SPECTROSCOPY OF PYROTECHNIC TRACER COMPOSITIONS UNDER DIFFERENT PRESSURE

V. Weiser*, S. Knapp, E. Roth, A. Raab, S. Kelzenberg Fraunhofer Institut für Chemische Technologie ICT, Germany *volker.weiser@ict.fraunhofer.de

D. Cegiel Rheinmetall Waffe Munition GmbH, Trittau, Germany

Dedicated to Beat Berger (1949-2014)

Abstract

The interior and exterior ballistics of tracer gun ammunition have a significant influence on the function of the tracer. In this study the burning behaviour in correlation to the tracer composition and the pressure is examined in the ICT optical bomb in air at 15 kPa to 100 kPa and 100 kPa nitrogen. Three tracer compositions with various oxygen balances were investigated using high speed photography and UV/Vis/NIR-spectrometry. The results indicate a strong correlation of sub-atmospheric pressure and the oxygen balance of the tracer composition with respect to ignition behaviour, burning temperature and luminance which is in a well agreement to ballistic firing test.

Introduction

The burning behaviour and photometric luminance of tracer gun ammunition is significantly influenced by the interior and exterior ballistics due to the abrupt pressure transition from high to sub-atmospheric pressure while leaving the gun barrel that can induce an extinction of the trace. During the flight of the bullet the tracer burns inside the slipstream that causes drastic low-pressure and prevents air to enter the tracer flame and avoids an intensive after burning process.

Objective of this work is to provide a relationship between the tracers function in real firing and the spectroscopic results in the ICT optical bomb. If this is possible, the spectroscopy of pyrotechnic tracer compositions in the ICT optical bomb can be an expressive and economy-priced development tool in future.

Experimentals

Samples

0.5 g tracer composition (s. Table 1) and 0.2 g igniter composition based on barium peroxide, magnesium und aluminium are pressed with 195 MPa into cylindrical pellets with 8 mm diameter and 7 mm height.

Table 1 summarises the three compositions, adiabatic temperatures, total burning time and the over-all photometric properties.

The burning time, candle power, wavelength and colour saturation of the three different samples are photometrical measurements performed by a calibrated colorimeter (type C3330, measuring head CHS 60; company LMT, Berlin, Germany). The measuring head contains silicon photo elements with spectral sensitivity matched exactly on the "CIE 1931 XYZ color space" [1]. With this measurement setup the CIE values are directly measured with 120 measurements per second.

| Composition | LS1 | LS2 | LS3 |
|---------------------------------|---------|---------|---------|
| Strontium nitrate | 39 | 33 | 46 |
| Magnesium | 44 | 51 | 40 |
| Additive | 17 | 16 | 14 |
| Oxygen balance | -34 | -41 | -27 |
| Adiabatic temperature | 1987 K | 1951 K | 2186 K |
| Burning time ¹⁾ | 3.3 s | 1.3 s | 1.6 s |
| Candle power ¹⁾ | 2.6 kcd | 9.6 kcd | 5.4 kcd |
| Wavelength ¹⁾ | 602 nm | 598 nm | 598 nm |
| Colour saturation ¹⁾ | 85 % | 81 % | 78 % |

¹⁾ Photometric measurement by calibrated colorimeter (type C3330, measuring head CHS 60; company LMT, Berlin, Germany)

Table 1Sample composition

Thermodynamic Considerations

Due to their different composition the three mixtures differ in their adiabatic combustion temperature.

Table 1 also compares these values calculated with the ICT-Thermodynamic Code [2] for isobaric conditions of p = 100 kPa. LS3 marked as the mixture with the highest oxygen balance also features in the highest temperature of nearly 2200 K. LS1 and LS2 do not differ significantly with values of 1987 K and 1951 K.

The negative oxygen balance implies that all mixtures are enabled for post-combustion with atmospheric air. Depending on the available amount of air the combustion temperature can increase as depicted in Figure 1 which shows the adiabatic combustion temperatures of all samples as a function of the available amount of air at 10 and 100 kPa also calculated using ICT-Thermodynamic Code [2]. In all cases the maximal achievable combustion temperature increases for several hundred Kelvin to about 2700 K for 10 kPa and 3050 K for 100 kPa independent to the composition. But due to the oxygen balance the maximum temperature is at different air concentrations. Remarkably is the high difference of the absolute values for 10 and

100 kPa. This correlates to a larger MgO content at the expense of lower Mg gas content at 100 kPa.

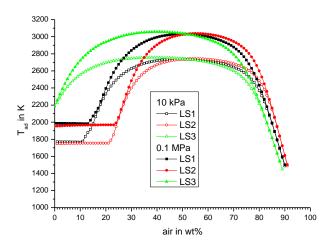


Figure 1 Adiabatic combustion temperature of all samples as function of available air at 10 kPa and 0.1 MPa.

