Research paper / Praca doświadczalna

Termite pyrotechnic compositions of iron and alkaline earth metals peroxides
Pirotechniczne mieszaniny termitowe żelaza z nadtlenkami berylowców

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Abstract: *The fallowing article presents the combustion studies of Fe/alkaline earth metals peroxides composition. It contains a literature review and the results of own research, which aim is to determine the possibility of using iron-based thermite compositions in time delay elements. The article focuses on the investigation of combustion front propagation rate as a function of a pressing load, the iron content and the purity of used oxidants. The DSC, TG and XRD analysis confirmed that reactions in this system occurs mainly in the solid state.*

Streszczenie: *Poniższy artykuł przedstawia badania procesu spalania mieszaniny żelaza z nadtlenkami berylowców. Obejmuje on przegląd literatury, jak również wyniki badań własnych, których celem jest określenie możliwości zastosowania w układach opóźniających mieszanin opartych na żelazie. Artykuł skupia swoją uwagę na określeniu prędkości propagacji frontu spalania mieszaniny w funkcji ciśnienia zaprasowania, zadanego w trakcie procesu elaboracji, zawartości żelaza oraz czystości wykorzystanych utleniaczy. Analiza DSC, TG oraz XRD potwierdziła, iż reakcje pomiędzy komponentami mieszaniny zachodzą głównie na granicy faz (ciało stałe)-(ciało stałe).*

Keywords: *time delay composition, detonator, gasless combustion, burn rate*
Słowa kluczowe: *mieszanina opóźniająca, zapalnik, spalanie bezgazowe, prędkość spalania*

Symbols and abbreviations:

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λ	thermal conductivity [W/m·K]
c	specific heat [J/kg·K]
ρ	density [kg/m³]
D	thermal diffusivity [m²/s]
t_r	time of increment determined on the base of the complementary Gauss function [ms]
v_{exp}	combustion rate determined experimentally [mm/s]
v_{calc}	calculated combustion rate [mm/s]

1. Introduction

A distinctive feature of pyrotechnic compositions is that once ignited, they combust at a constant rate, emitting heat that is utilised to produce a particular special effect [1]. Due to their properties, gasless thermite compositions often find application in chemical delay systems, used in turn in time delay detonators. Consequently, they are often referred to as delay compositions. Because of a weak dependence of burning rate on external pressure and temperature, they can be used to ensure the desired delay time in detonators for military and civilian usage. Delay compositions find the broadest application in the production of blasting agents, which in turn are commonly used by the mining industry, as well as in some types of civil engineering projects (demolitions, tunnel construction). The primary group of blasting agents, utilising delay compositions, consists of electric and non-electric detonators, whose development, since the second half of the twentieth century, served to greatly increase their sophistication and opened new avenues of application, particularly in the mining industry and civil engineering [2]. The burning rate, characteristic for each delay composition and determining its application, is expected to be only marginally affected by atmospheric pressure. The choice of burning rate as the main property, describing a pyrotechnic delay composition is justified and results from the direct correlation between the burning time of a path or column of a particular delay composition with its spatial dimensions (typically with the length of the path).

2. Components of iron based pyrotechnic time delay compositions

2.1. Chemical properties of iron

Metallic iron turned out to have potential for use in delay mixtures, to which Tribelhorn devoted a lot of attention in his works, *e.g.* [3, 4]. Iron, not having found significant application in delay compositions beforehand, due to it being oxidised relatively easily in most systems with reactive oxidising agents, may yet prove to be one of the best fuels, in mixtures with alkaline earth metal peroxides. An oxidation temperature in oxygen (150 °C), significantly lower than its melting point (1535 °C), is a characteristic feature of iron. The presence of humidity and acidic substances, which catalyse the process of iron oxidation by forming galvanic cells, has a significant impact on the behaviour of iron. If barium or strontium peroxides are used, such a problem is avoided, because both peroxides are strongly alkaline. Furthermore, the electrode potentials of Ba^{2+} and Sr^{2+} cations are significantly more negative than the electrode potential of iron. Consequently, their use in combination with iron does not produce any direct risk of deactivation of the system. The reactivity of iron is strictly linked with its grain characteristic and its morphology. Consequentially this factors have significant impact on the burn rate of a final delay composition. For industry it is common to use iron with an average grain size below 30 µm. To exemplify, carbonyl iron, manufactured by BASF has an average grain size (d50) in the range of 2-15 µm and purity of 97.0-99.5%. Iron of higher purity requires additional passivation. The main contaminants in carbonyl are carbon, oxygen and nitrogen. Figure 1 features SEM photographs, detailing the microstructure of standard and passivized, higher purity carbonyl iron.
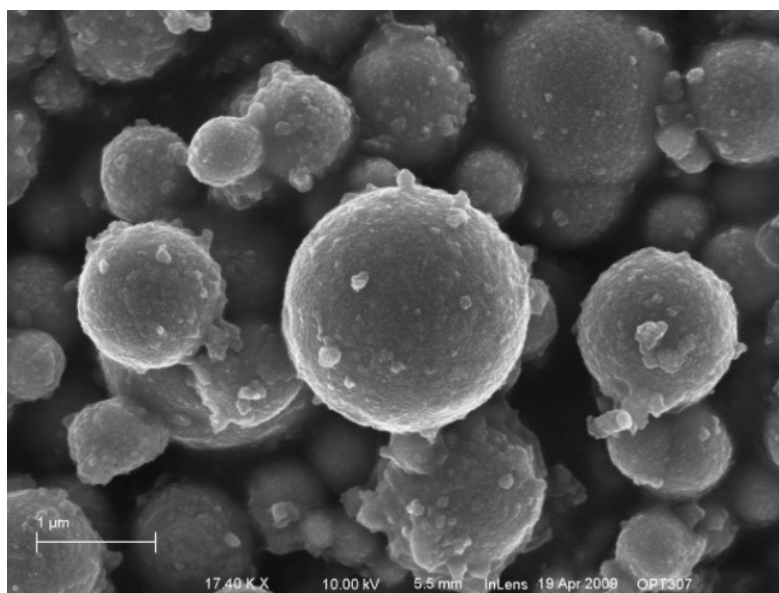
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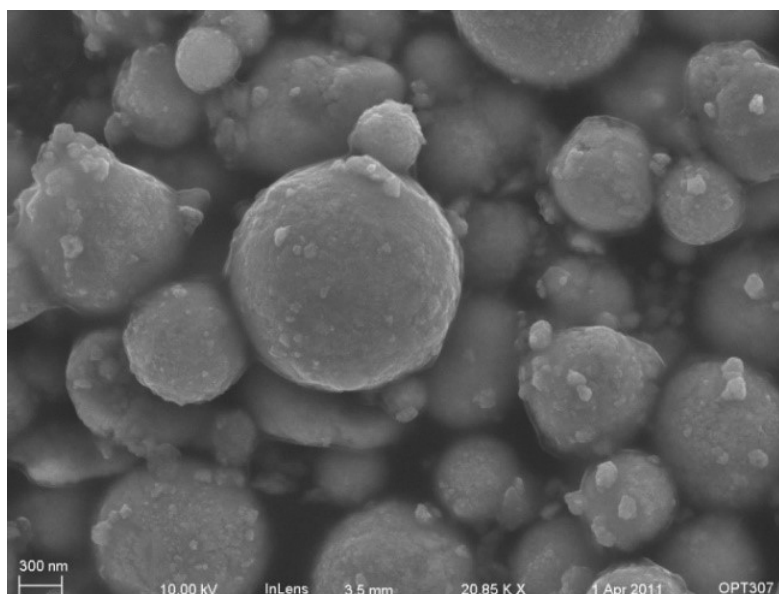
(b)

Figure 1. The microstructure of carbonyl iron – scanning electron microscopy (SEM) image captures: (a) pure carbonyl iron, (b) carbonyl iron coated with an organic passivation layer

