Determination of Ignition Sensitivity of Selected Heat Powders

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Abstract: Ignition sensitivity is one of the factors defining the characteristics of high calorific mixture with low emission of gaseous product. It was found that $Zr-BaCrO_4$ mixture is sensitive to ignition by electric spark energy of 0.82 J, whereas activation of $Fe-KClO_4$ mixture depends on the iron powder employed and the composition of its surface oxide layers. Energy required for the activation of high calorific mixture in form of powder designated as Fe_K, Fe_R or Fe_E is equal to 0.08, 0.59 and 1.1 J, while in the form of pellet 6.92, 10.2 and 14.1 J. Activation of $Fe-KClO_4$ mixture with a strip of heat paper as well as with the electric spark has revealed that the mixture containing iron powder obtained by atomization method (Fe_A) is not active.

Keywords: heat powder, ignition sensitivity, $Fe-KClO_4$, EDS test

Introduction

Resistance to electrostatic charge interaction is one of the most important characteristics of high calorific materials, mainly because of safety requirements during their production, conversion and storage.

Among these mixtures, inorganic heat powders are particularly sensitive to electrostatic charge. However, their components like metal powders and oxidants,

stored and modified separately are, in most cases, not sensitive to electrostatic charge. Their sensitivity increases if they exist as a homogeneous mixture.

The most precise methods for the determination of activation energy include activation by laser ray [1] or by electrostatic capacitor discharge (EDS) [2]. A significant disadvantage of the first method is the loss of laser radiation energy due to its dissipation on the sapphire window, which protects optical system against impurities evolved during mixture ignition. Another disadvantage is the necessity to select appropriate diameter of laser radiation beam in relation to the mixture density [3].

On the other hand, the major disadvantages of EDS method are: the difference between the energy accumulated in the capacitor and energy passed later to the mixture as a spark, time of energy transfer and the form of the pyrotechnic mixture (powder or pellet) [4].

In the present study, the value of energy necessary for activation of $Fe-KClO_4$ mixture, both in powder and pellet form, was determined using the heat paper. Additionally, differential thermal analysis (DTA) has been carried out. Both mixtures are characterized by a low emission of gaseous products. One of them, ($Fe-KClO_4$), is a good electric and heat conductor, while the other, ($Zr-BaCrO_4$) is nonconductive – reveals non-conductor's properties.

Furthermore, in accordance with the applicable standards, PN-EN 13938-2 [5] and STANAG 4490 [6], as well as our own solution, a new apparatus for the determination of pyrotechnic mixture resistance to electrostatic charge has been designed and constructed.

Materials and Methods

$Zr-BaCrO_4$ system

The mixture of zirconium powders (pyrotechnic purity) and barium chromate(VI) with grain size <10 μm applied on inorganic carrier is defined as a heat paper. The mixture employed in this work contained 22 and 78 wt.% of the above mentioned ingredients, respectively. The calorific value was 1675 J g^{-1}, which corresponds to 2 J mm^{-2} if calculated against the heat paper surface [7]. In the present work, only the heat paper has been tested.

$Fe-KClO_4$ system

Selected iron powders, standardized prior to the measurements, were mixed with potassium chlorate(VII) with grain size in the range of 1-10 μm.

Commercial iron powders were used in this study. Iron powders obtained

by atomization, iron carbonyl decomposition, electrolysis and reduction of the iron(II) compound are denoted as Fe_A, Fe_K, Fe_E and Fe_R, respectively. Specific surface area of the studied samples marked as Fe_K, Fe_E, Fe_R and Fe_A was 0.33, 0.43, 0.38 and 0.15 $m^2 g^{-1}$, respectively and had been defined in our earlier work [8]. The surface area of the sample (Riedel de Haen) produced by atomization method was 0.67 $m^2 g^{-1}$ [9].

Potassium chlorate(VII) used in the study was subjected to preliminary double crystallization from H_2O and to the main crystallization from EtOH-H_2O solution (1:1) [10].

After mixing the equivalent quantities of iron powder and potassium chlorate(VII) to obtain the content of 83 wt.% Fe and 17 wt.% $KClO_4$, the mixture was compressed into pellets of 25 mm in diameter. The procedure for the preparation of high calorific mixture both in form of pellets and as a powder has been described in our earlier work [11]. The above mixtures were investigated both as pellets and a powder.

