

HTPB BONDED PYRO-ORGANIC SPECTRAL FLARES

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Abstract

Recent missiles equipped with modern seeker technology are able to distinguish between target and decoy flares evaluating spectroscopic emission. So, future flares must be adapted to the thermal and spectral emissivity of the platform to be protected.

One way to achieve such spectral flares consists in the application of so-called pyro-organic flares. The idea is to combine hydrocarbon combustion to meet spectral requirements and pyrotechnic mixtures to increase the radiation intensity.

In this study HTPB bonded samples with AP as oxidizer and different pyrotechnical mixtures were prepared and tested with regard to potential use as a spectral flare. Two thermite mixtures, and a titanium/graphite mixture compared to pure titanium and a titanium carbide mixture were used. The combustion experiments were performed once in free atmosphere at normal pressure, and even at reduced pressure levels. It can be shown that all investigated samples have good combustion properties as well as very good spectral properties even at reduced pressure.

The oxidation of the binder and post combustion with ambient air of the pyrotechnic reaction products lead to a second reaction phase resulting in a favorable β/α -ratio. Most promising mixtures for further investigations are with thermite as pyrotechnic component.

Introduction

IR decoy flares are used for the protection of various military platforms and even for civilian airplanes. Recent missiles equipped with modern seeker technology are able to distinguish between target and decoy flares evaluating spectroscopic emission. So future decoy flares have to be adapted to the thermal and spectral emissivity of the platform to be protected.

Conventional MTV decoy flares emit a continuous IR spectrum, whereas the exhaust plume of a jet gives distinct band signatures of carbon dioxide and water [1][2].

Hence new spectral flares need an emissivity, which is similar to hydrocarbon flames of jet fuels according to their spectral characteristic, and with highest possible radiation power. This means that the flare needs a similar intensity ratio in defined spectral regions (β/α -band ratio) as the jet plume of an engine. Here the β/α -band ratio is defined by the quotient of the wavelength-integrated emission power within the spectral regions of the two bands (α - and β -band) and should range from 2-10 for a spectral flare.

One approach for the design of new spectral flares is the pyro-organic flare, which is based on the combination of hydrocarbon combustion to design the desired spectrum with pyrotechnic mixtures to improve the performance.

The combustion of hydrocarbons leads to intensive CO_2 band in mid infrared region to strengthen the spectral β -band and with low continuum radiation in the near infrared to get favorable β/α -band ratios. The pyrotechnic composition ensures highest possible heat release and combustion temperature optimizing the radiation intensity of the decoy [2] [3] [4].

In former work thermite mixtures were successfully used as pyrotechnic components providing high radiation intensity by enhanced temperatures [2]. A further aspect of pyro-organic flares is the use of atmospheric oxygen for a consecutive reaction to generate additional radiation power. Classical thermites produce pure metals, that may react exothermically with oxygen to form the metal oxide, but due to the noblesse of this metals the energy release is limited and the formation of hot oxide particles is unfavorable to emission in α -band. So the idea was to replace the thermite by a metal + carbon combination that should

react in a first step at the surface of the solid pyrolant to its metal carbide, which is able to burn also exothermically with ambient air to form the metal oxide and the aspired CO_2 . A detailed study of various metal + carbon reactions showed, that titanium + graphite is the most suitable pyrotechnic combination [3]. Also the previously studied pyro-organic flare mixtures based on a benzoic acid (BA) / ammonium perchlorate (AP) mixture showed convincing properties regarding their combustion behavior as well as their radiation characteristics [2]. In addition to the combustion and radiation characteristics also the mechanical stability and the formability of a flare are important and must be taken into consideration. Thus, for the first time a polymeric binder was used as organic part in order to achieve better mechanical properties.

Experimental part

Similar to earlier studies [2] [3] pyro-organic flares were formulated on the base of metal/carbon and thermite mixtures as shown in Table 1. As pyrotechnic part Ti/C was used and compared with Ti and TiC. As thermite mixtures Al/CuO and Mg/CuO were selected. These ingredients were combined with HTPB as organic component and AP as oxidizer for the organic part.

As reference a commercial MTV was investigated considering this is not a spectral flare and therefore, the comparability is limited.

SAMPLE PREPARATION

The powders of the energetic components were pre-mixed in a mortar mill (when necessary) and then granulated. The further processing with HTPB and AP was performed in a planetary centrifugal vacuum mixer (Thinky-Mixer® [5]). Then the mixtures were poured into a mold and after curing they were cut into strands of $4 \times 4 \times 40 \text{ mm}^3$.