2.2. Thermal analysis of barium and strontium peroxides

Figure 2 shows the DSC-TG thermograms of oxidising agents (BaO_2 and SrO_2) [5]. The thermograms of the BaO_2 oxidising agent (Fig. 2, curves (a) and (c)) contains two endothermic peaks at around 150 °C, coupled with

a small loss of sample mass, indicating the release of adsorbed moisture from the sample. A minor endothermic peak is observed at 380 °C, attributed to the dehydroxylation of $Ba(OH)_2$ traces present in the sample. In the range of 570-630 °C, the main decomposition stage is induced, ending in temperatures above 900 °C. The entire decomposition process results in a loss of about 8% of the initial mass of the sample. The change in enthalpy measured for this process by DSC is equal to 382 kJ/kg, whereas the value calculated using enthalpies of formation for the respective compounds equals 334 kJ/kg.
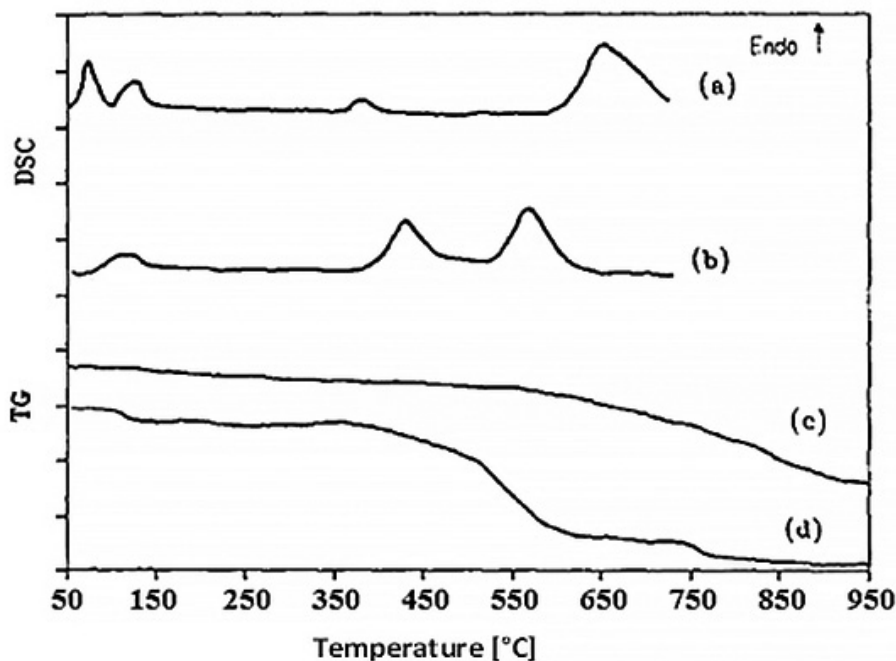

Figure 2. DSC-TG thermograms, recorded in nitrogen at a temperature scanning rate of $t = 10$ °C/min for BaO_2 and SrO_2: (a) DSC of BaO_2, (b) DSC of SrO_2, (c) TG of BaO_2, (d) TG of SrO_2

3. The overview of iron – alkaline earth metals peroxides compositions

3.1. Burn rate measurements

The first works on the use of iron, as a component of mixtures with barium and strontium peroxides, were published by Spice and Staveley [6, 7], and Hill *et al.* [8]. Binary systems of peroxides with molybdenum, manganese and sulphur have also been studied. Tribelhorn investigated the dependence of the combustion rates of pyrotechnic systems on the iron content of those systems, in which various oxidising agents, *i.e.* BaO_2, SrO_2 and $KMnO_4$ were used. The combustion of mixtures of iron with any of the abovementioned oxidising agents takes place on the solid(fuel)/solids(oxidising agent) or on the solid(fuel)/gas(oxidising agent) interface. Figure 3 presents general combustion profiles for systems composed of iron and peroxide oxidising agents, in comparison to the behaviour of the $Fe/KMnO_4$ system, where fineness and purity of the reagents are:

- Fe (99%): max 43 µm,
- BaO_2 (85%): max 20 µm,
- SrO_2 (85%): max 20 µm,
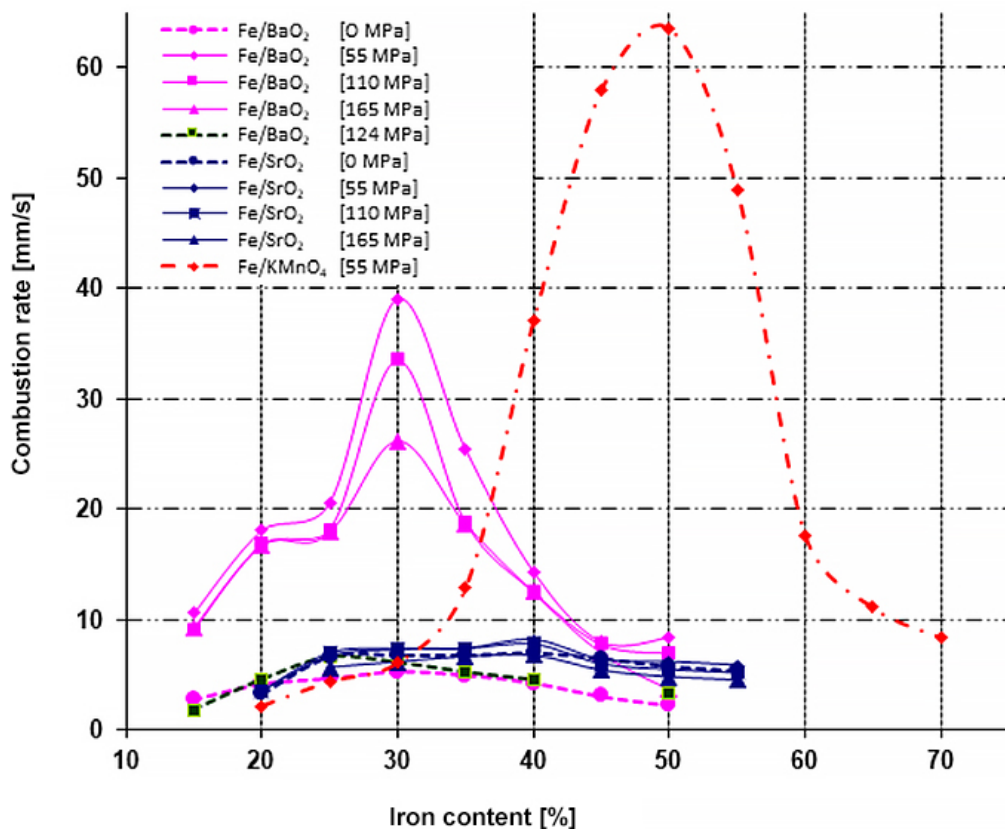- $KMnO_4$ (99.5%): max 53 µm.

Figure 3. Combustion rates of different delay systems, pressed at a pressure of 55 MPa, as a function of the share of iron in the composition [3]

The impact of the pressure of pressing on the combustion rate versus the fuel content in the Fe/BaO$_2$ and Fe/SrO$_2$ [3] systems is detailed in Figure 4. The results indicate that both mixtures are viable for use, in terms of their combustion rates and low sensitiveness to the pressure applied during pressing. Activation energies of the stoichiometric systems differ from each other and are:

– Fe/KMnO$_4$: 8.1 kJ/mole for 50% Fe,
– Fe/BaO$_2$: 13.8 ±1.8 kJ/mole for 18% Fe,
– Fe/SrO$_2$: 27.0 ±2.4 kJ/mole for 25% Fe.

