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A Study of the Influence of Selected Transition Metals on the Solid State Reactivity in a Fe-$KClO_4$ Mixture

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Abstract: The effect of selected transition metal powders (Zn, Ti, Mo and nano-Fe), in the concentration range from 0-5 wt.%, when used as activators in the highly calorific mixture Fe-$KClO_4$ (containing 16 wt.% $KClO_4$), has been studied. It has been established that zinc and molybdenum powders can act as factors in decreasing the activation temperature and increasing the effectiveness of the oxidant used. Titanium powder increases the oxygen conversion rate and the amount of energy released. Iron nano-powder has only a slight influence on the above mentioned parameters.

Keywords: Fe-$KClO_4$ mixture, activators, linear burn rate, electrostatic discharge sensitivity test (EDS), calorimetric measurements, oxygen conversion

1 Introduction

In some branches of technology, certain thermally initiated processes require the use of high calorific value mixtures usually based on a mixture of iron powder and potassium chlorate(VII). Moreover, very often, specific requirements involve the heating mixture's activity, which can be satisfied by modification of

the above mixture by the addition of certain metal powders in amounts much greater than stoichiometric ones [1]. These admixtures are used in order to limit the amount of gaseous components evolved during the decomposition of the $KClO_4$. Moreover the presence of these additives leads to an increase in the high calorific value of $KClO_4$, and an increased linear burn rate, these being necessary for the activation of a highly calorific mixture.

The high calorific mixture used in the thermal battery should not provide too much heat, so as not to decompose the cathode material in the cell. This effect occurs when using thermite [2].

Recently, molybdenum has become of much interest as an activator of highly calorific mixtures. It is usually used in the form of a powder introduced into the $KClO_4$ in the ratio range 7:3 to 1:9. It was observed that the decomposition temperature of such a mixture increases from 603 to 763 K with an increased quantity of $KClO_4$ [3]. Among the products of $KClO_4$ decomposition, besides KCl, such compounds as MoO_2, MoO_3, MoO_2Cl_2, Mo_4O_{11} and Mo_9O_{26} have been observed [4]. Similar observations were made on addition of Ti or W powder to $KClO_4$ (oxides of Ti or W) [5, 6].

The role of the metallic surface titanium powder on the ignition temperature of the Ti-$KClO_4$ mixture in the temperature range 298-1273 K has been investigated by XRD and AES methods. At a temperature of 573 K, the metallic titanium dissolves superficially in the oxygen-free atmosphere forming non-stoichiometric oxides. With increasing temperature to 623 K the appearance of a metallic surface completely free from oxygen was observed [7].

This paper is a continuation of our work on the physicochemical properties of the Fe-$KClO_4$ mixture used as a highly calorific mixture [8]. It deals with the influence of the selected metal powders Zn, Ti, Mo and nano-Fe, used in quantities of 1.0, 2.0, 3.0, 4.0 and 5.0 wt.%, on the thermal decomposition of a two-component heating mixtures containing 84 wt.% of iron powder and 16 wt.% of potassium chlorate(VII). It has been established that the introduction of these metallic powders into the calorific mixture, pressed into pellet form, leads to a modification of its properties, such as linear burn rate, energetic effect (reaction heat) and the amount of gases released to the atmosphere.

The introduction of molybdenum powder (up to 15 wt.%) as an activator into the Fe-$KClO_4$ mixture leads to a significant decrease in the initial decomposition temperature [9, 10]. In the literature, mainly patents, we found information concerning the possibility of using other metallic powders like Ni, Cu, W, and Ti, as activators. Unfortunately, there is no evidence of the changes in physicochemical properties of the highly calorific mixture that could be attributed to these powders [11, 12]. The results of our own investigation show that the

addition of metallic powders of Zn, Mo and Ti to the Fe-$KClO_4$ mixture in the ratio of 4.9:1, and with grain sizes of 25, 90 and 18 μm respectively, leads to modifications of its properties, such as oxygen conversion, linear burn rate and amount of heat released [13].

This study was undertaken to analyse the effects of the Zn, Mo, Ti (maxima of volumetric distribution <3 μm) and nano-Fe metallic powders, introduced into the heating mixture at the weight ratio of $KClO_4$:Fe+activator of 16:84 wt.%, on the performance of the mixtures.