Set-Up

The tests were performed inside the ICT optical bomb that allows to work under reduced air pressure of 10 to 100 kPa [3]. The cylindrical samples were ignited using a melting wire fixed at the upper surface with about 100 mg Mg/BaO₂ igniter paste. All samples were investigated at 15, 20, 25, 50 and 100 kPa in air and at 100 kPa in nitrogen.

Measuring techniques

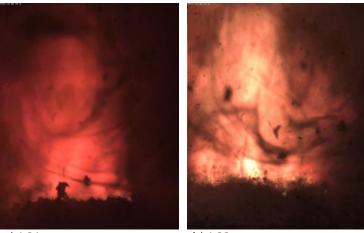
To observe the ignition behaviour and to characterize the reaction zone, a digital colour highspeed video camera (Motion Pro X3) was used. Frame rates from 100 to 1000 fps were sufficient and enabled to measure the linear burning rate applying the technique described in [4].

Temperatures were measured using a Plane Grating Spectrometer PGS-NIR 2.2 (Carl ZEISS GmbH) in the wavelength range from 1 to 2.17 μ m. Under the applied experimental conditions the field of view was about 10 mm in diameter. This allowed the determination of time history of overall reaction temperatures close to the burning surface. The NIR emission spectra were evaluated with the ICT-BaM code. The procedure compares each experimental spectrum with a calculated one using a least-squares-fit-method to determine the temperature (comp. [5]). For the recent application the continuum radiation from 1.2 to 2.1 μ m was regarded as grey-body emission.

Results and Discussion

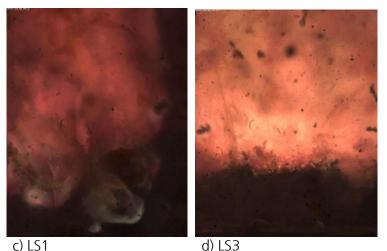
Burning Behaviour

At 100 kPa all samples ignited and burnt stable in air and nitrogen developing a red flame characteristic for strontium. Figure 2 compares LS1 and LS3. The flame of the better balanced mixture LS3 emits more intensive in both atmospheres. The combustion of the less stoichiometric mixture LS1 in air shows ejected particles burning with blue and green flamelets outside the visible flame which are characteristic for gaseous MgO emission and indicate post-combustion of magnesium particles in air (Figure 2c).



a) LS1

b) LS3





At reduced air pressure of 25 kPa all samples ignited and burnt down stable.

Figure 3 shows pictures of the ignition (green flame corona) and combustion (red corona) under these conditions. LS2 and LS3 burnt also at 20 kPa. At this pressure the less stoichiometric mixture LS2 featured in a less luminous flame. Below, at 15 kPa, only the igniter composition worked but could not induce a stable combustion of the tracer composition that extinguish after about 500 ms (Figure 3c). Although LS1 burnt stable at 25 kPa the combustion was characterized by an intermitting, strongly flickering flame (see also Figure 4b)



a) Combuston of LS2 at 20 kPa



b) Combustion of LS3 at 20 kPa



c) Ignition and extinctions of LS3 at 15 kPa

Figure 3 Ignition and combustion at low pressure in air.

In all cases when the combustion of the tracer composition could be induced a constant regression rate developed. This could be discovered from the regression images in Figure 4. The pictures were produced by analysing the movies from the high-speed camera using the procedure introduced in Ref. [1]. Each vertical line represents the local intensity distribution of a consecutive video picture. Time line goes to the right. Light colour represents the vertical position of emitting flame. Clearly the position of the pyrolant surface and its regression can be realized. In Figure 4a, the combustion stops after some millimetres when the igniter composition burnt out. Figure 4b illustrates the flickering flame after ignition. This video was recorded with a reduced frame rate. Figure 4c+d present stable combustion of LS2 at 25 kPa and LS3 at 25 kPa.

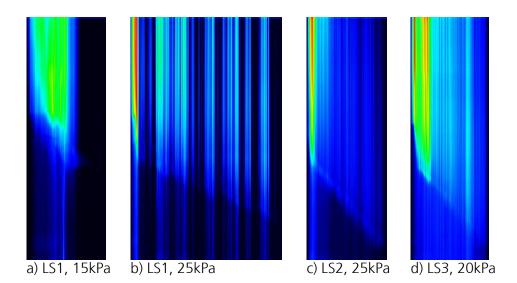


Figure 4 Regression images; a) extinction of LS1 at 15 kPa; b) intermitting combustion of LS1 at 25 kPa; combustion at 20 kPa of c) LS2 and d) LS3.