The combustion rates of a Fe/BaO$_2$ system, depending on the iron content (in the range of 15-50%) and the pressure of pressing (5-165 MPa), are in the range of 8-39 mm/s. The highest combustion rates were recorded for mixtures containing 30% Fe, regardless of the pressure applied to the mixture during pressing. The combustion rate profiles for non-compacted (bulk) peroxide/iron compositions are virtually identical. The differences manifest only after pressing. The combustion rate profiles of Fe/SrO$_2$ mixtures remain unchanged, because the system is practically insensitive to pressing, when the content of iron is in the range of 25-45%.
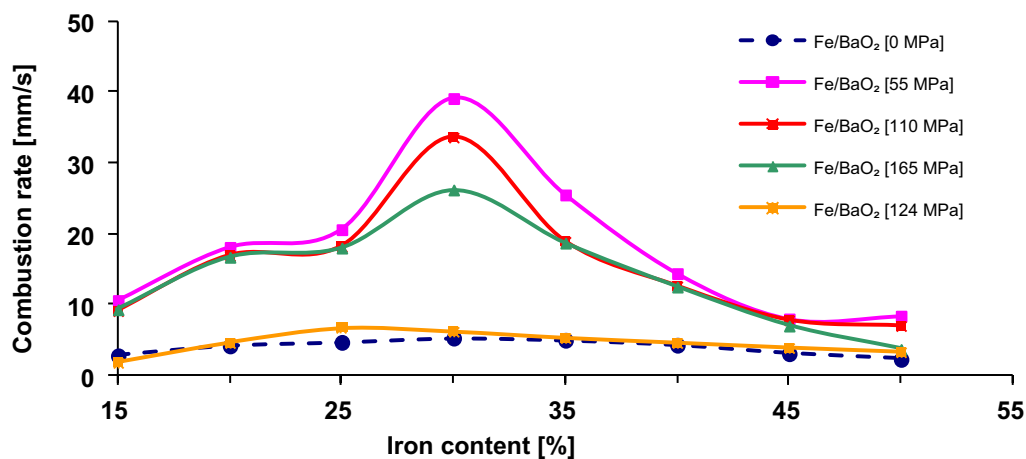
(a)
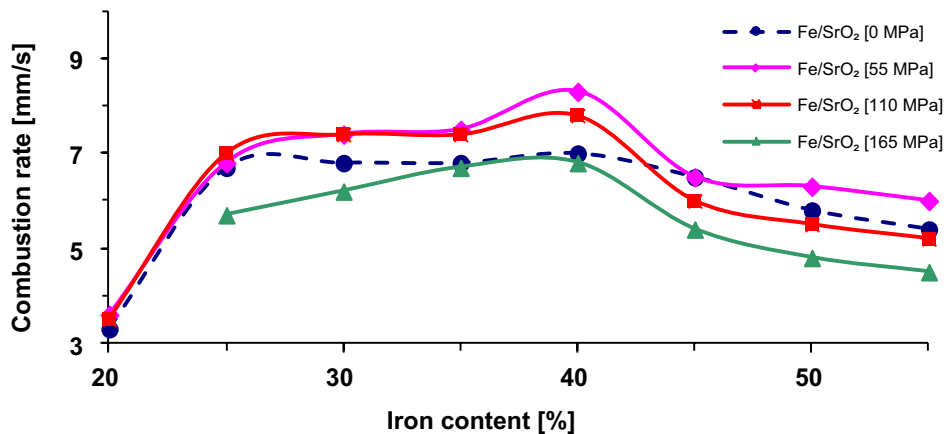
(b)

Figure 4. Combustion rate of iron-peroxide delay systems for different pressing pressures, *vs.* the share of iron in the (a) Fe/BaO₂; (b) Fe/SrO₂ composition [3]

Figure 4 shows that the combustion rate of the bulk Fe/BaO$_2$ mixture is low and reaches at most 5 mm/s (the propagation rate of the combustion front is slightly lower than for the Fe/SrO$_2$ system), however it increases, when the mixture is pressed at low pressure (up to 55 MPa); further increasing the pressure of pressing brings about a rapid decline of the combustion rate. Research, conducted by the author of this study, shows that the Fe/BaO$_2$ mixture withstands greater pressures of pressing and its combustion rate stabilises, when pressures in the range of 100-300 MPa are used for pressing, and is highly repeatable [3].

In comparison with the Fe/SrO$_2$ compositions, the combustion rate of Fe/BaO$_2$ compositions was investigated for iron contents in the range of 20-55%, at different pressures of pressing (0-165 MPa). The highest combustion rates were observed for mixtures, containing 40% Fe, regardless of the degree of compression (Fig. 4(b)). The investigated temperature profiles for that system fit in the range of 600-1100 °C (the time, required to reach the maximum temperature, was 400-700 ms). The shape of the temperature profiles is varied, depending on the iron content of the mixture, exhibiting a maximum for a 25% Fe content (the stoichiometric composition for this system is 23% of iron in the mixture). The combustion rates of the composition were

virtually unchanged over a wide range of iron contents; more importantly, they were not strongly dependent on the degree of compression (Figure 4(b)). The Fe/SrO_2 mixture is highly resistant (its parameters are only slightly affected) to changes in the pressure applied during pressing, in comparison to the Fe/BaO_2 system.

Combustion rates of a Fe/SrO_2 system, which was pressed using a pressure of 55 MPa, are within the range of 3.6-8.3 mm/s, whereas for a Fe/BaO_2 system they were significantly higher (8-39 mm/s) [3]. Such behaviour of the Fe/SrO_2 system indicates it as a good material for delay mixtures slower than what is required of systems with a decisecond delay.

Studies on the impact of additives on the combustion rate of Fe/BaO_2 and Fe/SrO_2 systems, containing near-stoichiometric amounts of fuel, indicate that for Fe/SrO_2 systems, the presence of $SrCO_3$ significantly affected the combustion rate. Conversely, the presence of $BaCO_3$ had negligible impact on Fe/BaO_2 systems. Interestingly, even a 1% addition of $SrCO_3$ to Fe/SrO_2 systems was sufficient to completely deactivate the system. Furthermore, it was observed that $SrCO_3$, as occurring on SrO_2 crystal surfaces (due to absorption of CO_2 from the air) has an even greater deactivating effect on the mixture, than its addition as a powdered component. This is explained by the nature of the absorption of CO_2 from the air, as it deactivates a larger surface area of SrO_2 and, therefore, hinders contact between the two main components of the composition. Similarly, a 1% addition of water and $Sr(OH)_2$ also completely deactivates the mixture. In the case of Fe/BaO_2 systems, the influence of such impurities was noticeably lesser, however water and elevated air humidity remain the biggest threats, as they may cause adverse reactions, leading to the formation of barium hydroxide and carbonate [4].

Brown and Tribelhorn have also studied (in comparison to mixtures of iron with peroxides) the combustion rate of $Fe/KMnO_4$ systems, with the iron contents in the range of 20-70)%. The tests were performed, using various pressures for pressing the mixtures (0-165 MPa). The combustion rates of the $Fe/KMnO_4$ system, pressed using a pressure of 55 MPa, are strongly dependent on the iron content of the mixture, and are found in the range of 2-64 mm/s. The study shows that the combustion rate increases sharply with an increasing degree of compression of the mixture, as for a $Fe/KMnO_4$ system, composed of a 1:1 ratio of the reagents and pressed at 55, 110 and 165 MPa, the combustion rates are respectively 64, 75 and 92 mm/s. The temperature profiles for this system are irregular, in comparison to those for other compositions, indicating an unstable course of the reaction. The highest combustion temperature (1500 °C) was recorded for a system containing 40% Fe; the lowest combustion temperature (1000 °C) was observed for a system with 70% Fe. The times, required for the system to achieve its maximum temperature, were in the range of 60-120 ms, shorter than for Fe/BaO_2 systems [3].
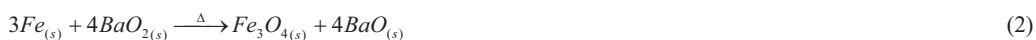
The above data indicates that the $Fe/KMnO_4$ system does not fulfil the fundamental requirements for delay mixtures, due to the overly high dependence of its combustion rate on the degree of compression and on the iron content. The Fe/SrO_2 system appears to be adequate, however it is not free from drawbacks, namely the presence of impurities has too big of an impact on its combustion process and it is more expensive than the Fe/BaO_2 system. The Fe/BaO_2 system is more predictable, in terms of the effect of impurities, however, it is more strongly dependent on the pressure of pressing and contents of the mixture than either the Fe/SrO_2 or $Fe/KMnO_4$ system. Reliability of operation, determined by the activation energy of the system, is another important factor to be considered when designing pyrotechnic compositions. Thermochemical data indicates that the activation energy of the Fe/SrO_2 system is approximately twice as high as that of the Fe/BaO_2 system, which is not without relevance for its application as a delay composition in detonators.

