



Modification of the Surface of the Iron Powder as an Ingredient of the High Calorific Mixture

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Abstract: Textural properties of iron powders obtained by reduction of iron(II) compounds and by electrolysis were determined. Their specific surfaces were 0.38 and 0.43 m²g⁻¹ respectively, and the prevailing grain sizes amounted to 10 and 43 μm respectively. Total content of the determined metallic impurities was 0.055 wt.% in the preparation obtained by the electrolysis while in the preparation obtained by reduction it was 0.025 wt.%.

It was proved that in initial samples the α-Fe₂O₃ phase occurred in the outer oxide layer present on the surface of Fe grains, and below this phase a layer of magnetite was found, the thickness of which was considerably greater in iron obtained by electrolysis.

Measurements of selected properties showed that modification of the iron powder surface carried out by reduction with dihydrogen led to decreasing the linear rate of burning of the high calorific mixture Fe/KClO₄ but it did not affect its calorific value. Moreover, it was found that modification of the iron powder surface resulted in lowering the temperature of ignition of the analysed mixture and decreasing

the quantity of the released oxygen generated by decomposition of the oxidant, which did not react with the iron powder.

Keywords: iron powder, Fe-KClO₄ mixture, Raman spectroscopy (RS), ellipsometry, thermo-programmed reduction (TPR), thermogravimetric analysis (TG/DTA)

Introduction

Literature sources indicate that from among the high calorific mixtures under consideration only Zr/BaCrO₄ and Fe/KClO₄ have found practical application in engineering. The first mixture is applied mainly in floating batteries, thermally activated and characterised by short time of action. The other one is used in floating batteries of the relatively long time of action (up to several dozen of minutes) [1]. Information regarding investigation of the ingredients of the second mixture is scarce [2]. Iron powders can be obtained by various methods the simplest of which is reduction of iron(II) compounds by hydrogen and mechanical breaking [3]. On the technical scale, these powders are obtained by atomization (by spraying the molten iron into the water vapour) [4], thermal dissociation of the appropriate iron carbonyls [4], and by the electrolysis of the iron(II) chloride or sulfate(VI) [5, 6]. These powders display diversified activity in reaction with a strong oxidant such as KClO₄ [7] the degree of grinding of which [8] and the presence of prevailing impurities (i.e. Cl⁻ and Na⁺) [9] only slightly affect its reactivity [10]. It was found that the presence of the Na⁺ ions occurring in the form of NaClO₄ leads only to the increase of the hygroscopicity of KClO₄ [10].

Specialist literature regarding this issue lacks the data concerning the influence of the superficial properties of iron powders upon their activity in reaction with the oxidant. Earlier studies showed that samples of iron powders obtained by atomization were characterised by little reactivity with KClO₄ resulting from the presence of a passivity layer consisting of α-Fe₂O₃ and Fe₃O₄ tightly adhering to their surface and also impurities occurring in superficial layers [7, 11].

In the investigation presented in this paper, influence of the modification of oxides occurring on grain surfaces of two selected, commercially available iron powders obtained by reduction of the iron(II) compound and by electrolysis upon some properties of the high calorific mixture prepared with their participation was studied.

Materials and Methods

Samples

Samples of the iron powders used in the study were commercially available products from Fluka (Switzerland) prepared by reduction of the iron(II) compound and from Höganäs (Sweden) obtained by electrolysis denoted in the text as Fe-R and Fe-E respectively. The powders were subjected to chemical processing consisting in their reduction at various temperatures: 293, 600, 670 and 750K in the dynamic hydrogen atmosphere ($350 \text{ cm}^3 \text{ min}^{-1}$).

Commercial KClO_4 p.a. Fluka (Germany) was subjected to the two-stage process of crystallization described earlier in the reports [7, 12].

Analysis of chemical composition

Analysis of superficial and near superficial layers of the samples was performed using the ICP-MC-LA method. A suitable, pellet-like sample was placed in a measuring apparatus in which a thin layer of the preparation was evaporated in the argon atmosphere.

