

Parameters Influencing the Pyrotechnic Reaction

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Abstract

Phenomena (reaction effects) such as varied light emissions, sound, varied burning rates, varied heats of reaction and reaction products occur during the reaction of inorganic redox systems used for pyrotechnics. The peculiarity of these redox reactions is, that they take place as solid-solid, solid-liquid or solid-gaseous state reactions. In opposite the theoretical redox reaction normally postulated in inorganic chemistry takes place in a solvent. By variation of different parameters as for example the reducing agent, the oxidizer, the oxygen balance and the particle size, it is possible to create the above-mentioned effects in a wide range.

Keywords: Pyrotechnics, Fireworks, Redox Reaction, Particle Size, Oxygen Balance

1 Introduction

This paper is a general review about pyrotechnic redox reactions. To generate certain effects most pyrotechnic compositions contain at a minimum one reducing agent (fuel) and one oxidizer, nevertheless complementary ingredients such as binders. Different additives, e.g. burn rate modifiers, colorants, processing aids are used as well.

The understanding of a pyrotechnic reaction can sometimes be very difficult, because in solid state chemistry factors, such as particle size, impurities and oxidation layers on the surface of fuels influence the reaction behaviour significantly. Since there is a lack for suitable models to account for these influences, the development of pyrotechnic compositions up to now is still based on trial and error, to say it more scientifically, occurs empirically. For a long time, experience was the fundamental base of pyrotechnics. By clever choice of reducing agents and oxidizers as well as variation of the compositions, the redox reaction can be influenced to generate the desired, well-defined effects. This is the main reason, why a few common compositions are used exactly in the same way all over the world. In military as well as in civilian pyrotechnics the way to generate effects (such as light, heat, smoke, as just to mention a few) is well known and has been published. Nevertheless the practical details (such as grain size distribution, amount and type of binder, mixing procedure etc.) to adjust a composition for a certain application has to be checked from case to case. Pyrotechnic

compositions often react at visibly observable rates, producing solid and liquid reaction products as well as gases.

In general, one can distinguish between endo- and exothermal reactions. Whereas endothermal reactions require heat input from the surrounding, exothermal reactions release heat. Sometimes the heat release rate is insufficient to cause a self-sustaining reaction. However if the reaction produces a flame or glow throughout the composition, either at high reaction rate or slowly, it may be suitable for pyrotechnic purposes.

A pyrotechnic reaction differs from an ordinary combustion, such as the burning of timber or charcoal in the way that it does not require the presence of ambient air [1].

In pyrotechnics the expression “effect” accounts for several parameters:

- Reaction rate, as described by the equation of Hill et al., Eq. (1)

$$v_B = k \cdot q/b \cdot c^2 \cdot \rho \cdot (T_i - T_a) \quad (1)$$

with

- v_B : Burning velocity [cm/s]
- k : Heat transfer [cal/cm s °C]
- q : Heat of reaction [cal/g]
- b : Length of the reaction zone [cm]
- c : Specific heat [cal/g °C]
- ρ : Density [g/cm³]
- T_i : Burning temperature [°C]
- T_a : Surrounding temperature [°C]

The burning rate can also be determined through various experimental application such as techniques of a burning rinse to probe the combustion rate of loose material or combustion of a strand of the pressed material in order to get the propagation rate in the compact state.

- Heat of reaction which can be calculated either by applying the balanced chemical equation or by application of thermodynamical codes such as e.g. EKVI Code or ICT Code. The heat of combustion can also be determined experimentally in an adiabatic calorimeter
- The reaction temperature can be calculated by applying thermo-dynamical codes such as e.g. EKVI Code or ICT Code. The reaction temperature can also be determined experimentally by using an emission spectrometer

