Burning rate of solid homogeneous energetic materials with a curved burning surface

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Abstract. We study experimentally the combustion of a double-based solid propellant NB at a pressure of $p = 1$ bar, and show that combustion occurs in the cellular-oscillating mode: combustion occurs in the form of separate cells that periodically appear on the burning surface, move along it and disappear. We show that in this mode, a carbonized skeleton is formed on the burning surface, consisting of products of incomplete decomposition of propellant. This skeleton is associated with the burning surface and plays an important role in maintaining the cellular-oscillating mode of combustion of the double-based propellant. To explain the experimental data, we consider a combustion model with a curved burning surface. We show that the burning rate depends on the curvature of the burning surface: with increasing curvature of the burning surface, the local burning rate decreases and combustion becomes impossible if the nondimensional radius of curvature (Michelson-Markstein criterion) of the burning surface becomes less than some critical value. The calculated critical value of the Michelson-Markstein criterion is in good agreement with that obtained in experiments. Using the developed model of combustion of solid homogeneous energetic materials (SHEMs) with a curved burning surface, we calculate the critical combustion diameter of various SHEMs and the shape of stationary cells on the burning surface. The critical combustion diameters of various SHEMs calculated in this way we compare with the available experimental data. A good agreement between the theory and experiments was obtained.

1. Introduction

Solid homogeneous energy materials (SHEMs) are used in various applications, both as the individual energetic materials, and as the energetic binders in solid propellants.

To explain the regularities of combustion of SHEMs and to simulate the combustion, as a rule, one-dimensional stationary combustion models are used [1,2], which is completely justified at high pressures $p > 1$ bar.

For some technical applications, it is of interest combustion of energetic materials at low pressures $p > 1$ bar.

Experimental data [3] indicate that under such conditions, the combustion of SHEMs occurs in a nonstationary and non-uniform (cellular-oscillating) mode. A possible cause of such a process is the instability of a one-dimensional stationary burning wave in SHEMs at low pressures.

The stability of a one-dimensional stationary combustion wave in SHEMs was studied theoretically by [4,5] et al. It is established that two types of instability are theoretically possible: (i) one-dimensional instability, when the burning surface remains flat, but the burning rate becomes oscillating, and (ii) the two-dimensional instability, when different points of the burning surface burn with different local burning rates that oscillate in time.
The one-dimensional stability of combustion of SHEMs has been studied in detail using one-dimensional nonstationary combustion models [1, 2]. In many cases, the combustion of SHEMs under nonstationary conditions (for example, at variable pressure) is analyzed from the standpoint of the one-dimensional nonstationary combustion theory. However, the experimental data [3, 6, 7] indicate that the two-dimensional instability of combustion of SHEMs occurs earlier than the one-dimensional instability.

This means that one-dimensional stationary and nonstationary combustion models of SHEMs [1, 2] are not applicable at low pressures. Instead, more complex non-uniform combustion models should be used, in particular, those that take into account the curvature of the burning surface and the effect of the curvature of the burning surface on the burning rate [8].

The goal of this work is an experimental study of the structure of the burning surface of SHEMs at pressures \( p = 1 \) bar and an analysis of the possibility of using the combustion model of SHEMs with a curved burning surface [8] to describe the nonstationary and non-uniform burning modes of such energetic materials.

2. Experimental part

We used a double-based propellant NB (which contains 56.44 wt.% of coloxylin with 11.7–12.2% of nitrogen, 27.72 wt.% of nitroglycerin, 10.89 wt.% of dinitrotoluene, 2.97 wt.% of ethyl centralite, 0.99 wt.% of petroleum jelly, and 0.99 wt.% of water) as a SHEM.

The experiments were conducted both on cylindrical samples and on samples in the form of thin plates.

The sizes of the samples were chosen so that the effective diameter of the burning surface was greater than the critical diameter of combustion.

The samples were mounted vertically and ignited from the top end; burning (displacement of the burning surface) occurred from the top down.

Samples were burned at different pressures under a nitrogen environment. To prevent ignition along the lateral surface of the sample, it was blown with nitrogen in a vertical direction (bottom-up).

A detailed video recording of combustion process was carried out.

Two methods of ignition were used:

- using a nichrome spiral heated by an electric current, which was pressed against the upper end of the sample and was removed after ignition;
- contactless (radiant) ignition, using an electric heater in a ceramic shell; the distance from the radiant heater to the top end of the sample was from 2 to 5 mm.