	Ti	TiC	Ti+C	Al/CuO	Mg/CuO
Titanium carbide		19,52			
Titanium powder, 2,5 μm	19,52				
Titanium + Graphite, granulated			19,52		
Aluminium/Copper(II)-oxide				19,52	
Magnesium/Copper(II)-oxide					19,52
AP	58,56	58,56	58,56	58,56	58,56
HTPB + Isocyanate + Catalyst	21,93	21,93	21,93	21,93	21,93

Table 1 Compositions of the investigated flare-mixtures

MEASUREMENT TECHNIQUES

High-speed digital camera

Movies were recorded with a color high-speed (HS) digital camera Motion Pro X3 from Redlake equipped with an active-pixel-CMOS sensor and a resolution of 1280×1024 pixels. Depending on the reaction speed a frame rate up to 8000 fps can be used. In the present study, movies were recorded with a rate of 50-200 fps and evaluated with the program AVICOR [6] to get the burning rates.

NIR-spectrometer

For non-intrusive determination of flame temperatures during the combustion process a fast scanning MMS-spectrometer (ZEISS MCS 611 PGS-NIR 2.2) with a wavelength ranging from 950 nm to 2.15 μm was applied to record emission spectra with scan rates up to 60 spectra per second. As optical entrance, a 600 μm glass fibre equipped with an SMA-connector is used. The spectra were calibrated for intensity per wavelength using a technical black body radiator. Temperatures were achieved from the recorded spectra by using ICT-BaM-code fitting theoretical spectra calculated from Planck's law by variation of temperature and of a wavelength-independent factor adjusting intensity using a chi-square function [7].

MIR-spectrometer

A fast scanning CVF-spectrograph built at ICT consisting of a rotating circular variable filter (CVF) wheel equipped with three interference filter segments was used to obtain MIR emission spectra. CVF continuously vary the transparency in the wavelength regions from 1500 to 2500 nm (InSb-detector) and 2450 to 14000 nm (InSb/HgCdTe-sandwich-detector). The system operates at a frequency of 100 cycles per second with a complete spectrum at each cycle. The optic structure consists in a 1 to 1 projection using ZnSe-lenses. For the calibration of the spectrometer system a black body radiator was used.

COMBUSTION EXPERIMENTS

The combustion experiments were performed in free atmosphere at normal pressure, and in an optical bomb at reduced pressures of 300, 400 and 500 hPa.

Free atmosphere

The strands were fixed on a ceramic plate and ignited at the top with a blow torch (1700-1800 K). The combustion was observed with the HS-video camera to receive characteristic flame pictures and regression rates. Since the seekers head acts by the IR-spectrum, the radiation in this spectral range is essential for a flare. So a fast filter wheel spectrometer was used to get IR-spectra. To determine the radiation temperatures, an NIR spectrometer and the BaM software were used [7].

Reduced pressure

The investigations under reduced pressure were carried out in the optical bomb specially modified for this measurement. For ignition a melting wire enforced by an ignitable booster paste [8] is used. At least the same measurement technique as it is used for the tests in free atmosphere is applied, but without the filter wheel-spectrometer.

Results and discussion

FREE ATMOSPHERE

All samples could easily be ignited and burned down completely with a brightly shining and voluminous flame (see Figure 1). Thereby the titanium-containing samples particularly the

one containing titanium and graphite (Figure 1d) show a higher tendency for particle formation. The thermite-containing samples (Figure 1e+f) show a bluish shimmer within the flame, which is caused by the thermally excited copper oxide (CuO).



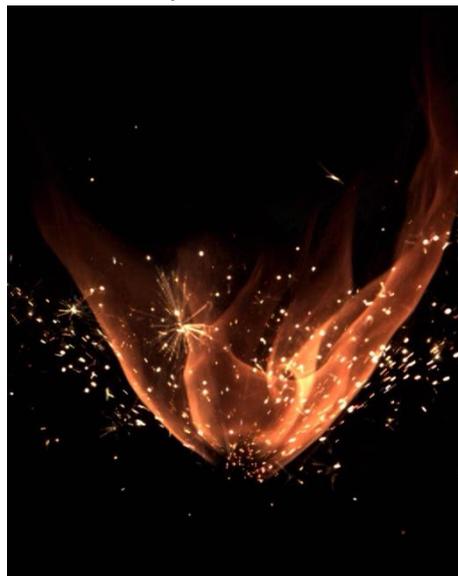
a) MTV



b) Ti + AP/HTPB



c) TiC + AP/HTPB



d) Ti/C + AP/HTPB



e) Al/CuO + AP/HTPB

f) Mg/CuO + AP/HTPB

Figure 1

Typical screenshots of the burning flare-mixtures b) Ti+AP/HTPB c) TiC+AP/HTPB d) Ti/C+AP/HTPB e) Al/CuO+AP/HTPB f) Mg/CuO+AP/HTPB in comparison to a) MTV

All examined samples show stable and highly reproducible flame propagation speeds between 3 and 10 mm/s, which are in the same order of magnitude as the measured reference MTV with (3 to 5 mm/s). Only the pure titanium sample burns much faster with about 10 to 19 mm/s (see Figure 2).