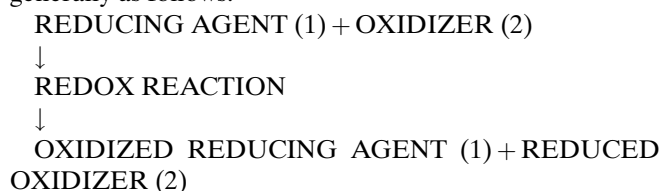
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- The thermal behavior can be investigated with Differential Scanning Calorimetry (DSC) or Thermal Gravimetry Analysis (TGA)
- The ignition temperature can be measured with Differential Scanning Calorimetry (DSC)
- The evolved gas can be calculated with thermodynamical codes such as e.g. EKVI Code or ICT Code
- Experimentally the evolved gas as well as the amount of produced gas can be determined by using Differential Scanning Calorimetry followed by mass spectrometry
- The reaction products can be calculated by using thermodynamical codes such as e.g. EKVI Code or ICT Code. The reaction products can also be determined experimentally with Differential Scanning Calorimetry followed by mass spectrometry or XRD
- The emitted light can be measured with an emission spectrometer

2 Principles of Pyrotechnics

2.1 Pyrotechnic Reaction

The basis of a pyrotechnic reaction can be displayed generally as follows:



During the redox reaction, the reducing agent (fuel) is oxidized and the oxidizer is reduced. The pyrotechnic reaction is mostly a solid-solid, solid-liquid or solid-gaseous state reaction. To predict the reaction behavior of a pyrotechnic composition, it is not or only partly possible to apply the theory of inorganic chemistry which bases on chemical redox reactions in solutions. Pyrotechnic reactions are high temperature redox reactions. They take place in a temperature range of 1500 to 4000 °C. Due to this fact also the reaction products of a pyrotechnic redox reaction are in most cases not the same as expected according to the theory of classical chemistry.

3 Chemicals

To produce pyrotechnic compositions, it is important to use well-defined chemical products. The following important parameters for chemicals used in pyrotechnics must be known:

- Purity
- Particle size
- Particle shape
- Particle surface
- Crystal structure
- Water content

3.1 Reducing Agents (Fuels)

There are several types of reducing agents with different reactivity available, e.g. zirconium, titanium, silicon and boron. The physicochemical data [2] of some reducing agents used in military pyrotechnics are listed in Table 1.

Today very often alloys of zirconium and nickel containing 70% zirconium and 30% nickel, 50% zirconium and 50% nickel or 30% zirconium and 70% nickel are used as fuels.

3.2 Oxidizers

Table 2 shows the physicochemical data of oxidizers [2] often used in pyrotechnic compositions. Oxidizers such as for example nitrates, perchlorates and peroxides of barium, strontium and lithium are also used as auxiliary substances. Depending on their emission spectra, they produce colored light during the redox reaction [3, 4].

3.3 Additional Substances

Most pyrotechnic compositions are mixtures consisting of very fine powders. To produce granules it is necessary to add so called binders. Different types of binders are in use:

- Natural products (e.g. Acaroids resin, Arabian rubber)
- Semi-synthetic products (e.g. Cellulose nitrate, Dextrin)
- Synthetic products (e.g. Polyvinyl chloride (PVC), Polynitropoly-phenylene (PNP), PolyGLYN, PolyNIMMO and other polymers)

Additional pyrotechnic compositions contain auxiliary supplies. Due to their large variety it is not possible to present a detailed overview in this paper. To produce different colored light emissions, it is necessary to have auxiliary substances in a pyrotechnic composition. Very often such substances have a double function, they act on one hand as an oxidizer and on the other hand they are responsible to produce colored light during the redox

Table 1. Physicochemical data of the most important reducing agents used in pyrotechnics

Substance	Molecular Weight	Density [g/cm ³]	Mp* [°C]	Bp** [°C]
Zr	91.22	6.52	1530	2900
Ni	58.71	8.90	1455	3177
Mg	24.32	1.74	650	1102
Ti	47.90	4.50	1727	3000
W	183.9	19.32	3380	6000
B	10.82	1.73	2050	2550
Si	28.09	2.33	1440	2630
C	12.01	2.25	subl. 4350	–
S	32.06	2.07	112.8	444.6
P	30.97	2.2	590 (4.3 MPa)	–

* Melting point

** Boiling point

Table 2. Physicochemical data of the most important oxidizers used in pyrotechnics

Formula	Molecular Weight [g/mol]	Density [g/cm ³]	Mp [°C]	Bp [°C]
KNO ₃	101.11	2.109	339	dec. 400
Ba(NO ₃) ₂	261.38	3.24	592	–
NaNO ₃	85.00	2.257	312	–
KClO ₄	138.65	2.52	dec. 610	–
BaO ₂	169.36	4.96	450	diss. 795
PbO ₂	239.21	9.375	dec. 290	–
Pb ₃ O ₄	685.63	9.1	dec. 500	–
BaCrO ₄	253.37	4.498	–	–
PbCrO ₄	323.22	6.12	844	–
CaCrO ₄	192.09	–	–	–

reaction. Some famous emitters of colored light are the oxides or nitrates of sodium, potassium, barium, copper and strontium [5, 6].

