Wave Combustion Modes of Hafnium in Nitrogen

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INTRODUCTION

The foundations of research on the combustion of group IV–V metals in gaseous nitrogen were laid by Merzhanov et al. [1–3] in which the basic ideas of the mechanism for this process were developed. In an extension of this work [4] the combustion of hafnium in nitrogen at pressures above atmospheric was studied in detail. Recently, interest in these systems has arisen again, but also at gas pressures below atmospheric [5–8]. This is apparently because of the discovery of new, previously unobserved, combustion modes in these systems and the development of new experimental techniques for tracing the phase formation dynamics in combustion waves [9].

The purpose of this paper is to study experimentally the wave modes of combustion of hafnium in nitrogen at reduced pressures.

EXPERIMENTAL TECHNIQUE

The test samples (Fig. 1) consist of a pipe with an outside diameter $D = 3$ mm, a wall thickness $\delta = 0.75$ mm, and a length $L = 20–28$ mm pressed from hafnium powder (particle size $d \approx 10 \mu m$) to a density $\rho = (6.2 \pm 0.05) \cdot 10^3$ kg/m$^3$. The samples were prepared by axial compression on a 1.5-mm-diameter, 45-mm-long alundum capillary. In order to ensure the required durability and a uniform density of the sample along its length, the pressing was done step-by-step in layers of $\approx 3$ mm from a paste of hafnium powder with a 0.1% alcohol solution of polyvinyl butyral. The amount of the latter in the sample was less than 0.01%. After a sample was prepared, it was dried in an oven at a temperature of 423 K until a constant mass was attained. A tungsten wire heater with a diameter of 0.4 mm was mounted inside the capillary.

A sample was mounted vertically in the reaction vessel and a flat tungsten–rhenium thermocouple with a junction diameter of 20 $\mu$m was clamped to its surface in the middle. After the required initial temperature of the sample surface $T_0$ (controlled by varying the electrical power to the heater), and the nitrogen pressure $p_{N_2}$ in the vessel were reached, combustion was initiated with a semicircular electrical spiral on the end of the sample. The pres-

Fig. 1. The experimental setup: 1) spiral initiator; 2) heater wire; 3) layer of Hf powder; 4) tungsten–rhenium VR 5/20 thermocouple; 5) capillary insulator; 6) video camera.
sure change in the vessel during combustion was less than 2%.

The use of fairly extended samples \((L/D = 7-9)\) made it possible to avoid distortions in the process by the initiating spiral and end effects and to conduct the main measurements in the middle of samples up to 10 mm in length, for which it was possible to obtain an isothermal section with the initial temperature distribution along the sample. Wave combustion of the Hf–N system was recorded on a video camera at a framing rate of 25 sec\(^{-1}\). The average propagation velocity of the combustion wave (flare) along the sample \((u_d)\) and \((u_r)\) the circular velocity of the spin flare were measured (with an error of ±5%). The average pitch \(h = H/n\), where \(H = 5-7\) mm is the base length, was determined on cooled samples from the number of turns by the spin \(n \approx 10-15\).

The phase composition of the samples was studied in two ways: using x-ray phase analysis on a DRON-3M diffractometer (Cu \(K\alpha\) radiation) and directly during combustion using a laboratory dynamic x-ray radiography method \([9]\). In the first case, as a rule, an integral analysis of the sample was made (the entire sample was ground to powder in an agate mortar), but a layer-by-layer analysis was done for some of the samples (for this layers up to 50 \(\mu\)m thick were removed from their surface). In the second case, the x-ray radiation from the sample surface was analyzed (the penetration depth of the x rays was less than 50 \(\mu\)m) for transverse and longitudinal localization of the radiation beam (diffractometer slit) relative to the axis of the sample.

The diffraction patterns of the phase composition of the samples before and after burning obtained by dynamic x-ray radiography correspond to the analogous diffraction patterns of the samples obtained by x-ray analysis. However, here we shall just note some of the results of this study, without given a detailed discussion of the dynamics of the phase conversions in the various combustion wave modes.

An x-ray phase analysis of the initial hafnium powder revealed the presence of a small amount of the hydrides \(\text{HfH}_1.53\) and \(\text{HfH}_1.98\). But there is fairly weighty evidence for assuming that, because of their relatively low dissociation temperatures, the hydrogen is already released in the heating zone and has no significant effect on the combustion process, as such.

The Hf–N system includes several nitrides (\(\text{Hf}_3\text{N}_2\), \(\text{Hf}_4\text{N}_3\), and HN) and a solid solution of nitrogen in hafnium. The solid solution was identified from the x-ray emission of a compound corresponding to the composition \(\text{HfN}_{0.4}\) in the set of data.

RESULTS

Depending on the initial temperature of the sample surface and nitrogen pressure, four major modes of combustion wave propagation were observed in the reaction vessel (Fig. 2): two spin modes (region II) and two layer-by-layer modes (region III). Self-ignition of the sample took place for surface temperatures exceeding 900 K (region IV).

Spin Modes. The spin mode region becomes narrower as the pressure is reduced, and for \(p < 0.015 \cdot 10^6\) Pa only layer-by-layer wave combustion can be observed. Single-flare spin occurs only near the boundary separating the spin modes from the absence of combustion (see Fig. 2). As a rule, it is unstable: usually at least 3–4 continuous turns are observed followed by a transition to two-flare spin or quenching. Two-flare spin is more typical and takes place over almost all of region II. Nevertheless, near the boundary with region III, the number of flares in the spin mode increases rapidly to three or more.

The longitudinal spin propagation speed increases with rising initial temperature (for \(p_{\text{N}_2} = \text{const}\)) by an average of 2–3 times and the tangential velocity, by 1.5–2 times (Figs. 3 and 4). The pitch in the spin regime is essentially independent of the initial temperature and increases as the nitrogen pressure is reduced (Fig. 5).

Integral x-ray phase analysis of samples that had burned in the spin mode in atmospheric pressure nitrogen (high pressure spin, \(p_{\text{N}_2} \approx 0.035 \cdot 10^6\) Pa; Fig. 2) showed that in this case, the main combustion product is the nitride HfN (Fig. 6). The rel-