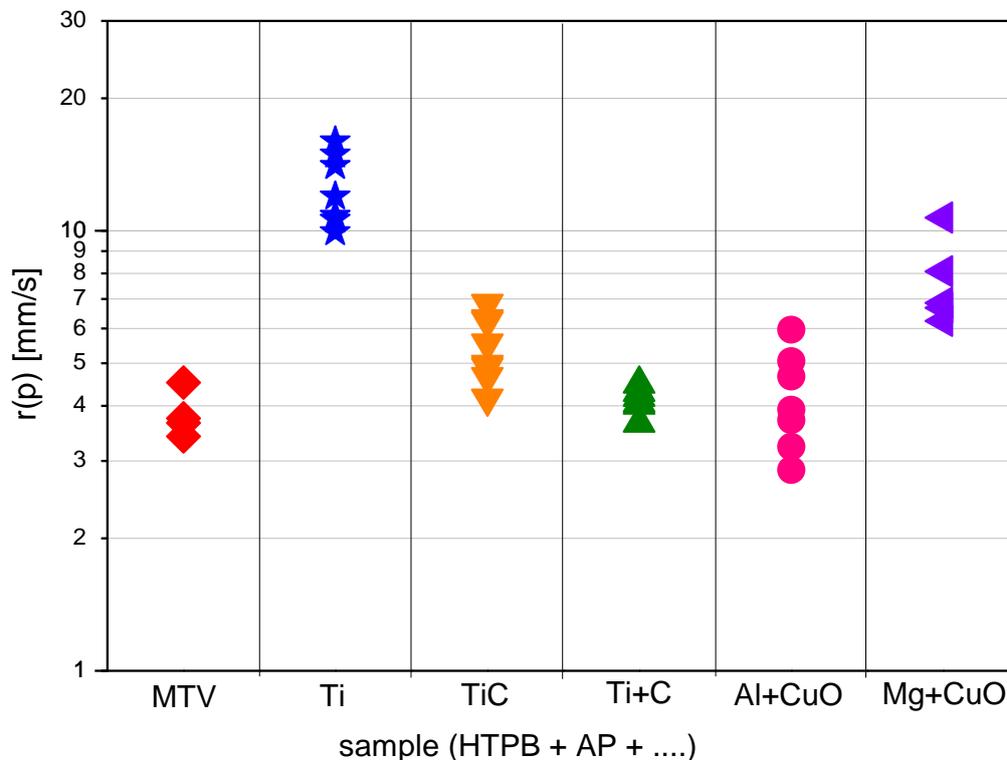


Figure 2

Flame propagation speed of the pyro-organic flares with different energetic components in comparison to MTV

The mean burning temperatures were determined by taking the average over all calculated temperatures of a spectra series. Due to the measurement setup, where the spectrometer

focus was always on a fixed point, the mean temperature is an average of the temperatures of various reaction zones. More interesting are the maximum temperatures, indicating the reaction phase with the highest temperature.

The mean radiation temperatures of all the investigated samples are significantly higher than those of MTV, which is only 1800-1900 K. The highest mean temperatures are reached by the two thermite mixtures with 2300 K for Al/CuO and 2400 K for Mg/CuO.

The maximum combustion temperatures of MTV are between 2250 and 2400 K, which is in the expected range for MTV. Also the maximum temperatures for the burning of pure titanium and titanium carbide are in the same order of magnitude (about 2300 K). With about 2500 K, the maximum temperatures of the titanium/graphite mixture are significantly higher. This indicates that besides of the exothermic formation of TiC ($\Delta_f H^\circ(\text{TiC}) = -184 \text{ kJ/mol}$) its consecutive reaction with atmospheric oxygen ($\Delta_f H^\circ(\text{TiO}_2) = -945 \text{ kJ/mol}$ and $\Delta_f H^\circ(\text{CO}_2) = -394 \text{ kJ/mol}$) is involved in the whole reaction process [9].

With values around or just above 2500 K, the two thermite mixtures show the highest maximum temperatures due to their high reaction enthalpies ($\Delta_f H^\circ(\text{Al/CuO}) = -402 \text{ kJ/mol}$ and $\Delta_f H^\circ(\text{Mg/CuO}) = -445 \text{ kJ/mol}$ [9]).