4 Preparation of Pyrotechnic Compositions

The mixing and granulating process is an important procedure during the manufacturing of pyrotechnic compositions. The fuel and the oxidizer must be in a close contact to each other. Usually the reducing agent and the oxidizer are mixed repeatedly in a Turbula mixer intermitted with passing the mixture through sieves with defined meshes. After mixing, the fine powder has to be granulated by adding a dissolved binder. The formed dough is then passed through sieves with adequate mesh sizes to get well-defined granules.

5 Parameters Influencing the Pyrotechnic Redox Reaction

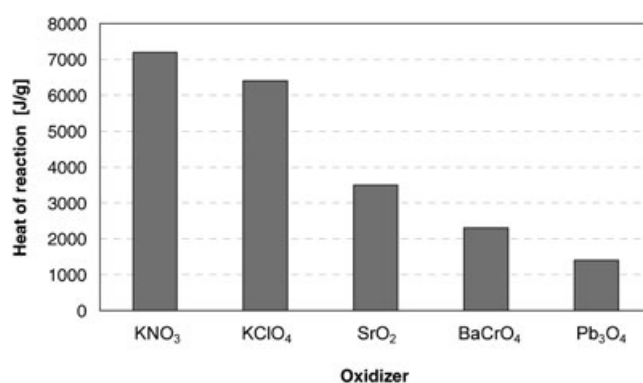
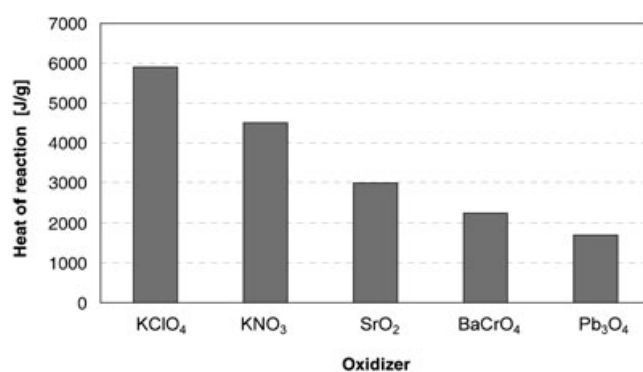
Some of the most important parameters which influence the pyrotechnic performance of a chemical redox reaction are listed below:

- Type of chemicals
- Oxygen balance
- Particle size/active surface
- Binder type/content
- Mixing process

It has to be mentioned that the measured reaction rates are relative values based on a well-defined experimental setup. All reaction rate data presented in this paper were measured with the same experimental setup. The pyrotechnic compositions were filled in a burning rinse [7].

5.1 Type of Chemicals

The influence of the chosen substances can be demonstrated with the heat of reaction ($\Delta_R H$) of compositions

**Figure 1.** Measured maximum heats of reaction of pyrotechnic compositions containing boron and different oxidizers [6].**Figure 2.** Measured maximum heats of reaction of pyrotechnic compositions containing zirconium and different oxidizers [6].

containing various oxidizers and boron or zirconium as reducing agent [8]. These data are measured with an adiabatic calorimeter (helium, 3 MPa). Figure 1 presents the maximum measured heats of reaction of different pyrotechnic redox systems. These systems contain boron as a reducing agent and potassium perchlorate, potassium nitrate, strontium peroxide, barium nitrate and lead III, IV oxide as an oxidizer. Due to different enthalpies of formation, a change of the oxidizer in compositions containing boron as reducing agent results in heats of reaction between 7330 J/g (B/KNO₃) and 1360 J/g (B/Pb₃O₄). Using zirconium instead of boron as reducing agent, the measured heats of reaction are found between 4470 J/g (Zr/KNO₃) and 1710 J/g (Zr/Pb₃O₄). A comparison of the maximum heats of reaction of different pyrotechnic redox systems containing the reducing agent zirconium is plotted in Figure 2.