In the contactless ignition of a sample, local melting of the surface layer of the sample, boiling of the melt with the formation of bubbles on the burning surface (bubble sizes reached 3 mm) and subsequent ignition of the surface were observed. After that, the combustion zone spread rapidly over the surface of the sample, and further combustion occurred throughout the combustion surface without appreciable formation of a melt.

Experiments have shown that at low pressures (\( p \leq 1 \) bar) the combustion of the propellant is unstable. This is due to the fact that the heat released in the reaction zones (both in the condensed phase and in the gas phase) is not sufficient for self-sustaining stationary combustion. As a result, either the extinction of the propellant occurs over the entire surface, or the combustion proceeds in a non-stationary and non-uniform (cellular-oscillating) mode. In the latter case, the combustion of the propellant does not occur in the layer-by-layer mode, but in the form of separate cells on the burning surface, which have finite sizes (figure 1a and 1b). These cells periodically appear on the burning surface, move along it and disappear. In this mode, a complete combustion of the propellant sample can occur, but the mean “burning rate” of the sample, defined as the ratio of the sample height to the burning time, can be 2–5 times smaller than the local burning rate inside the cells.
Figure 1. Cellular structures on the burning surface of double-base solid propellant NB (a and b) at pressure 1 bar (cylindrical sample with a diameter of 12 mm). For a comparison, the cellular structures (c) on the burning surface of extinguished ammonium perchlorate at pressures 35 bar [7] is shown.

Measurements of the characteristic sizes of the cells on the burning surface showed that they depend on the pressure and decrease with increasing pressure. Given the monotonous dependence of the burning rate of propellant on pressure, it seems preferable to consider not the dependence of the sizes of the cells on the pressure, but the dependence of the sizes of the cells on the burning rate of the propellant, which will make it possible to compare the cells for propellants having different burning rates, both in level and in their dependence on pressure.

The dependence of the characteristic sizes of the cells on the burning surface, on the burning rate of the propellant, is shown in figure 2. The maximum size of the cells is approximated by the dependence $L_{\text{max}} = 2.6 \, r^{-1.17}$.

When combustion of propellant occurs in the cellular-oscillating mode, the carbonized skeleton is present on the burning surface, which is periodically formed and detached from the burning surface (figure 3).

The carbonized skeleton has a well-defined network structure, formed by carbonized fibers of $50\div100$ microns in thickness. The characteristic size of the grid cells of carbonized skeleton is $100\div1000$ μm. The results of a quantitative analysis of the chemical composition of the carbonized skeleton showed that it mainly consists of carbon ($\sim 66 \text{ wt.\%}$), calcium ($\sim 11 \text{ wt.\%}$) and oxygen ($\sim 15 \text{ wt.\%}$), with small impurities, apparently oxides metals (Na, Mg, Al, K, Ca, Fe), sulfur and silicon.

The mechanism of formation of the carbonized skeleton is as follows.

When combustion of propellant occurs in the cellular-oscillating mode, the temperature of the surface layers is still quite high on that part of the burning surface on which local extinction occurred. As a result, the chemical reactions (for example, the thermal destruction and the release of volatile compounds) can continue on these areas of the burning surface due to the accumulated heat. These processes, however, proceed relatively slowly, with no appreciable exothermic effect and are not self-sustaining. As a result of low-temperature destruction of the surface layer of propellant, its incomplete decomposition takes place, which leads to the formation of an appreciable quantity of liquid products (with a sufficiently high melting point) which, under the action of surface tension, gather into droplets and solidify on the burning surface. The contacting drops can stick together forming long (up to several mm) filamentary structures (“garlands”) lying on the burning surface of the propellant and firmly connected to the burning surface (figure 4).

When a transverse wave passes through the burning surface, a local intensification of the thermal decomposition of the surface layers of propellant occurs, which leads to local disruption of adhesion between the filamentary structures and the surface of propellant. As a result, there is a local detachment of the filamentary structure from the burning surface, however, the integrity of the filament is not disturbed, because the part of the filament that has detached from the surface is connected with its part that remains firmly connected with the burning surface. As the transverse burning wave passes along the surface of the propellant, the detached part of the filament, located in the gas flame zone, elongates. Neighboring filamentary structures can join (coalesce), forming a
carbonized skeleton, located above the burning surface and connected to the burning surface (figures 3a and 3b). This skeleton has the form of a grid with very high porosity or it is a separate dendritic structure (figure 3c).

