

Influence of Percolation Threshold of Structural Phase Transition in a Solid Two-Component Propellant Mixture on Thermal Efficiency of Combustion Chamber of a Rocket Engine

S.I. Futko*, I.A. Koznacheev, E.M. Ermolaeva

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus

Abstract

Solid multi-component heterogeneous propellant mixtures have been found widespread aerospace applications in engines of different power (up to microthrusters MEMS). For improving overall engine performance it is helpful to know how thermal efficiency of combustion chamber of a rocket engine depends on structural characteristics of solid fuel mixture composition. Recently we found out that two-component propellant mixture GAP/RDX undergoes structural phase transition when mass fraction of RDX in GAP approaches 60.8 %. It corresponds to a percolation threshold dividing predominantly amorphous and mainly polycrystalline solid-fuel structure. We considered Clausius-Rankin thermal cycle of operation of combustion chamber of a typical rocket engine on solid fuel. Calculations show that for higher pressures dependence of thermal efficiency of combustion chamber of such engine on mixture composition has two maximum values. Main trends of the calculated parametrical dependencies for the thermal efficiency can be understood according to the Le Chatelier principle.

Introduction

Mixtures based on high-energy polymers are used widely as solid fuels in rocket engine systems designed for different purposes [1–5]. Considerable recent attention has been focused on the study of the possibility of use of solid-fuel mixtures based on the glycidyl azide polymer (GAP) in the mini-engines of microelectromechanical systems (MEMS) with combustion chambers in which the pressure is lower than 10 atm [6–11]. In particular, in [8–11] the possibility of use of fuel mixtures in the mini-engines of microelectromechanical systems based on crystal silicon was theoretically investigated. In [12,13], it was shown that fuel mixtures GAP/RDX can experience a structural phase transition at pressures of 1–100 atm and that the thermodynamic parameters of combustion of such a mixture change drastically at the point of its structural phase transition. It was also established that it occurs when mass fraction of RDX $Y_{\text{RDX}} = 0.608$ and mole fractions of the C and O atoms in the mixture become equal ($X_{\text{C}} = X_{\text{O}}$). The data obtained show that, at the point of structural phase transition, the mainly amorphous structure of a solid-fuel mixture is changed to the predominantly polycrystalline one [12,13].

The aim of the present work is to show that this structural phase transition corresponds to the percolation threshold for the structure of GAP/RDX mixtures and to investigate main parametrical dependencies of thermal efficiency of combustion chamber of a rocket engine in the vicinity of such structural transition point.

Thermodynamic calculation of percolation threshold in combustion characteristics of the solid mixtures GAP/RDX.

The adiabatic temperature T_{max} and the equilibrium composition of the products of combustion of a solid fuel mixture were calculated for different mass fractions of its components with the use, as in [8–13], of the

CHEMKIN subprogram package [14,15]. A two-component mixture of the GAP (component 1) and RDX (component 2) was used as a model solid fuel. The calculations were carried out on the basis of the comprehensive thermodynamic model including 67 gas-phase components and three solid-phase components [8,9,12,13]. It was assumed that the GAP represents a polymer-triol of chemical composition $\text{C}_{78}\text{H}_{131}\text{O}_{27}\text{N}_{66}$ with a molecular weight $W_1 = 2425.3$ g/mole and that the initial temperature of the GAP/RDX mixture $T_0 = 300$ K.

Figure 1 presents the results of calculations of the adiabatic temperature of combustion of the model mixture T_{max} at pressures falling within the wide range $P = 3\text{--}100$ atm corresponding to the working pressure ranges of the combustion chambers of the mini-engines of microelectromechanical systems [6,7,9] and of rocket engine systems designed for different purposes [1,5,16].