Figures 3 and 4 show the influence of the reducing agents boron and zirconium mixed with various oxidizers on the maximum measured reaction rates. These reaction rates vary in a range of some mm/s to about 290 m/s. The reaction temperature is also influenced by the selected reducing agents and oxidizers, respectively. Figure 5 shows the reaction temperatures of redox systems using three different reducing agents and as oxidizer always potassium perchlorate. The reaction temperatures were calculated with the

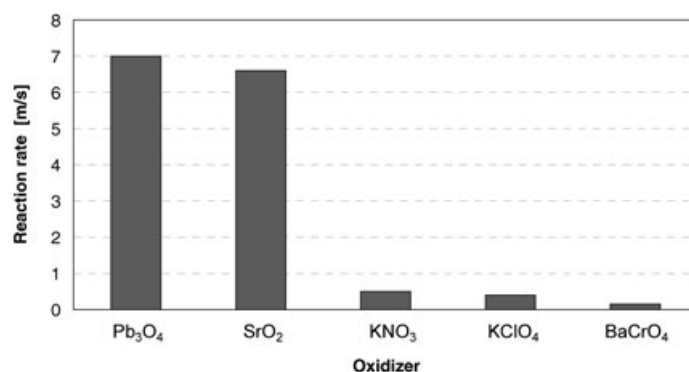


Figure 3. Measured maximum reaction rates of pyrotechnic compositions containing boron and different oxidizers [6].

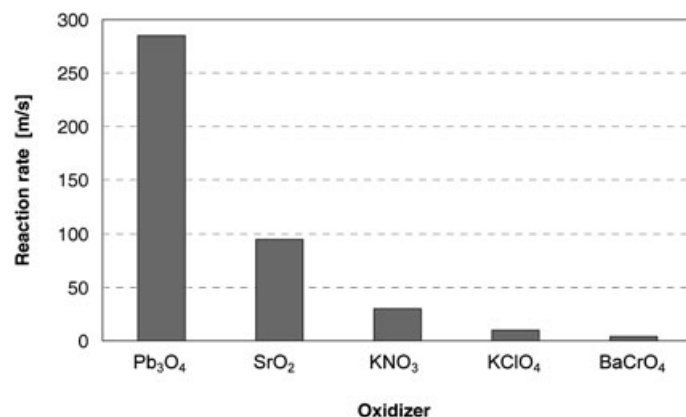


Figure 4. Measured maximum reaction rates of pyrotechnic compositions containing zirconium and different oxidizers [6].

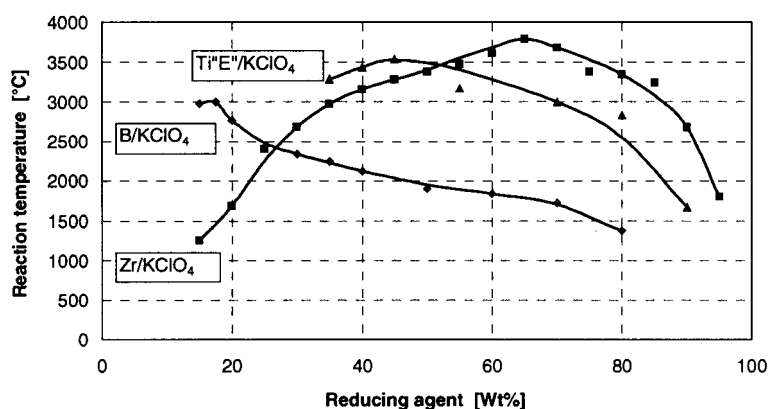


Figure 5. Calculated reaction temperatures of compositions containing titanium, boron or zirconium as a reducing agent and potassium perchlorate as oxidizer.

EKVI code. The temperature maxima are in the range of 3000 and 3700 °C. Figure 6 shows three redox systems with titanium as reducing agent and different oxidizers. In this case the temperature maxima are in a temperature range of 3050 and 3500 °C.