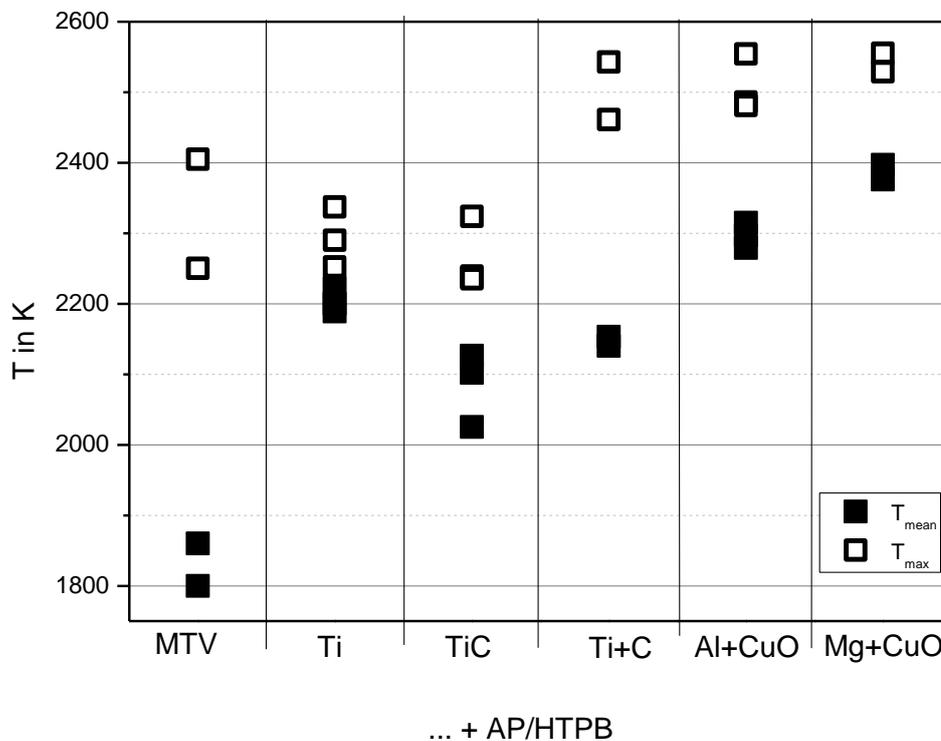


Figure 3 Mean and maximum radiation temperatures of the pyro-organic flares with different energetic components in comparison to MTV

Figure 4 and Figure 5 show typical IR emission spectra of the different flare-mixtures. Compared to MTV they show two significant differences. While MTV is only emitting continuum radiation all other mixtures show distinct bands of CO_2/CO , water and little HCl. Additionally and in contrast to MTV all investigated flare mixtures show two reaction stages. The first phase shows a more intensive continuum radiation, while in the second phase, the CO_2/CO -band rises significantly. So actually it seems that first the energetic component is reacting and afterwards mainly the binder with the oxidizer. As it will be shown, the products formed during the first step also react with the atmospheric oxygen - in case of carbon containing mixtures to CO_2/CO or to metal oxide, when they include metals. At least an increased CO_2 formation is reached resulting in an increase of β -band and an increase of β/α

ratio. Figure 6 shows the β/α ratio of the investigated flare-mixtures. They all show two reaction phases, where the β/α value for the first phase is with 0.5 to 1 in the same range as for MTV. In the second reaction phase values significantly above 1 are reached, which comes close to the characteristics of a real exhaust plume. The thermite mixtures tend to provide higher β/α ratio values; they even reach values up to 10.

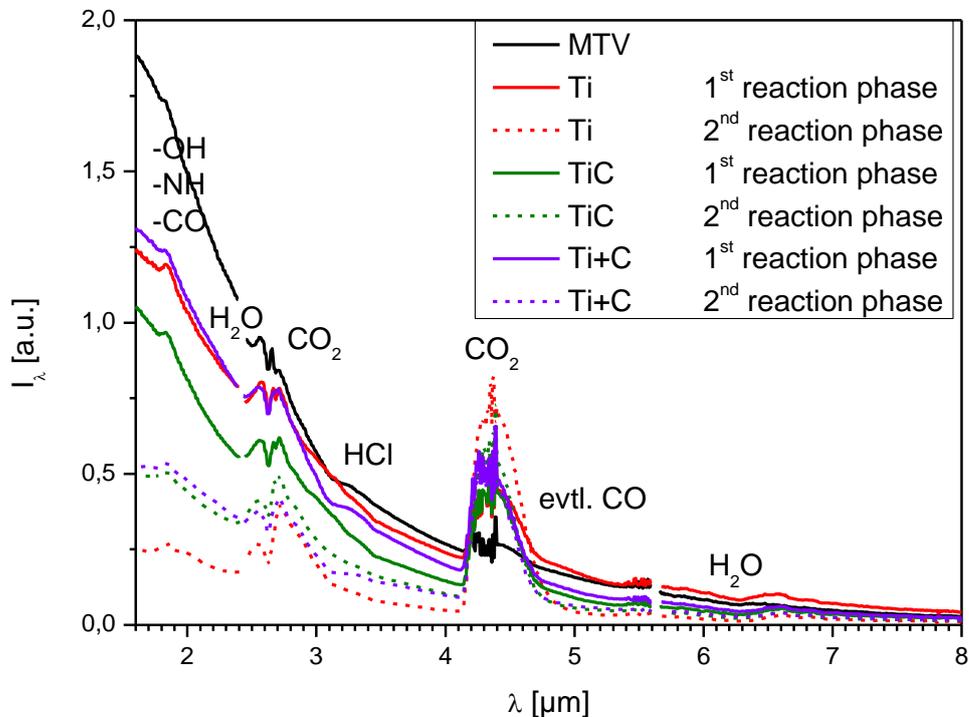


Figure 4 Typical IR-spectra of the first and second reaction phase of Ti-, TiC- and Ti + C- mixtures in comparison to MTV