3.2. The thermochemistry of Fe/BaO₂ composition

Among the abovementioned systems, containing iron and oxidising agents, which satisfy the criteria for use as delay compositions for decisecond delay detonators, the system based on iron and barium peroxide shows the best performance. The parameters of the Fe/BaO_2 system, its profile and properties prove that, with minor modifications, it could meet the basic requirements for high precision decisecond delay compositions.

The binary pyrotechnic mixture Fe/BaO_2 features a relatively low combustion temperature between 800-1300 °C

and negligible emission of gaseous products. The reaction between iron and barium peroxide occurs mainly in the solid and liquid phases and the amount of its gaseous products is very small. The maximum combustion temperature (approximately 1300 °C) is achieved for a system, whose oxygen balance is negative, with 20% Fe, a near-stoichiometric amount. The following reactions occur in this system [9]:

$$2Fe_{(s)} + 3BaO_{2(s)} \xrightarrow{\Delta} Fe_2O_{3(s)} + 3BaO_{(s)} \tag{1}$$

$$3Fe_{(s)} + 4BaO_{2(s)} \xrightarrow{\Delta} Fe_3O_{4(s)} + 4BaO_{(s)} \tag{2}$$

$$Fe_{(s)} + BaO_{2(s)} \xrightarrow{\Delta} FeO_{(s)} + BaO_{(s)} \tag{3}$$

The stoichiometric iron contents for each of the above iron oxidation reactions (1)-(3) are respectively 15.8, 17.4 and 21.9%. The main gaseous products are oxygen, produced during decomposition of the oxidising agent, and carbon dioxide, produced during combustion of the binder. The heat of combustion for a stoichiometric system (18.03% Fe) is 900 kJ/kg of the mixture. Increasing the fuel content above 25% significantly limits emission of free oxygen during the combustion of the mixture. A study of gas evolution properties revealed that a mixture, containing 25% Fe, releases no more than 6 cm^3 of oxygen per 1 g of the mixture [10]. The main solid products of combustion of this system are BaO and Fe$_3$O$_4$, with small amounts of FeO and Fe$_2$O$_3$ also being found. Investigations, apart from revealing the qualitative composition of the samples (found, using X-ray diffraction), have confirmed the presence of solid phases of intermetallic oxides in the post-combustion residue, namely, the following spinels: Ba$_3$Fe$_2$O$_6$, Ba$_3$FeO$_5$, BaFeO$_3$, Ba$_2$FeO$_4$ and BaFe$_2$O$_4$, formed according to the following reactions [11]:

$$Fe_2O_{3(s)} + BaO_{(s)} \xrightarrow{\Delta} BaFe_2O_{4(s)} \tag{4}$$

$$FeO_{(s)} + BaO_{2(s)} \xrightarrow{\Delta} BaFeO_{3(s)} \tag{5}$$

$$Fe_{(s)} + 2BaO_{2(s)} \xrightarrow{\Delta} Ba_2FeO_{4(s)} \tag{6}$$

$$FeO_{(s)} + 2BaO_{(s)} + BaO_{2(s)} \xrightarrow{\Delta} Ba_3FeO_{5(s)} \tag{7}$$

A review of the available literature reveals that the combustion reaction of the Fe/BaO$_2$ system has low activation energy, in the range of 7-16 kJ/mole (Fig. 5). The activation energy decreases when the fuel content in the mixture is increased above the stoichiometric. This is a characteristic feature of combustion processes that are mostly diffusion-limited, taking place for a mixture, with a very negative oxygen balance [9]. The maximum activation energy was recorded for a Fe/BaO$_2$ mixture, containing 35% of metallic iron. Increasing the fuel content to 45% reduces the activation energy to about 7 kJ/mole, the lowest value observed in the entire range of compositions, in which the mixture is combustible. Considering the value of the activation energy practically, it is most beneficial to use systems containing either about 25% or about 45% of the fuel. This is because a system, with low activation energy is clearly more advantageous for application in delay detonators, as it removes the need of using an additional igniting mixture.
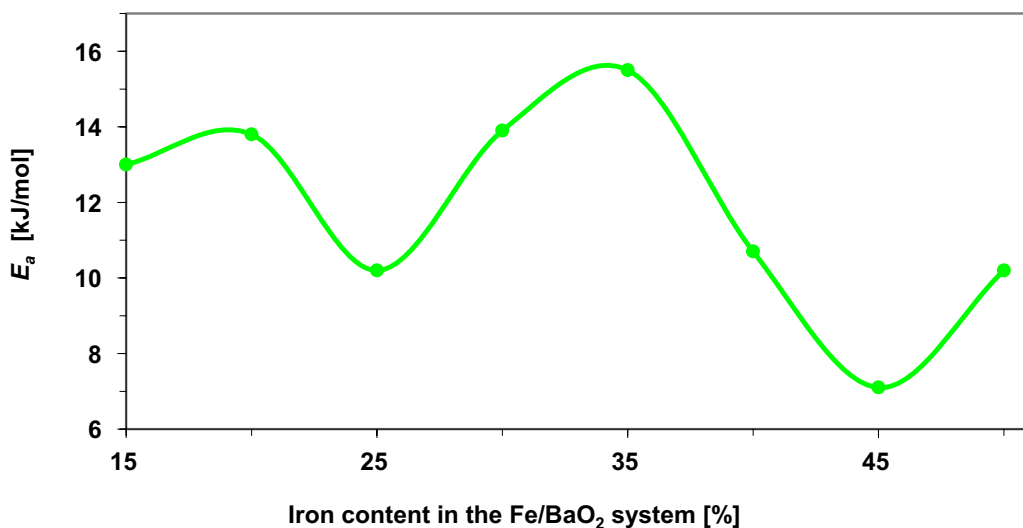
Figure 5. Activation energy of the Fe/BaO₂ system plotted *vs.* the iron content in the mixture [12]

Figure 6 presents the dependence of the enthalpy of reaction of the Fe/BaO₂ system as a function of the contents of the mixture [3]. Tribelhorn *et al.* have extrapolated the temperature gradient (using temperature profiles) to obtain their data, which is shown alongside the enthalpy of reaction that was calculated, based on the enthalpy of formation of the reagents. The abovementioned data is compared with the results reported by Spice and Staveley [6, 7], who experimentally determined the enthalpies of the reaction, through measuring the heats of combustion (marked with a yellow dashed line in Figure 6).
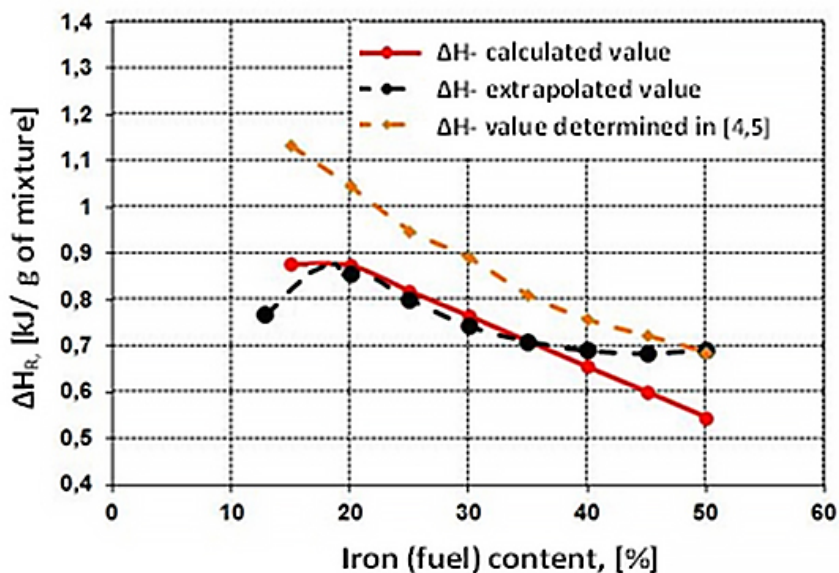

Figure 6. Enthalpies of reaction for the Fe/BaO₂ system, plotted as a function of the iron content: calculated using Hess's law and determined experimentally [3, 6, 7]

The above dependences of reaction enthalpy on the fuel content show that the enthalpy values calculated and determined by the extrapolation method (Tribelhorn) are convergent for 20-35% Fe in the mixture. However, in case of iron contents above 35%, the extrapolated values are higher than the ones calculated, using the formation enthalpies of the reagents. Some discrepancies pertain to mixtures, whose contents correspond to the upper flammability limit of the mixture, for which the enthalpy differs by 20-25%. Spice and Staveley have reported reaction heats much higher than what was found by Tribelhorn. This discrepancy may be attributed to the participation oxygen from the reaction environment in the oxidation of iron oxidation, as Spice and Staveley carried out their measurements in a bomb calorimeter, in oxygen [7]. The heat of reaction, changes by 35% of the maximum value (achievable for a stoichiometric system) across the entire combustibility range of the mixture, enabling precise control of the course and rate of the reaction. The decrease in the heat of the reaction, with increasing fuel content in the mixture, takes place at a gradient of 1%/1 °C. This is beneficial, in terms of matching the amount of generated heat to the thermal conductivity and heat capacity of the delay element.