5.2 Particle Size and Specific Surface of Particles

The particle size and the specific surface also significantly influence the reaction rate of pyrotechnic compositions. In

Figure 7 this effect is demonstrated as an example with different reaction rates of the redox system titanium/potassium perchlorate [9]. As already mentioned the reaction is influenced by the type of reducing agent as well as by the particle size and its active surface. Depending on the reducing agent, a reduction of the mean particle size by a factor of two leads to a decrease of the reaction rate by a factor four to five. This can be seen in Figure 7. The reason for this effect is the fact that a decrease of the particle size results in an increase of the specific surface of the reducing agent. In the case of the investigated titanium powder, the

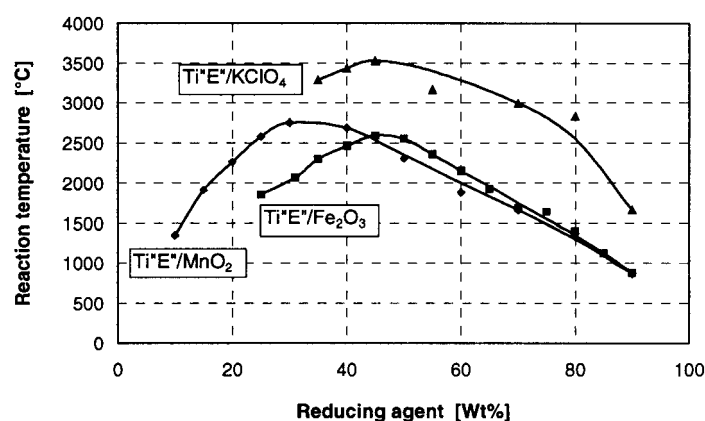


Figure 6. Calculated reaction temperatures of compositions containing titanium as a reducing agent and potassium perchlorate, iron oxide or manganese dioxide as an oxidizer.

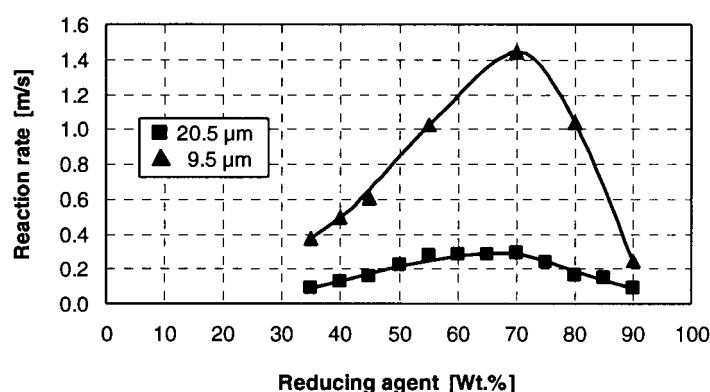


Figure 7. Reaction rates of the redox systems titanium/potassium perchlorate using different particle sizes of titanium [8].

decrease of the medium particle size by a factor 2 leads to an increase of the specific surface by a factor 3.

The particle size and the specific surface influence the kinetic of a redox reaction. However, the particle size of a reducing agent does not influence the heat of reaction [9]. This fact can be seen in Figure 8.

5.3 Oxygen Balance

Very important parameters of a pyrotechnic composition are the reaction rate and the heat of reaction. By varying the oxygen balance of a pyrotechnic redox system, it is possible to vary the heat of reaction as well as the reaction rate in a wide range. It is assumed and can be demonstrated by experiments, that the composition of a pyrotechnic system with an equalized oxygen balance shows the highest heat of reaction, but not the highest reaction rate. This is due to the fact that pyrotechnic reactions are usually solid-solid state reactions. Figures 9 and 10 show, as an example for the statement, the measured heats of reaction as well as the reaction rates of compositions with a positive and a negative oxygen balance as well as the composition with equalized

oxygen balance of the redox system zirconium nickel alloy 50:50 / potassium perchlorate.

$$OB = 100 \frac{n_{Ox} M_{Ox} u}{n_{Red} M_{Red} + n_{Ox} M_{Ox}} \quad (2)$$

OB Oxygen balance
M_{Ox} Molecular weight of oxygen
M_{Red} Molecular weight of reducing agent
u Number of oxygen atoms in the oxidizer
n Number of moles

5.4 Binder and Binder Content

The type of binder as well as the content of binder influences the two main parameters of redox reactions used in pyrotechnics. However, the influence of the binder on the heat of reaction is much smaller than it is on the reaction rate. The influence of variable binder content on the reaction rate and on the heat of reaction is demonstrated with the pyrotechnic system titanium/potassium perchlorate, using polynitropoly-phenylene as an energetic binder [10]. Figures 11 and 12 show the measured data.