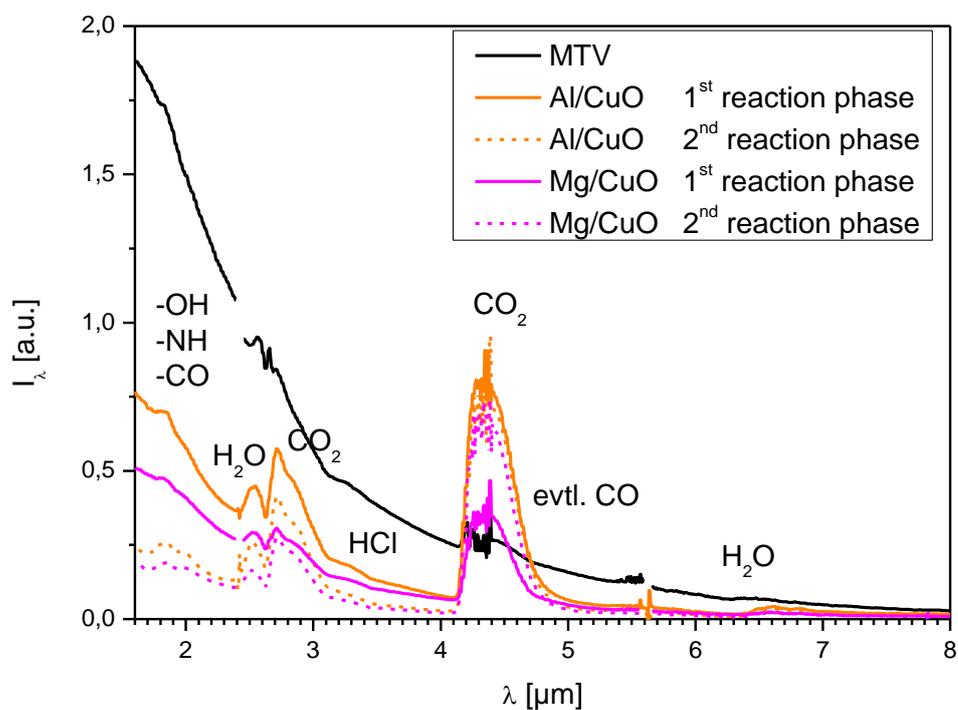


Figure 5 Typical IR-spectra of the first and second reaction phase of thermite mixtures (Al/CuO and Mg/CuO) in comparison to MTV