Temperature programmed reduction (TPR)

The temperature-programmed reduction (TPR) by hydrogen experiments was carried out by means of a specially constructed instrument described earlier [13]. All the TPR profiles were converted into mass equivalent.

Raman spectroscopy (RS)

The Raman spectra were recorded with LabRAM HR800 HORIBA Jobin Yvon spectrometer. The spectra were excited with 632.8 nm radiations from an air-cooled He-Ne laser and with 488, 514 nm from argon laser Stabilite 2017; the resolution was better than 2 cm^{-1} . The laser power was kept from 1 to 20 mW at the sample, to avoid sample degradation.

Ellipsometry

Ellipsometric measurements were carried out using the pressed tablets of appropriate iron powders with the spectral range of 280-1000 nm, every 10 nm, and the glancing angle 65° . A Variable Angle Spectroscopic Ellipsometer with RAE-Rotated Analyser Ellipsometry - by J.A. Woollam, Co. Inc. USA was used for the measurements.

Burning rate

Burning rate of a heating tablet was determined with the help of TPS-2

manufactured by ARET Poland [14]. A tablet, 25 mm in diameter, was fastened in a special holder-enabling ignition by heating paper, and then a measuring device was started automatically as soon as the first probe received a signal. The time of burning was measured upon receiving a signal from the second instrument stalk.

Determination of calorific value

Calorific values of heating tablets were measured using a KL-12 Mn calorimeter produced by Precyzja-BIT Sp. z o.o. Eight tablets of the diameter of 25 mm and weight of ca 10 g each were placed 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 the atmospheric pressure. The amount of heat released by the heating coil and the heating paper was taken into consideration while calculating the calorific value.

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. Details of the reactivity measurements are described in the paper [12].

Measurements were performed on tablets composed of 17 wt.% of KClO_4 powder and 83 wt.% of metallic powders including the commercial and modified iron powders.

Results and Discussion

Samples

Iron powder preparations denoted Fe-R and Fe-E were subjected to textural tests regarding the size of their specific surface, grain size distribution and the picture of the surface under the electron microscope obtained by the SEM technique [11].

The surface areas of all samples studied are rather very small and vary from 0.38 and 0.43 $\text{m}^2 \text{g}^{-1}$ respectively for sample Fe-R and Fe-E. Numerical distribution of the size of iron powder particles for the range of 1-14 μm for preparation marked Fe-R and the volumetric distribution for the range of 1.5-90 μm (maximum at $\sim 10 \mu\text{m}$). Numerical distribution is of the monodisperse nature, while the volumetric one is bidisperse. In preparation marked Fe-E, polydisperse nature of numerical distribution (two maxima) pointing to the presence of grains of two different sizes (i.e. 0.6 and 3 μm). Volumetric

distribution of grains in these samples showed the monodispersive nature and maximum diameter of $42 \mu\text{m}$. The shape of the Fe-R particles under observation was close to spherical, whereas grains of Fe-E were clearly flat with numerous fissures [11]. As regards the volumetric distribution, differences resulting from application of different methods of obtaining the powder samples can be noted. Particles of the powder preparation obtained by reduction of iron compounds were smaller in size.

Results of the granulometric analysis suggest that preparation marked Fe-R constitute a strictly defined fraction of the grain size, which was probably obtained by grain segregation or carrying out the process of obtaining in some strictly determined regime of the synthesis.

Results of the analysis of impurities occurring in the investigated iron powders preparations presented in Table 1 show that they occur in trace quantities. Total contents of the determined metallic impurities in iron powders are small and they amount to 0.055 and 0.025 wt.% in preparations obtained by the electrolysis and by iron(II) compounds reduction respectively. The content of the elemental carbon and silicon in the above-mentioned preparations was not determined, and also it was not indicated in the certificates granted to the respective commercial preparations.