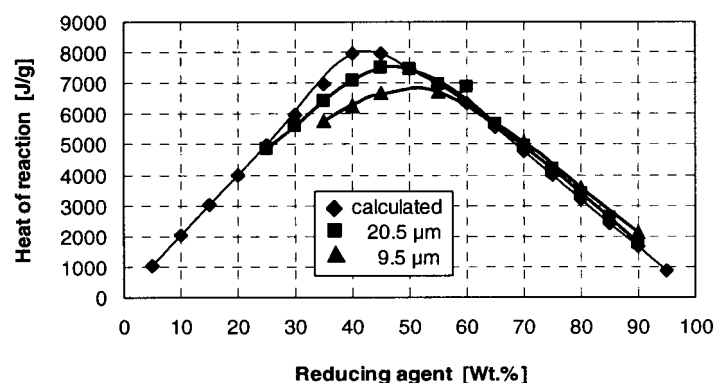


Figure 8. Heats of reaction of the redox systems titanium/potassium perchlorate using different particle sizes of titanium [8].

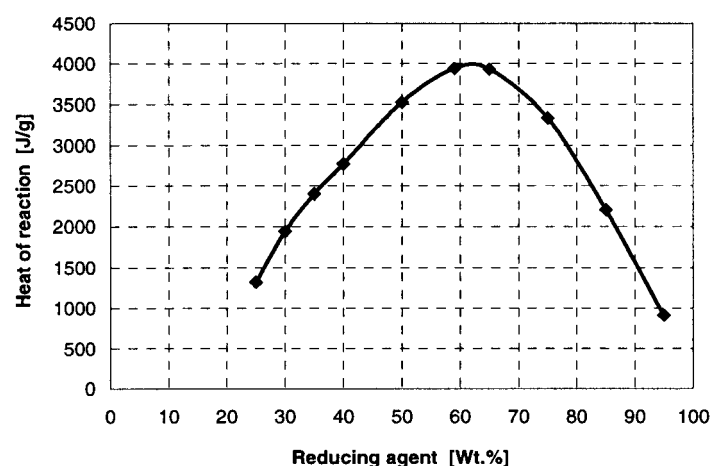


Figure 9. Heats of reaction of compositions based on the redox system titanium/potassium perchlorate with different oxygen balances.

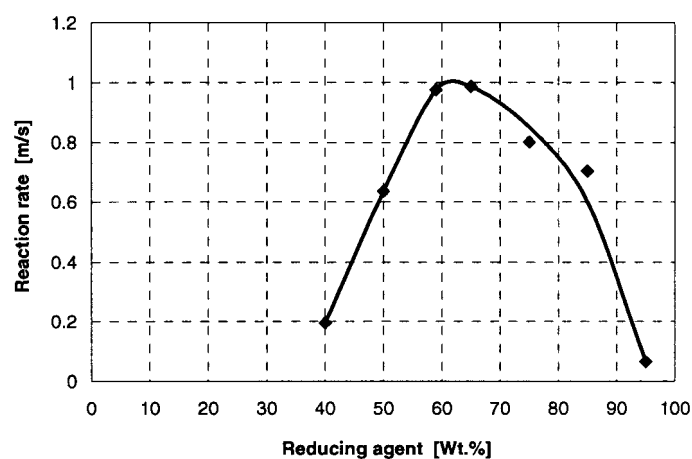


Figure 10. Reaction rates of compositions based on the redox system titanium/potassium perchlorate with different oxygen balances.