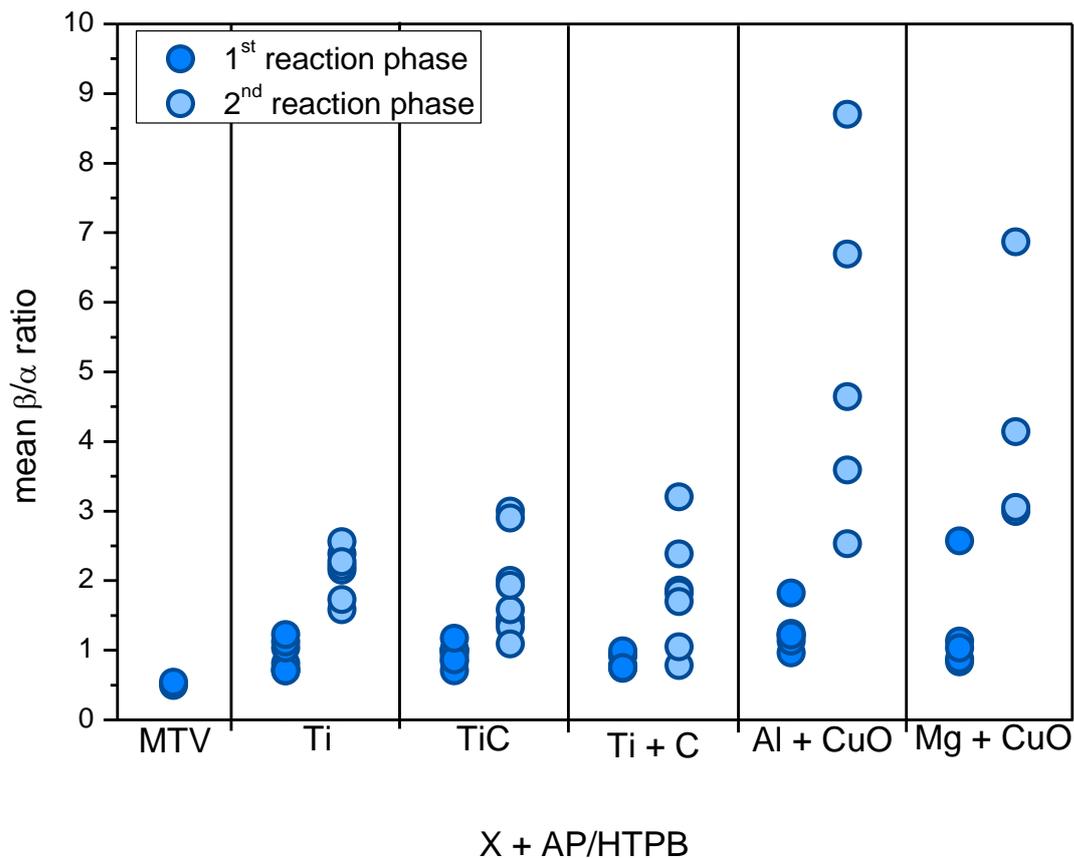


Figure 6 Mean β/α ratio of the different flare-mixtures in comparison to MTV

REDUCED PRESSURE

Under reduced pressure, all samples could be ignited at 500, 400 and 300 hPa and burned down completely, only the reference sample MTV could not be ignited below 400 hPa. In Figure 7 typical screenshots of the combustion are shown. The flames are not as distinctive and voluminous as under atmospheric pressure (comp. Figure 1), but the burning surface can clearly be seen in all cases. In general the combustion process is much slower than at atmospheric pressure and with decreasing pressure the whole process tends to become unstable, but reproducible regression speeds could be determined (see Figure 8). The sample containing titanium and carbon, which burned very well and quickly under atmospheric pressure, shows a remarkably low regression speed under reduced