Table 1. Content of impurities in the samples of iron powder determined by the ICP-MS-LA method

Element	Sample Fe-E	Sample Fe-R
	wt. %	
Cr	0.005	0.002
Cu	0.005	0.005
Mn	0.002	0.001
Mo	0.005	0.001
Ni	0.022	0.005
Co	0.010	0.005
Zn	0.005	0.005

Figures 1 and 2 show the TPR profiles for the investigated preparations. The profile of the initial preparation obtained by the electrolysis (marked 293K) reveals the presence of the huge quantity of the oxide phase. Almost identical shape of the peak corresponding to the Fe_3O_4 in the investigated magnetite powder was observed in the report [15]. Processing Fe-E with hydrogen at the temperature of 600K showed that it contained considerably smaller quantity of oxide phases with two maxima present [16]. On the basis of the shape and

positioning of the profiles of the respective phases i.e. Fe_2O_3 , Fe_3O_4 and FeO , one can assume that the investigated preparation contains the phases Fe_3O_4 and Fe_2O_3 . This preparation being reduced at 670K and 750K respectively is characterised by profiles with only one small maximum present. Probably, it corresponds to the presence of the Fe_3O_4 phase generated under the influence of trace quantities of dioxygen present in the dry-box or during placing the sample of the preparation in the quartz reactor in the apparatus for determining the TPR profiles. The TPR profiles of Fe-R presented in Figure 2 were made for the initial preparation and for the one subjected earlier to reduction with hydrogen at the temperature of 600K. The shape of the TPR line for this preparation points to the presence of two maxima of low intensity. On the basis of the calibration carried out, one can assume that there are phases Fe_2O_3 and Fe_3O_4 present on the surface of this preparation. Chemical processing of Fe-R with dihydrogen at 600K results in reducing the quantity of oxide phases present on the surface of its grains. Intensity of the signal presented on the Y-axis in Figure 1 and Figure 2 was adjusted so that it was possible to half-quantitatively compare contents of oxide phases in both preparations under examination using the size of peaks' surfaces as a criterion. As regards Fe-E and Fe-R subjected to reduction at 670K and 600K respectively, it was found that comparable quantities of oxide phases occurred. In these conditions, as already shown in [17], the phase composition of the iron powder surface undergoes restructuring with simultaneous thinning of the layer of $\alpha\text{-Fe}_2\text{O}_3$ and thickening of Fe_3O_4 . Formation of oxide phases at 523K in the atmosphere of nitrogen leads to formation of the Fe_3O_4 phase only, while in the atmosphere of air Fe_3O_4 and Fe_2O_3 , 2 and 7 nm thick respectively, are initially formed and then thickness of the first phase increased while that of the second one went down to 2 nm [17].

However, on the basis of the TPR measurements carried out, it is not possible to unambiguously assign the observed maxima to the specific iron oxide phases. Along with elimination of oxide phases by dihydrogen, alteration of the arrangement of existing oxide layers can take place on the surface of the preparation leading to formation of the passivating layer of the corresponding oxide closely adhering to the surface of iron grains.

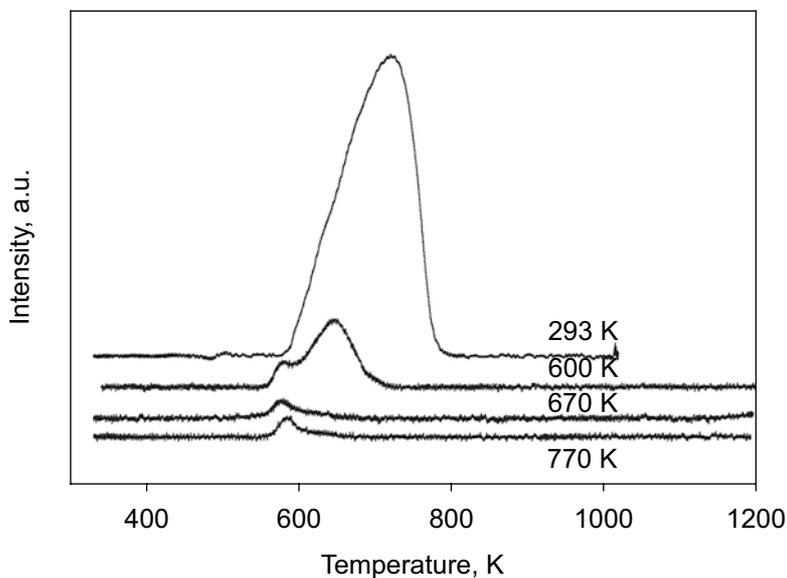


Figure 1. TPR profiles of the Fe-E sample reduced by dihydrogen in different temperatures.