5.5 Mixing Process

The secret of maximizing the rate of reaction for a given pyrotechnic composition can be revealed in a single word – homogeneity [11]. Because of cost savings, pyrotechnic compositions are often mixed in dry state, passing the

composition several times through a sieve with defined mesh size. Due to the fact that a lot of pyrotechnic reactions are solid-solid state reactions, any operation that increases the degree of closeness of participating particles of a high-energy mixture results in an enhancement of reactivity. Reactivity, in general, refers to the rate – in grams or moles

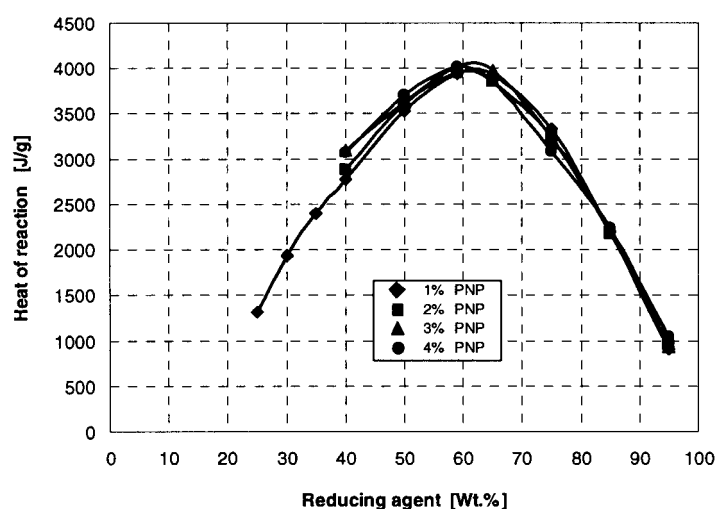


Figure 11. Heats of reaction of compositions of the redox system titanium/potassium perchlorate with different binder content [9].

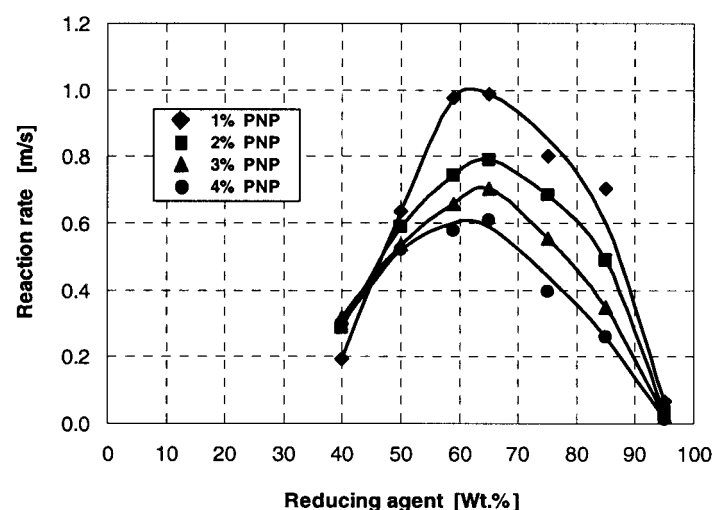


Figure 12. Reaction rates of compositions of the redox system titanium/potassium perchlorate with different binder content [9].

per second – at which initial materials are converted into products.

Figures 13 and 14 show very clearly the differences of a bad and a good mixing process with a composition containing boron and barium chromate [12]. As can be seen, many compositions are not in an ideal state of mixing.

6 Thermal Behavior of Pyrotechnic Compositions

The knowledge of the thermal behavior, the stability and the compatibility of pyrotechnic compositions is very important for safety and shelf life assessment. To investigate these important parameters, Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Thermal Gravimetry Analysis (TGA) coupled with Mass Spectroscopy (MS) [13, 14] and Heat Flow Calorimetry (HFC) are used. Figures 15–17 show the thermal behavior

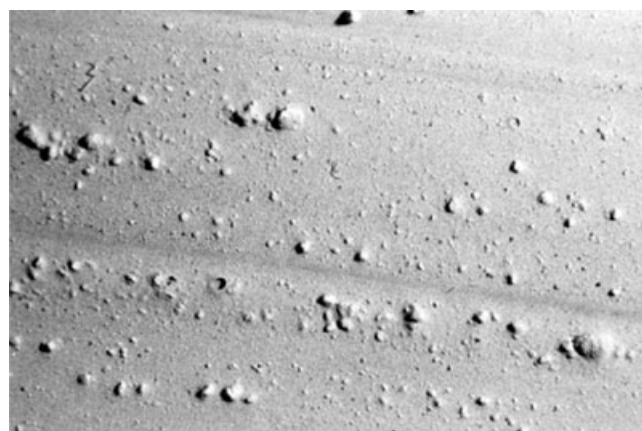


Figure 13. Composition containing boron and barium chromate mixed in a Turbula mixer [10].