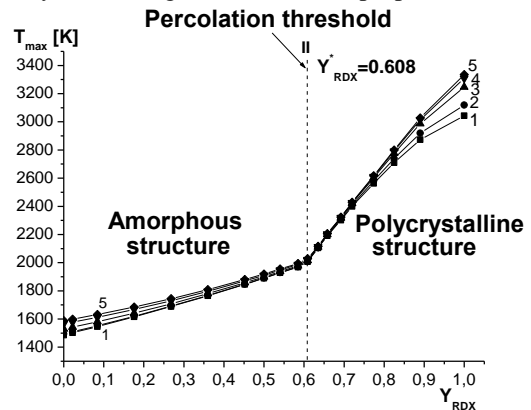


Fig. 1: Dependences of the adiabatic temperature of combustion of the GAP/RDX mixture in the combustion chamber of an engine system on the mass fraction of RDX for $P = 3$ (1), 6.8 (2), 30 (3), 68 (4), and 100 atm (5).

* Corresponding author: foutko@itmo.by

It is seen from Fig. 1 that, when the mass fraction RDX increases from 0 to 60.8%, the adiabatic temperature of the system, e.g., at $P = 3$ atm, increases smoothly from 1486 to 2007 K; however, at $Y_{\text{RDX}} = 60.8\%$, the curve $T_{\text{max}}(Y_{\text{RDX}})$ has a characteristic break, and the adiabatic temperature increases much more rapidly from 2007 to 3042 K with change in the values of Y_{RDX} in the range of $Y_{\text{RDX}} = 60.8\text{--}100\%$. When the pressure in the combustion chamber increases to 100 atm, the temperature T_{max} increases somewhat too; however, the behavior of the curve $T_{\text{max}}(Y_{\text{RDX}})$ remains unchanged in this case. Figure 2 presents calculation data on the main gas-phase (H_2 , CO , H_2O) and solid-phase (C_s) products of combustion of the GAP/RDX mixture in the combustion chamber of an engine system, obtained for different ratios between these components and pressures falling within the wide range.

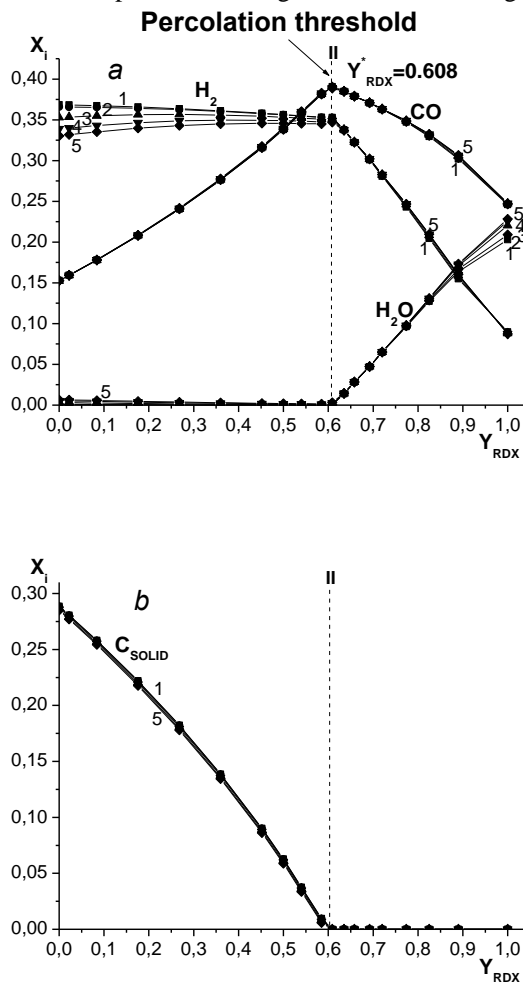


Fig. 2: Dependences of mole fractions of the main gas-phase components H_2 , CO , and H_2O of the GAP/RDX mixture (a) and mole fraction of the solid carbon C_s (b) in the combustion products on the mass fraction of RDX Y_{RDX} for $P = 3$ (1), 6.8 (2), 30 (3), 68 (4), and 100 atm (5).