Figure 2. Dependences of the cell size $L$ (left) and the ratio of $L$ to thickness $\delta_T$ of thermal layer in condensed phase (right) on the burning rate for double-base solid propellant NB. (1) is the characteristic size of the cells; (2) is the mean surface size of the equivalent cells; (3) is the size of the cells obtained from the video recording data; line is the approximation $L_{\text{max}} = 2.6 r^{-1.17}$.

Figure 3. The carbonized skeleton formed during combustion of propellant NB (a and b), and the carbonized residue remaining after the combustion of the sample (c); (a) is a cylindrical specimen with a diameter of 12 mm and a height of 20 mm, (b) is the sample in the form of thin plate (sizes $11 \times 4 \times 16$ mm) with a central vertical slit ($0.6 \times 9$ mm).

Figure 4. Burning surface of the extinguished sample of propellant NB with traces of filamentary structures.
The upper part of the carbonized skeleton, as it grows, enters the high-temperature zone of the gas flame and heats up to high temperatures, as evidenced by its luminosity. Having high thermal conductivity, the carbonized skeleton returns some of the heat back from the high-temperature zone of the gas flame to the burning surface at the place of its attachment to the surface (i.e., plays the role of a thermal bridge). Increasing by this way the heat flux to the burning surface, the carbonized skeleton has a stabilizing effect on the propellant burning process. This is manifested in the fact that the front of the transverse wave (the boundary of the cell) moving along the burning surface usually coincides with the place where the carbonized skeleton is attached to the burning surface. This front moves along the burning surface and, together with it, the “point” of joining the carbonized skeleton to the surface moves. Simultaneously, new parts of filamentary structures are released from the burning surface, which contributes to the growth of the carbonized skeleton over the burning surface. It can be concluded that the carbonized skeleton promotes the propagation of a transverse wave along the burning surface, while the transverse wave, in turn, contributes to the formation and growth of the carbonized skeleton.

If the carbonized skeleton, for any reason, leaves the high-temperature zone of the gas flame, its cooling occurs, which is manifested in a sharp decrease in the luminosity of the skeleton. In this case, at the place where the carbonized skeleton is attached to the burning surface, the local extinction of propellant occurs, because its own heat generated in the condensed phase is not enough to support the process.

The carbonized skeleton periodically completely detaches from the burning surface under the action of gaseous combustion products. The condition of detachment is the excess of the detached aerodynamic force over the strength of the skeleton [9]. The detached aerodynamic force increases with the growth of the size of the carbonized skeleton, and the detachment occurs when its size reaches a certain critical value. In the place of detachment of the carbonized skeleton, there is also a local extinction of the propellant.

At contactless ignition of the sample (by radiant heater), combustion occurs in a stationary layer-by-layer mode without the formation of appreciable cells and carbonized skeleton. The burning surface remains smooth throughout the entire operation of the radiant heater, and the burning rate is constant. If the radiant heater is turned off before the sample was completely burned, its further combustion occurs in a cellular-oscillating mode with the formation of a carbonized skeleton, as described above. It can be concluded that the radiant heater provides additional heat flux to the burning surface in the form of thermal radiation, which stabilizes the propellant combustion. In this case, the combustion of propellant is forced but not self-sustaining.

3. Influence of the burning surface curvature on the burning rate and the critical diameter of combustion

The experimental data obtained in this work and in [3,6,10] show that the burning surface of even SHEMs at low pressures and without additional heat supply is not flat, and the burning process is not one-dimensional. The curvature of the combustion surface is particularly pronounced near the combustion limit when the sample size approaches the critical diameter of combustion [3,10].

The dependence of the burning velocity on the curvature of the flame front is well known for premixed gases [11].

The combustion theory of SHEMs with a curved surface was developed in [8,12] and the dependence of the burning rate of SHEMs on the curvature of the burning surface was found. It is established [8,12] that the burning rate of a SHEM \( r \) satisfies the equation

\[
Z = \exp \left( -\frac{2kK_2}{\bar{z}} \right) \tag{1}
\]

if the dependence of the steady-state burning rate on the initial temperature of the grain has the form

\[
r_0 = r_{0N} \exp (\beta \Delta T_0) \tag{2}
\]

and the equation

\[
5
\]
if the dependence of the steady-state burning rate on the initial temperature of the grain has the form

\[ r = r_0 (1 + \beta \Delta T_0) \]  

where

\[ Z = \frac{r}{r_0} \]

