Chromium nitride synthesis in co-flow filtration mode

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Abstract. In this work, we considered an original setup that allows us to study the combustion of metal powders in a co-flow gas stream, and also presents the results of experimental studies on the combustion of chromium powder in a confined nitrogen-containing gas stream. This method has high energy efficiency and allows to get nitrides without the use of high pressures. The study of chromium combustion is justified by its high melting point at a relatively low exothermicity, which eliminates the influence of melting of the initial powder and synthesis products on the filtration process. This article presents the results of combustion of chromium powder with particle size $\delta = 63-80 \mu m$ and $\delta = 500-1000 \mu m$. X-ray phase studies of the obtained powders were carried out. The effect of nitrogen-containing gas consumption on the degree of nitriding of combustion products is shown. It is established that the forced filtration mode allows the synthesis of non-stoichiometric chromium nitride Cr$_2$N. The nitrogen content in the obtained Cr$_2$N samples reached 9.6%.

1. Introduction

The development of modern technology is impossible without the creation of new materials. The wide use of metal nitrides is due to their physical and chemical properties, such as heat resistance, corrosion resistance, and wear resistance. Metal nitrides are used as abrasive materials, wear-resistant and decorative coatings, raw materials for the production of nitride ceramics, alloying additives [1-5].

Filtration combustion of metal powders in nitrogen and self-propagating high-temperature synthesis of nitrides are experimentally studied under conditions of natural filtration [6], while maintaining the pressure drop, which contributes to the supply of reaction gas to the combustion region.

In this work, another type of filtration combustion is considered, in which the reacting gas is forcibly supplied to the combustion zone and moves in the direction of combustion through the reaction products following the moving combustion front. This type of combustion is theoretically described in sufficient detail [7-14], but at the same time, it has been little studied experimentally [15-17]. However, this method is energy efficient and has high applied value.

Thus, an experimental study of the combustion of metals in a nitrogen environment under forced filtration and the study of the properties of synthesized combustion products is a very actual task.

The aim of this work is an experimental study of the combustion of chromium powder under forced filtration conditions and the study of the properties of SH synthesis products during the combustion of chromium in a satellite stream of nitrogen-containing gas.
2. Materials and methods

As starting materials, chromium powders PH1S (Technical Specifications TU 14-1-1474-75) with a chromium content of 99.5% and a dispersity of less than 80 μm were used.

The particle size distribution of the initial powders was determined using an ANALYSETTE 22 MicroTec plus device from FRITSCH by laser diffraction. The nitrogen content was determined using a TCH600 device from LECO. X-ray phase analysis of the initial powders and synthesized samples was carried out using a Rigaku diffractometer with CuKα radiation, as well as the Crystallographica Search Match program (Oxford Cryosystems - UK) based on the Powder Diffraction File database.

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 installation – laboratory SHS reactor, the scheme of which is shown in figure 1. 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).

During the experimental work, the following actions were carried out. A portion of the initial powder was poured into a quartz tube. The size of the samples was constant: diameter 16 mm., height 40 mm. The upper part of the powder is brought into contact with an electric spiral. Using a reducer, reaction gas is supplied to the quartz tube from a cylinder, in which a mixture of gases of a given composition is preliminarily prepared. By applying an electrical impulse to the spiral in the surface layer, an exothermic reaction is initiated. A flat combustion front forms, which begins to propagate along the sample. Pressure control is carried out according to the testimony of a manometer and a pressure detector. The gas flow at the inlet to the reactor and at its outlet is carried out by electronic micro-flow meters of the “Red-y” hot-wire anemometric type. The reaction temperature is measured by a W / Re thermocouple WR5 / 20, the signal of which is fed through an amplifier to a recording device. Process parameters are recorded by a RealLab multi-channel meter.

![Figure 1. Scheme of an experimental setup for studying combustion metals under forced filtration.](image)

3. Results

The first experiments showed that the initial powders have a large fraction of small particles, which, when placed in a reactor, impede the gas flow and impede the combustion process. In this work, two
approaches were used to increase the porosity of the powder layer. The essence of the first one is excluding of the fine fraction, which resulted in the production of particles with a size of $\delta = 63 \div 80$ μm, which were used in further experiments. The second method of increasing the porosity of the powder layer was the granulation of the initial chromium powders (the granulation operation is described in paragraph above). As a result of granulation, granules of size $\delta = 500 \div 1000$ μm were obtained.