3.3. Temperature profiles

Nakahara and Hikita [13] have studied the pressure and temperature profiles for the combustion of the Fe/BaO_2 and Mo/BaO_2 systems, reporting that the propagation wave, developing in the Fe/BaO_2 system, is preceded by intensive emission of oxygen, resulting from the endothermic decomposition of barium peroxide. The investigated temperature profiles of the Fe/BaO_2 system fit within the temperature range of 700-1300 °C (Figure 7).
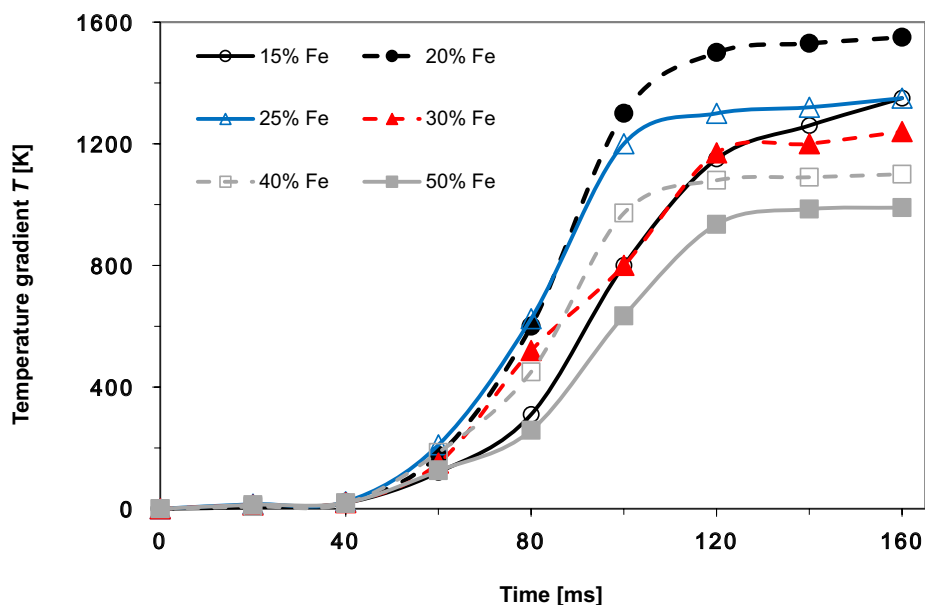

Figure 7. Temperature profiles of the combustion of a binary Fe/BaO_2 system in time t [3, 13]

The shape of the temperature profiles depends on the iron content, exhibiting the highest temperature gradient for 20% fuel in the mixture. The temperature profiles of the Fe/BaO_2 are smooth and the maximum temperature of the system is reached after about 120-140 ms. The reaction rate at the solid$_{(fuel)}$/solid$_{(oxidising agent)}$ interface proves that the contents of the mixture are near-stoichiometric (18.0% Fe, according to calculations). One of the tests for determining the extent, to which the mixture retains its parameters, is the verification of heat retention in the combusting mixture and heat exchange with the environment. Repeatable temperature

profiles, recorded by Tribelhorn *et al.* indicate that the Fe/BaO$_2$ composition is highly stable during heat exchange with the environment. The repeatability of the temperature profiles of the 20% Fe/BaO$_2$ mixture compressed at the pressure of 55 MPa is illustrated in Figure 8.
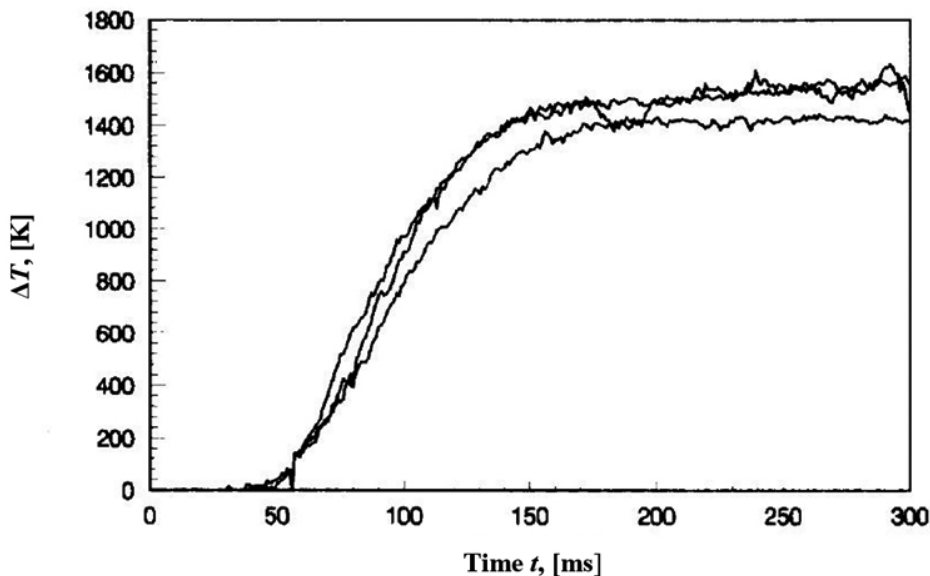

Figure 8. Series of temperature profiles recorded for the combustion of 20% Fe/BaO$_2$ mixture, which was pressed at the pressure of 55 MPa [3]

Systems containing BaO$_2$ are sensitive to change in the contents of the mixture and in the fineness of its components [3]. Presumably, the combustion process in this system can be controlled to a larger extent, through varying the fineness of iron. Spice and Staveley's earlier research into this subject indicates that the fineness of both the fuel and oxidising agent has significant impact on the combustion profiles of Fe/BaO$_2$ compositions. These same researchers have used BaO$_2$ of much greater fineness (*i.e.* grain-size of 125 μm) to achieve significantly reduce the combustion rates for this system [6]. Comparing the combustion rates of the Fe/BaO$_2$ system reported by Spice and Staveley with the rates obtained by Tribelhorn for similar pressures applied to press the mixtures (110 MPa used by Tribelhorn compared to 124 MPa used by Spice and Staveley) reveals that their values are more than 3 times higher for components with finer grains. In light of the current availability of reagents, which fulfil the requirements for decisecond delay compositions, the suitability of the Fe/BaO$_2$ system, as a basis for producing such mixtures, is confirmed. The requirements for the reagents include a desired average grain-size, which is largely responsible for the reaction rate in a system with given contents; in the case of iron an average grain-size in the range of 20-40 μm, including at most 15% of the 40-63 μm grain fraction is the most advantageous. The presence of a small amount of larger-grained fuel is advantageous, because it alters the reaction rate somewhat, preventing it from developing in an uncontrolled manner. Larger fuel grains require a longer time to be heated up to the temperature, at which they undergo the reaction, thereby absorbing more heat from the reaction zone. It is worth noting that all earlier studies have shown that the fineness of the metallic iron has a greater impact on the reaction rate than the fineness of barium peroxide, for which the optimal average grain-size should be in the range of 10-30 μm.