2 Experimental

2.1 Preparation of samples

The iron powder used in this study was a commercial sample from Fluka (Germany), prepared by the reduction of an iron(II) compound. Its volumetric distribution of particles and surface area were 1.5-90 μm (maximum 10 μm) and 0.38 m^{-2}, respectively. Prior to any measurements, the preparation was standardised at 553 K, under an atmosphere of 95% Ar and 5% H_2 for 12 h and was then held under Ar at 563 K [14].

A commercial sample of potassium chlorate(VII) p.a. from Fluka (Germany) was subjected to preliminary crystallisation from H_2O and to the second crystallisation from EtOH solution in order to eliminate detectable quantities of the majority of impurities, *e.g.* Na^+, Cl^-, using AES-ICP and nephelometric methods respectively. The concentration of Na^+ ions was 0.055 wt.%, while the Cl^- ion content was <0.0005 wt.% [15]. The above procedure ensured that sufficiently small grains were obtained without additional grinding. Its volumetric distribution of particles was 1-30 μm with maxima at 4 and 8 μm, exactly as described in our earlier paper [14].

The zinc (minimum 97.5 wt.%) and titanium (minimum 93 wt.%) powders used in this study as activators, were commercial samples from Alfa Aesa Johnson Matthey GmbH (Germany). Their volumetric distribution of particles were 6-9 μm and <20 μm, respectively. The molybdenum powder (minimum 97.5 wt.%) was a commercial sample from Sigma-Aldrich (Germany). Its volumetric distribution of particles was 3-7 μm [16]. Nano-iron powder, prepared by reduction of an iron(II) salt by sodium borohydride ($NaBH_4$), was also used as an activator in this study. Its volumetric distribution of particles was 2 μm [16].

Measurements were performed on mechanical mixtures of the commercial preparations composed of 16 wt.% of $KClO_4$ and 84 wt.% of metallic powder, including the Fe and the appropriate transition metal used as an activator, the

latter being varied from 0-5 wt.%. The mixtures were pressed into tablets about 0.8 mm thick and diameter 25 mm, at a pressure of 400 MPa [16].

2.2 Linear burn rate of the tablets

The burning rate of a heating tablet was determined with the help of a TPS-2 model photocell apparatus manufactured by ARET Poland [17], using two instrument probes. A tablet, 25 mm in diameter, was fastened in a special enabling ignition device by mixture of zirconium powders and barium chromate(VI) with the grain <10 μm applied on inorganic support and then the measuring device was started automatically as soon as the first instrument probe received a signal. The burning time was measured upon receiving a signal from the second instrument probe. The distance between probes was kept at 15 mm.

2.3 Electrostatic discharge sensitivity test (EDS)

Measurements of ignition sensitivity of the high calorific mixtures were performed using an electric spark of defined energy, generated by an EDS apparatus model PMEZ-1.0 manufactured by ARET (Poland), as the ignition source. The electric spark was generated by voltages in the range of 8-12 kV, and its energy was in the range 0.01-14.4 J. The ignition energy determined for the mixtures corresponded to the minimum energy required for the activation of five samples [17].

2.4 Reactivity of the Fe/$KClO_4$ mixture with activators

The reactivity of the iron powder preparations with potassium chlorate(VII) was tested in the solid state in the form of tablets, using mixtures with a weight ratio $KClO_4$:Fe+activator of 16:84. The reaction was carried out in a differential thermo-analyser made by Netzsch; DTA/TG model STA 409 C 3F. The samples were heated at 40 $K \cdot min^{-1}$ from room temperature to 1070 K in a dynamic atmosphere of inert gas (Ar) at a flow rate of 150 $cm^3 \cdot min^{-1}$. The reaction of Fe with $KClO_4$ in the solid state was investigated using pellets of diameter 6.2 mm prepared from the appropriate mixtures. The procedure adopted permitted simultaneous determination of the ignition temperature, the amount of energy released during the reaction and the degree of potassium chlorate(VII) reaction with Fe. The ignition temperature of the heating tablet was determined on the basis of the DTA and TG curves. It corresponded to the temperature of weight loss on the TG curve and the beginning of the exothermic peak on the DTA curve ("onset"). The amount of thermal energy released during the reaction was determined from the area under the DTA peak. On the basis of the weight loss at 873 K, the quantity of $KClO_4$ which, during decomposition, released oxygen

which did not react with the iron powder was determined. The degree of its conversion was determined by subtracting the appropriate value from the total quantity of $KClO_4$ introduced to the mixture [14].