The regression rates are measured by analysing these images and the results are summarized in Figure 5 as a function of pressure. It also contains the values achieved at 100 kPa nitrogen. As with most condensed energetic materials the regression rates increase with pressure for all samples. The reproducibility of the values is good. The ranking is in a good agreement with the photometric measured burning times in

Table 1. LS1 is the slowest burning composition. At sub-atmospheric pressure LS2 and LS3 burn comparably fast. The more balanced composition LS3 burns faster at the lowest pressure. But at atmospheric pressure LS2 burns about 3 mm/s faster. At 100 kPa nitrogen the ranking is equal but the burning rates are some mm/s slower as in air.

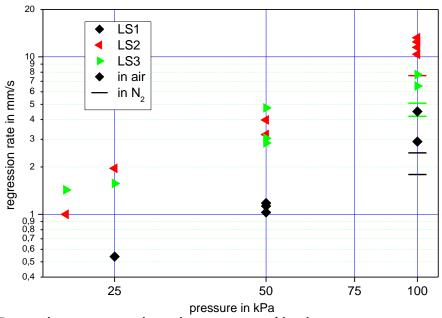


Figure 5 Regression rates at various air pressures and in nitrogen.

Spectra series

Time resolved emission spectra are best gualified to evaluate the emission and combustion behaviour of the samples. Figure 6 presents waterfall plots of the ignition and combustion period of LS1 and LS3 at several pressure levels. Time scale runs from the rear to the front. In Figure 6a and d a non successful ignition of the samples LS1 and LS3 at 15 kPa is shown. Obviously the near infrared emission of BaO indicates a proper function of the igniter composition but the transmission to the tracer composition did not operate. This is different on the other plots of Figure 6. Here the igniter composition works identical but then emission peaks in the orange to red spectral range indicate hot strontium oxide burning from the tracer composition. Assuming that the intensity of the IR-igniter emission is more or less independent of pressure this emission may be used to quantify the tracer luminescence. In Figure 6b ignition of LS1 performed at a minimum pressure of 25 kPa but the low red spectrum indicates flickering and unstable combustion behaviour. This improves drastically in Figure 6c at 50 kPa. In contrast the better balanced tracer composition of LS3 burns much more intensive even at the lower pressure of 20 kPa in Figure 6e. The oxygen balance of this mixture is good enough also to burn at 100 kPa nitrogen, but with lower red emission. An intensive continuum spectra in NIR indicate a high fraction of condensed materials probably particles of only partially burnt material.

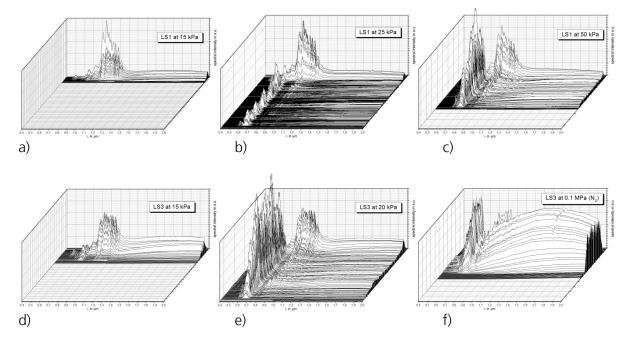


Figure 6 Waterfall plots of spectra series of LS1 at a) 15 kPa (extinction), b) 25 kPa, c) 50 kPa and of LS3 at d) 15 kPa, e) 20 kPa (air), f) 0.1 MPa (N_2)

Temperatures

Between 1.1 µm and 2.1 µm all spectra feature in a continuum spectrum and do not exhibit any significant line spectra. Using ICT-BaM this continuum could be fit in nearly perfect agreement with Planck's law assuming a constant emissivity to determine the grey emission temperature. In Figure 7 the achieved temperature histories of LS2 are plotted at various air pressure levels and in 100 kPa nitrogen. All profiles start with a temperature peak. This points to the burning of the igniter composition. When the ignition was successful the profile goes over to a period with more or less constant temperature which can be assigned to the combustion of the tracer composition. According to the regression rates in Figure 5 the burning times increases with decreasing pressure. This is also in a good agreement with

Table 1.

In the case of extinction (15 kPa) the temperature decreases steadily after ignition. Obviously the tracer temperature increases with pressure. The lowest temperature is determined in nitrogen atmosphere. This indicates co-combustion with available air. Interestingly the temperature of the igniter composition is correlated to the atmosphere in a similar way.

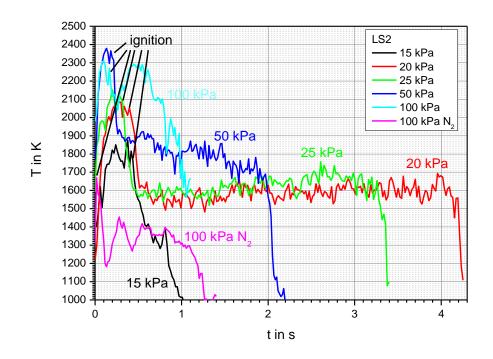


Figure 7 Temperature history of LS2 at different pressure levels in air and at 0.1 MPa in N₂.

