An evaluation of the combustion temperature profile of $Ba(NO_3)_2$-based composition

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ABSTRACT

The study examined both theoretical and experimental combustion temperatures of $Ba(NO_3)_2$-based samples of composition with an oxidizer excess coefficient of $\alpha \sim 0.72$ under various pressures. The results indicate that at low pressures, the combustion temperature of the samples is significantly lower than the calculated value. The temperature profile in the combustion wave at atmospheric pressure was determined, revealing that the samples exhibit a high surface combustion temperature. The majority of the heat required for the propagation of the sample's combustion is released in the condensed phase. These findings underscore the influence of pressure on combustion characteristics and emphasize the importance of considering phase interactions in understanding combustion behaviors.

Keywords: Barium nitrate; Combustion; Temperature profile; Condensed phase.

1. INTRODUCTION

Barium nitrate is widely used in the development of green light compositions, as well as in the production of signaling, and pyrotechnic products [1-5]. Currently, many studies have been conducted to elucidate the combustion behavior of compositions containing $Ba(NO_3)_2$ [3-8]. In [8], the combustion behaviors of samples based on various nitrates and phenol formaldehyde resin at a wide range of pressures (0.99-177.65 atm) were studied. It is important to note that the $Ba(NO_3)_2$-based samples with oxidizer excess coefficient $\alpha \leq 0.91$ were burned completely at atmospheric pressure. The results of measuring the combustion temperature at atmospheric pressure indicated that the experimental combustion temperatures of $Ba(NO_3)_2$-based samples match the calculated temperatures only at low α values (0.48-0.57). At slightly higher α values (0.72-0.91), the experimental temperatures are significantly lower than the calculated ones. Hypotheses were proposed to explain the causes of these discrepancies: For preparations based on $Ba(NO_3)_2$, the following observations are made: at 0.99 atm, for samples with a high α (0.72-1), the experimental values are lower than the calculated ones [9]. This discrepancy is due to the incomplete reactions involving nitrogen oxide at low pressures, as well as the combustion of energy-dense materials (such as double base propellants). For $Ba(NO_3)_2$-based samples with a lower α value, various factors may have opposing effects on the combustion temperature. Under certain conditions, the positive effect (e.g., increased CO_2 and C content in the combustion products) and the negative effect (e.g., NO content in the combustion products) can balance each other out, resulting in the experimental temperature matching the calculated temperature [8, 10].

However, the research results on experimental combustion temperatures for the $Ba(NO_3)_2$-based samples under high-pressures have not yet been clearly shown [11]. Besides, the temperature profiles of the samples have not been clarified. The objective of this study is to evaluate the experimental combustion temperature of the $Ba(NO_3)_2$-based samples of composition with α value ~ 0.72 under different pressure conditions and analyze the combustion temperature profile of the sample at atmospheric pressure conditions. This analysis will allow for the calculation of the reaction zone, which determines the burning rate of the sample.

2. MATERIALS AND METHODS

2.1. Materials

All raw materials are from Russia. The tested charges of the sample based on 9.3% phenol-formaldehyde resin (with 2.3% free phenol) and 82.5% $Ba(NO_3)_2$ were studied [6-11]. Particles of $Ba(NO_3)_2$, with sizes ranging from 90 to 160 µm and purity ≥ 99.3%, were used. Dibutyl phthalate served as a plasticizer. Dibutyl phthalate has a relative density of 1.046. The ratio of phenol-formaldehyde resin to dibutyl phthalate is 3:2. 1.5% Teflon and 0.5% calcium stearate are included in the sample to make the processing and production process more convenient. So, the $Ba(NO_3)_2$-based samples with α value ~ 0.72 were prepared for investigation.

2.2. Methods

2.2.1. Sample preparation method

The sample preparation method was prepared similarly to those described in references [6, 8]. The components were pre-dried and mixed with resin and processing additives, followed by the addition of a plasticizer. The mixture was then subjected to a rolling process.

