wave (Figure 4b, 4d curve 2).

Figure 5 presents diagrams showing the temperature and burning rate of the powder (1) and chromium granules (2) depending on the argon content.

![Graph showing temperature and burning rate](image)

**Figure 5.** The temperature and burning rate of the powder (1) and chromium granules (2) depending on the argon content.
Figure 6 shows the appearance of the samples obtained by combustion chromium of different dispersion. Moreover, Figures 6a and 6b show a sample formed by combustion of 63–80 µm chromium particles, and Figures 6c and 6d - as a result of combustion of 500–1000 µm chromium granules. In both cases, the original structure is preserved.

Titanium powder has a high exothermicity compared to chromium, which makes it possible to study the combustion of titanium at a higher concentration of inert argon. The combustion of titanium in nitrogen and at low concentrations of argon was accompanied by a rapid increase in temperature exceeding the melting point of titanium. at the same time, melting affected the filtration process. To lower the burning temperature of titanium, titanium nitride powder was added to the charge, and the amount of argon in the gas mixture was increased.

![Figure 6. Physical configuration of combustion products of chromium.](image)

Figure 7 shows pictures of synthesized samples of titanium nitride (the largest craters are marked with arrows).

![Figure 7. The samples of titanium nitride: a) [N₂] = 100%, Ti =100%; b) [Ar] = 24%, 50% Ti+50% TiN; c) [Ar] = 39%, 30% Ti+70% TiN.](image)

The temperature profile obtained by combustion 50% Ti+50% TiN is illustrated in Figure 8. The depression in the graph reflects titanium melting.
Figure 8. The temperature profile at the combustion of titanium:
\[ q = 12 \text{ sm}^3/(\text{s} \cdot \text{sm}^2); \]  
\[ [\text{Ar}] = 24 \%; 50\% \text{ Ti}+50\% \text{ TiN}. \]

Figure 9 presents diagrams showing the temperature and burning rate of the mixture 30\% \text{ Ti}+70\% \text{ TiN} depending on the specific flow rate and argon content. The figure shows that the argon concentration in the binary mixture significantly affects the maximum burning temperature.

![Figure 9](image.png)

**Figure 9.** Temperature and burning rate of the mixture 30\% \text{ Ti}+70\% \text{ TiN}:
blue – \( q = 5 \text{ sm}^3/(\text{s} \cdot \text{sm}^2);\) [Ar]=24 \%;
red – \( q = 12 \text{ sm}^3/(\text{s} \cdot \text{sm}^2);\) [Ar]=24 \%;
green – \( q = 12 \text{ sm}^3/(\text{s} \cdot \text{sm}^2);\) [Ar]=24 \%;
orange – \( q = 12 \text{ sm}^3/(\text{s} \cdot \text{sm}^2);\) [Ar]=39 \% .

A typical XRD (X-ray diffraction analysis) patterns of combustion products of (a) titanium and (b) chromium powders in the co-flow filtration mode are presented in Figure 10.
Figure 10. Typical X-ray diffraction patterns of combustion products of (a) titanium and (b) chromium [14] powders in a co-flow combustion mode: a) \( q=12 \text{ sm}^3 / (\text{s} \cdot \text{sm}^2) \), [Ar] = 12.8%; b) \( q=12 \text{ sm}^3 / (\text{s} \cdot \text{sm}^2) \), [Ar] = 24%

In the first case TiN was detected. In the second case Cr\(_2\)N nitride and chromium were detected. According to XRD-analysis (Table 2), the Cr\(_2\)N unit cell is trigonal [15], while the TiN unit cell is cubic.

Table 2. XRD-analysis results of synthesized products.

| Sample | Type of lattice | Lattice parameters, Å | Coherent scattering region, nm | \( \Delta d/d \cdot 10^{-3} \) |
|--------|-----------------|-----------------------|-------------------------------|--------------------------|
| Cr\(_2\)N | trigonal | a = 4.7756, c = 4.4617 | 32 | 1.1 |
| TiN | cubic | a = 4.2334 | 38 | 0.9 |

4. Conclusion

The paper presents the results of experimental studies on the combustion of chromium and titanium powders in a co-flow of nitrogen-containing gas. A laboratory co-flow reactor is considered, which makes it possible to study filtration combustion of metal powders in a gas flow. The results of experimental studies of filtration combustion of metal powders are presented on the example of titanium and chromium. It was found that in the mode of cocurrent filtration, the combustion products of chromium are mainly represented by the phase of nitride Cr\(_2\)N. With an increase in the concentration of argon in a binary gas mixture, a decrease in the rate and temperature of combustion is observed. It was found that the combustion of chromium in the forced filtration mode of the phenomenon of superadiabatic heating takes place. Titanium powder has a high exothermicity compared to chromium, which makes it possible to study the combustion of titanium at a higher concentration of inert argon. The cocurrent filtration mode makes it possible to apply SHS in the Cr-N\(_2\) system to the region of lower pressures and large sizes of metal particles. This method has high energy efficiency and allows you to get nitrides without the use of high pressures.

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