Despite its low activation energy, the Fe/BaO$_2$ system does not exhibit increased sensitiveness to simple mechanical stimuli, such as friction or impact. An additional advantage of the Fe/BaO$_2$ pyrotechnic composition is the relatively low toxicity of its ingredients. The drawbacks of this system undoubtedly include sensitiveness to water and to high air humidity. The above property stems from high reactivity of the oxidising agent,

which decomposes in the presence of water, forming barium hydroxide, which strongly deactivates the Fe/BaO$_2$ pyrotechnic composition. Consequently, during production of this mixture any probability of the oxidising agent becoming deactivated by water should be eliminated, because its presence in an amount higher than 1% in the system may completely deactivate the Fe/BaO$_2$ pyrotechnic mixture. It is, therefore, prudent to introduce the most optimal binder into the composition, in order to limit the negative effect of humidity on the delay mixture that contains barium peroxide. During combustion of the Fe/BaO$_2$ mixture, water is released from the endothermically decomposing Ba(OH)$_2$, which evaporates, consuming the heat released by the system. It additionally affects the system, by diminishing the contact between the particles of the components of the mixture. Water can also deactivate the system by reacting with iron, present in the mixture, forming oxides and hydroxides on the surface of iron grains. Barium peroxide rapidly reacts with carbon dioxide, present in air, readily forming a thin layer of BaCO$_3$ on the surface of BaO$_2$, however, research has shown that, because the amount of BaCO$_3$ is marginal (less than 1%) and stable over time, it does not substantially affect the pyrotechnic characteristics of the Fe/BaO$_2$ system [3, 14-16]. The presence of BaCO$_3$ in the composition, in an amount up to even 15% does not cause deactivate the composition completely.

3.4. Fe-BaO$_2$ combustion kinetics

In the case of a reaction taking place at the Fe/BaO$_2$ interface (of two solid phases), its rate, as for most pyrotechnic mixtures, is primarily dependent on the contents of the mixture and on the grain-size distributions of each of its components, however, some pyrotechnic systems and slow-burning delay compositions, in particular, are also sensitive to the pressure of pressing. This pertains mainly to compositions, whose combustion is in the diffusion or diffusion-kinetic (mixed) area and also depends on the thermal conductivity of the composition. This issue can be partially limited by the use of appropriately fine and pure components in the mixture. It is worth to analyse the data about the key parameters, affecting the reaction mechanism. Table 1 contains most of the data that allows the mechanism of the reaction of iron with barium peroxide to be followed.

Table 1.   Summary of the key parameters which decide the mechanism of the reaction [3]

Fe [%]	λ [W/m·K]	$c \cdot 10^2$ [J/kg·K]	$\rho \cdot 10^3$ [kg/m^3]	$D \cdot 10^{-8}$ [m^2/s]	t_r [ms]	v_{exp} [mm/s]	v_{calc} [mm/s]
15	0.221	5.31	4.10	0.1	2.2	10.6	6.7
20	0.216	5.73	4.01	9.4	1.6	18.1	7.7
25	0.153	5.91	3.67	7.1	1.2	20.6	7.7
30	0.123	6.03	3.50	5.8	0.9	39.1	8.0
35	0.150	6.18	3.80	6.4	1.1	25.5	7.6
40	0.155	6.34	3.92	6.2	1.6	14.4	6.2
45	0.146	6.52	3.88	5.8	1.9	8.0	5.5
50	0.121	6.73	3.46	5.2	2.5	8.4	4.6

λ – thermal conductivity, c – specific heat, ρ – density, D – thermal diffusivity, t_r – time of increment determined on the base of the complementary Gauss function, v_{exp} – combustion rate determined experimentally, v_{calc} – combustion rate determined using a model based on thermal conductivity and heat capacity of the system

Correlating the data compiled in Table 1 with the curves presented in Figure 6, which illustrate the dependence of reaction enthalpy on the iron content in the mixture, allows the high stability of the energy efficiency parameters of the composition to be explained. Despite the fact, that an increasing fuel content in the mixture is the main cause of a decreasing value of reaction heat (because it results in an increasing deficit of the oxidising agent), the influence of the decreasing thermal conductivity and density and increasing specific heat value is observed. Equation 8 gives the dependence of thermal diffusivity on the above parameters:

$$D = \frac{\lambda}{c \cdot \rho}$$
(8)

where: D – thermal diffusivity [m²/s], λ – thermal conductivity coefficient of the material [W/m·K], c – specific heat [J/kg·K], ρ – density of the material [kg/m³], $c·\rho$ – heat capacity of the material [J/m³·K].

In turn, the combustion rate, in a model based on the theory of thermal conductivity, is calculated using the following equation:

$$v_{calc} = \sqrt{\frac{\lambda}{c \cdot \rho \cdot t_r}} \tag{9}$$

Low activation energies unequivocally show that the process is largely controlled by the diffusion mechanism. It is worth noting that the reaction order (n) for the chemical system Fe/BaO₂ is in the range of 0.5-0.7, which indicates that the process takes place with significant participation of the solid phase. Related to the decline in diffusivity, caused by the growth of the heat capacity of the system, this mechanism of reaction is greatly limited, due to a significant decrease in the thermal conductivity of the mixture (for 30% Fe content). The reaction takes place mainly due to conduction, convection and, partially, radiation in the area of the reaction, because heat exchange in the system can take place only in this way. In the zone, where the reaction takes place violently, due to convection, the kinetic mechanism plays a greater role. The molecules of the reagents have such high energy that most of them do not exchange heat with each other through conduction. The equilibrium state is shifted towards the formation of a larger amount of gaseous products, produced through the decomposition of the oxidising agent. The highest linear combustion rate, for the combustion front, of 39 mm/s, is achieved for low thermal conductivity and thermal diffusivity. In this way, the heat exchange through conduction is somewhat limited, while the share of convection and radiation tends to grow. Figure 9 shows the percentage share of the diffusion mechanism, based on the correlation v_{calc}/v_{exp}. The data about the percentage share are correlated with the thermal conductivity of the mixture and with the values of the increment time t_r, determined using the complementary Gauss function.
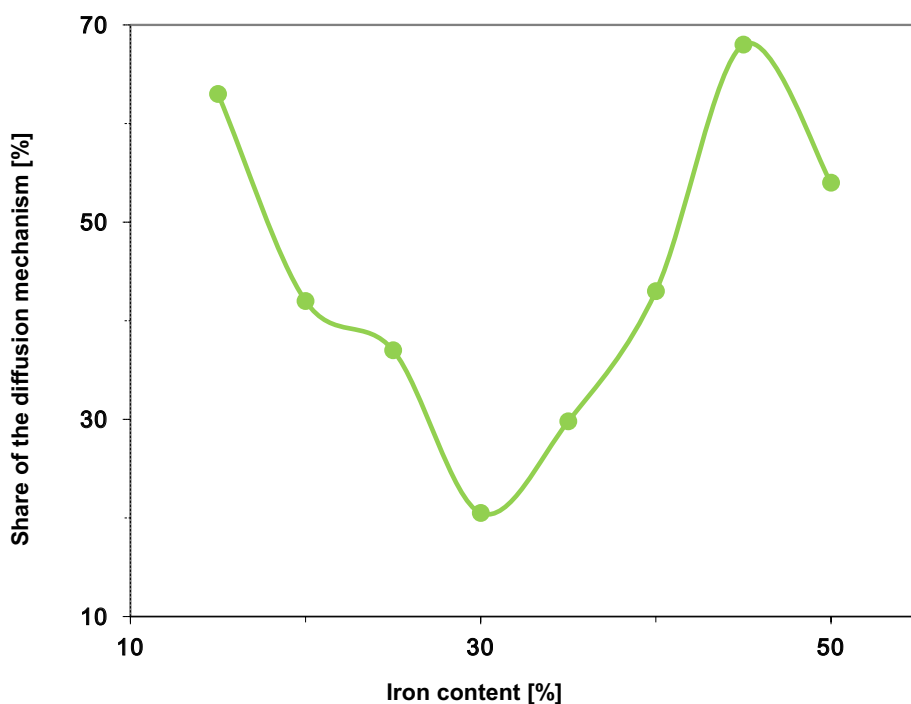

Figure 9. Share of the diffusion mechanism in the full rate of combustion, expressed as v_{calc}/v_{exp} [3]