The obtained mixture was rolled in a rolling mill with a rolling step that was four times larger than the size of the oxidizer. The rolling was performed on a roller that included a rolling device. The rolling process was carried out at a temperature of 75-80 °C. After rolling, thin sheets are produced and passed on for pressing. The pressing of the wire from the obtained flat was performed on a press with loads of up to 10 tons, and the diameter of the pressed sample of the medication was ~7 mm.

2.2.2. Method for determining the burning rate of samples

The methods for determining the burning rate (r_b, mm/s) were similar to the ones described in studies [8, 12]. The experiments were conducted on cylindrical charges with a diameter of approximately 7 mm and a height of approximately 15 mm. The charges were enclosed on their lateral surfaces. The burning rates were determined by the ratio of the height of the test sample to the time it took for it to burn completely. At atmospheric pressure, the burning time was recorded using a high-speed camera, which was subsequently used to calculate the burning rate. At high-pressure conditions, the burning time was determined by increasing the pressure using the angular point method, thereby determining the burning rate [13, 14].

2.2.3. Method for determining the combustion temperature of samples

Thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer, which records the change in mass as the temperature increases. The experiments were carried out in a nitrogen atmosphere from 40 ^oC to 900 ^oC (from 313 K to 1173 K) with a heating rate of 20 °C per minute [13].

2.2.4. Method for determining the combustion temperature of samples

The combustion temperature of the samples was determined using tungsten-rhenium thermocouples (TY CY0.021.142), which were positioned within charges enclosed in plexiglass tubes, as in [13]. To ensure accurate measurement, a special procedure was followed to insert the thermocouples into the samples. Initially, two half-charges of a unique shape were prepared. One of these half-charges served as the base for the thermocouple, which was then carefully placed on it. After positioning the thermocouple, the two half-charges were sealed together by compressing them at high temperatures to achieve a hermetic closure.

Once assembled, the entire block containing the thermocouples was placed inside a constant pressure bomb. This setup was then subjected to a controlled nitrogen atmosphere during the combustion process. The nitrogen atmosphere was essential to prevent any interaction between the combustion products and oxygen in the air, which could otherwise affect the results. The combustion process was carefully monitored, and the temperature data collected was plotted to create a characteristic graph illustrating the relationship between combustion temperature and time [14]. Experimental combustion temperatures at different pressures were determined by thermocouples with a thickness of 100 µm. Combustion temperature profiles were investigated by thermocouples with thickness 5-10 µm.

3. RESULTS AND DISCUSSION

3.1. Calculation of theoretical combustion temperature

The theoretical combustion temperature (T_t) of the samples was determined using the fundamental thermodynamic principle of maximum entropy. It states that for a given set of reactants, the final composition of combustion products at equilibrium will be the one that maximizes entropy. This principle helps calculate the most probable distribution of species and energy, ensuring that the system reaches a state where entropy is at its maximum possible value. Figure 1 illustrates a graph depicting the relationship between theoretical temperatures and the coefficient α under different pressure conditions.

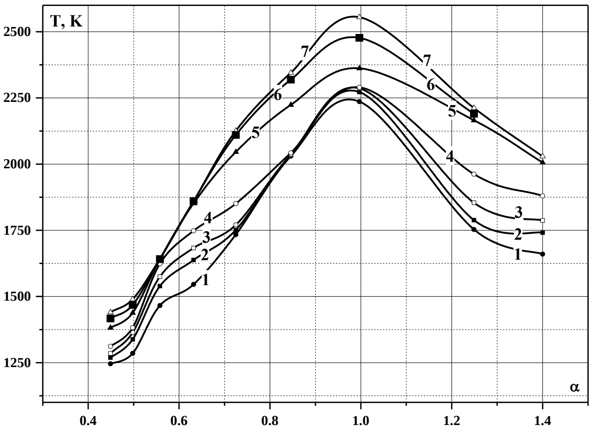


Figure 1. *The dependence of theoretical combustion temperature of Ba(NO*$_3$*)*$_2$*-based samples on the value of α within the pressure range from 0.99 to 98.69 atm:*