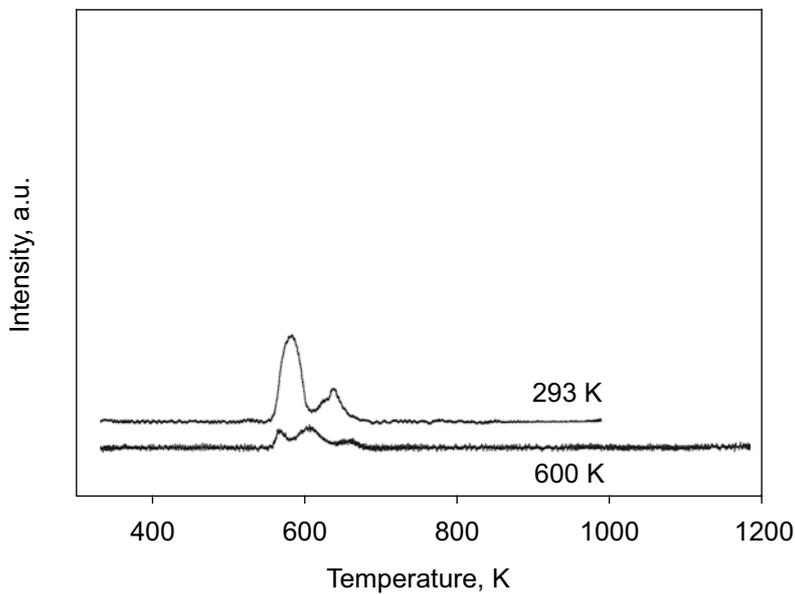


Figure 2. TPR profiles of the Fe-R sample reduced by dihydrogen in different temperatures.

A Raman spectrum (RS) of a commercial iron powder denoted as Fe-E presented in Figure 3 reveals the presence of phases, among which, α -Fe₂O₃ is the dominating one [18]. Also, there are present some low intensity signals derived from the Fe₃O₄ phase visible on the presented spectrum (Table 2) [19]. It was observed that the Raman spectra of commercial Fe-R and Fe-E powders (Figures 3 and 4) reveal considerable similarity regarding the number and positioning of bands. Significant differences in the intensity of vibrational bands, which were observed, can be explained by different ways of obtaining them [11].

Table 2. Position of bands related to the presence of the α -Fe₂O₃ and Fe₃O₄ phases observed in the Raman spectra ν cm⁻¹ of the investigated iron powders versus the literature data

Literature data [18]				Experimental data			
Fe ₃ O ₄	α -Fe ₂ O ₃			Fe - R		Fe -E	
	Symetry	P=0.7 mW	P=7 mW	P=1 mW		P=10 mW	
	A _{1g}	226.7	219.6	225.2		217.6	
	E _g	292.5	282.7	290.9		281.1	
	E _g	410.9	395.9	409.0		396.7	
	A _{1g}	497.1	492.3	501.7		487.7	
534					537.5		544.5
	E _g	611.9	596.0	611.2		595.8	
663					663.1		645.6

Increasing the laser power applied caused broadening of the Raman bands and their simultaneous shifting to lower wavenumbers as shown in Figure 3 (graph in the right upper corner). This effect is fully reversible i.e. decreasing the laser power causes the bands to shift to higher wavenumbers. These alterations can be ascribed to the increase of unharmonic interactions in the system to which thermal energy is supplied. This phenomenon has been the first time observed by Beattie and Gilson [20].

The bands occurring in the Raman spectra of the studied powders can be attributed to the presence of the iron oxide phases: α -Fe₂O₃ and Fe₃O₄ (Table 2) [18]. Hematite α -Fe₂O₃ belongs to the D_{3d}^6 crystal space group, and for this reason seven phonon lines are expected in the RS spectrum: two A_{1g} modes (225, 498 cm⁻¹) and five E_g modes (247, 293, 299, 412, 613 cm⁻¹) [21].

