

Features of the thermal structure of reaction waves in the Ti - Mo – N₂ system

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Abstract. The thermal structure of filtration combustion waves in the metallic Mo – Ti system in nitrogen is studied by dynamic color pyrometry. It's shown that the combustion of the samples is conducted in the surface mode. This mode is characterized by the propagation of a reaction wave in a narrow near-surface layer of the sample followed by the penetration of combustion from the surface to the centre. The peculiarities of combustion observed are the presence of local reaction sources in the surface reaction wave and the complex three-dimensional structure of the temperature field in the reaction wave (local reaction source – surface reaction wave - inside reaction wave). The measurements have shown that with increasing nitrogen pressure, the maximum temperature inside the sample rises by 200 K.

1. Introduction

In recent decades, titanium-based alloys have found wide use in several fields, including the aerospace, automotive, marine, construction, and biomedical device industries [1-6]. Significant attention has been paid to investigating the suitability of titanium alloys as structural materials due to their desirable microstructural, mechanical, and physical properties [7]. Titanium has two allotropic forms: the α - and β -forms. If alloy Ti-Mo is nitrated [8], titanium nitride precipitates and leads to precipitation hardening of surrounding molybdenum matrix. This improves the hot strength and the recrystallization temperature of alloy. A particular interest, understanding the behavior and mechanism of combustion of metal-containing systems in gas media is important for solving urgent problems of the synthesis of functional inorganic materials [9].

It was shown in [2] that the microstructure, mechanical properties, and corrosion resistance of dense Ti – Mo alloys are sensitive to Mo content.

In this work, the thermal structure of the combustion wave in the powders with the ratio of Ti + 35 wt.% Mo in gaseous nitrogen media is studied using dynamic color pyrometry. The basis of color pyrometry applied in the work and its approbation are given in work [10].

2. Materials and Methods

The initial reaction components were metal powders the mass fraction of which was not less than 99.5 wt.%: Mo (average particle size - $< 10 \cdot 10^{-4}$ m) and Ti (average particle size - $< 63 \cdot 10^{-4}$ m). The powders were mixed in the ratio Ti + 35 wt.% Mo. The prepared mixtures were used to form



cylindrical samples with a flat lateral surface (figure 1), a diameter of $20 \cdot 10^{-3}$ m and a maximum relative density of 0.37. The combustion of the samples was initiated at the top by a heated electrosprail in an experimental setup (figure 1) under nitrogen (purity is not less than 99.9%) at a pressure 2 and $50 \cdot 10^5$ Pa. The setup was a sealed reaction chamber equipped with optical glass and electrical inputs to initiate combustion and record electrical signals. After the initiation of combustion, a self-sustaining reaction wave propagated along the samples.

Synthesis was recorded with a Panasonic DA 1EV video camera (frame rate is up to 50 s^{-1} , spatial resolution is 10^{-5} m) that was used for direct monitoring the velocity and structural characteristics of the surface combustion wave of mixtures. Temperature was controlled with a WRe5/20 thermocouple (thickness is $1 \cdot 10^{-4}$ m) that was placed at the bottom of the sample. The signal of thermocouple was recorded by an analog-to-digital converter (sampling frequency rate is up to 1 kHz) and analyzed on a computer. In addition, the temperature of the combustion wave was measured by the method of color pyrometry [9]. For simultaneous measurement by the method of color pyrometry in thermograms of the internal and surface combustion waves, a blind cylindrical hole was drilled on the flat lateral surface for the extraction of radiation (figure 1).

The software “Temp” was developed for the processing of video recording data obtained by color pyrometry. “Temp” can be used for:

1. Construction of the temperature distribution on an arbitrarily selected reaction wave. The temperature range is limited to ~ 500 K, which is related to the brightness of CCD matrix of the video camera used.

2. Conversion of video frames into colors corresponding to a specific temperature range. The minimum size of the combustion wave to measure the distribution of thermal fields is $\sim 55 \text{ } \mu\text{m}$ (10×10 pixels).

3. Construction of temperature chronograms of the reaction wave.

The error in the determination of temperature by color pyrometry did not exceed 50 K. The error was determined in the test temperature measurements of Ni, Ti and Mo wires during melting due to the heating by electric current under Ar (at a pressure $2 \cdot 10^3$ Pa). The temperature measurements of Ni–1750 K, Ti–1990 K and Mo–2905 K have a minimum deviation from the known melting points: Ni–1726 K [11], Ti–1940 K [11] and Mo–2890 K [11].

