



Activator – Induced Modification of Selected Properties of Heat Generating Fe-KClO₄ Mixture

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Abstract: The effect of the kind (Zn, Mo, or Ti) and amount (the concentration range 0-5 wt.%) of the metallic powder used as an activator introduced into the highly calorific mixture of Fe and KClO₄ has been studied. In all samples studied, with increasing amount of the activator introduced into the system Fe-KClO₄ the energy effect has been found to increase in the following sequence Ti<Zn<Mo, while the degree of conversion of KClO₄ in the sequence Mo<Zn<Ti. The obtained results have indicated the powders of Ti, Mo as promising from the point of view of future applications, on condition of using them at proper proportions.

Keywords: Fe-KClO₄ mixture, activators, granulometric analysis, TPR, SEM and X-ray methods

Introduction

In some branches of technology certain thermally initiated processes require the use of high calorific value mixtures, among others, those based on a system of iron powder – potassium chlorate(VII). Usually the specific demands can be satisfied by modifications of the system through introduction of its activators [1]. The activators are known to modify the system's properties, e.g. change the

temperature of initiation of the reaction between its components or the volume of liberated volatile substances. In our previous papers we have shown that there is a possibility of application of commercial iron and potassium chlorate(VII) powders as a components of the high calorific mixture after their previous modification [2, 3].

This study was undertaken to analyse the effect of small admixtures of highly dispersed metallic powders introduced into the heating mixture on the performance of the latter. The metal powders can act in the mixture as factors decreasing the activation temperature or increasing the effectiveness of the oxidant used. Some authors have indicated a possibility of using molybdenum powder as an activator of the heating mixture [4, 5]. Considering the fact that properties of Fe-KClO₄ mixture are influenced by addition of an activator, we have analysed the effect of the Zn, Mo and Ti powders on selected physicochemical properties of the above mixture.

Materials and Methods

Samples

The iron powders used in the study were samples of commercial products from: POCh Gliwice (Poland), Alfa Aesar, Johnson Matthey GmbH (RFN) and KOCH LIGHT Laboratories Ltd. (GB) denoted respectively in the text as **Fe-1**, **Fe-2** and **Fe-3**. Commercial KClO₄ p.a. Fluka (BRD) was subjected to the two-stage process of crystallization as it was described earlier in the papers [3, 6, 7].

The zinc and molybdenum powders used in this study as an activators were samples of commercial products from Fluka A.G. Chemische Fabrik CH-9470 Buchs (Swiss), marked in the text as **A-1** and from Alfa Aesar, Johnson Matthey GmbH (RFN)), denoted as **A-2**. Moreover as an activator was used sample of titanium from POCh Gliwice (Poland) subjected special procedure, which has been described below and marked as an **A-3**.

Pulverisation of titanium powders in the hydriding-dehydriding process

The commercial preparation of titanium powder was pulverised in a specially constructed device ensuring the control of the atmosphere of the process [8]. The weighted portion of the powder was placed in a quartz tube and heated at 500 °C under a pressure of 2×10^{-6} MPa for 2 hours. After cooling the content to the room temperature, highly pure hydrogen liberated from titanium hydride (placed in a special dosing device) was inserted by doses. The introduction of

hydrogen by doses was continued until its constant pressure above the sample was achieved, and then the hydrogen from the sample was desorbed at 500 °C and under pressure 2×10^{-6} MPa. The above process of hydriding-dehydriding was three times repeated. As a result of the process the commercial preparation of titanium powder was refined to the grain size below 40 μm .

Granulometric analysis

The grain size distribution of the KClO_4 powder and the commercial iron powder preparations was determined by laser scattering using a granulometer made by Malvern Instruments model Mastersizer S, of the measuring range 0.04-900 μm . The conditions of the granulometric analysis of KClO_4 were described in [7], while the conditions of measurements of the commercial iron powders in paper [9].

X-ray diffractometry

X-ray analysis was performed for powders of potassium chlorate(VII) subjected to a two-stage process of crystallization, selected commercial iron samples and powders metallic zinc, titanium and molybdenum on a Philips powder diffractometer model PW 1070, using CoK_α radiation and an iron filter. The conditions are specified in paper [6].