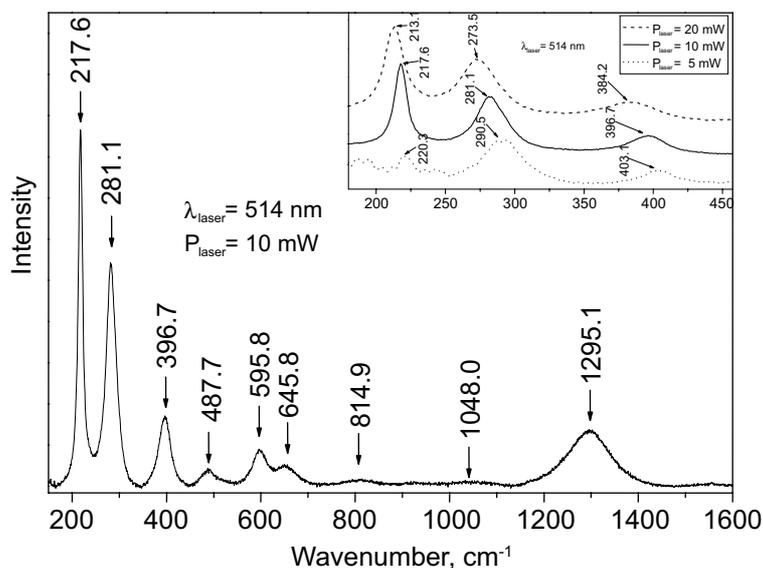


Figure 3. Raman spectra of the Fe-E sample recorded with varying laser power: 20 mW, 10 mW and 5 mW.

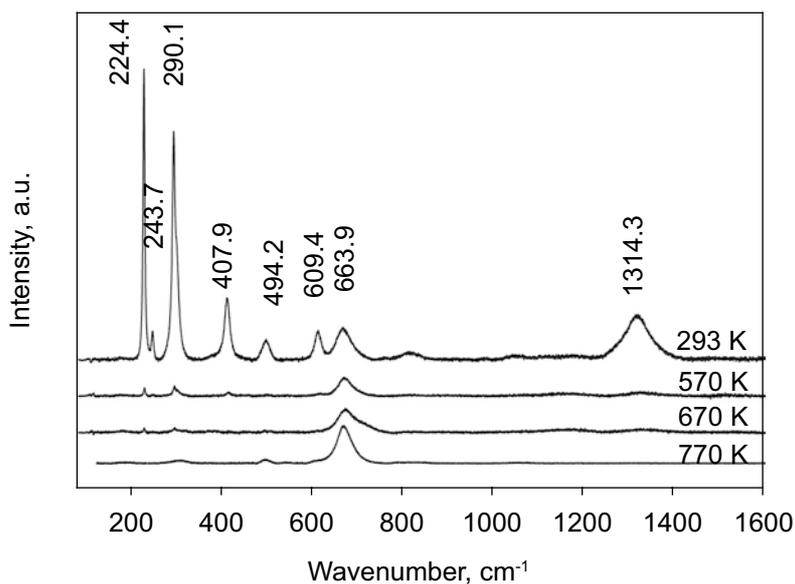


Figure 4. Raman spectra of the initial Fe-R iron powder and Fe-R processed with dihydrogen at 570, 670 and 770 K respectively obtained at the wavelength 633 nm and power 8 mW.

It can be noticed that with identical laser power values applied positions of the bands differ only a little. Moreover application of the excessive laser power can make some bands invisible (e.g. two E_g modes in Fe-E). It resulted from caused by overlapping of two lines situated close to each other; therefore determination of the optimum laser power was necessary.