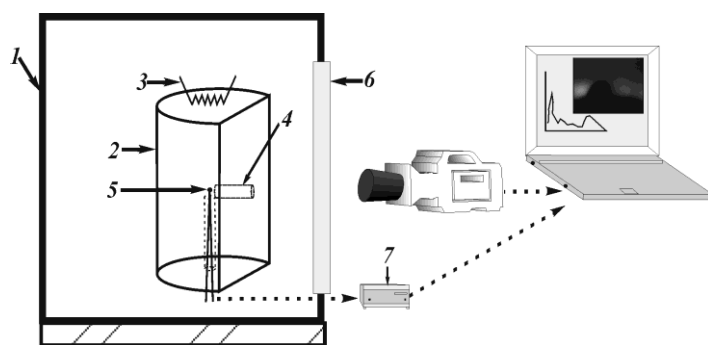


Figure 1. Scheme of the experimental setup.

(1) reaction chamber, (2) sample, (3) igniting spiral, (4) the hole in the sample, (5) thermocouple, (6) quartz glass, (7) analog-to-digital converter.

3. Results

According to the video recording data, the combustion of the powder mixture Ti + 35 wt. % Mo in nitrogen ($P(\text{N}_2) = 2 \cdot 10^5$ Pa) is conducted in the surface mode. This mode is characterized by the propagation of reaction wave in a narrow near-surface layer of the sample (figure 2, frames 0–0.48 s) followed by the penetration of combustion from the surface to its center, as can be seen from the increase in the glow intensity of the hole (figure 2, frames 1 to 13 s) after the passage of surface wave.

The features of combustion observed are the presence of local reaction sources in the surface reaction wave (figure 2). The observation shows that the local reaction sources occur stochastically in the combustion wave. After ignition, a plane decaying reaction wave propagates from the end of the sample at a velocity monotonically decreasing along its axis. Then, in the temperature zone ($T=1500$ K, according to the data of color pyrometry) the wave reactions are initiated and develop

across the sample with an average temperature of 2240 K (according to the data of color pyrometry) and a rate of up to $3\div 5.3$ mm/s. A similar combustion mode was observed earlier in the Ti-N₂ system [12].

Another feature of combustion is a complicated three-dimensional thermal structure of the reaction wave (figure 3). Figure 3 shows the temperature chronograms for the surface combustion wave with and without combustion sources, as well as for the central part of the sample (powder mixture Ti + 35 wt. % Mo in nitrogen ($P(N_2) = 2 \cdot 10^5$ Pa)). The measurements have shown that the maximum temperature of surface wave outside the combustion source (T_1) is 200 K lower than the temperature in the center of the sample (T_2). This is explained by the effect of heat accumulation during nitrogen filtration in the central part of the sample. This fact corresponds to the observed fusion in the central part of the sample (figure 4a), where the temperature is 150 K higher than the melting point of titanium. The temperature of surface combustion wave inside the combustion source (T_3) exceeds the temperatures T_1 and T_2 , which is explained by the known effects of heat accumulation in local combustion sources due to the thermal and chemical instability of nitriding reactions [13]. The time difference (Δt) in reaching the maximum temperature on the surface and inside the sample allows the linear propagation velocity to be estimated ($V=R/\Delta t \approx 0.9$ mm/s, where R is a sample radius). The latter value is substantially less than the rate of combustion over the surface and is equal to 6.2 mm/s.