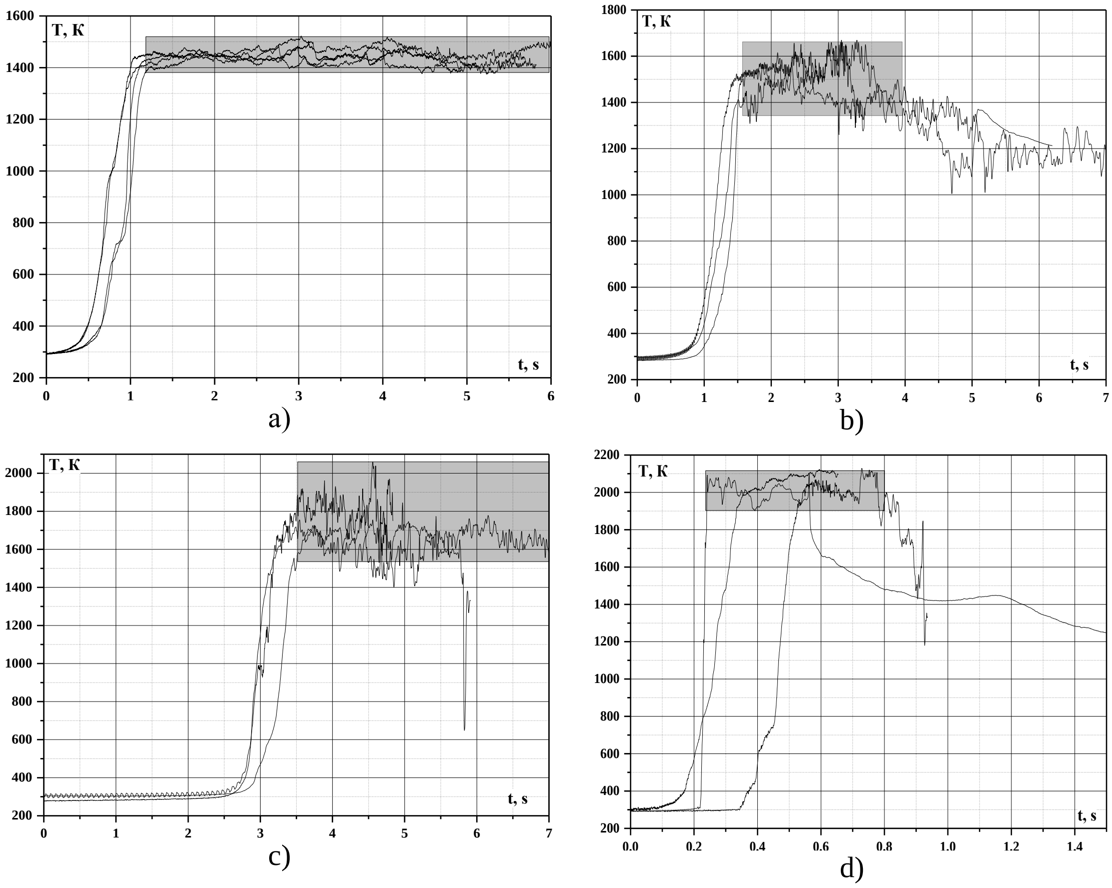
1- 0.99 atm; 2- 2.96 atm; 3- 4.93 atm; 4- 9.87 atm; 5- 39.48 atm; 6- 69.08 atm; 7- 98.69 atm.