A comprehensive analysis of the dependences of the temperature T_{max} and concentration of the products of combustion of a solid-fuel mixture on its composition

has been performed in [12,13] for the working pressures 1–6.8 atm of the mini-engine of a microelectromechanical system. It should be noted that a characteristic of the combustion of the GAP/RDX mixture with $Y_{\text{RDX}} \approx 60.8\%$ as well as of other rich fuel mixtures [8] in the combustion chambers of engine systems designed for different purposes [1,5,15] at pressures lower than 6.8 atm [12,13] and at higher pressures ($P = 30\text{--}100$ atm), is the formation of large amounts of H_2 , CO , CH_4 , and C_s . In the GAP/RDX mixture with a mass fraction of RDX $Y_{\text{RDX}} = 60.8\text{--}100\%$, the concentrations of CO_2 and H_2O are large and the solid phase carbon C_s is not formed, which points to the thermal decomposition of RDX.

It is known that pure RDX has a crystal structure. For instance, in [17] it was shown by the method of molecular dynamics modeling that RDX molecules form crystals with different types of crystal surfaces: 001, 010, and 100. Noteworthy, unlike RDX molecules, polymeric chains of the GAP form amorphous configurations that can take widely differing forms [17].

These results also show the necessity of existence of a transition point in the structure of the solid fuel mixture from the predominantly amorphous structure of the GAP to the mainly polycrystalline structure of pure RDX. The data presented in Figs. 1, 2 show that such a transition point is realized rather sharply, "stepwise" and, obviously, takes place at an RDX content in the GAP of approximately 60.8 mass %.

Another way to look at this phenomenon is provided by the percolation theory [18]. In fact, as it is illustrated in the Fig. 3, in describing the process of the structural transition in the GAP/RDX mixture mass fraction of RDX Y_{RDX} can serve as critical parameter so that percolation threshold takes place at $Y_{\text{RDX}}^* = 0.608$.

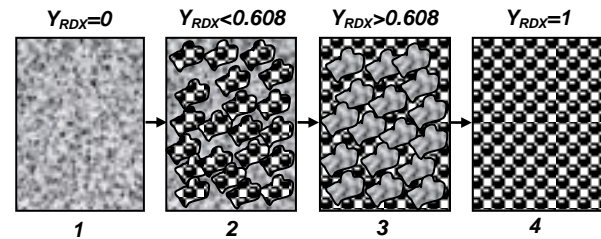


Fig. 3: Schematic of the structural phase transition in solid-fuel mixture GAP/RDX according to the value of the critical parameter Y_{RDX} : 1- pure GAP, 2- GAP/RDX structure just before the percolation threshold ($Y_{\text{RDX}}^* = 0.608$), 3- GAP/RDX structure after the percolation threshold, 4- pure RDX.

The above and other thermodynamic considerations [12,13] allow the conclusion that, in the case where $Y_{\text{RDX}} = Y_{\text{RDX}}^* = 0.608$ in the GAP/RDX mixture, this mixture experiences a structural phase transition, with the result that two regions can be distinguished in it. In the region where $Y_{\text{RDX}} < 0.608$, the amount of the

atomic oxygen is insufficient for oxidation of the fuel; therefore, the thermodynamic parameters of combustion of the mixture in this region are similar to that of the combustion of GAP and the structure of the mixture is distinctly amorphous. In the second region with $Y_{RDX} > 0.608$, the amount of the atomic oxygen becomes gradually sufficient for practically complete oxidation of the fuel to CO_2 and H_2O , and the mixture in this region has progressively more polycrystalline structure characteristic of RDX (Fig. 1,3). In [12,13], it was also shown that the point of structural phase transition of the GAP/PDX mixture is independent of its pressure in both the cases where this pressure is small ($P = 1-6.8$ atm) and large ($P = 30-100$ atm), defined by condition $X_C = X_O$ and coincides with the minimum on the dependence of the combustion velocity of the mixture on the concentration of RDX in it, which, according to the experimental data of [3], is also independent of the pressure.

Thermal Efficiency of the Combustion Chamber of a Rocket Engine.