Figure 8 compares the temperature histories of the different samples at a) 20 kPa and b) 25 kPa. At both pressure levels the function of the igniter composition (peak between t = 0 and 0.5 s) works identical. At 25 kPa its peak temperature is about 50 K higher. This is enough to ignite all samples. At 20 kPa sample LS1 starts to burn but cannot built a stable combustion and extinguishes by cooling. Although it burns completely at 25 kPa its temperature history shows strong temperature fluctuations which indicate intermittent combustion. The long burning time of LS1 at 25 kPa correlates with the low regression rate measured in Figure 5. LS3 burns with the highest temperature between 1550 to 1800 K. LS2 burns about 100 K lower, at least at 25 kPa with similar temperature as LS1. But in average LS2 seems to burn with slightly higher temperature as LS1.

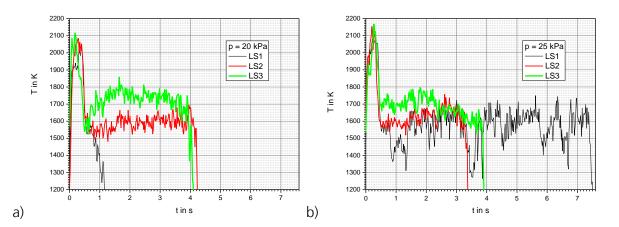


Figure 8 Temperature history of the samples at a) 20 kPa and b) 25 kPa.

The mean temperatures and temperature ranges are summarized and compared in Figure 9 at various pressure levels and also in 100 kPa nitrogen atmosphere. In general, temperature increases with pressure. The best balanced mixture LS3 burns with the highest temperature in all cases. The temperatures of LS1 and LS2 are in comparable dimension. But at least in average LS2 is slightly higher despite to its lower oxygen balance. This should be explained by lower heat losses due to its higher regression rate equal to a faster reaction rate.

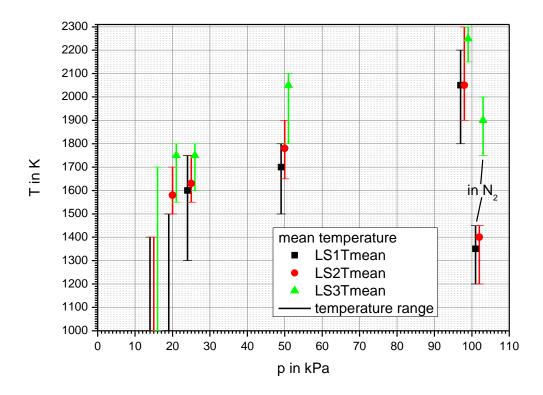


Figure 9 Summary of mean temperature and temperature range of burning tracer compositions at various air pressures and in nitrogen. (no mean temperatures, if temperature decreases continuously after ignition)

Conclusions

At sub-atmospheric pressure the ignitability of a tracer composition is inversely correlated with their oxygen balance but this can be counteracted by the reaction rate. An important indication is the combustion temperature that can easily and non-intrusively be measured by evaluating the spectral emission. This also indicates the luminance of the tracer at various pressure conditions and enables to distinguish the transmission phenomena from the igniter to the tracer composition.

A correlation between tracer composition, pressure and burning behaviour (visual and spectroscopic analysis, burning rate and temperature) can be pointed out. A relationship between the tracers function in real firing and the spectroscopic results in the ICT optical bomb is given. For future tracer development, spectroscopy of pyrotechnic tracer compositions in the ICT optical bomb can be an expressive and relatively economy-priced development tool.

References

- [1] CIE Technical Report Colorimetry, CIE 15:2004, 3rd Ed.
- [2] F. Volk, H. Bathelt, User's Manual for the ICT-Thermodynamic Code, Volume 1, ICT-Bericht 14/88, T/RF 11/I 0001/I 1100, Pfinztal, Germany, 1988.
- [3] V. Weiser, E. Roth, S. Knapp, A. Raab, E.-C. Koch, Combustion Behaviour of MTH under Reduced Atmospheric Pressure, 42nd International Annual Conference of the Fraunhofer ICT, June 28 - July 01, 2011, Karlsruhe, Germany, 91-(1-10)
- [4] V. Weiser, H. Ebeling, M. Weindel, W. Eckl, T. Klahn, Non-intrusive burning rate measurement under pressure by evaluation of video data, 35th International Annual Conference of ICT, June 29-July 2, 2004, Karlsruhe, pp. 158-(1-6)
- [5] V. Weiser, N. Eisenreich, Fast Emission Spectroscopy for a Better Understanding of Pyrotechnic Combustion Behaviour, Propellants, Explos., Pyrotech., Vol. 30, p. 67, 2000.