is the nondimensional burning rate; \( \beta = \frac{\partial \ln r}{\partial T_0} \) is the temperature sensitivity of the burning rate; \( k = (T_s - T_0) \beta \) is the nondimensional temperature sensitivity of the burning rate in the phenomenological ZN-theory [4]; \( T_s \) is the temperature of the burning surface; \( T_0 \) and \( \Delta T_0 \) are the initial grain temperature and its deviation from the accepted nominal value; \( r_0 \) is the burning rate of the same propellant with a flat burning surface under the same conditions at the nominal temperature;

\[ K_0 = \frac{aK}{r_0} \equiv \text{Mi}^{-1} \]

is the nondimensional mean curvature of the burning surface; \( \alpha \) is the thermal diffusivity of the propellant condensed phase; \( K = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \) is the mean curvature of the burning surface; \( R_1 \) and \( R_2 \) are the principal radii of curvature of the burning surface; \( \text{Mi} = \frac{r_0}{ak} \) is the Michelson-Markstein criterion. Curvature (for each principal direction) is considered positive if the burning surface is convex towards the condensed phase and negative if the burning surface is convex toward the gas phase.

Dependences (1) and (3) are shown in figure 5.

According to (1) and (3), the burning rate decreases with increasing curvature of the burning surface and reaches a minimum value \( r_{\text{min}} \) for a certain curvature \( K_{\text{cr}} \); while at \( K_0 > K_{\text{cr}} \) steady-state combustion of the SHEM becomes impossible [8,12]. For the equation (1), \( K_{\text{cr}} = (2k\epsilon)^{-1} \), \( \text{Mi}_{\text{cr}} = 2k \epsilon \) and \( r_{\text{min}} = r_0 e^{-1} \); for the equation (3), \( K_{\text{cr}} = 0.125/k \), \( \text{Mi}_{\text{cr}} = 8k \) and \( r_{\text{min}} = 0.5r_0 \).

The theory [8,12] allows explaining the existence of the critical diameter of combustion.
In experiments [3,10] on measurement of the critical diameter of combustion, either flat samples with transverse dimensions \( L \times d \), where, usually, \( L \gg d \), or cylindrical samples of diameter \( d \), are usually used.

When analyzing the experimental data obtained on flat samples, its real thickness is not considered as a characteristic size, but it is used the effective diameter \( d_{ef} = 4F/\Pi \), which is equal to

\[
d_{ef} = \frac{2}{L/a}
\]

where \( F \) is the area of the burning surface, \( \Pi \) is its perimeter. In experiments [3,10] and similar experiments, the critical effective diameter \( d_{ef,cr} \) for flat samples and the critical diameter \( d_{cr} \) for cylindrical samples are determined.

It should be noted that the transition from real dimensions of flat samples to their effective diameter and comparison with the diameter of a cylindrical sample is done without any physical justification. The SHEM combustion model with a curved burning surface [8,12] allows justifying the use of effective diameters in calculating the critical diameter of a flat sample.

As noted in [10], at the combustion limit (when its transverse dimension approaches a critical value), the burning surface becomes curved, convex toward the condensed phase and the radius of curvature of the burning surface approaches the radius of the cylindrical sample, or the half-thickness of a flat sample; in other words, the critical radius of curvature of the combustion surface

\[
R_{cr} \approx d/2
\]

where \( d \) is the actual size of the sample: the width for the flat sample or the diameter for the cylindrical sample.

From a physical point of view, this means that the existence of a critical diameter of combustion is associated with a supercritical curvature of the burning surface at which the sample is extinguished (Fig. 5).

Consider the critical radii of curvature of the burning surfaces for flat and cylindrical samples, determined by theory [8,12].

For a flat sample, \( R_2 = \infty \) and \( R_{cr} = \frac{1}{2\kappa_{cr}} \). As a result, one obtains

\[
R_{cr} = \frac{a}{2\kappa_{cr} \kappa_{acr}}
\]

For a cylindrical sample \( R_1 = R_2 \) and \( R_{cr} = \frac{1}{\kappa_{cr}} \). Therefore

\[
R_{cr} = \frac{a}{\kappa_{cr} \kappa_{acr}}
\]

Taking into account (8), (9) and (10), for the critical thickness of a flat sample, one obtains

\[
d_{cr} = \frac{a}{\kappa_{cr} \kappa_{acr}}
\]

while for the critical diameter of a cylindrical sample, we obtain

\[
d_{cr} = \frac{2a}{\kappa_{cr} \kappa_{acr}}
\]