Figure 4 shows a diagram of the typical working cycle of a rocket engine operated by a solid fuel, which corresponds to the Clausius–Rankin cyclic process [15].

In this thermal cycle, process 1–2 is the ignition of the solid-fuel mixture, process 2–3 is the combustion of the mixture at a constant pressure, process 3–4 corresponds to the adiabatic expansion of the combustion products in the exhaust nozzle of the engine, and, in process 4–1, the combustion products come into thermal equilibrium with the environment at a constant pressure P . The thermal efficiency of this cyclic process is calculated by the formula [15]

$$\eta_{th} = 1 - (1/\varepsilon)^{(n-1)/n} \quad (1)$$

where $n = c_p / c_v$ is the adiabatic exponent of the gas-phase combustion products and $\varepsilon = P / P_{out}$ is the degree of expansion of the combustion products in the exhaust nozzle. It was assumed in the further calculations that $P_{out} = 1$ atm.

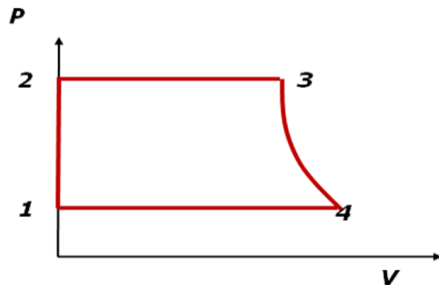


Fig. 4: Thermal cycle of the combustion chamber of a rocket engine operated by a solid fuel (the Clausius–Rankin cyclic process) [15].

As a result of the calculations of the thermal efficiency of the combustion chamber of a rocket engine by

formula (1) at increased pressures ($\varepsilon > 30$) for the wide range of ratios between the mass fractions of the GAP/RDX mixture components, we obtained the dependence $\eta(Y_{RDX})$ presented in Fig.5. This dependence has two characteristic maxima: I and II.

The position of maximum I depends on the pressure of the mixture in the combustion chamber: with increase in the pressure, it shifts to the side of the larger concentrations of RDX in the mixture. Maximum II appears on the dependence $\eta(Y_{RDX})$ when $Y_{RDX} = Y_{RDX}^* = 0.608$. This maximum is independent of the pressure in the combustion chamber and coincides with the point of structural phase transition of the mixture [12,13]. It was shown in [12] that, at this point, the dependence of the rate of combustion of a solid-fuel mixture on its composition has a minimum, the position of which is independent of the pressure.

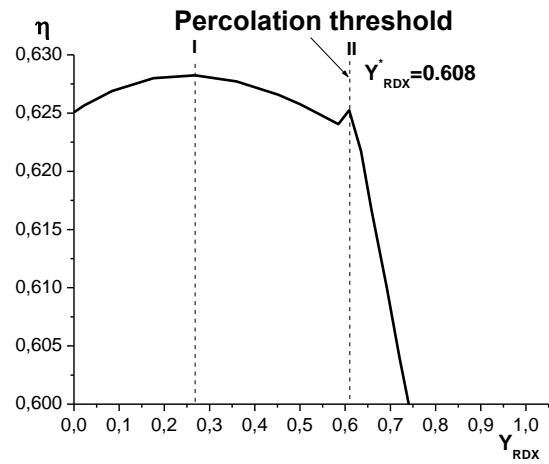


Fig. 5: Dependence of the thermal efficiency of the combustion chamber of a rocket engine on the mass fraction of RDX Y_{RDX} in the GAP/RDX mixture with two maxima (I and II) at $P = 68$ atm.

Dependence of the Thermal Efficiency of the Combustion Chamber of a Rocket Engine on the Composition of the Solid-Fuel Mixture.

Figure 6 presents dependences of the thermal efficiency of the combustion chamber of a rocket engine as well as of the adiabatic exponent and the specific capacities of the gas-phase combustion products at a constant volume and a constant pressure on the composition of the GAP/RDX mixture at pressures falling within the range $P = 3-100$ atm.