It can be observed that, even under varying pressure conditions, the theoretical value always reaches its maximum ($T_t$max) when α ~ 1, for example, at 0.99 atm - $T_t$max= 2242 K, higher 506 K than the sample with α ~ 0.72 (T_t = 1736 K). This is entirely appropriate because, at value α ~ 1, the oxygen balance is zero, creating almost complete combustion products (according to theoretical predictions). At that time, the combustion heat generated is the greatest. When the α value deviates from position 1, the combustion products obtained are incomplete, and the heat of combustion and the combustion temperature are reduced. As the pressure increases, the theoretical combustion temperature also rises. For example, for the sample with α ~ 0.72, at a pressure of 9.87 atm, the theoretical combustion temperature is 1849 K, while at a pressure of 39.48 atm, the temperature increases to 2046 K, representing a rise of 197 K.

3.2. Experimental combustion temperatures at different pressures

Figure 2 shows the oscillograms of the experimental combustion temperatures (T_c) of the samples. Fluctuations appear on the combustion temperature oscillograms, possibly due to some condensation products during the combustion process sticking to the surface of the thermocouple and making it difficult to record. Therefore, determining the exact experimental combustion temperature is relatively difficult. The provided experimental combustion temperature is taken as the average of the highest value area over an extended time.

The results show that, at pressures from 0.99 to 9.87 and 29.6 atm, the experimental combustion temperatures of the $Ba(NO_3)_2$-based samples are lower than the theoretically calculated values. It should be noted that at 29.6 atm, there is a brief peak where the experimental temperature exceeds the theoretical value, reaching 2060 K for a very short duration of 0.01 seconds, making it unrepresentative of the overall process.



a) b) c) d)

Figure 2. *Oscillograms of the combustion temperature of* $Ba(NO_3)_2$*-based samples with* $\alpha \sim 0.72$ *at different pressures: a- 0.99 atm; b- 9.87 atm; c- 29.6 atm; d- 69.08 atm.*

This observation reaffirms that for the studied samples under low-pressure testing conditions, the experimental combustion temperature is consistently lower than the calculated value. This behavior is likely linked to the two-stage decomposition process of $Ba(NO_3)_2$, as documented in several previous studies [15, 16]:

$$Ba(NO_3)_2(liq.) \rightarrow BaO(s) + NO\ (g) + NO_2\ (g) + O_2\ (g) \qquad (1)$$

$$Ba(NO_3)_2(liq.) \rightarrow BaO(s) + N_2\ (g) + 5/2O_2\ (g) \qquad (2)$$

It means that in the combustion products of the $Ba(NO_3)_2$-based samples, NO_2 and NO (N_xO_y) gases may appear. As it is known, the combustion temperature of double base propellants at low pressure is significantly lower than the calculated value due to the incomplete reaction involving $NO_2 \rightarrow NO \rightarrow N_2$ [17]. As pressure increases, the reaction series proceeds in a completely circular direction $NO_2 \rightarrow N_2$. This likely also occurred during the combustion of the investigated samples.

Calculations based on the fixation of various amounts of NO in gaseous combustion products (in the absence of carbon) are shown in table 1. It can be seen that assuming the combustion products contain incompletely converted NO gas, the corresponding experimental combustion temperatures result in 2.8, 2.27, and 1.05 mol/kg of NO at pressures of 0.99, 9.87, and 29.6 atm, respectively. At a pressure of 69.08 atm, with the average experimental temperature recorded, the NO content in the product could be 0.15 mol/kg. However, at this pressure, the experimental combustion temperature can be considered equal to the theoretical value, as the graph shows many points matching the calculated temperature within the measurement error.

Table 1. *The calculation results for some gaseous combustion products at different combustion temperatures.*

Pressure, atm	r_b, mm/s	Combustion temperature, K	N_2, mol/kg	NO, mol/kg	CO_2, mol/kg	CO, mol/kg	H_2O, mol/kg	H_2, mol/kg
0.99	1.3	T_t=1736	3.16	0	3.88	6.31	3.07	1.68
		T_c =1466	1.76	2.80	0.81	6.55	1.28	4.24
9.87	1.6	T_t=1850	3.16	0	3.29	6.27	3.66	1.72
		T_c =1625	2.02	2.27	0.91	6.44	1.68	3.83
29.60	3.1	T_t=2046	3.16	0	2.05	6.00	3.25	1.97
		T_c =1875	2.62	1.05	1.27	6.11	2.52	2.93
69.08	5.0	T_t=2110	3.16	0	1.72	5.87	3.10	2.12
		T_c =2077	3.08	0.15	1.63	5.90	3.04	2.23