As regards magnetite belonging to the symmetry group O_h , five bands should occur in the Raman spectrum: three T_{2g} , one E_g and one A_{1g} [22]. A comparison of our data with results obtained by other investigators is presented in Table 2. Furthermore, the intense features observed at 1309 cm^{-1} in Fe-R and at 1292 cm^{-1} and 1295 cm^{-1} in Fe-E were ascribed to a two-magnon scattering arising from the interaction of two magnons created on the antiparallel close spin sites in the net of the phase $\alpha\text{-Fe}_2\text{O}_3$. In Figure 4 the Raman spectra for the Fe-R samples subjected to thermal processing in the dihydrogen atmosphere are shown. In the initial sample, like in the Raman spectrum shown in Figure 3 regarding the Fe-E sample, the presence of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 phases was observed. Significant difference between the presented spectra results from the weak signal emerging at 243.7 nm in the initial Fe-R preparation. This signal is probably caused by considerably smaller quantities of oxide phases present on the iron powder surface. Hydrogen processing at 570K leads to almost total elimination of the $\alpha\text{-Fe}_2\text{O}_3$ phase, which is confirmed by the TPR measurements (Figure 2).

In the Raman spectrum (see Figure 4), a signal coming from the magnetite phase is visible at 663.9 nm . Thermal processing at 670K does not alter the spectrum of this preparation in any significant way. Hydrogen processing at 770K causes total elimination of the $\alpha\text{-Fe}_2\text{O}_3$ phase and – probably – restructuring of the superficial layer, which can be evidenced by smaller half-intensity width of the magnetite peak. No conversion of magnetite into hematite, a common phenomenon known as martitization, was observed in this sample. Martitization consists in conversion of magnetite Fe_3O_4 into hematite $\alpha\text{-Fe}_2\text{O}_3$ through the $\gamma\text{-Fe}_2\text{O}_3$ phase along with the temperature increase [23].

Analysis of the results of the ellipsometric results obtained for the glancing angle 65° (close to the Brewster angle for the analyzed structure) [24] revealed good adjusting between the experimental and theoretical results. In all investigated cases the mean square error (MSE) ranged from 10^{-9} to 10^{-12} .

For determination of optical properties of the studied oxides, the Cauchy formula referring to normal dispersion was adopted [25]. On the basis of the high absorption level observed in the full spectrum range being measured, considerable difference was noticed between the superficial oxide and the oxide lying just below it (coefficient of extinction exceeding one) what can point to the electric conductivity of this oxide. Ellipsometric measurements of

the initial Fe-R sample showed that thickness of the oxide layer was ca 26 nm. This layer consists mainly of α -Fe₂O₃. Hydrogen processing of this preparation leads to increasing the relatively high value of the coefficient of light refraction amounting to ca $n_{630}=3.2$.

Because of the surface of tablets of the analyzed preparations not being perfectly smooth, it was not possible to determine at the same time thicknesses of oxide layers of both phases: α -Fe₂O₃ and Fe₃O₄. Such measurements are possible only when surfaces are very smooth, like e.g. steel [26]. Subjecting sample denoted as Fe-R to the dihydrogen processing at 670K results in elimination of α -Fe₂O₃ from its surface. Coefficient of light refraction for samples of the iron powder marked as Fe-E subjected to reduction at 670K and 720K amounted to $n_{630}= 2.8895$ and $n_{630}= 2.8396$ respectively. Thickness of the Fe₃O₄ phase calculated for Fe-E subjected to the dihydrogen reduction at 670K amounted to 29 nm.

Literature sources quote the value of the coefficient of light refraction for α -Fe₂O₃ calculated at 630 nm corresponding to $n_{630}=2.6250$. Typical dependence of the Fe (Fe₂O₃) refractive index and the Fe (Fe₃O₄) extinction index on the wavelength (denoted as Fe₂O₃ literature data) was taken from J.A. Woolam Co. Inc. WVase32 program v.3.668, tabulated at UNL (Lincoln University, Nebraska, USA).

Formation of the oxide layer on the iron powder surface is usually of thermal origin and results from the reaction between dioxygen and the surface of the metallic powder during its obtaining and storage [27]. Measurements carried out using the TPR, RS and ES techniques showed that the outside oxide layer is formed by hematite while the inside one – by magnetite. Dihydrogen processing of the investigated iron powder preparations allows only to considerably, but not fully eliminate the α -Fe₂O₃ phase, which leads to thickening of the Fe₃O₄ layer.