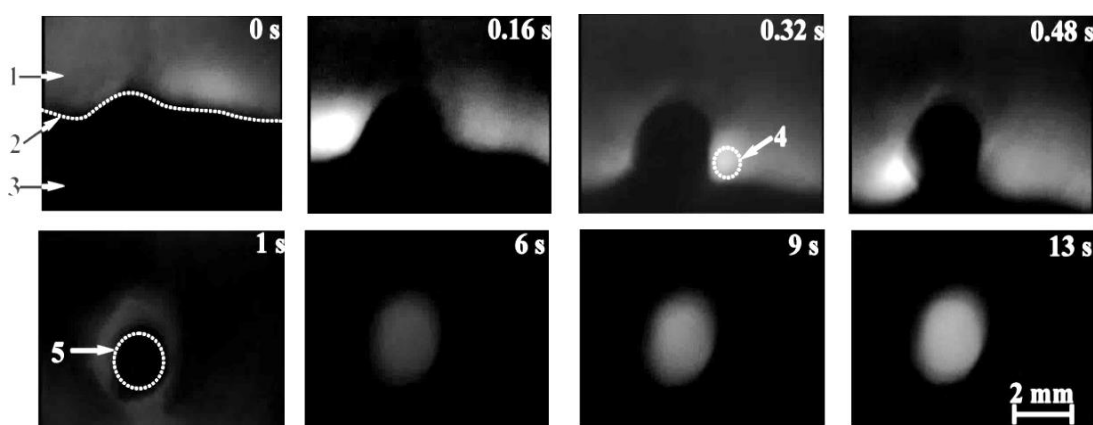


Figure 2. Frames of video recording of combustion in the powder mixture Ti + 35 wt. % Mo under the nitrogen atmosphere ($P(N_2) = 2 \cdot 10^5$ Pa); the relative density of the sample is 0.37.

(1) product, (2) front of surface combustion wave, (3) a reaction mixture, (4) a reaction source, (5) a hole in the sample.

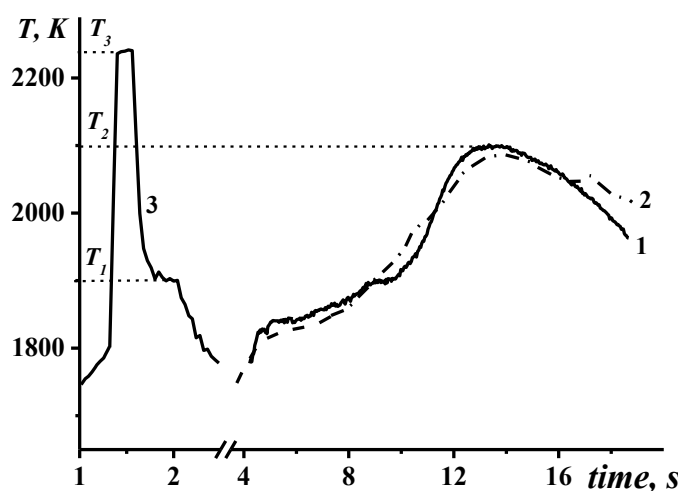


Figure 3. Temperature chronogram (1, 2 - in the center and 3 - on the surface of the sample) during the combustion of the powder mixture Ti + 35 wt. % Mo in nitrogen ($P(N_2) = 2 \cdot 10^5$ Pa). (1-3) dynamic pyrometry measurements, (2) thermocouple measurements.

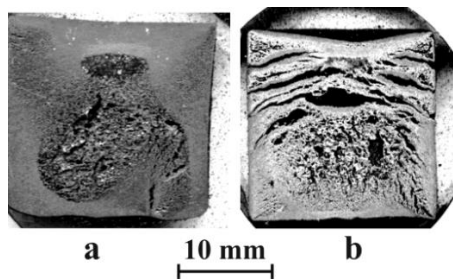


Figure 4. Structure of the cross-section of the combustion product obtained from the powder mixture of Ti + 35 wt. % Mo.
(a) nitrogen pressure is $2 \cdot 10^5$ Pa,
(b) nitrogen pressure is $50 \cdot 10^5$ Pa

Combustion of the powder mixture Ti + 35 wt. % Mo in nitrogen ($P(N_2) = 50 \cdot 10^5$ Pa) is conducted in the layered combustion mode, and the combustion wave propagates from layer to layer. Here, the filtration resistance of the oxidizer in the center of the sample is minimal, and gas pressure in the center of the sample is close to the ambient pressure. With the passage of a surface wave near the hole, in contrast to combustion at a nitrogen pressure of $2 \cdot 10^5$ Pa, the temperature difference (figure 5) in the center and in the adjacent area on the sample surface is ~ 80 K (the temperature difference between the isothermal sections T_1 and T_0 , figure 6). Figure 6 shows the temperature chronogram for the surface combustion wave with and without combustion sources, as well as for the central part of the sample in nitrogen at pressure of $50 \cdot 10^5$ Pa. According to the data (figure 6, the regions with the measured reaction wave temperature are marked in figure 5), increasing the pressure of the gaseous medium accelerates the spread of the reaction wave propagating from the surface to the center of the sample ($V \approx 2.3$ mm/s) with a surface combustion rate of 12 mm/s. Filtered gas, heated to temperature T_1 (figure 6), redistributes heat between the outer and inner parts of the sample, increasing the maximum internal temperature to 2290 K that is ~ 200 K higher than the maximum combustion temperature at a nitrogen pressure of $2 \cdot 10^5$ Pa. An increase in temperature leads to the stratification of the sample and a significant expansion of its melted part (figure 5b). In the work [14] it is reported that during the nitriding of chromium, the maximum temperature in the central part of the samples exceeds the calculated adiabatic temperature due to the nonuniform combustion front. Overheating of the central part leads to the melting of the product and a decrease in the conversion depth.