Electrostatic discharge sensitivity test (EDS)

Measurements of ignition sensitivity of high calorific mixture were performed using electric spark of definite energy, generated by the EDS apparatus model PMEZ-1.0 manufactured by ARET (Poland), as the igniting factor. The electric spark was generated by the voltage in the range of 8-12 kV, and its energy was suited in the range 0.01-14.4 J. The ignition energy determined for the mixture corresponded to the minimum energy required for the activation of five samples.

Differential thermal analysis (DTA)

DTA method was used for the determination of ignition temperature of the pelletized samples only. It employed differential thermo-analyzer Netzsch, model STA 409 C/3F. Measurements were performed in the following experimental conditions: heating rate 40 K min^{-1} from room temperature to 1070 K in dynamic atmosphere of inert gas (Ar) at the flow rate of 150 cm^3 min^{-1}. Endothermic peaks observed on DTA curve in temperature 575 and 1040 K, respectively, were applied as the internal standard for a precise determination of the ignition temperature of the mixture [8, 11].

Activation of high calorific mixture with the heat paper

A strip of the heat paper, size 35x5 mm, was suitably aligned to the side edge of 0.8 mm thick heating pellet to form a contact area of 4 mm^2. After that, the pellet was placed on a ceramic plate. The ignition of the heat paper strip occurred under the ceramic plate (see Figure 1) [12].
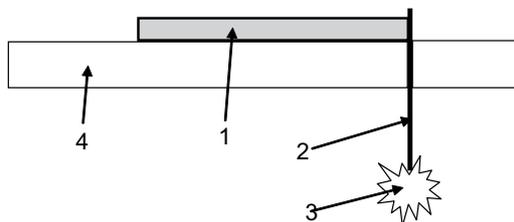
Figure 1. Experimental set: 1 – heating pellet, 2 – strip of heat paper, 3 – flame, 4 – ceramic support with slit.

Results and Discussion

In present study, measurements started with a simple test to determine the ignition sensibility of high calorific mixture containing 83 wt.% Fe and 17 wt.% $KClO_4$ when activated by a strip of heat paper. The above systems were investigated both in powder and pellet form. The activation procedure applied in this study is alike to the real activation conditions. This heat paper was capable of delivering energy of about 8 J.

Table 1. The different forms of energy values indispensable for high calorific mixture activation in the function of its form (powder, pellet) determined by electrostatic discharge method (column 3), differential thermal analysis method (column 4) and heat paper ignition susceptibility (column 5)

Chemical composition of sample	Form of sample	Spark energy J	Differential thermal analysis K	Heat paper test
1	2	3	4	5
Fe_A 83 wt.%-$KClO_4$ 17 wt.%	B	14.2	717	-
Fe_A 83 wt.%-$KClO_4$ 17 wt.%	A	14.2	-	-
Fe_E 83 wt.%-$KClO_4$ 17 wt.%	B	14.1	732	+
Fe_E 83 wt.%-$KClO_4$ 17 wt.%	A	1.11	-	+
Fe_K 83 wt.%-$KClO_4$ 17 wt.%	B	10.2	751	+
Fe_K 83 wt.%-$KClO_4$ 17 wt.%	A	0.59	-	+
Fe_R 83 wt.%-$KClO_4$ 17 wt.%	B	6.92	736	+
Fe_R 83 wt.%-$KClO_4$ 17 wt.%	A	0.08	-	+
$Zr/BaCrO_4$ (stoichiometric)	B	0.82	897	no tested

Legend: Fe_A – iron powder obtained by atomization, Fe_K – iron powder obtained by iron carbonyl decomposition, Fe_E – iron powder obtained by electrolysis, Fe_R – iron powder obtained by iron(II) compound reduction, A – the mixture in powder form, B – the mixture in pellet form.

Results presented in Table 1 show that, except for the inactive mixture containing iron powder obtained by atomization (Fe_A), (see column 5), all the other mixtures were activated by the energy of approx. 2 J mm^{-2}. Activation deficiency observed in powder Fe_A can be explained by the presence of a passive layer of iron oxide on its surface formed during high temperature treatment [11].