The system should also produce only a relatively small amount of gaseous products, whose presence can adversely affect the stability of the combustion of the composition. Systems, fulfilling these criteria, in which the reaction is mostly diffusion-limited, are less sensitive to the pressure of pressing. Data presented by Tribelhorn indicates that the linear combustion rate of the bulk (non-pressed) Fe/BaO_2 composition is low and does not exceed 5 mm/s, whereas the pressed composition shows a rate greater by one order of magnitude, although it declines with increasing the pressure applied during pressing (in the range of p = 55-165 MPa). Figure 10 illustrates the combustion profiles of the Fe/BaO_2 mixture, containing 20-50% Fe, pressed at a pressure of 110 MPa.
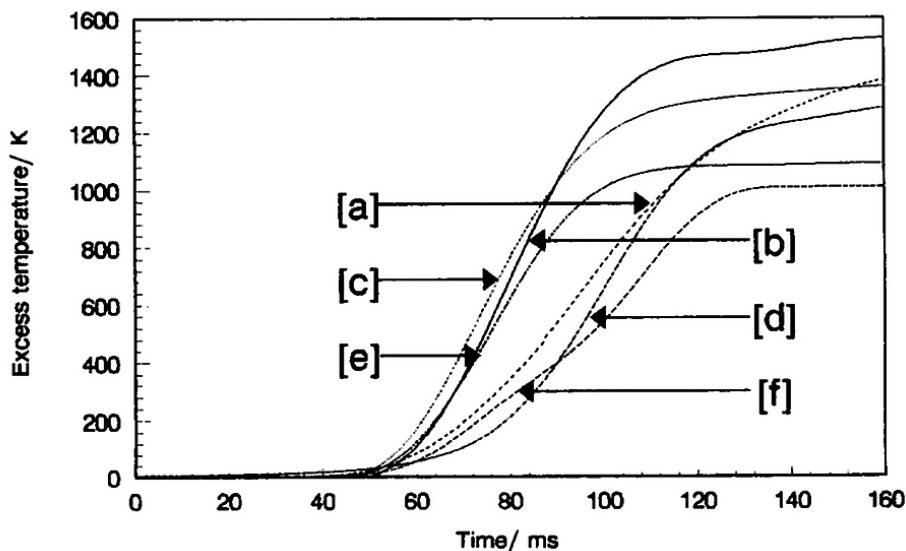

Figure 10. Temperature profiles for combustion of the Fe/BaO_2 composition, pressed at a pressure of 110 MPa with the iron content of: a) 15%, b) 20%, c) 25%, d) 30%, e) 40%, f) 50% [3]

Figure 10 indicates that the composition containing 20% of iron is characterized with the greatest exothermic effect of all other compositions, pressed with the pressure of 110 MPa. The temperature of combustion of that composition reaches a temperature of about 1500 °C. The lowest combustion temperatures are achieved by mixtures with a strongly negative oxygen balance (*i.e.* 40 and 50% Fe content). Assuming that iron oxides are the main and primary reaction products between iron and barium peroxide, the stoichiometric iron content for reactions (1)-(3) is 15.8, 17.4 and 21.9, respectively. This fact justifies the release of the greatest amount of heat by a mixture containing 20% Fe.

The combustion of Fe/BaO_2 composition is a diffusion-limited process. In the case of Fe/BaO_2 pyrotechnic mixtures, a dependence of the combustion rate on the degree of compression is observed, however, increasing the pressure applied during pressing improves contact between the reagents and the combustion rate of the entire system stabilises. Temperature profiles of the combustion front indicate that the induction time shortens significantly with increasing the pressure of pressing [3]. At pressures above 110 MPa, the diffusion mechanism of the reaction plays an important role in the combustion process and the combustion rate of the mixture is significantly decreased. Increasing the degree of compression brings about improved contact between the components of the mixture; the surface area, available for the reaction diminishes as gaseous and liquid intermediate products are formed. The gaseous products, produced in the course of the reaction, are not removed sufficiently rapidly from the interface of the two reacting components, which contributes to enforcing a low combustion rate. Gaseous oxygen is unable to migrate into and penetrate the fuel phase to the same extent it does in mixtures pressed at lower pressures. Therefore, in the production of delay compositions,

particularly those, which exhibit low combustion rates, much higher pressures of pressing are used, in order to ensure that the combustion process is predominantly diffusion-limited.

4. Burn rate dependence on the purity grade of the oxidant

Figure 11 shows a comparison of the combustion rates as a function of the fuel content in the examined Fe/BaO_2 system, based on two grades of barium peroxide (manufactured by REACHIM and FLUKA), for selected values of pressures of pressing.
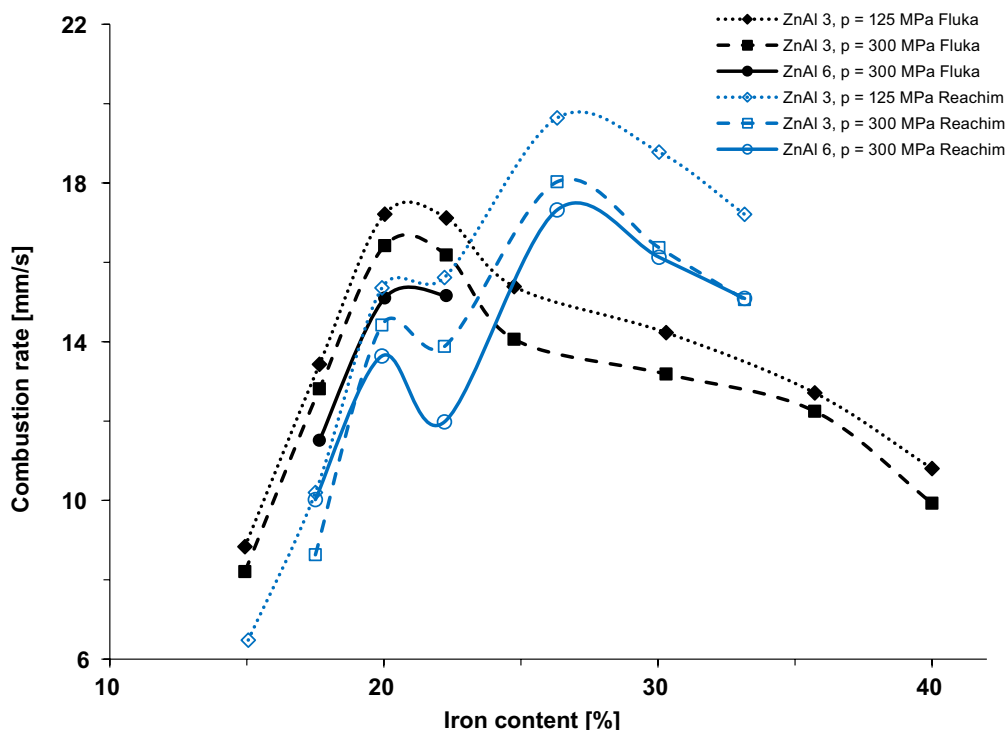

Figure 11. Comparison of the combustion rates versus fuel content for the Fe/BaO_2 system, relating to the use of two different purity grades of barium peroxide (produced by FLUKA and REACHIM) in two types of ZnAl delay elements [10]