2.5 Calorimetric measurements

Calorific values of the heating tablets were measured using a KL-1 calorimeter produced by Precyzja-BIT Sp. o.o. (Poland). Eight tablets, of 25 mm diameter and weight 10 g each, were placed individually in a quartz crucible. They were ignited with the help of the heating paper. The heating mixture was burning in the presence of an inert gas (argon) under atmospheric pressure. The amount of heat released by the heating paper was taken into consideration when calculating the calorific value.

The values of energy release, ignition temperature and conversion of oxidizer ($KClO_4$) presented in this paper are the mean values obtained from three measurements. The mean values of the linear burn rate and the amount of indispensable energy of the high calorific mixture were calculated from four measurements. The values of the standard deviation for the above parameters were 8 $J \cdot g^{-1}$, 6 K, 0.5%, 0.82 $cm \cdot s^{-1}$ and 0.02 J, respectively.

3 Results and Discussion

3.1 Energy evolved

Figure 1 shows the relation between the quantity of thermal energy evolved by the calorific mixture and the amount of activator, *e.g.* Zn, Ti, Mo or nano-Fe introduced into the Fe-$KClO_4$ mixture. The quantity of heat energy released from the investigated calorific mixtures was determined using the values of the molar enthalpy of formation of the corresponding oxides, expressed in $kJ \cdot mol^{-1}$.

In all of the cases investigated, a significant decrease in the evolved energy with increasing amounts of activator in the mixture was observed. Introduction of zinc powder decreased the evolved energy by about 180 $J \cdot g^{-1}$. Our earlier research using the DTA method showed that the addition of metallic zinc powder to the Fe-$KClO_4$ mixture fundamentally modifies some properties of this mixture. Ignition leads initially to melting. Upon further heating to 1200 K, the pellet undergoes change into the vapour state. Consequently, vapour of zinc react with the oxygen present in the intergranular space, which explains the observed changes in released energy due to the replacement of iron powder by zinc powder in the calorific mixture [14]. Physicochemical parameters related to the enthalpy of ZnO and iron oxides formation indicate that the amount of released energy

for zinc oxide formation is much lower than for iron oxides; the values are: ZnO (-350.5); FeO (-272.0); Fe_3O_4 (-1118.4); Fe_2O_3 (-824.0) kJ·mol^{-1} respectively [18].

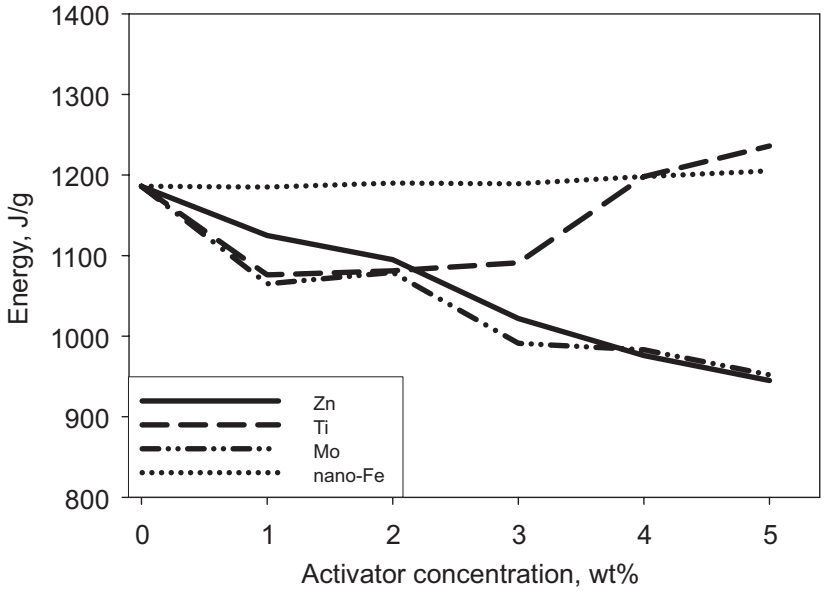

Figure 1. Amount of energy (mean values) evolved during the interaction in the solid state reaction of the Fe-$KClO_4$ mixture as a function of the activator concentration.