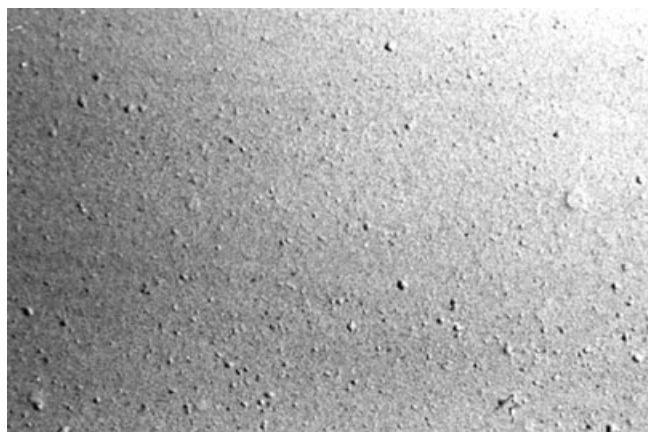


Figure 14. Composition containing boron and barium chromate mixed with an ultra sonic process [10].

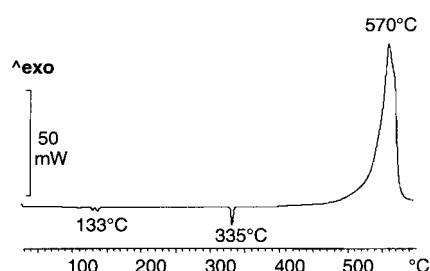


Figure 15. Thermal behaviour of a composition containing boron/potassium nitrate 20:80 wt%.

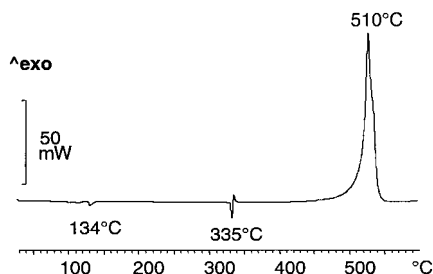


Figure 16. Thermal behaviour of a composition containing boron/potassium nitrate 30:70 wt%.

of a commonly used igniter composition for rocket propellant based on boron and potassium nitrate containing different amounts of ingredients. In a temperature range of 133 – 135 °C at all three compositions a first endothermal process can be observed due to a crystal state change of potassium nitrate (literature data 129 °C). At the second endothermal peak (335–336 °C) potassium nitrate melts (literature data 334 °C) and finally at a peak temperature in a range of 570 °C (composition containing 20 wt% boron) and 510 °C (composition containing 50 wt% boron) the exothermal redox reaction takes place. This data show that the temperature of the highest reaction rate is influenced by the oxygen balance of a pyrotechnic composition.

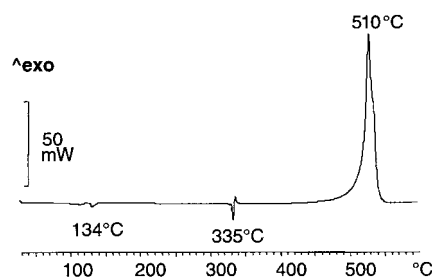


Figure 17. Thermal behaviour of a composition containing boron/potassium nitrate 50:50 wt%.

7 Conclusions

The influence of different parameters on the pyrotechnic redox reaction is demonstrated. Important parameters are the chosen reducing agent as well as the oxidizer, the particle size of the reducing agent, the oxygen balance and the binder and the binder content respectively.

As already mentioned, the distribution, the particle size and the morphology affect the sensitivity and the reactivity of pyrotechnic compositions. Today, much research is done on new pyrotechnic compositions containing nano structured metal oxides produced by sol-gel technology [15, 16, 17] and nanometer sized reactive metal powders. The goal of this research is to introduce nanometer sized metal powder into the pores of a nano structured metal oxide during the gelatinizing process. It was already found, that such pyrotechnic composites show a ten fold reduced sensitivity to mechanical influences and a two to three times increased performance (combustion rate) [18, 19].

8 References

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