It is seen from Fig. 6 that the thermal efficiency of the combustion chamber decreases sharply when the mass fraction of RDX in the mixture becomes larger than $Y_{RDX} = Y_{RDX}^* = 0.608$, and, in accordance with Eq. (1), to higher pressures correspond larger values of the thermal efficiency of the combustion chamber.

However, when the pressure reaches the values $P = 70-100$ atm, the dependence $\eta(P)$ saturates, and a further increase in the pressure in the combustion chamber does not cause a marked increase in its efficiency.

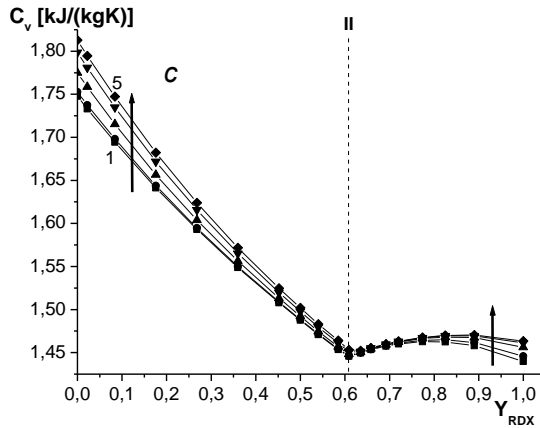
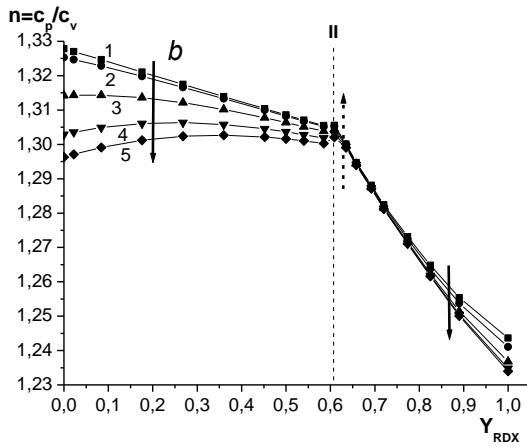
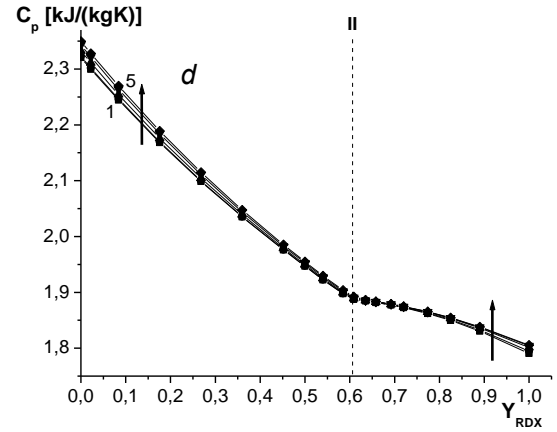
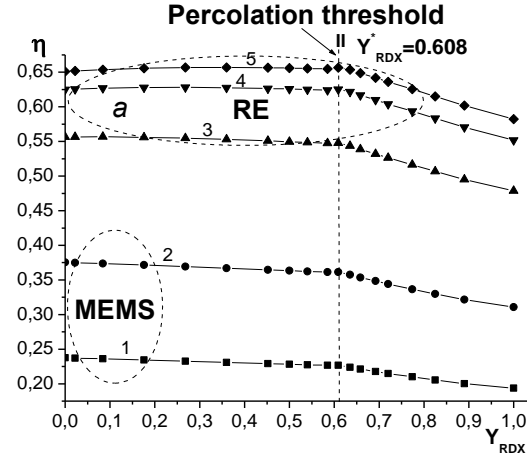


Fig. 6: Dependences of the thermal efficiency η of the combustion chamber of a rocket engine (a), the adiabatic exponent n (b), and the specific heat capacities c_v (c) and c_p (d) of the products of combustion of the GAP/RDX mixture on the mass fraction of RDX Y_{RDX} for $P = 3$ (1), 6.8 (2), 30 (3), 68 (4), and 100 atm (5); solid arrows show directions of the "resistance" of the system to an increase in its compression in accordance with the Le-Chatelier principle outside the percolation threshold point $Y_{RDX}^* = 0.608$ and dashed arrow corresponds to the same in the vicinity of the percolation threshold point of structural phase transition; dashed lines show characteristic ranges of change in the parameters of the combustion chamber of the mini-engines of microelectromechanical systems (MEMS) [6–11] and rocket engine (RE) [1,5,15].