Scanning electron-microscopy (SEM)

The commercial zinc and molybdenum powders were subjected to the three-stage refinement process. During the first stage, the appropriate powder was placed in a quartz tube inside an electric furnace, and then the atmosphere was changed to helium. Next, the atmosphere was modified again by introducing hydrogen into the tube ($20 \text{ cm}^3 \text{ min}^{-1}$), gradually increasing the temperature inside the furnace up to 230 °C and maintaining it for 2 h. At the third stage, after cooling the tube together with the powder to the room temperature, the atmosphere was again changed to helium and then the sample was transferred to the dry box. The above samples were observed under a scanning electron microscope (SEM) 515 made by Philips (Netherlands) in the following conditions: working distance of 14 mm, accelerating voltage of 15 kV and digital image recording DISS.

Temperature programmed reduction (TPR)

The temperature-programmed reduction (TPR) by hydrogen experiments was carried out by means of a specially constructed instrument described earlier [6, 10]. All the TPR profiles were converted into mass equivalent.

Study of the reactivity in the solid state between KClO_4 and Fe

The reaction progress was followed by measuring the thermal effects in a differential thermo-analyser made by Netzsch, model STA 409 C 3F [3, 6, 7]. Details of the reactivity measurements are described in the paper [2].

Measurements were performed on tablets composed of 17 wt.% of KClO_4 powder and 83 wt.% of metallic powders including the commercial iron powder and an appropriate activator Zn, Mo or Ti in the amount varied from 0 to 0-5 wt.%, i.e. 0, 0.5, 1.0 and 5.0.

Results and discussion

Samples

Physical and chemical properties of potassium chlorate(VII) powder and its modifications are given in detail in [3]. As a result of the modifications, we obtained a preparation characterised by a low content of the main impurities that is chlorine ions <0.0005 wt.% and sodium ions <0.084 wt.%. The bulk density of this preparation was 0.51 g cm^{-3} , and its grains were planar of irregular shape and characterised by a low degree of crystallinity as indicated by the low intensity of the reflexes from this phase. The iron powder preparations used for the study were obtained in different ways as evidenced by the shape and diameter of the grains and the surface area of 0.84 , 0.38 and $0.67 \text{ m}^2 \text{ g}^{-1}$ for **Fe-1**, **Fe-2** and **Fe-3**, respectively. The content of iron oxides on the surface of the iron powder preparations studied was obtained in a semi-quantitative way to decrease in the series **Fe-3** $<$ **Fe-1** $<$ **Fe-2** [9].

Similarly as for the heating mixture components (metallic iron powders [9] and potassium chlorate(VII) [2], also for the activators studied (Zn, Mo and Ti metallic powders) the volumetric and numerical distributions of grain size, the shape of grains, phase composition and the content of oxide phases on the activators' surface were determined.

Granulometric analysis

Granulometric analysis of the commercial metallic powders used as activators has shown the monodisperse grain distribution in all samples. The maxima of the distribution were obtained at the grain diameter of 25 , 90 and $18 \mu\text{m}$ for zinc, titanium and molybdenum. The numerical distribution revealed maxima at the grain sizes of 5 , 7 and $0.9 \mu\text{m}$ for zinc, titanium and molybdenum powders. The theoretical and experimental curves of the volume and numerical distribution differed significantly, the differences were characterised by the residual of about

6%, so much more than the limit of 1% given by the producer, which indicates significant deviations of the grains shape from the oval or spherical one.

Granulometric analysis of the commercial titanium powder subjected to hydriding-dehydriding process has shown a significant decrease in the dominant size of the molecules to about 40 μm in the volume distribution and about 10 μm in the numerical distribution. The above values imply the presence of a small population of large size grains whose contribution is important only when analysing the volume distribution.