3.3. Thermogravimetric analysis

The results of TGA at a heating rate of 20 ^oC/min show that the investigated sample begins to lose mass at a temperature of 373 K (100 ^oC). The mass loss in the temperature range from 673 to 713 K is 32.08%. The greatest mass loss at a single temperature is recorded at 713 K, amounting to 17.45%. Thus, it can be said that the flash point temperature of the sample is 713 K (figure 3). This temperature is significantly lower than the temperature at which the decomposition of $Ba(NO_3)_2$ begins (above 849 K), as documented in many previously published researches [15, 16]. The studied phenol-formaldehyde resin is significantly less thermally stable compared to $Ba(NO_3)_2$ [13]. In the temperature range above 673 K, the decomposition products of phenol-formaldehyde resin may be H_2, CO, CO_2, CH_4, H_2O,… [18, 19].

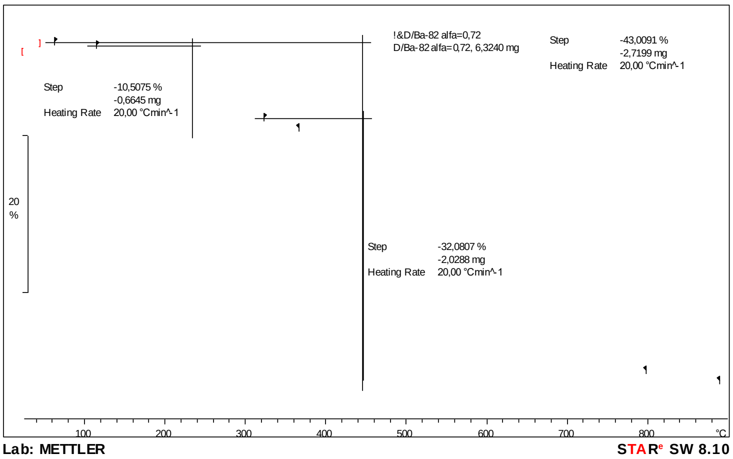


Figure 3. *Graph TGA of $Ba(NO_3)_2$-based sample with α ~ 0.72.*

So, some chemical reactions that can occur during process decomposition of $Ba(NO_3)_2$ are as follows:

$$Ba(NO_3)_2(liq.) \rightarrow BaO(s) + NO\ (g) + NO_2\ (g) + O_2\ (g) \quad (3)$$
$$Ba(NO_3)_2(liq.) \rightarrow BaO(s) + N_2\ (g) + 5/2O_2\ (g) \quad (4)$$
$$BaO + CO_2 \rightarrow BaCO_3 \quad (5)$$
$$CO + NO_2 \rightarrow NO + CO_2 \quad (6)$$

$$NO_2 + CO \rightarrow N_2 + CO_2 \quad (7)$$

$$CH_4 + 2NO_2 \rightarrow N_2 + 2H_2O + CO_2 \quad (8)$$

The total mass loss of the sample during the heating process is 43%. The residual mass is 57%. Based on calculations, if the solid combustion products of the studied sample consist solely of BaO or $BaCO_3$, the remaining solid mass would be 48.3% and 62.19%, respectively. According to the TGA results, the remaining solid product can contain both BaO, $BaCO_3$, and other products.

3.4. Combustion temperature profiles at atmospheric pressure

The combustion temperature profiles of the samples are shown in figure 4.