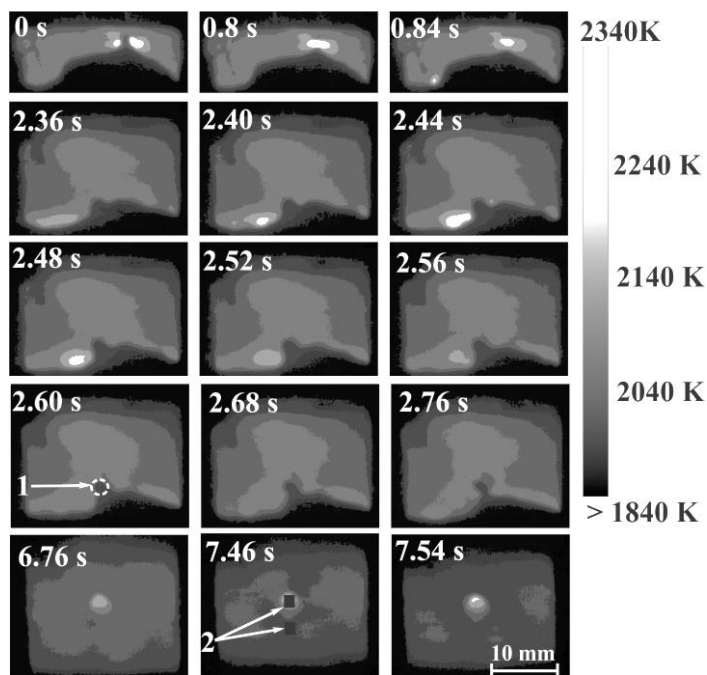


Figure 5. Frames of video recording of combustion in the powder mixture of Ti + 35 wt. % Mo in nitrogen ($P(N_2) = 50 \cdot 10^5$ Pa, the relative density of sample is 0.37) after color pyrometry processing.
(1) hole in the sample
(2) region for the temperature measurements in the sample.

The temperature change from T_1 to T_2 corresponds to the stage of volume nitriding (afterburning) of the sample and is caused by the permeability of the surface layer, through which gas is filtered in the center.

The feature of the process is the similarity of the maximum temperatures in the reaction source T_3 that occurs in the front of the surface wave (figure 5) with T_2 (figure 6). On the surface of the reaction product the trajectory of the reaction source over the surface takes the form of a groove. As can be seen in figure 4b, the macrostructure of the cross-section of the combustion product is characterized by the stratification of the sample and a substantially melted central part.

The characteristic microstructure of the combustion product at a pressure of $2 \cdot 10^5$ Pa is shown in figure 7. Elemental analysis showed the formation of triple nitrides that were solid solutions where titanium atoms were substituted with molybdenum (Ti, Mo) N in the TiN lattice and which can be described by the relation $\beta\text{-Ti}_x\text{Mo}_{2(1-x)}\text{N}_y$ ($0 < x < 1$, $0 < y < 5$). The structure of the product during the combustion of a mixture in nitrogen at a pressure of $50 \cdot 10^5$ Pa is homogeneous throughout the whole volume and corresponds to the case shown in figure 7 a, b.