For flat samples, the condition \( L \gg d \) is usually satisfied, therefore, taking into account (7), one obtains \( d_{ef} \approx 2d \) for a flat sample, while for a cylindrical sample, by definition, \( d_{ef} = d \). Then, taking into account (11) and (12), we see that, for both flat and cylindrical samples, the effective critical diameter of combustion is the same:

\[
d_{ef,cr} = \frac{2a}{\kappa_{cr} \kappa_{acr}}
\]

Thus, indeed, an analysis of the critical sizes of a sample based on effective diameters (7) allows including the experimental data both on cylindrical and on flat sample into a single set of data.
If the dependence of the burning rate on the curvature of the burning surface is described by equation (1), then relation (13) takes the form

$$d_{ef,cr} = \frac{4ek}{r_0}$$  \hspace{1cm} (14)

In the case when the dependence of the burning rate on the curvature of the burning surface is described by equation (3), relation (13) takes the form

$$d_{ef,cr} = \frac{16ek}{r_0}$$  \hspace{1cm} (15)

A comparison of the critical diameters for several SHEMs, calculated using expressions (14) and (15), with experimental data [7,13,14] is given in table 1. In the calculations, $a = 1.5 \cdot 10^3 \text{cm}^2/\text{s}$ is used.

**Table 1. Parameters of different SHEMs.**

| Energetic material | $k$ (mm/s) | $r_0$ (mm) | Theory (14) $d_{cr,ef}$ (mm) | Theory (15) $d_{cr,ef}$ (mm) | Experiment $d_{cr,ef}$ (mm) |
|--------------------|------------|------------|-------------------------------|-------------------------------|----------------------------|
| Propellant N       | $2.4p^{-0.1}$ | 0.047$p^{0.67}$ | $7.7p^{-0.77}$ | $11.3p^{-0.77}$ | $7p^{-0.74}$ |
| Propellant A       | $2.4p^{-0.1}$ | 0.1$p^{0.64}$ | $3.6p^{-0.75}$ | $5.3p^{-0.75}$ | $6p^{-0.75}$ |
| Propellant NB      | $2.4p^{-0.1}$ | 0.09$p^{0.65}$ | $4p^{-0.75}$ | $5.9p^{-0.75}$ | $6.8p^{-0.76}$ |
| RDX                | 2.3        | 0.037$p^{0.82}$ | $9.3p^{-0.82}$ | $13.7p^{-0.82}$ | $9.2p^{-0.88}$ |

Thermal sensitivity of burning rate for this SHEMs has been taken from [13,15-18]; experimental data for critical diameters has been taken from [10,13,14].

One sees that the hypothesis of existence of the limiting curvature of the burning surface allows explaining the critical conditions of combustion of various SHEMs.

Experimental data on thermal sensitivity allows estimating the critical value $\text{Mi}_{cr}$.

Thus, at a pressure $p = 1$ bar, for the variant corresponding to equation (1), we obtain $\text{Mi}_{cr} = 12.5$, while for the variant corresponding to equation (3), we obtain $\text{Mi}_{cr} = 18.4$, which (taking into account the inaccuracy in the values of the parameters $a$ and $k$) agrees with the estimates values $\text{Mi}_{cr} = 10\div14$, obtained in [14,19] in the analysis of cells appearing on the combustion surface of double-based propellant $N$ at a pressure $p = 1$ bar.

4. **Conclusions**

Thus, it is shown that at low pressures ($p \leq 1$) the burning of the double-based propellant NB is unstable and occurs in the cellular-oscillating mode. The burning surface in this case has a complex inhomogeneous and nonstationary structure: burning does not occur over the whole surface, but it proceeds in the form of separate cells that periodically appear on the burning surface, move along it and disappear. In this mode, a carbonized skeleton is formed on the burning surface. This skeleton consists of products of incomplete decomposition of propellant, associates with the burning surface, and connects the burning surface with a high-temperature zone of the gas flame. The carbonized skeleton, apparently, plays a principal role in maintaining the cellular-oscillating combustion mode of double-based propellant.

Despite the fact that for such a combustion mode, it is possible to formally determine the mean burning rate of the sample as a whole, it can differ 3-5 times from the local burning rates within the cells.

The inhomogeneous and nonstationary structure of the burning surface does not allow using the one-dimensional stationary models (which are usually widely used in the theory of combustion of SHEMs) to describe such combustion mode. In describing the cellular-oscillating combustion modes, it is necessary to take into account the effect of the local curvature of the burning surface on the local
burning rate. The analysis of the combustion model of a SHEM with a curved burning surface shows that it allows describing some observed features of the cellular-oscillating combustion mode.

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