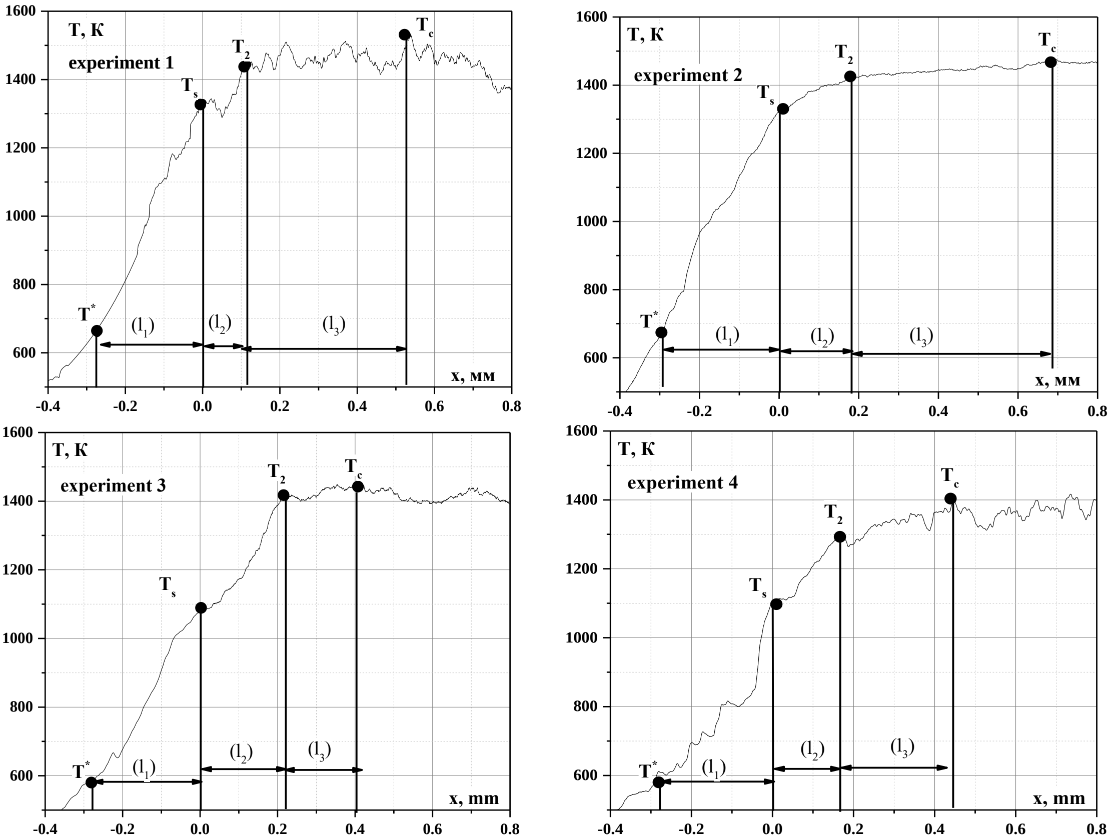


Figure 4. *Temperature profiles in the combustion wave of a $Ba(NO_3)_2$-based samples.*

Analysis of the obtained oscillograms reveals that all temperature profiles exhibit typical bends and distinct regions. The first bend, occurring at x=0 (considered the surface temperature, T_s), may be associated with the thermocouple transitioning from the melt state to the gas phase [13]. Below T_s lies the condensed phase, which includes a narrow reaction zone and a heated zone. The thickness of the heated zone (l_1) is defined as the distance over which the temperature decreases by a factor of e (from T_s to T^*). Above the combustion surface is the gas phase, which consists of two regions. The first region has a thickness of l_2, within which the temperature changes from T_s to T_2. This region is characterized by a temperature gradient, with T_2 being the temperature above which fluctuations are observed. The second region, with a thickness of l_3, is where the temperature reaches the experimental combustion temperature.