It can be seen from the Fig. 6 that, at $P \leq 30$ atm, the dependences $n(Y_{RDX})$ and $\eta(Y_{RDX})$ decrease monotonically with increase in Y_{RDX} from 0 to 58%. At larger pressures ($P > 30$ atm), these dependences have maximum I, which shifts to the side of the larger values of Y_{RDX} with increase in the pressure P . Thus, maximum I appears in the case where $Y_{RDX} = 5.3, 26.6,$ and 36.1% at $P = 30, 68,$ and 100 atm, respectively.

Maximum II appears at $Y_{RDX} = Y_{RDX}^* = 0.608$, and it is independent of the pressure in the combustion chamber in the wide range of its change $P = 3\text{--}100$ atm (Fig. 6). The detailed shapes of maxima II on the dependences $n(Y_{RDX})$ and $\eta(Y_{RDX})$, obtained for different pressures, are shown in Fig. 7, from which the values of the local peaks Δn and $\Delta \eta$, corresponding to maximum II, can be determined graphically. The values of Δn , $\Delta \eta$, $\Delta n/n$, and $\Delta \eta/\eta$ increase practically linearly with increase in the pressure P and can be determined approximated from the following expressions:

$$\Delta n = 7 \cdot 10^{-5} + 1.8 \cdot 10^{-5} \cdot (P - 3), \quad (2)$$

$$\Delta n/n = 5.36 \cdot 10^{-3} + 1.39 \cdot 10^{-3} \cdot (P - 3), \quad (3)$$

$$\Delta \eta = 5.3 \cdot 10^{-5} + 1.69 \cdot 10^{-5} \cdot (P - 3), \quad (4)$$

$$\Delta \eta/\eta = 0.023 + 2.42 \cdot 10^{-3} \cdot (P - 3). \quad (5)$$

The theoretical efficiencies of the mini-engines MEMS are much smaller ($\eta < 0.4$), which is mainly due to the lower pressures in their combustion chambers ($P \leq 10$ atm) as compared to the pressures 30–100 atm characteristic of a rocket engine operating at elevated pressures [1,5,15]. In accordance with definition (1), the behaviors of the dependences $n(Y_{RDX})$ and $\eta(Y_{RDX})$ should be similar.

Note that the value of $\Delta\eta$ corresponding to maximum II can be also determined directly from the known value of Δn . Differentiation of Eq.1 gives the following equation to define $\Delta\eta$:

$$\Delta\eta = -\Delta n \cdot \ln\left(\frac{1}{\varepsilon}\right) \cdot \left(\frac{1}{n} - \frac{n-1}{n^2}\right) \cdot \left(\frac{1}{\varepsilon}\right)^{\frac{n-1}{n}} \quad (6)$$