X-ray diffractometry

The activators of the heating mixture studied were commercial metallic powders of Zn, Mo and Ti, labelled as **A-1**, **A-2** and **A-3**, respectively. Results of the diffractometric analysis of the Zn-based activator labelled as **A-1** the reflexes appear at 2θ of about 42, 46, 51, 64, 83, 84 and 99° and can be assigned to metallic zinc phase. The reflexes at the angles of 37, 40, 56, 67, 75, 81° evidence the presence of the ZnO phase. Although the intensity of these reflexes is relatively low, the amount of ZnO in the sample **A-1** is of an order of a few wt.%. Figure 1 presents the X-ray spectrum of the sample **A-2** showing only the reflexes assigned to the Mo phase. Detailed analysis of the background did not reveal the presence of the oxide phases of molybdenum such as MoO₂, MoO₃, Mo₂O₃, Mo₄O₁₁, Mo₈O₂₃ or Mo₉O₂₆. The diffraction pattern of the sample **A-3** shows reflexes at 2θ of 41, 45, 47, 62, 75, 85, 92, 93, 99, 106 and 114°, indicating the presence of the metallic titanium phase. Detailed analysis of the background did not reveal the presence of the TiO₂ phase. However, the diffraction pattern shows four low-intensity reflexes at the angle of about 42, 48, 70 and 89° whose assignment has not been resolved yet.

Pulverisation of titanium powders in the hydriding-dehydriding process

The size of grains in the commercial metallic titanium powder is much greater than that of the grains of the iron powders used in the heating mixture. Hence the raw material has been subjected to pulverisation in the process of hydriding-dehydriding. As a result of this process the grain size of the preparations decreased as indicated by the results of the granulometric analysis.

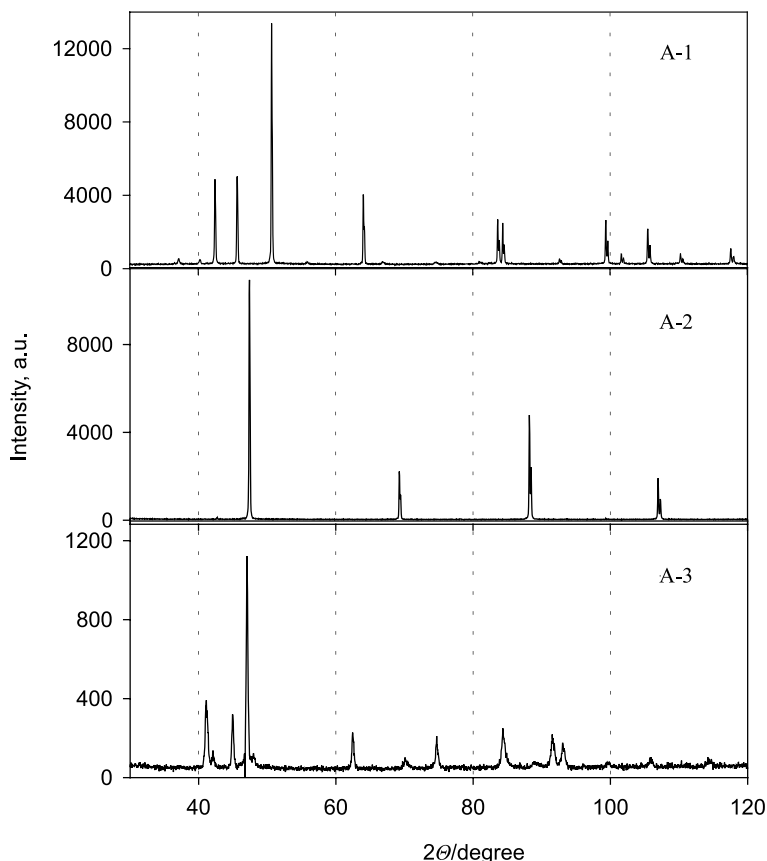


Figure 1. X-ray diffraction patterns of the samples used as activators: **A-1** (Zn); **A-2** (Mo); **A-3** (Ti).

Scanning-electron microscopy (SEM)

The effect of pulverisation performed in the above process of hydriding-dehydriding is illustrated in the SEM photographs shown in Figure 2. The above photographs also reveal the effect of subsequent stages of the hydriding-dehydriding process on the type of the grains of metallic titanium. Photograph a) in Figure 2 shows the commercial titanium powder (**A-2**) composed of two types of solid and spongy grains of relatively large size. After the first stage of the hydriding-dehydriding process numerous crevice pores started appearing in the solid grains, but the grains did not deteriorate yet (see Figure 2b). No crevice pores were detected on the surface of the spongy grains. At the second stage of the process, pulverisation of solid grains occurs as a result of numerous breaks

(see Figure 2c). A magnified image of a spongy grain with many crevices on the surface indicating that the process of its deterioration has already started is shown in Figure 2d.