pressure. All other samples show an analogous behavior except for MTV, which seems to get faster. Due to the fact, that the flame quickly spreads over the entire surface of the MTV-sample and that no defined burning zone parallel to the cross-sectional area is formed, the determined regression speeds are too high.

All investigated samples show a decrease in the maximum radiation temperature under reduced pressure, except for MTV showing nearly the same maximum temperatures. This might be an indication that post combustion of reaction products with atmospheric oxygen plays an important role in reaction behavior of the pyro-organic flare mixtures.

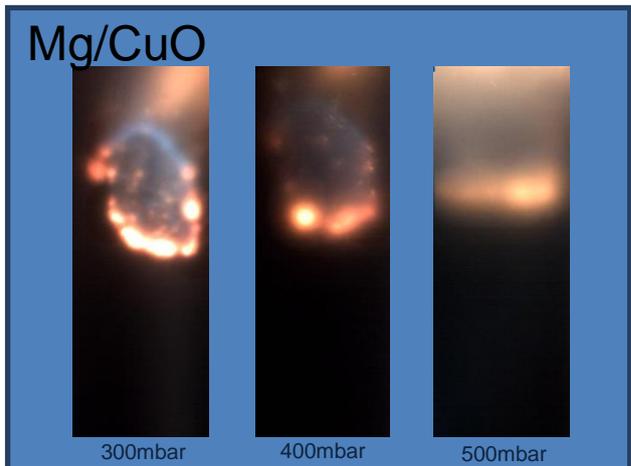
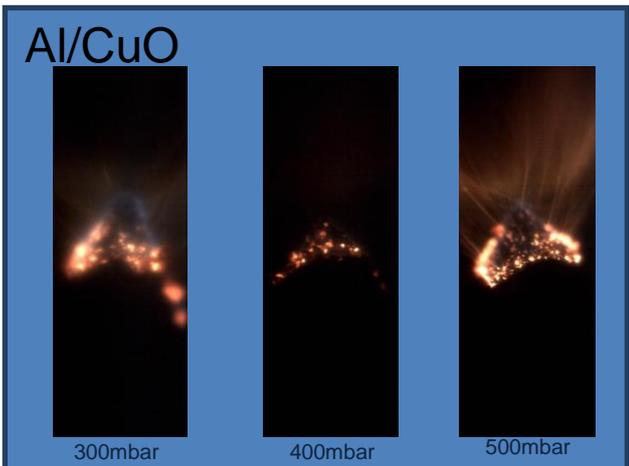
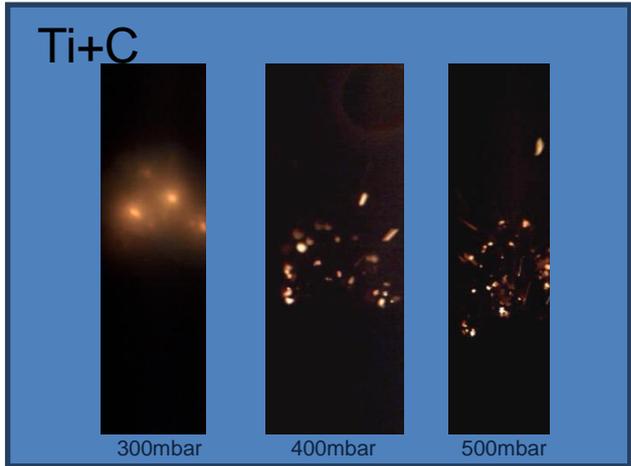
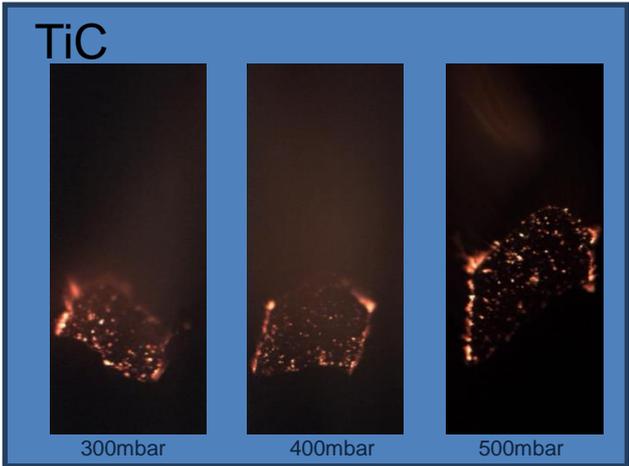
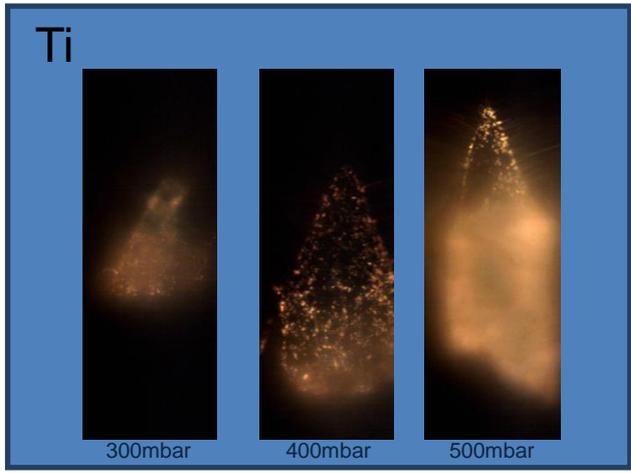
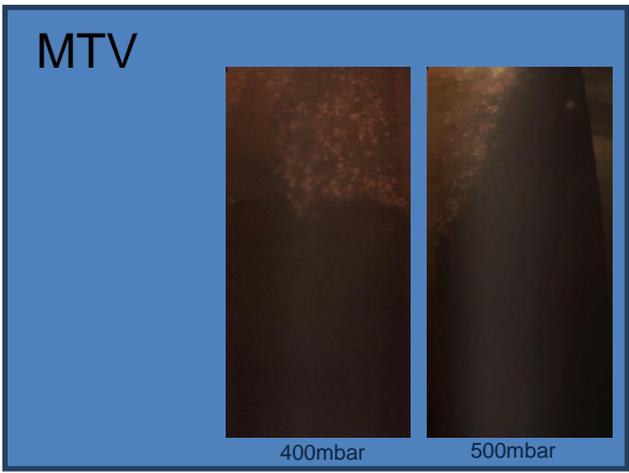