The determination of ignition temperature of high calorific mixture pellets was performed by differential thermal analysis using adequate DTA curve [13].
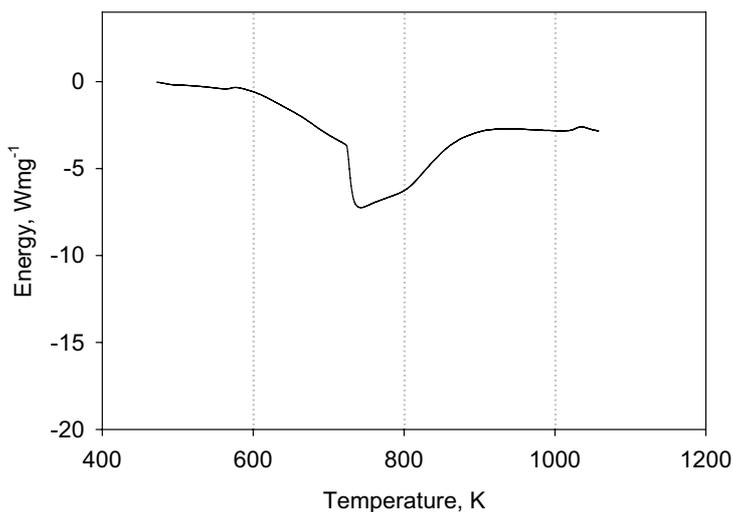
Figure 2. DTA curve of Fe-KClO$_4$ system containing F$_A$ and 17 wt.% of potassium chlorate(VII).

Figure 2 shows DTA curve of the mixture containing 83 wt.% iron powder Fe_A and 17 wt.% $KClO_4$. The ignition temperature determined for this system was 717 K (see Table 1). Two peaks can be noticed on this curve. The first one, with maximum at 575 K, can be assigned to a partial decomposition of $KClO_4$ and reaction of evolved oxygen with iron powder, whereas the second one, at 800 K, results from potassium chlorate(VII) decomposition.

The ignition temperatures of high calorific mixtures containing iron powder Fe_E, Fe_K and Fe_R, were 732, 751 and 736 K, respectively (Table 1, column 4). Figure 3, similarly as Figure 2, represents the temperature dependence of the mixture on the amount of energy released. Based on the peak area, it can be noticed that most of the oxygen evolved reacts with iron powder, and the above process starts at 732 K. Similar shape of DTA curve was observed for the mixture containing iron powder Fe_K and Fe_R.
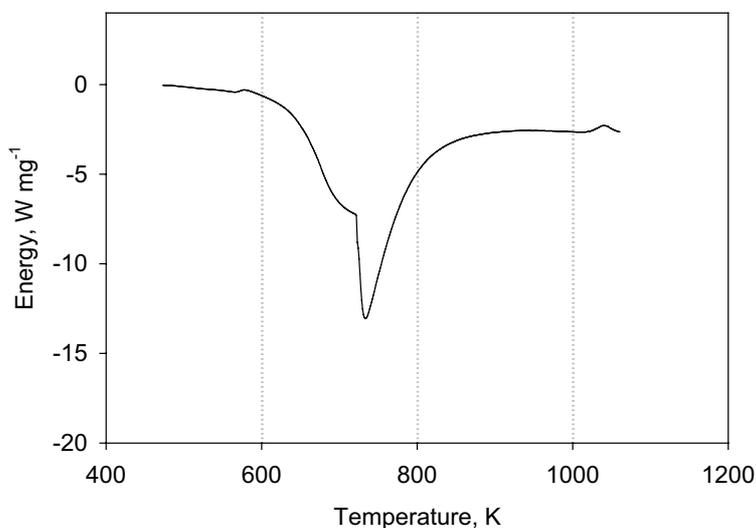
Figure 3.   DTA curve of Fe-KClO$_4$ system containing Fe$_E$ and 17 wt.% of potassium chlorate(VII).