The value of T_s for the samples is approximately 1214 K. The width of the heated and reaction layers in the condensed phase is 289 µm. The temperature gradient above the combustion surface, φ_1, is about $1.0 \cdot 10^4$ K/cm, which is significantly lower compared to φ_1 for the KNO_3-based samples [13]. The measured temperature (1469 K) is lower than the calculated value. All the parameters of the combustion wave are presented in table 2.

The all-experimental values on temperature profiles exhibit relative differences for different testing experiments. This characteristic may be due to the reaction process of the components in the samples, especially $Ba(NO_3)_2$, as the mass of the condensation product (BaO, $BaCO_3$…) produced by this oxidant is substantial, strongly affecting the accurate determination of experimental values.

Table 2. *Parameters of the temperature profile in the combustion wave of the studied samples.*

№ experiment	T^*, K	l_1, µm	$\chi.10^3$, cm^2/s	T_s, K	$\varphi_1.10^{-4}$, K/cm	T_2, K	l_2, µm	T_c, K	l_3, µm
1	678	275	3.6	1337	0.9	1439	115	1536	411
2	670	300	3.9	1315	0.6	1414	174	1478	509
3	590	287	3.7	1099	1.4	1409	217	1460	186
4	592	289	3.8	1104	1.2	1300	165	1400	278
The average value	633	289	3.8	1214	1.0	1390	168	1469	349

Based on the results obtained, the heat balance of the condensed phase was compiled [13]:

$$C_p(T_s-T_0) + \Sigma(\Delta H) = Q_c + Q_\lambda$$

Where: T_0 - Initial temperature; C_p - Average heat capacity of the samples in the temperature range T_s - 293 K; $\Sigma(\Delta H)$ - The sum of the heats of phase transitions of the components, J/g; Q_c - Heat released in the condensed phase, J/g; Q_λ - Heat supplied from the gas zone, J/g.

Table 3. *Heat balance for studied samples in condensed phase.*

№ experiment	Q_λ, (J/g)	ΣQ, (J/g)	Q_c, (J/g)	$Q_c/\Sigma Q$, (%)
1	22	945	923	98
2	81	941	860	91
3	11	1097	1085	99
4	17	1028	1010	98

According to the above table, the majority of the heat required for the combustion propagation process is released in the condensed phase (over 91%).

4. CONCLUSIONS

In this article, the combustion temperature and temperature profiles of the $Ba(NO_3)_2$-based sample with α~0.72 were analyzed. The research results indicate that as the experimental pressure increases, the combustion temperatures of the sample gradually rise and approach the theoretically calculated values. The discrepancy between the calculated and experimental combustion temperatures is attributed to the incomplete reaction of nitrogen oxide. At a pressure of 69.08 atm, the combustion temperature of the sample matches the calculated value. The sample exhibits a high burning surface temperature (~1214 K), and the main heat required for the combustion propagation is released in the c-phase.

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TÓM TẮT

Một đánh giá về nhiệt độ cháy của vật liệu trên cơ sở $Ba(NO_3)_2$

Bài báo nghiên cứu về nhiệt độ cháy lý thuyết và thực nghiệm của các mẫu của thành phần trên cơ sở $Ba(NO_3)_2$ *có hệ số oxy là* α*~0,72 ở nhiều điều kiện áp suất khác nhau. Kết quả cho thấy ở áp suất thấp, nhiệt độ cháy của mẫu thấp hơn đáng kể so với giá trị tính toán. Biên dạng nhiệt độ trong sóng cháy ở áp suất khí quyển đã được xác định, cho thấy mẫu có nhiệt độ bề mặt cháy cao. Phần lớn nhiệt cần thiết cho quá trình lan truyền cháy của mẫu được giải phóng trong pha ngưng tụ. Những đặc điểm này làm rõ ảnh hưởng của áp suất đến các đặc trưng cháy và nhấn mạnh tầm quan trọng của việc xem xét các tương tác pha trong nghiên cứu quá trình cháy.*

Từ khoá: Bari nitrat; Cháy; Biên dạng nhiệt độ; Pha ngưng tụ.