Figure 7

Typical screenshots of the burning flare-mixtures under reduced pressure: Ti+AP/HTPB, TiC+AP/HTPB, Ti/C+AP/HTPB, Al/CuO+AP/HTPB, Mg/CuO+AP/HTPB in comparison to MTV

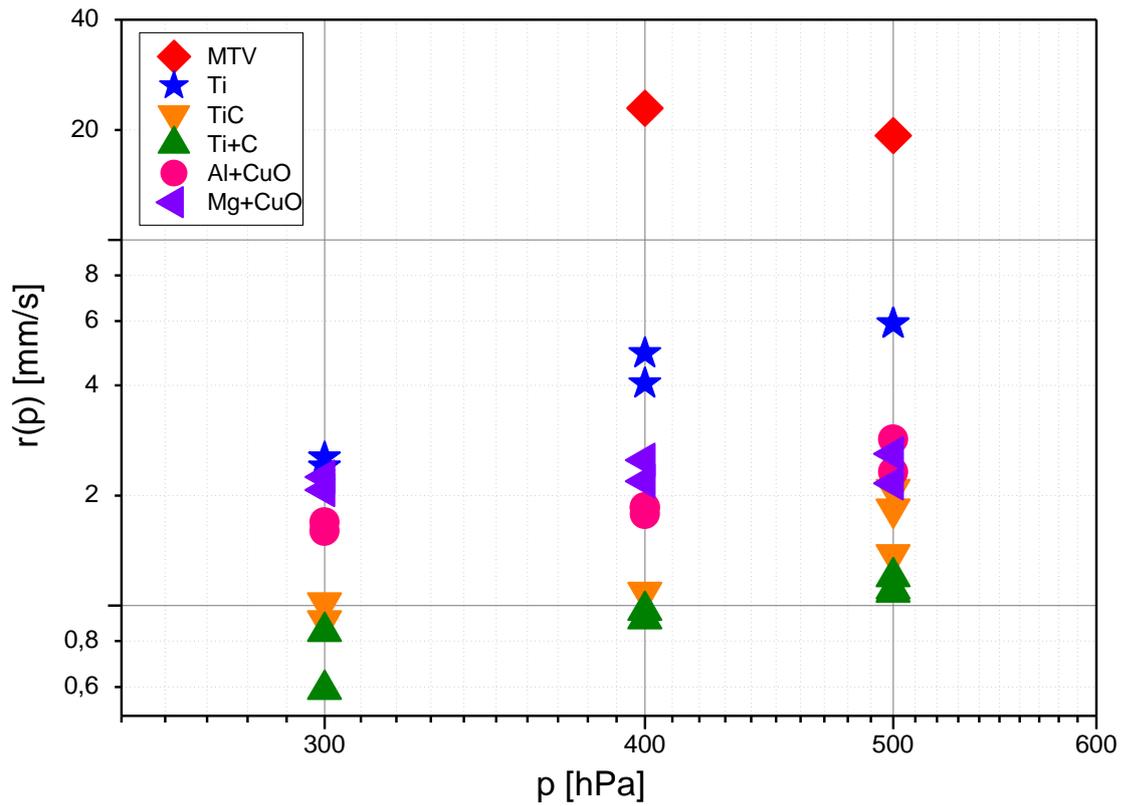


Figure 8 Flame propagation speed of the pyro-organic flares with different energetic components under reduced pressure in comparison to MTV

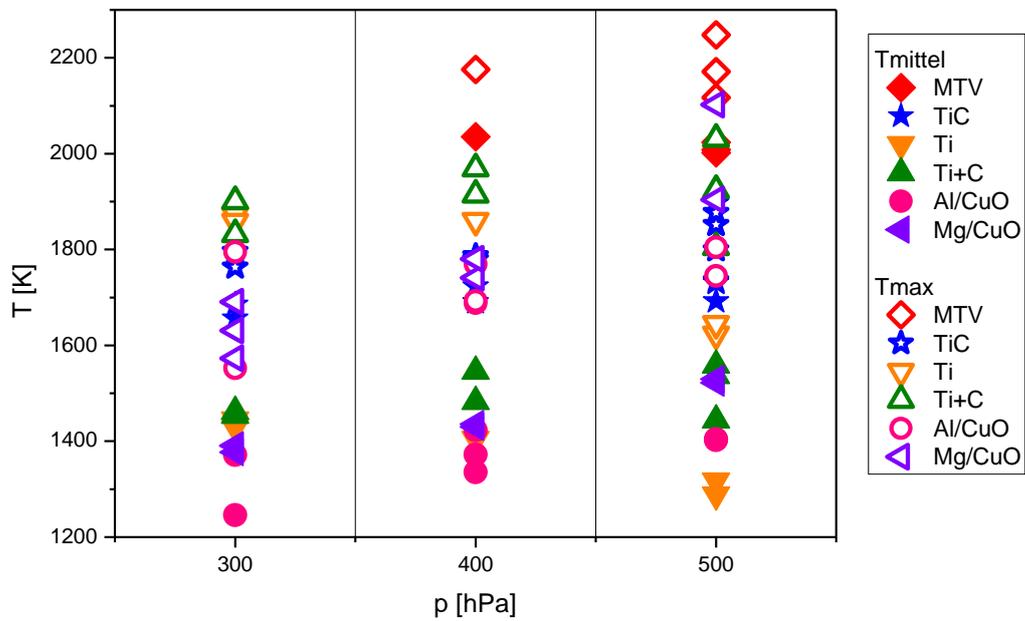


Figure 9 Mean and maximum radiation temperature under reduced pressure of the pyro-organic flares with different energetic components in comparison to MTV

Conclusion

Several HTPB-bonded pyro-organic flares were tested successfully. All investigated laboratory scaled samples show good combustion and radiation properties - even at reduced pressure - as well as very good spectral properties (Table 2). Very promising are the samples containing thermite mixtures which feature in highest temperatures and highest spectral band ratios. Ti+C mixture is also a very interesting energetic component which shall introduce additional CO₂ by post combustion in atmospheric air. At atmospheric conditions it shows, high radiation temperatures and a good β/α ratio. While titanium carbide has a similar favorable β/α ratio, but less radiation power it validates the energetic advantage of the Ti+C reaction. The mixture with pure titanium shows higher temperatures but tends to have a worse β/α ratio. At reduced pressure, the Ti+C mixture shows the best properties. All mixtures react reliably even at low pressure, but with a sufficient oxygen supply after-reactions are possible, providing additional energy and/or CO₂ for a favorable β/α ratio.

	MTV	Ti	TiC	Ti+C	Al/CuO	Mg/CuO
Atmospheric pressure						
Regression rate [mm/s]	4	15	5	4	4	7
Max. radiation temp [K]	2300	2300	2250	2500	2500	2550
β/α -ratio	0.5	1-3	1-4	1-4	1.5-12	1.5-12
Reduced pressure						
Regression rate [mm/s]						
300 hPa	--	2.5	1	0.7	1.6	2.1
400 hPa	-	4.5	1	1	1.8	2.2
500 hPa	-	5.9	1.8	1.1	2.5	2.3
Max. radiation temp [K]						
300 hPa		1780	1560	1870	1700	1650
400 hPa	2150	1780	1740	1930	1710	1760
500 hPa	2150	1850	1870	1910	1870	2000

Table 2 Summary of properties of investigated samples

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