The ignition temperature estimated by DTA method allows for determining the reactivity of iron powder with the oxidizer and ranking iron powders in order according to their activation: Fe$_A$>Fe$_E$>Fe$_R$>Fe$_K$. Powder mixtures have not been investigated due to a very small contact of oxidizer and reductant grains as well as a low degree of reaction of oxygen evolved from KClO$_4$ with iron powder. Ignition temperature was investigated also on thermally nonconductive mixture containing 22 wt.% Zr and 78 wt.% BaCrO$_4$. As compared to thermally conductive mixtures, the above material is characterized by considerably high activation temperature of 897 K (Figure 4). Based on the literature data, it can be concluded that Zr/BaCrO$_4$ system is very sensitive to electrostatic charges and can be activated by electric spark with very low energy [14]. In case of temperature as the activating factor, it can be assumed that the above mentioned mixture reveals low sensitivity in comparison with some conductive mixtures described in this paper [15].

The above measurements, i.e. activation by a strip of heat paper and differential thermal analysis (DTA) were performed in inert gas atmosphere, as opposed to EDS's method.
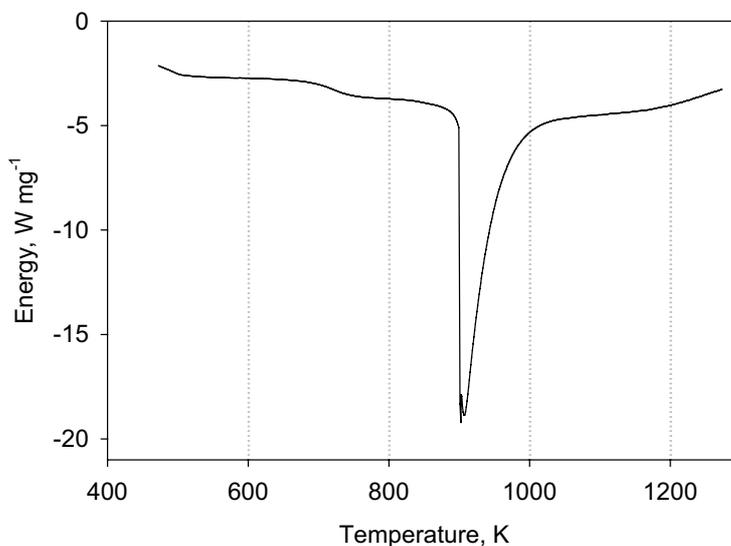
Figure 4.   DTA curve of Zr-BaCrO$_4$ system containing 22 wt.% of Zr and 78 wt.% of barium chromate(VI).

In this case, the activation by electric spark of high calorific mixture, both in pellet and powder form, was performed in air atmosphere, what is very significant especially for powder mixture. The results obtained by this method are summarized in Table 1, column 3. Both forms of mixture, i.e. powder and pellet, containing iron powder Fe$_A$ appeared to be resistant to electric spark of energy equal to 14.2 J.

Figure 5.   View of the upper surface of a heating pellet with Fe$_A$ which has contact with positive pole.

Figure 6.   View of the lower surface of a heating pellet with Fe_A which has
            contact with negative pole.

Figures 5 and 6 show the view of upper and lower surface of a pellet prepared
from the above mixture. The pellet was positioned in such a way that its upper
side was at a 2 mm distance from the positive pole, whereas the lower one was
in a direct contact with the negative pole.

The above pictures represent the pellet after activation by electric spark
with energy of 14.2 J. In Figure 5, no differences in the appearance of the upper
surface of the pellet can be notice before and after activation, whereas significant
difference is observed on its lower face (Figure 6). White spot, originating from
melted KCl formed as the result of potassium chlorate(VII) decomposition, is
well seen exactly in the place where the electric spark was generated. The energy
delivered by the spark and generated by potassium chlorate(VII) decomposition
was too low to initiate the reaction in the whole volume of the pellet.

High calorific mixtures in pellet form, containing iron powder Fe_R, Fe_K
and Fe_E, are activated by electric spark with energy of 6.92, 10.2 and 14.1 J,
respectively. Tests carried out on powder mixtures reveal that the minimum
energy values of the iron powders designated as Fe_R, Fe_K and Fe_E, are 0.08, 0.59
and 1.1 J, respectively. It shows that activation energy values obtained for pellets
are much higher than for the powder in powder form.