Figure 2 shows a typical photographic recording program for the extension of a stationary combustion front in the co-flow filtration mode.

![Figure 2](image_url)

**Figure 2.** Propagation of the combustion front in the co-flow filtration mode.

Figure 3 shows the X-ray diffraction pattern of the combustion product during the combustion of chromium in the satellite filtration mode and the temperature profile at a gas flow rate of $5.5 \times 10^{-5} \text{m}^3/\text{s}$.

![Figure 3](image_url)

**Figure 3.** Is an X-ray diffraction pattern of a sample obtained by combustion of chromium powder in a co-flow reactor and a temperature profile.

The maximum temperature recorded is about 1560 °C. The stoichiometric nitrogen content in chromium nitride is 21.2%, and in Cr$_2$N – 11.8%. Elemental analysis showed that the nitrogen content in the obtained samples reached 9.6%. X-ray studies confirmed the existence of a Cr$_2$N phase and chromium. No other phases have been established. Information regarding the region of existence of the Cr$_2$N phase is quite contradictory. However, in [18], the homogeneity region is presented in the range of 9.2–11.9% N. Thus, the forced filtration mode allows the synthesis of non-stoichiometric Cr$_2$N of various compositions.

The data of x-ray diffraction analysis are presented in table 1. It was found that the Cr$_2$N unit cell has the trigonal lattice parameters $a = 4.7756 \text{Å}$, $c = 4.4617 \text{Å}$. 
Table 1. X-ray analysis data.

| Sample  | Detected phases | Lattice parameters [Å] | Coherent scattering region [nm] | Δd/d*10⁻³ |
|---------|-----------------|------------------------|---------------------------------|-----------|
| Cr₂N     | Cr₂N            | a = 4.7756             | 32                              | 1.1       |
|          |                 | c = 4.4617             |                                 |           |

In the samples obtained using both sifted and granular chromium as the starting component, a decrease in the degree of nitriding is observed depending on the increase in the flow rate of the gas mixture (table 2).

Table 2. The degree of nitriding of chromium nitride, depending on the volumetric flow rate of the gas mixture at the inlet to the reactor.

| Source powder size δ [µm] | G_in=3.3⋅10⁻⁵ [m³/s] | G_in=1.1⋅10⁻⁴ [m³/s] |
|---------------------------|------------------------|-----------------------|
| 63÷80                     | 8.4 %                  | 8.0 %                 |
| 500÷1000                  | 9.5 %                  | 8.7 %                 |

4. Conclusion
The paper presents the results of experimental studies on the combustion of chromium powder in a coflow stream of nitrogen-containing gas. It is established that the forced filtration mode allows the synthesis of non-stoichiometric chromium nitride Cr₂N. The nitrogen content in the obtained Cr₂N samples reached 9.6%. X-ray phase studies of the obtained powders were carried out, which confirmed the presence of chromium in the synthesis product, which indicates that combustion occurs in the mode of incomplete conversion and chromium does not burn out. At the same time, all of the nitrogen entering the reaction zone interacts completely with chromium. This is supported by data recorded by the flowmeters at the inlet and outlet of the reactor.

Thus, the degree of nitriding of Cr₂N, for which the starting material was chromium with a particle size of δ = 63 ÷ 80 µm, decreased from 8.4% to 8.0% with an increase in the volumetric flow rate of the gas mixture at the inlet to the reactor. For Cr₂N, the initial component of which was granular chromium powder with a granule size of δ = 500÷1000 µm, the degree of nitriding decreased from 9.5% to 8.7%.

For combustion of a larger particle size of chromium powder under natural filtration conditions, the use of high pressures is necessary. The use of forced filtration allows one to extend the implementation of SHS in the Cr – N₂ system to the region of lower pressures and large metal particle sizes.

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