For titanium powder used as an activator, a decrease in the amount of released energy was observed for the range 0-1 wt.% concentration. When the concentration of Ti was 1-4 wt.% the released energy increased by up to 32 J·g^{-1}. Granulometric analysis of the metallic titanium powder has shown that its volumetric distribution contains grains of diameter <20 μm. The grains are probably covered by a thin passive layer of titanium dioxide. It is worth mentioning that the molar enthalpy of formation of TiO and TiO_2 is 519.7 and 944.0 kJ·mol^{-1}, respectively [16]. Replacing some of the iron powder in the calorific mixture with a small quantity of titanium results in an increase in the released energy as larger amounts of activator are added (see Figure 1).

The use of metallic molybdenum powder as an activator caused a sharp decrease in the amount of liberated energy across the full range of concentrations. This could be explained by a high vapor pressure of the forming MoO_3. The values of the molar enthalpy of formation of MoO_2 and MoO_3 are equal to -588.9 and -745.1 kJ·mol^{-1}, respectively [16]. Partial replacement of the metallic

iron powder in the Fe-KClO mixture with iron in its nano-form does not have any influence on the amount of energy liberated.

In all of the calorific mixtures investigated after activation, vaporization of KCl was observed in the form of a white deposit on elements of the devices at temperatures less than 1000 K. The above effect decreased the amount of thermal energy liberated.

3.2 Activation temperature

Figure 2 shows activation temperature of the Fe-$KClO_4$ mixture as a function of the concentration of metallic powder activator, determined by the DTA/TG method.

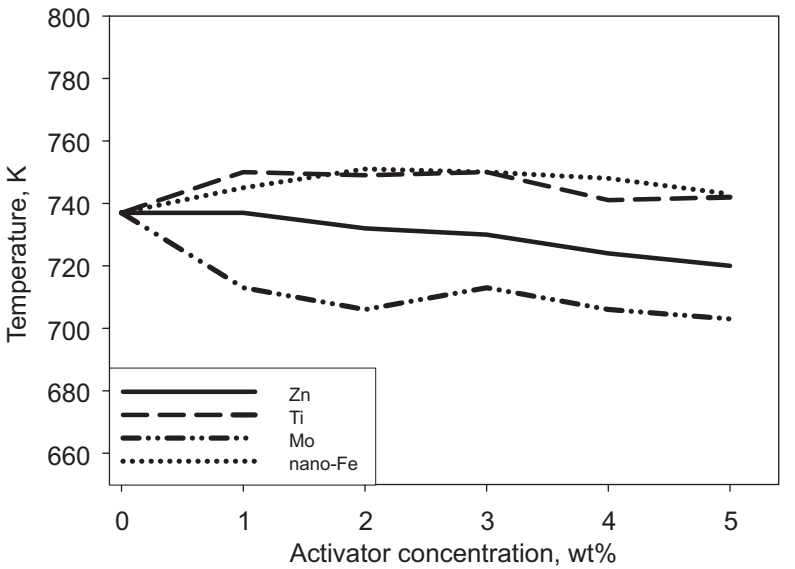

Figure 2. Activation temperature (mean values) of Fe-$KClO_4$ mixtures as a function of the activator concentration.

If metallic zinc is used as an activator, the activation temperature is decreased by 17 K with 5% Zn additive. In the case of titanium powder, the influence of the concentration of the activator on the activation temperature of the Fe-$KClO_4$ mixture was negligible.

Titanium does not perform the function of an activator because activation of the Fe-$KClO_4$ mixture is initiated by iron powder, the oxygen later released from the oxidizer then reacting with the titanium powder. A similar phenomenon was observed for Ti-KNO_3 and Zr-KNO_3 mixtures, where the reaction initiation

temperature of the titanium powder was 270 K higher than that of the zirconium powder [19].

Completely different behavior was observed when molybdenum powder was used as an activator (see Figure 2). An increase in its concentration in the heating mixture was accompanied by a decrease in the activation temperature of the mixture of about 40 K.

For iron nano-powder, its introduction leads to a relatively slight increase in the activation temperature of the heating mixture.

3.3 Oxygen conversion

An important factor influencing the decomposition temperature of $KClO_4$ is earlier subjection to pressure or grinding, for crushing the polycrystalline powder [20]. We have found that high purity of $KClO_4$ obtained by crystallization (without grinding) is characterized by a decomposition temperature of 873 K. The observed mass loss during decomposition of $KClO_4$ corresponds to the mass of oxygen which does not react with the powdered Fe and activator.