Additionally, a series of tests involving the change the distance between
the positive pole and the sample surface were carried out. In the range of 0.5 to
3 mm, no influence of the distance change was observed.

The electric spark of 0.82 J caused the heat paper activation despite the fact
that in previous findings, this material was considered to be highly sensitive to
electrostatic charge. As compared to the mixture in a pellet form, containing
iron powder Fe_R and being both, electric and thermal conductor, the mixture

containing zirconium is eight times more sensitive to electrostatic charges, despite the presence of insulating under layer (ceramic fibre) in direct contact with the negative pole of the capacitor.

Based on the analysis of data in Table 1, it was found out that determination of ignition temperature of high calorific mixture by DTA method is not possible. The explanation of above observation is that most of the oxygen evolved during $KClO_4$ decomposition does not react with iron powder, due to a low contact area of their grains.

Application of above method for the investigation of high calorific mixture in the pellet form, leads to a precise determination of activation temperature value.

It was previously revealed that, from 619 K to the mixture ignition temperature, a solid phase reaction between oxidizer and reducer is observed. In case of the mixture containing carbonyl iron powder (Fe_K), it takes only 210 s to react 14% of potassium chlorate(VII).

Employing a strip of heat paper for ignition of the particular mixture allows for a quick and effective elimination of non active systems, and, what is more, in similar to real conditions.

Based on data of the specific surface area presented in paper [8] it would appear that the surface area value has an influence on the electric sparks energy needed to activate a high calorific mixture. In the case of two iron powders with surface area of 0.15 and 0.67 $m^2\,g^{-1}$ [11], obtained by the atomization method, it was found that the activation of mixtures in the form of pellets by a heat paper test was impossible. The inactivity of iron powder mixed with $KClO_4$ is associated with the presence in the surface layers of metallic impurities and passivation layer at high temperatures generated during the preparation process [8].

Sensitivity of the investigated system to electrostatic charge was precisely determined using electric spark with specified energy, generated by MPEZ-1.0 apparatus. This method revealed that the energy required for the activation of $Fe-KClO_4$ mixture in powder form is much lower than that for the pellets.

Another reason is a higher participation of atmospheric oxygen in the oxidation of iron powder as compared to the pellets.

In pressed conductive mixtures, certain amount of energy may be dissipated in the pellet; therefore long duration spark was not applied.

Due to the presence of inactive iron powder in the compressed high calorific mixture, melted KCl occurs in the contact surface between the mixture and the anode. This indicates that iron powder employed does not react with oxygen evolved from $KClO_4$.

Summary and Conclusions

In accordance with applicable standards, PN-EN 13938-2 and STANAG 4490, as well as our own solution, new apparatus for the determination of pyrotechnic mixture resistance to electrostatic charge has been designed and constructed. This installation allows for direct measurement of ignition sensitivity of both electrically conductive and nonconductive high calorific mixtures characterized by low gaseous products emission.

The results obtained in this work allow for drawing the following conclusions:

- the method of activation by a strip of heat paper enables fast evaluation of conducting mixture suitability, as revealed for Fe-$KClO_4$ system;
- differential thermal analysis (DTA) allows to determine precisely the activation temperature of high calorific mixture in pellet form and establish whether a two-step oxidizer decomposition is taking place, due to activation deficiency of iron powder in reaction with oxygen evolved during $KClO_4$ decomposition;
- activation of high calorific mixture in powder form requires much lower electric spark energy than the pellet which may be explained by a strong dissipation of energy in compressed bulk material;
- both quantitative and qualitative composition of oxide phases present on the iron powder surface are responsible for the activation energy value of high calorific mixture;
- high calorific mixture containing commercial iron powder labelled as Fe_K, Fe_R and Fe_E, respectively, is characterized by an increasing value of activation energy in the electric spark method, independently of the form of the sample;
- commercial preparations of iron powder for calorific mixture obtained by different procedures have an essential influence on the activation energy of these mixtures. It has been found that the energy increases in the following order: Fe_K (obtained as the iron carbonyl decomposition), Fe_R (obtained by iron(II) compound reduction), Fe_E (prepared by electrolysis), independently on the form high calorific mixture i.e. powder or pellets.

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