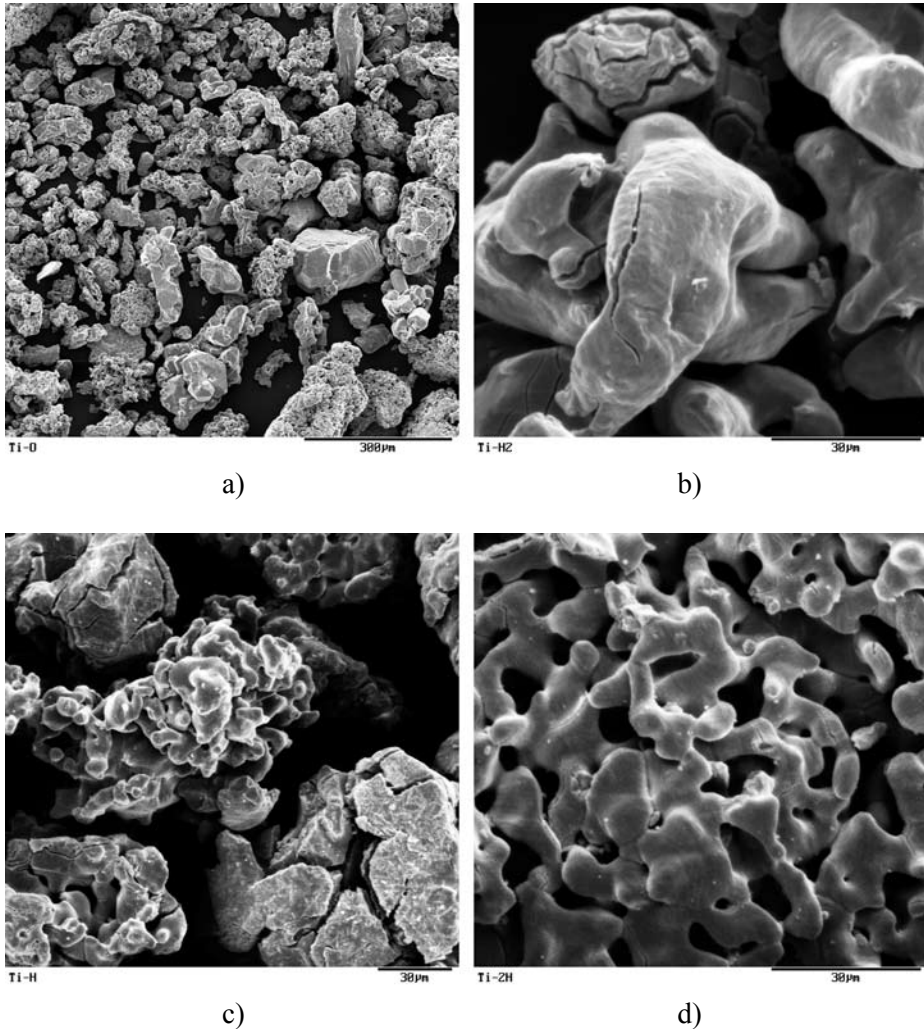


Figure 2. SEM micrographs of the commercial titanium powder sample: a) raw material; b) after the first step of the hydrogen treatment – solid grain; c) after second step of the hydrogen treatment – solid grain d) after second step of the hydrogen treatment – spongy grain.

After the third cycle of hydriding-dehydriding process of titanium powder, the majority of the spongy grains break down, as confirmed by the granulometric analysis. Figure 3 presents the SEM photographs of commercial metallic Zn (A-1) and Mo (A-3) powders. Figure 3a shows the Zn powder whose grains assume the shape of long needles of relatively large size. The dominant type of grains in this sample have the shape close to chips and some areas reveal structures resembling a three-dimensional net. The SEM of the molybdenum powder (A-2) is shown in Figure 3b. The dominant grains in this sample have the size of about $10\ \mu\text{m}$ or $1\text{-}2\ \mu\text{m}$.