If the content of the Zn activator in the heating mixture is higher than 1 wt.%, a slight increase in the unaccountable value of the conversion was observed (Figure 3). Further increase in its concentration up to 5 wt.% resulted in a maximum conversion value of about 99%.

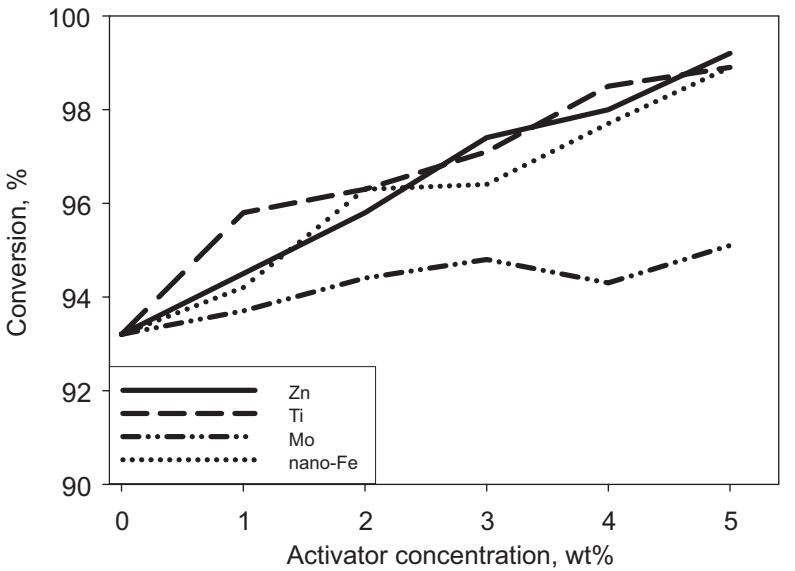

Figure 3. Conversion degree (mean values) of potassium chlorate(VII) in the mixture Fe-$KClO_4$ as a function of the activator concentration.

Ignition of the mixture composed of $KClO_4$, Fe powder and metallic titanium activator releases heat due to the interaction between $KClO_4$ and Fe. The released heat energy increases the rate of oxygen diffusion through a less tight TiO_2 passivation layer on the surface of the titanium powder.

Figure 3 shows the change of the $KClO_4$ conversion rate if molybdenum powder is used as the activator of the Fe-$KClO_4$ mixture. The $KClO_4$ conversion process in the presence with metallic molybdenum, as compared to the other activators, could be explained by a high vapor pressure of MoO_3 being formed. At of 900 K, MoO_3 undergoes sublimation and is deposited on the pellet surface, exposing the raw surface of the molybdenum powder. During transfer to ambient atmosphere, it causes enlargement of the existing channels. This, however, allows only an approximate estimation of the heat energy released; a precise determination of the amount of oxygen released to the atmosphere is not possible.

Figure 3 also shows the effect of iron nano-powder on the $KClO_4$ conversion rate. Generally, the addition of iron nano-powder increases the conversion rate by about 6% and simultaneously reduces the emission of the gaseous products.

3.4 Linear burn rate and electrostatic sensitivity

Other important features of the heating mixture, besides the physicochemical characteristics described above, are its linear burn rate and its sensitivity to electrostatic discharges [21]. As in the previous study of the two-component heating mixture [14], in this work we have determined selected physicochemical parameters for Zn, Ti, Mo and nano-Fe powders as activators.

Tables 1 and 2 show that the selected parameters have been determined by measurement of the linear burn rate and by the EDS test. They indicate that the linear burn rate of the three-component mixtures containing either molybdenum or titanium is higher than that of the mixture without an additive.

Table 1. Mean values of the linear burn rate ($cm \cdot s^{-1}$) of the Fe-$KClO_4$ mixtures as a function of the concentration of the activator

Activator	Concentration range of activator, wt.%					
	0	1	2	3	4	5
Zn	3.73	3.70	3.58	3.62	3.28	3.12
Mo	3.73	3.75	3.89	4.31	5.80	7.48
Ti	3.73	3.70	3.93	4.28	4.73	5.35
nano-Fe	3.73	3.62	3.74	3.69	3.79	3.85

Table 2. Amounts (mean values) of the indispensable energy of the high calorific mixture (J) as a function of the activator concentration determined by the electrostatic discharge test (EDS)

Activator	Concentration range of activator, wt.%					
	0	1	2	3	4	5
Zn	0.62	0.61	0.58	0.62	0.60	0.55
Mo	0.62	0.55	0.41	0.30	0.22	0.15
Ti	0.62	0.59	0.63	0.64	0.61	0.62
nano-Fe	0.62	0.63	0.60	0.59	0.58	0.58

In the case when using more than 4 wt.% Mo, a disadvantageous phenomenon occurs, that is, vigorous ejection of small, oval and molten iron particles. During the measurement of the linear burn rate of a three-component mixture containing 10 wt.% Mo, the above effect caused almost 30% pellet mass loss.