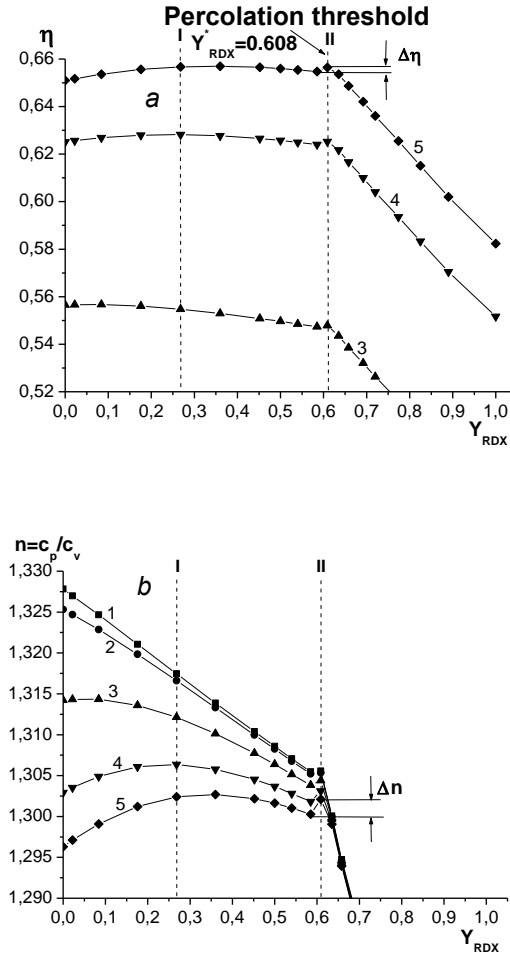


Fig. 7: Dependences of the thermal efficiency of the combustion chamber of a rocket engine (a) and the adiabatic exponent of the gas-phase products of combustion of the GAP/RDX mixture (b) on the mass fraction of RDX Y_{RDX} , calculated for $P = 3$ (1), 6.8 (2), 30 (3), 68 (4), and 100 atm (5); maximum I corresponds to the pressure $P = 68$ atm.

Interpretation via Le-Chatelier principle of the Dependences of the Thermal Efficiency of the Combustion Chamber of a Rocket Engine on the Composition of the Fuel Mixture and Pressure.

It is known that the intensity of the gas-phase processes generating combustion products depends on the calorific value of a unit volume of the reacting gas. Such a process proceeds with a combustion wave velocity u_w propagating in the combustible mixture and its pressure. Figure 8 presents dependences of combustion velocity u_w of the GAP/RDX mixture on

Y_{RDX} for different pressures, calculated in [12] along with the experimental data from [3].

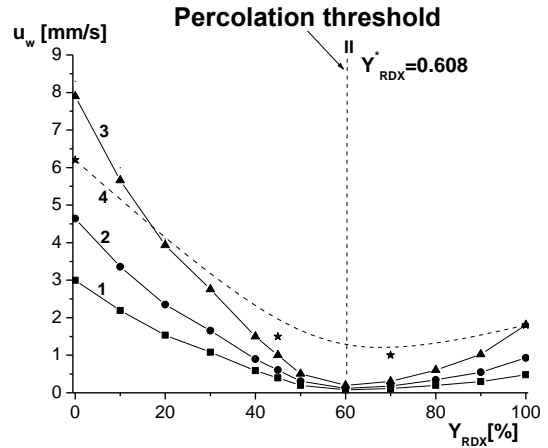


Fig. 8: Theoretical (1–3) [12] and experimental (4) [3] dependences of the combustion velocity of the GAP/RDX mixture u_w on the mass fraction of RDX Y_{RDX} at $P = 1$ (1), 3 (2), and 6.8 atm (3, 4).

The increase in the velocity u_w with increase in the pressure P is due to the additional compression of the mixture, which increases the intensity of its combustion. It should be noted that the curves representing the dependence of the rate of combustion of the GAP/RDX mixture on the mass fraction of RDX Y_{RDX} have an U-like shape with a minimum at $Y_{RDX} \approx 60\%$, which is supported by the experimental data obtained for the wide range of change in the pressure in the combustion chamber ($P = 1$ –136 atm) [3]. Thus, within the experimental error, the minimum on the dependence of $u_w(Y_{RDX})$ coincides with the percolation threshold $Y_{RDX}^* = 0.608$, and this minimum is independent of the pressure in the combustion chamber.