The combustion profile of the composition, using barium peroxide produced by REACHIM (85% purity), shows a "plateau" in the area of increasing combustion rate (for 20-22.5%) of fuel in the Fe/BaO_2 system), that is not observed in the case of the composition, containing barium peroxide produced by FLUKA (95% purity). The De Brouckere Mean Diameter (D[4,3]) of the carbonyl iron, that was used in this research was 7.94 μm. Both for FLUKA and REACHIM the D[4,3] diameter of barium peroxide was about 8.5 μm. The "plateau" can be observed for mixtures based on REACHIM barium peroxide, regardless of the pressure applied during pressing. Similar combustion profiles for the Fe/BaO_2 system were reported by Tribelhorn *at al.*, in studies, using similar purity and quality of barium peroxide [3]. Discrepancies in the shapes of the profiles are most probably the result of differences in the grade of purity and grain-size distributions of the utilised peroxides. The presence of the "plateau" may also result from a larger amount of contaminants being present in the 85% purity barium peroxide, produced by REACHIM (mainly strontium peroxide, significantly reducing the combustion rate of the mixture, and calcium peroxide, whose effect on the combustion rate of delay

compositions has not yet been thoroughly explored). Earlier studies have shown that the behaviour of barium peroxide and strontium peroxide during decomposition, in systems with a given fuel, differs sharply. This is mainly due to the mass of the cation of the oxidising agent. The composition, in which BaO_2 of higher purity (produced by FLUKA) is used, exhibits a combustion rate approximately 15% higher for pressing at a pressure of 125 MPa, and about 10% higher for pressing at a pressure of 300 MPa (in the area of maximal combustion rate). In the case of compositions, in which BaO_2 of higher purity was used, the maximum combustion rate is observed for fuel content of approximately 21%, while for compositions, in which lower purity BaO_2 (manufactured by REACHIM) was used, the maximum combustion rate is achieved for an iron content of about 27% [3]. In terms of technology, it is advantageous to use barium peroxide of the best possible purity and fine grain-sizes, because the behaviour of such a system, during combustion in the delay element, is more predictable. Although the unit cost of manufacture is higher, the risk of encountering unforeseen problems, concerning quality assurance during production or subsequent use of detonators, can be eliminated. When designing a decisecond delay composition, it is favourable to work with a range of fuel contents, in which only small changes in combustion rate are observed and the pressure of pressing has a limited impact on the rate and stability of combustion. For a system based on barium peroxide, containing more than 25% Fe, the above requirements are all met.

5. DSC analysis of Fe/BaO$_2$ composition

Differential scanning calorimetry (DSC) is used to discover the reactions and the nature of chemical transformations, occurring in the investigated samples of delay compositions. The DSC method allows determination not only of the net heat generated during decomposition of the pyrotechnic mixture, but also the partial heats of occurring transformations, the temperatures of individual processes and their relative rates.

In the temperature range of 60-715 °C, in which DSC investigations have been conducted, two main groups of signals are observed, originating from exothermic transformations, occurring during combustion of the Fe/BaO$_2$ mixture. The first peak is a composite signal, produced by the overlap of two exothermic transformations, whereas the second peak, whose intensity is significantly higher, is attributed to the main reaction, in which the final products are formed: Fe_2O_3 and Fe_2O_3/BaO spinels. The thermograms, recorded for this process, indicate that the oxidation of iron in the investigated delay composition is highly complex. The oxidation of iron in this system is a multi-stage process, which can be accompanied by the occurrence of several parallel reactions. The first peak is observed in the range of 360-380 °C and is attributed to slow decomposition of barium peroxide, accompanied by evolution of active oxygen, with pre-oxidation of iron to Fe_3O_4 (exothermic reaction) occurring alongside it. The intensity of this peak is a function of the iron content in the sample; it increases with increasing the iron content. The second (main) peak is found in the range of 500-550 °C and corresponds to the main iron oxidation reaction, which yields Fe_2O_3 and Fe_2O_3/BaO spinels, whose structure varies. The amount of heat, released during the reaction of iron with barium peroxide is in the range of 680-910 kJ/kg, depending on the contents of the composition.

Increasing the iron content, in the Fe/BaO$_2$ system, results in accelerating the iron oxidation reaction, which is observed as an overlap of both peaks; the temperature of the main exothermic reaction is also lowered, to about 487 °C. In some samples a small endothermic peak at 600 °C is observed, attributed to the decomposition of unreacted BaO_2.

The mechanism of the reaction consists of the following stages:
– the oxidation reaction between iron and the gaseous oxygen trapped in the mixture (reaction at the solid/gas interface),
– a series of exothermic reactions between iron and barium peroxide, that occurs in solid state,
– endothermic decomposition of unreacted BaO_2.

The decomposition of a small amount of barium peroxide, after the main oxidation reaction runs its course, indicates that the obtained products are highly defected. This stems mainly from the high formation rates of various products, whose occurrence is preferred under given conditions.

6. XRD analysis of the combustion products

Analysis of the phase composition of samples of Fe/BaO_2 compositions, containing 20, 25 and 30% Fe, using the XRD (X-Ray diffraction) method, confirm, based on the d_{hkl} value, that the main phase, present in the post-combustion residue, is the $2BaO \cdot Fe_2O_3$ spinel (compound core oxide) [11]. The d_{hkl} values on the diffractogram are respectively: 0.409, 0.371, 0.293, 0.289, 0.237, 0.204 and 0.167 nm. All of these values correspond to the reference values of d_{hkl} for this compound, found in the ICDD reference file (JCPDS prior to 1978). The diffraction maximum $d_{hkl} = 0.289$ nm is a characteristic maximum of the strongest intensity for a compound, whose molecular formula is $BaFe_{12}O_{19}$, which most likely corresponds to the $BaO \cdot 6Fe_2O_3$ core oxide. The other diffraction maxima, corresponding to this compound, *i.e.* 0.258 and 0.214 nm, are characteristic for it, however, the signals at 0.182 and 0.167 nm coincide with the peaks originating from $2BaO \cdot Fe_2O_3$. Due to the numerous overlapping reflections, produced by defected compounds, significant noise was observed, making it impossible to analyse the sample more accurately. Apart from that, a small signal is observed at 0.169 nm, attributed to iron(III) oxide, Fe_2O_3. The reaction does not run stoichiometrically to the end, as a signal of iron, at 0.203 nm was observed in the identified sample. Most likely, the investigated sample contains a mixture of $2BaO \cdot Fe_2O_3$ and $BaO \cdot 6Fe_2O_3$. Due to the presence of a large amount of reflections, which are characteristic for $2BaO \cdot Fe_2O_3$, it can be considered to be the dominant phase in the examined sample and occurring in the defected form.

7. Fe/BaO₂ sensitivity testing

Investigations of friction sensitiveness, conducted on a Peters' friction apparatus, as per the requirements of the EN 13631-3:2004 standard, indicate that Fe/BaO_2 compositions, containing 20, 25 and 30% carbonyl iron, meet the requirements of sensitiveness to friction for the maximum load of 360 N, producing no observable response (inflammation, sizzling or sparks) [17] in 6 consecutive attempts. Similarly, investigations of impact sensitiveness, conducted using the Kast method (BAM pile driver test), in adherence to the EN 13631-4:2004 standard, show that compositions with carbonyl iron contents of 20, 25 and 30% do not show any observable response (inflammation, sizzling or sparks) [18] in 5 consecutive attempts for each series. The only notable effect of the tests was that the compositions have only become compressed. All compositions, whose impact sensitivity was tested by the Kast method, have shown impact resistance of above 50 J. Therefore, the Fe/BaO_2 composition meets all the technological requirements and can be regarded as safe in use and applications in decisecond delay detonators.

8. Conclusions

The application of pyrotechnic compositions in time delay elements, comes with the need to determine the dependence of fuel content, composition density and combustion mechanism on the burn rate of the time delay composition. The mixtures of iron and alkaline earth metals peroxides turn out to have huge application potential due to their combustion mechanism, which makes their burn rate independent of the pressure inside the detonator shell. The comparison of the results obtained by the authors of the work with the burn rate values presented in the literature indicates a large dependence of the burn rate on components grain size characteristics. Authors found, that the burn rate of Fe/BaO_2 composition yields burn rate between about 3.0-20.0 mm/s, while the literature indicates the range of 2.3-39.0 mm/s. Apart from mentioned grain size characteristics, all parameters of the studies were selected to be identical to those presented in the literature (due to the lack of information in the literature on the grain size of the components). Hence it seems obvious that it was the components grain size that influenced lower burn rates while maintaining the burn rate-iron content curve profile. The composition of iron and strontium peroxide characterizes with significantly lower burn rate (in the range of 3.3-8.3 mm/s). Despite significantly higher price of strontium peroxide than barium peroxide, this oxidiser can be also considered as a component of pyrotechnic time delay compositions. It should be emphasized that the temperature profiles recorded for these compositions indicate that the combustion

temperature of the iron/(alkaline earth metals peroxides) compositions is about 1600 K, which is 400 K higher than for the Fe/KMnO$_4$ composition. By pointing to the low activation energy of solid state reactions, that take place in the system, the image of the mixture with stable combustion is shaped, the use of which will limit the possibility of the local combustion front quenching.

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