The ignition temperature of the high calorific mixture, energetic effect of the reaction and mass loss were determined by the thermogravimetric method (DTA /TG), which allowed estimating the amount of oxygen derived from decomposition of the potassium chlorate(VII) did not participating in the reaction with the iron powder.

Hypothetical results analysis of the Fe-R preparation containing 17 wt.% of KClO₄ is presented in Figure 5. There are seen two endothermic effects on the DTA curve: the first occurring at ca 573K and related to the reversible phase conversion of KClO₄ from the rhombic into regular phase and the second – occurring at ca 1040K and attributed to melting of KCl. The temperature of these effects was used as an internal standard for correction of the decomposition

temperature of potassium chlorate(VII) (onset). In the TG curve, there are three mass losses visible. The first loss is connected with liberation to the atmosphere of oxygen generated by decomposition of KClO_4 not participating in the reaction with iron powder. Modification of the iron powder surface caused significant decreasing of the amount of oxygen liberated to the environment [12]. The second mass loss is most probably related to conversion of Fe_2O_3 generated during the first stage of the reaction into Fe_3O_4 . The third one is attributed to slow evaporation of KCl .

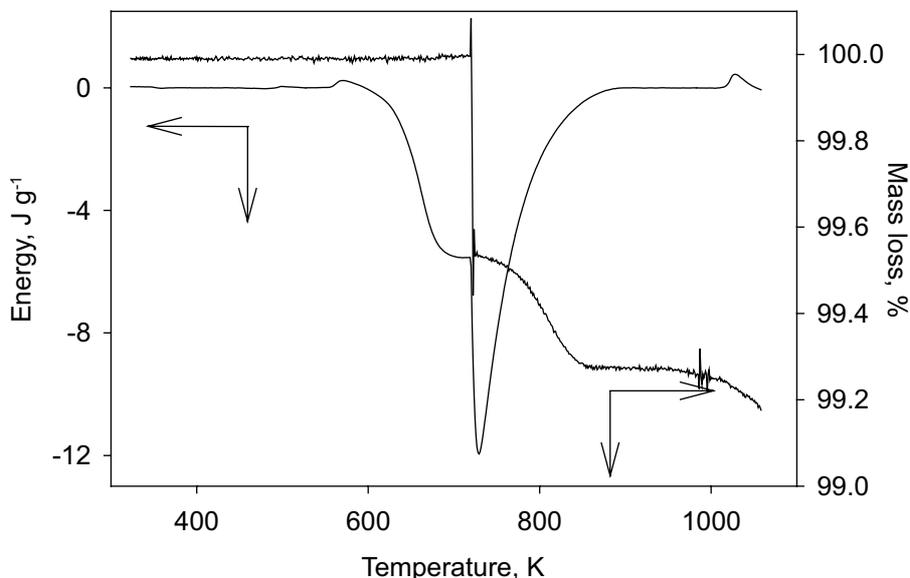


Figure 5. TG-DTA curves of the Fe- KClO_4 system containing Fe-R and 17 wt.% of potassium chlorate(VII).

Energetic effect connected with this last process is not reflected on the DTA curve. Strong exothermic effect noticed at 737K is related to decomposition of KClO_4 and reaction of thus generated dioxygen with the iron powder. Relatively high thermal capacity of the tablet containing a big excessive quantity of iron does not allow separation of the above-mentioned signals. The energetic effect accompanying this process was assessed on the basis of the five-point calibration curve DTA. The data regarding the temperature of starting the reaction, level of the energetic effect and the degree of utilizing KClO_4 is presented in Table 3.