It is interesting that the behavior of the reacting system can be explained by the Le-Chatelier principle [12,13]. For the GAP/RDX mixture with $Y_{RDX} \leq 58\%$, the adiabatic exponent n (or the coefficient of adiabatic compression of the gas) decreases substantially with increase in the pressure P (Figs. 6,7), which points to the fact that the system resists to its additional compression at an increased pressure in the combustion chamber. This process is shown by the arrows in Fig. 6. It is seen from Figs. 6 and 7 that it is precisely the additional compression of the combustible mixture leads to the appearance of maximum I on the dependences $n(Y_{RDX})$ and $\eta(Y_{RDX})$ at fairly high pressures in the combustion chamber of an engine system ($P > 30$ atm). The system behaves analogously at $Y_{RDX} \geq 62\%$.

The behavior of the system in the region of the percolation threshold Y_{RDX}^* is more difficult to explain. The data in Fig. 8 shows that pure GAP burns much better (with higher value of u_w) than pure RDX. In this case, addition of RDX to GAP ($Y_{RDX} < Y_{RDX}^*$) leads to a decrease in the value of u_w of the GAP/RDX mixture up to the point of the percolation threshold $Y_{RDX}^* = 0.608$,

i.e., an increase in Y_{RDX} degrades the conditions of combustion of the mixture (Fig. 8). Since, at $Y_{\text{RDX}} = Y_{\text{RDX}}^* = 0.608$, the predominantly amorphous structure of the GAP/RDX mixture changes abruptly to the mainly polycrystalline one (Fig. 1,3) and where the adiabatic exponent and the thermal efficiency of the combustion process decrease sharply, the conditions for combustion of the mixture deteriorate accordingly thus, at the point of structural phase transition of the GAP/RDX mixture ($Y_{\text{RDX}} = Y_{\text{RDX}}^*$) the "resistance" of the system is manifested as the appearance of a local maximum II on the dependences $n(Y_{\text{RDX}})$ and $\eta(Y_{\text{RDX}})$ in the immediate vicinity of the percolation threshold point (Figs. 5–7).

In this case, since the intensity of combustion of the mixture is proportional to the pressure in the combustion chamber [12], the linear form of the dependences $\Delta n(P)$ and $\Delta \eta(P)$ (Eqs. 2,4), as a quantitative measure of such system "resistance" seems to be quite natural. It is interesting that the trend of this process (the "resistance" of the system in accordance with the Le-Chatelier principle) in the vicinity of the percolation threshold point is opposite to the "response" of the system on increase in the pressure in the combustion chamber outside this point (Fig. 6).

It should be noted that the Le-Chatelier principle allows one to explain the features of the behavior of the dependences $c_V(Y_{\text{RDX}})$ and $c_P(Y_{\text{RDX}})$ in the case of change in the pressure P in the combustion chamber (shown by the arrows in Fig.6). An increase in this pressure increases the adiabatic temperature of the mixture (Fig.1). Therefore, since this temperature is inversely proportional to the specific heat capacity of the combustion products, the "resistance" of the system to its additional heating caused by an increase in the pressure P leads to an increase in the specific heat capacity of the combustion products, which explains the characteristic increase in the values of c_V and c_P with increase in the pressure in the combustion chamber (Fig. 6).

Acknowledgements

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Conclusions

For improving overall engine performance it is helpful to know how thermal efficiency of combustion chamber of a rocket engine depends on structural characteristics of solid fuel mixture composition. We found out that two-component propellant mixture GAP/RDX undergoes structural phase transition when mass fraction of RDX in GAP approaches 0.608.

The percolation threshold value is pressure-independent, corresponds to change from mainly amorphous to predominantly polycrystalline solid-fuel structure, coincides with the minimum point of combustion velocity of the mixture as a function of its composition and can be obtained from condition of

equality of mole fractions of C and O atoms in the mixture composition.

Calculations show that dependence of thermal efficiency of combustion chamber of a rocket engine on mixture composition has two maximums at elevated pressures. Main trends of the parametrical dependencies for the thermal efficiency can be understood according to the Le Chatelier principle.

Analogous results can be obtained, with necessary modifications, also for a wider class of solid-fuel mixtures of the type of polymeric binder/explosive.

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