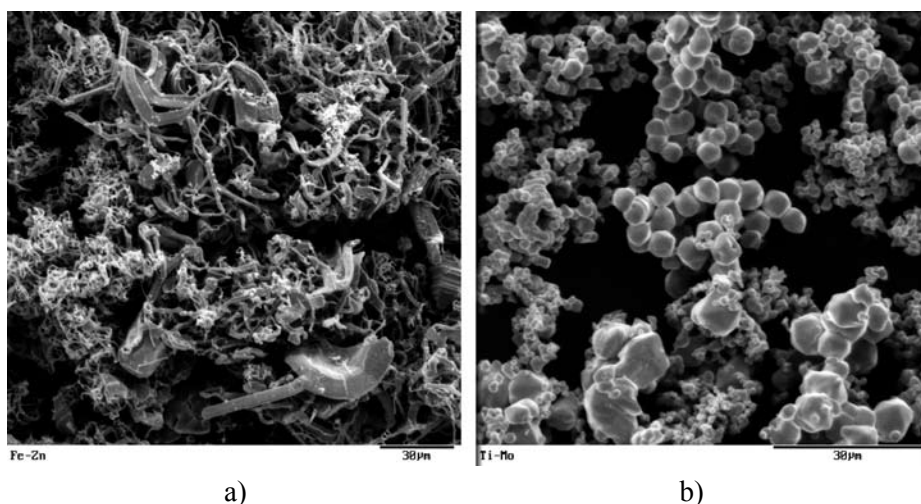


Figure 3. SEM micrographs of the commercial powder samples used as activators: a) Zn; b) Mo.

Temperature programmed reduction (TPR)

The content of the oxide phases on the metallic grains surface of the samples A-1, A-2 and A-3, used as activators in the heating mixture, was determined by the temperature-programmed reduction by hydrogen. The TPR curves of the preparations studied are shown in Figure 4. The TPR profile of A-1 sample indicates the presence of considerable amounts of ZnO, what has been confirmed by diffractometry. Starting from about $600\ ^\circ\text{C}$ a zinc mirror appeared on the reactor walls testifying to its slow evaporation. The TPR profile of activator A-2 in the temperature range studied shows a single maximum at about $400\ ^\circ\text{C}$ of low intensity, and can be assigned to the presence of trace amounts of oxides present on the grain surface of this preparation.

The course of the TPR profile of A-3 was untypical. The peak appearing at

about 380 °C was assigned to reduction of the surface oxides to metallic titanium. Another narrow peak of high intensity was noted at about 400 °C, and it was assigned to the volumetric sorption of hydrogen by metallic titanium accompanied by formation of titanium hydride of the formula TiH_2 . This compound undergoes decomposition at 630 °C. The thermal desorption of hydrogen from the sample is evidenced by the peak whose maximum is directed towards the abscissa – see Figure 4 (A-3). The application of pressure of 2×10^{-6} MPa during the dehydriding process of metallic titanium powder led to decomposition of titanium hydride at temperatures below 500 °C.