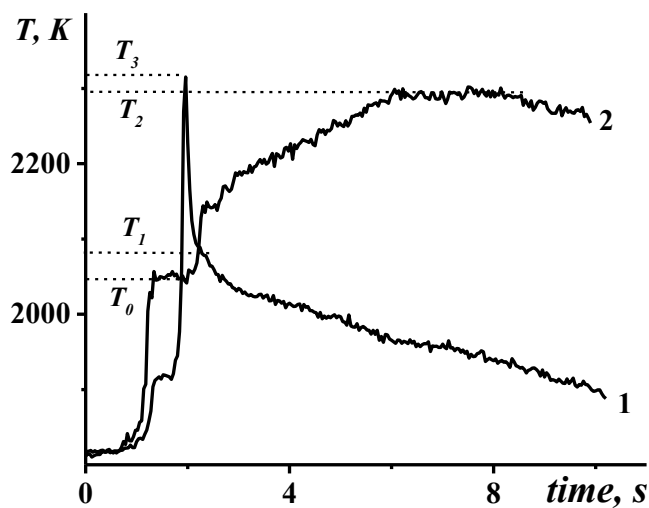


Figure 6. Chronogram of the temperatures (2 - in the center and 1 - on the surface of the sample) during the combustion of the powder mixture Ti+35 wt. % Mo in nitrogen ($P(\text{N}_2) = 50 \cdot 10^5$ Pa). (1, 2) dynamic pyrometry measurements.

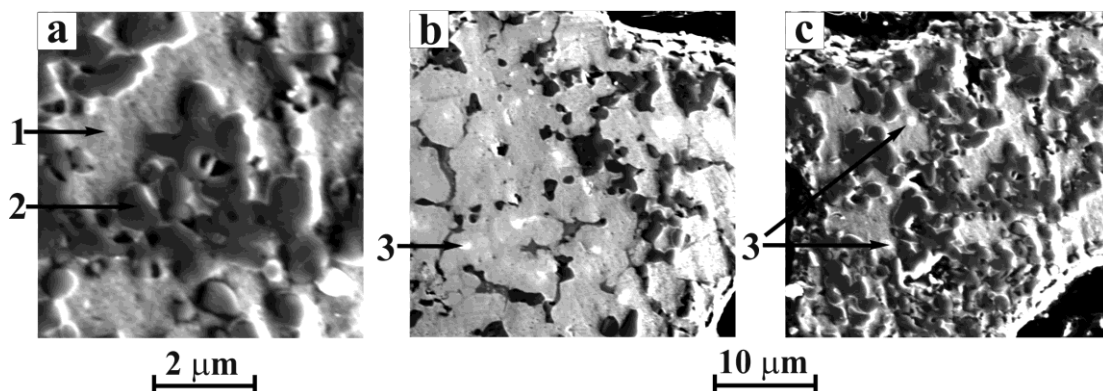


Figure 7. Microstructure of the product during the combustion of the powder mixture Ti + 35 wt. % Mo in nitrogen ($P(\text{N}_2) = 2 \cdot 10^5$ Pa). (a, c) central part of sample, (b) near-surface layer. Microanalysis of elements (at. %): (1) 28 Ti - 72 Mo and 56 Ti - 39 Mo - 5 N, (2) 85 Ti - 4 Mo - 22 N and 74 Ti - 4 Mo - 22 N, (3) 0.2 Ti - 95 Mo - 5 N and 0.8 Ti - 92 Mo - 7 N.

It is of interest to investigate combustion by widely varying the concentration of the mixture, dispersion of components, and pressures of the gaseous medium. Also, it is of interest to conduct

combustion of titanium and molybdenum powders on a substrate to form a protective coating and obtain a product with less porosity. Further research will be devoted to the solution of these tasks.

Conclusions

The thermal structure of the SHS wave was studied in the Ti-Mo-nitrogen system using the video recording data processed by the color pyrometry method. The peculiarities of combustion observed are the presence of local reaction sources and the complex three-dimensional structure of the temperature field in the reaction wave. It's shown that the maximum temperature of surface wave outside the combustion source is 200 K lower than the temperature that is reached at the center of the sample.

Increasing the pressure of the gaseous medium accelerates the spread of the reaction wave propagating from the surface to the center of the sample ($V \approx 2.3$ mm/s) with a surface combustion rate of 12 mm/s. Filtered gas, heated to temperature ~ 2080 K, redistributes heat between the outer and inner parts of the sample, increasing the maximum internal temperature to 2290 K that is ~ 200 K higher than the maximum combustion temperature at a nitrogen pressure of $2 \cdot 10^5$ Pa. The feature of the process (at a nitrogen pressure of $50 \cdot 10^5$ Pa) is the similarity of the maximum temperatures in the reaction source that occurs in the front of the surface wave.

Notification

WRe5/20 - tungsten-rhenium thermocouples [15]

SHS - Self-propagating high-temperature synthesis [9]

Acknowledgments

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