Table 3. Comparison of selected properties of high calorific mixtures prepared with non-modified and modified iron powders

Property	Fe-R		Fe-E	
	Unmodified	Modified	Unmodified	Modified
Ignition temperature, K	744	735	745	730
Conversion of KClO_4 , %	82.3	95.2	89.0	93.4
Caloricity, J g^{-1} (DTA)	989	1240	924	1244
Caloricity, J g^{-1}	1188	1186	1171	1166
Burning rate, cm s^{-1}	3.77	3.69	3.39	2.53

Ignition temperature, degree of reaction of oxygen derived from decomposition of KClO_4 with the iron powder and calorific value (DTA) were determined on the basis of the thermogravimetric analysis curves. With the modified iron powders, ignition temperature of the mixture is lower than with the non-modified ones, and the difference is 9 and 15K respectively. Degree of oxygen utilization is an important parameter of the high calorific mixture Fe- KClO_4 . The amount of energy released during thermal decomposition of KClO_4 only (decomposition at 883K) is increased also as a result of the reaction of dioxygen with the iron powder. The value of energy determined on the basis of the thermogravimetric analysis presented in Table 3 can be regarded as semi-quantitative only. Significant differences between high calorific mixtures containing the modified and non-modified iron powders can be noticed regarding the value of the registered energy. In turn, calorific values of two iron powders (Fe-R and Fe-E) are very similar (Table 3). Actual calorific values were determined following the calorimetric measurements presented in Table 3. Energy values obtained during combustion of the mixtures are almost identical, and they indicate that neither modification of the surface nor the type of the iron powder used affect their energetic properties. It was found that experimental conditions were of importance there. When the thermogravimetric method was employed, these conditions were: the value of the atmospheric pressure, argon flow rate and mass of the analyzed sample. Measurements with application of a calorimeter require the static argon atmosphere and using a sample of a hundred times greater mass. Also the fact that the calorimetric measurement is carried out in a closed vessel, which increases the degree of dioxygen reaction, is of significance.

Immediately after burning of a tablet of the high calorific mixture, the maximum pressure inside the calorimeter amounts to ca 0.4 MPa, which is the reason that the conditions differ from those present during thermogravimetric measurements. Because of a relatively small amount of gas products emitted during burning of the high calorific mixture, increase of pressure inside a tightly closed measurement cell caused mainly by the temperature increase and conversion of some small quantity of the moisture present in the mixture and elements of the measurement cell into gas, calculation of the actual combustion rate using the method described in [28] would be charged with a considerable error.

It was found that modification (by dihydrogen) of the surface of the iron powder resulting from its restructuring is reflected by significant reduction of the thickness of the α -Fe₂O₃ layer accompanied by simultaneous increase of the degree of ordering of Fe₃O₄. This leads to slight slowing down of the linear rate of burning of the high calorific mixture tablet.

After modification of the surface of both iron powders at ca 770K, a significant decrease of the rate of tablets burning down to ca 1 cm s⁻¹, decrease of the amount of the energy released down to ca 600 Jg⁻¹ as well as greater demand for energy required to ignite the mixture were observed. The burning rate values presented in Table 3 point to their significant dependence upon the type of the iron powder used in the investigated high calorific mixtures.

Comparison of selected physical and chemical properties of iron powders obtained by reduction of the iron(II) compound Fe-R to Fe-E obtained by electrolysis and comparison of the high calorific mixtures based on them allows to draw the following conclusions:

- analysed powders are characterized by similar size of specific surfaces BET and similar total quantity of metallic impurities; significant differences result only from grain size distribution and grain shape;
- the surface of initial preparations is covered with a layer of iron oxides of varying thickness with α -Fe₂O₃ on the outside;
- the surface of the iron powder obtained by electrolysis is covered with a very thick oxide layer which undergoes considerable reduction after its dihydrogen processing at 670K;
- the amount of oxides occurring on non-modified surfaces of the grains of iron powders does not affect the temperature of ignition of high calorific mixtures nor the energy released during the reaction with an oxidant;
- the amount of oxides present on non-modified surfaces of the grains of iron powders determines the rate of burning and the degree of utilization of oxygen derived from decomposition of KClO₄;

- modification of the surface of Fe-E with dihydrogen at 570K results in significant decrease mainly of the phase α -Fe₂O₃ and smaller of Fe₃O₄ with simultaneous lowering of the temperature of ignition of the mixture and the rate of its burning; this leads to the increased reaction of oxygen with iron powder;
- reaction of dioxygen with iron powder at 770K causes decrease of the activity of relevant high calorific mixtures demonstrated as difficulties in initiating the reaction and slowing down of the rate of mixture burning (not in full).

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