A similar effect of mass loss due to vigorous ejection of metal particles (molten iron or iron-titanium alloy) outside the measuring grip was observed at 3 wt.% Ti in the mixture. The linear burn rate of the pellet containing 10 wt.% Ti was very high, 115 $cm \cdot s^{-1}$, while the burn rate of the two-component mixture was 3.73 $cm \cdot s^{-1}$. It was also discovered that only 50% of the initial pellet mass remained after completion of the experiment with the measuring grip. Microscopic investigation of the pellet with 4 wt.% Ti revealed the presence of large areas of molten iron inside the pellet.

Table 1 shows a slight decrease in the linear burn rate of the Fe-$KClO_4$-nano-Fe pellets as a function of activator concentration. The results obtained for nano-Fe metallic powder show that an increase in concentration leads to a slight increase in the linear burn rate and at 5 wt.% it reaches the value of 3.85 $cm \cdot s^{-1}$. During activation, the temperature of the pellet surface is much lower and does not exceed 1200 K. Moreover, a slight increase in KCl vapor emission is observed and a pellet temperature higher than 620 K is maintained for about 45 s.

The testing of solid pellet samples revealed that if the energy supplied by the heating paper is 2 $J \cdot mm^{-2}$, 100% efficiency of mixture activation is obtained and the linear burn rate is only slightly decreased, by about 0.2 $cm \cdot s^{-1}$ on average.

Table 2 shows the sensitivity of the heating mixture to electrostatic discharge, with energy expressed in J. These data illustrate the influence of the activator concentration on the minimum energy value required for burning of the Fe-$KClO_4$ powder mixture. The energy value necessary for activation of the initial two-component mixture is 0.62 J. The presence of metallic zinc in the concentration range studied has no significant effect on the value. Mixtures containing the molybdenum activator required lower ignition energies as compared to mixtures

with the zinc activator. The energy value for a mixture with 5 wt.% Mo is 0.15 J and, in this respect, it is comparable with a Zr-$BaCrO_4$ mixture [22]. Upon addition of 10 wt.% Mo, the Fe-$KClO_4$ mixture may be activated by the electrostatic charge created during mixing.

In the case of powder mixtures with the titanium activator, no influence of the activator on the energy required for activation was observed. The use of iron powder with nano-metric grain size in the heating mixture reduces the value of the energy necessary for mixture activation.

The testing of solid pellets with activators specified in Table 2 revealed that 100% activation efficiency is obtained if the energy of a heat pulse delivered by the heating paper is 8 J (2 $J \cdot mm^{-2}$).

4 Conclusions

- The use of zinc powder as a heating mixture activator causes the temperature of activation to decrease with a simultaneous increase in the conversion rate of oxygen evolved during $KClO_4$ decomposition; zinc powder with nanometric grain size significantly reduces the amount of heat energy released from the mixture.
- The use of titanium powder activator increases the oxygen conversion rate and the amount of released energy but has little influence on the activation temperature of the heating mixture; activation of this mixture involves Fe and $KClO_4$, while Ti reacts only at higher temperatures. It is a fast process (high linear burn rate) accompanied by a significant release of energy, which results in melting of the iron powder and formation of Fe-Ti alloy.
- The addition of molybdenum activator in the form of nano-grain powder lowers the temperature of activation and the amount of released energy; this is probably due to the appropriate powder grain size.
- Iron nanopowder used as a heating mixture activator causes only a slight change in the linear burn rate and the amount of reacted $KClO_4$. The change is accompanied by uniform burning of the activated pellet.
- Molybdenum powder could be applicable practically as the activator of the Fe-$KClO_4$ heating mixture; if used in not more than 3 wt.% concentration, it considerably reduces the value of the activation temperature and eliminates the risk of self-ignition during mixture homogenization. While preparing the mixture with 4 and 5 wt.% molybdenum for 5 experiments, we observed 2 and 4 self-ignitions of the mixture, respectively.

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