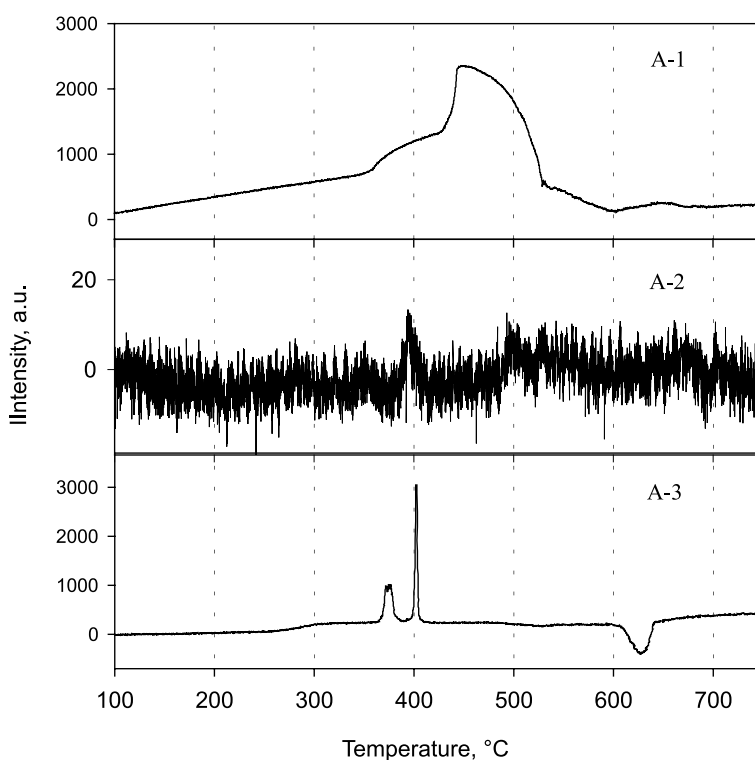


Figure 4. TPR patterns of the commercial powder samples: A-1 (Zn); A-2 (Mo) and A-3 (Ti).

The reactivity of $KClO_4$ and Fe in the solid state

The effect of the amount and kind of the activator on the reactivity of the heating mixture was studied on the mechanical mixtures of particular iron powder preparations (Fe-1, Fe-2 and Fe-3) and potassium chlorate(VII) at the ratio of 4.9:1. Figure 5 presents the mean parameters describing the efficiency

of the heating mixtures, including the temperature of the beginning of KClO_4 decomposition, the degree of its conversion and amount of the heat released.

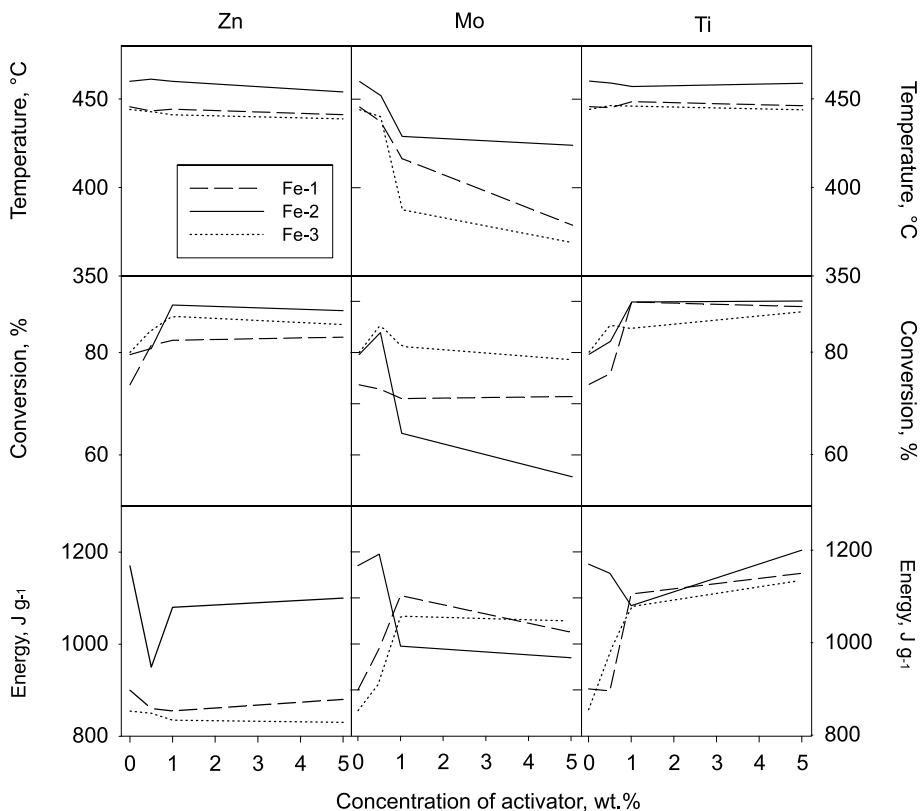


Figure 5. Parameters of reactivity (temperature of the initial decomposition of KClO_4 ; conversion of KClO_4 ; amount of energy evolved during the interaction in the solid-state reaction of the KClO_4 -Fe mixture as a function of the activator concentration Zn, Mo and Ti, respectively).

For titanium powder as an activator, no effect on the ignition temperature was observed, irrespective of the type of iron powder used in the mixture (**Fe-1**, **Fe-2** or **Fe-3**). The conversion of KClO_4 irrespective of the amount of the titanium activator used reached a maximum, which for the iron powder **F-2** reached almost 90%. The heat released in these conditions slightly decreased with increasing amount of introduced Zn to the heating mixture.

The situation was different for molybdenum powder used as an activator.

With increasing concentration of Mo powder in the heating mixture, the ignition point of the mixture decreased by 40-75 °C, depending on the type of iron powder used. Also with increasing concentration of molybdenum powder the conversion of KClO_4 was slightly decreased, except the situation when the reducer was the iron powder labelled as **Fe-2**.

The use of metallic titanium powder as an activator has no effect on the ignition point of the heating mixture, similarly as the use of zinc powder in the same role. The effect of metallic titanium on the degree of conversion of potassium chlorate(VII) is relatively strong in the concentration range used. The energetic effect caused by the presence of metallic titanium is similar to that metallic molybdenum.

In general, all the activators studied affect the parameters of the heating mixture. The presence of metallic zinc and titanium in the concentration range studied has no significant effect on the ignition point of the heating mixtures. This means that the ignition point is determined by the physical and chemical properties of the iron powder used. The grains of metallic zinc covered with a thick layer of zinc oxide have no effect on the initiation of KClO_4 decomposition. A similar situation takes place for the commercial powder of metallic titanium whose grains are also covered with a passivating oxide film.

The data presented in Figure 5 show that introducing small quantities of metallic powders used as activators into the heating mixture is variedly reflected in its physicochemical properties. When metallic zinc is used as an activator the ignition of the heating mixture causes its melting. At a temperature close to 1000 °C, in the inside of the tablet, it is transformed into vapour and interacts with oxygen present in the intergrain space. This leads only to the increase in the degree of KClO_4 conversion, whereas the energetic effect resulting from introduction of the metallic zinc powder into the heating mixture is relatively small, which can be explained by the low value of the molar enthalpy of ZnO formation amounting to 350.5 kJ mol⁻¹. A similar course of the dependencies of the ignition point of the heating mixture on the activator concentration is observed also for titanium powder. After ignition of the heating mixture, oxygen undergoes a fast diffusion inside the titanium grains through the passivating layer followed by titanium oxidation, which leads to an increase in the degree of KClO_4 conversion in the heating mixture. High values of the molar enthalpy of TiO and TiO_2 formation – 519.7 and -944.0 kJ mol⁻¹ respectively – are the reason that using titanium powder as an activator results in liberation of greater quantities of thermal energy [11].

The use of metallic molybdenum as an activator causes a strong decrease of the ignition point of the heating mixture, to about 370 °C for the mixtures

containing iron powders **Fe-1** and **Fe-3**. When molybdenum powder is used as an activator, the course of KClO_4 conversion is different, which can be explained by high vapour pressure of the forming MoO_3 . Assuming the total use of the activator introduced into the heating mixture to replace a part of the iron powder, the observed dependence of the heat released on the activator concentration are obvious.

Conclusions

- The presence of metallic powders of zinc and titanium used as activators of a heating mixture composed of metallic iron powder and potassium chlorate(VII) at the ratio of 4.9:1 has no effect on the ignition point of the mixture.
- The presence of zinc or titanium metallic powder in the range of their concentration up to 1 wt.% in the heating mixture leads to an increase in the degree of KClO_4 conversion, so to an increase in the mixture efficiency.
- Introduction of metallic zinc into the heating mixture leads to a slight decrease in the energy released, while the introduction of titanium metallic powder causes its significant increase.
- The use of metallic molybdenum powder as an activator in the heating mixtures studied leads to a significant decrease in their ignition point and an increase in the heat released.
- The origin of the metallic iron powder used in the heating mixture, significantly affects its efficiency in the case when it contains zinc powder as an activator.
- From among the metal powders studied as activators of the heating mixture, the most promising are the metallic powders of molybdenum and titanium.

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