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Metal-Fluorocarbon Pyrolants. XIV: High Density-High Performance Decoy Flare Compositions Based on Ytterbium/Polytetrafluoroethylene/Viton®

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In Memory of Dr. Uwe Krone

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Abstract. Three pyrotechnic compositions based on ytterbium /polytetrafluoroethylene/Viton® (**YTV**) 77/18/5, 82/13/5 and 87/8/5 wt.-% were compared to a baseline magnesium /polytetrafluoroethylene/Viton® (**MTV**) 60/35/5 wt.-% composition. **YTV** though energetically inferior to **MTV** both gravimetrically and volumetrically exhibit a radiance L_λ ($W{\cdot}sr^{-1}{\cdot}cm^{-2}$) superior to **MTV** in the important beta-band (λ = 3.5–4.6 µm). This is assumed to be due to the selective emissivity of Yb_2O_3 which is formed in the afterburning zone of YTV. The emissivity of Yb_2O_3 is 7–10 times higher than that of MgO in the same spectral range. Due to the high density of ytterbium and the formulations based thereon **YTV** are promising candidates for autophagous nose cones for kinematic blackbody flares.

Introduction

Expendable decoy flares protect aerial platforms against infrared guided weapon systems such as *surface-to-air* or *air-to-air* missiles.[1] Decoy flares applied against first and second generation missile seekers comprise pyrotechnic compositions based on magnesium and fluorocarbons such as magnesium/polytetrafluoroethylene(Teflon®)/ hexafluoropropenevinylidene fluoride-copolymer (Viton®) (MTV) and magnesium/poly(carbon monofluoride)/Viton® (MPV). Upon combustion these payloads yield an intense black body type signature.[2]

In order to be effective flares must have a fast rise time (d*I*/d*t*) and must separate at a suitable rate (d*x*/d*t*) from the platform to be protected. A fast rise time can be achieved with the above compositions without problems. However, a proper separation of a burning decoy pellet requires either aerodynamic stabilization of the flare grain by fins or winglets and/or a shift of the center of gravity of the flare payload to the front in order to maintain a stable flight lowering the drag. Hitherto flare designers have used inert steel or tungsten ballasts to shift the center of gravity to the front as is done in the MJU-57 A/B flare.[3] Recently it has been proposed by *Hahma* to apply high density payloads based on Zr/W/PbO_2/Viton®.[4] However, the spectral efficiency of these payloads is very low per unit weight. Even though nose cones based on this material are autophagous and reduce the probability of damage to the aircraft due to debris in the air, they contribute only up to 10 % of the total energy radiated in an ideally weighted flare. As an inert nose cone contributes no radiated energy, high density combustible compositions for the nose cone with a similar performance to MTV would be highly desirable.

Recently it has been found by *Koch* et al. that ytterbium metal undergoes vapor phase combustion similarly to magnesium.[5] The combustion temperatures of the formulations based on Yb/PTFE are similar to those of Mg/PTFE.[5b] As powdered ytterbium costs about the same as special grades of zirconium, an investigation of its use in practical applications is reasonable. Considering these findings and the higher density of ytterbium (ρ(Yb) = 6.965 $g{\cdot}cm^{-3}$ vs. (ρ(Mg) = 1.738 $g{\cdot}cm^{-3}$) we decided to explore the potential of ytterbium as a fuel in metal/fluorocarbon based decoy flare compositions.

Results and Discussion

The combustion enthalpy of MTV flares, Δ_cH ($J{\cdot}g^{-1}$) is the sum of both the primary fluorination reaction enthalpy, $q_{anaerobic}$, and the secondary afterburn enthalpy of magnesium with the atmospheric oxygen, $q_{aerobic}$, according to the following simplified equations:

$$a\ Mg_{(s)} + b\ –(C_2F_4)– + c\ –(C_{10}F_{13}H_7)– \rightarrow d\ MgF_{2(s)} + a–d\ Mg_{(g)} + e\ C_{(soot)} + f\ H_2 + q_{anaerobic}, \quad (1)$$

$$a–d\ Mg_{(g)} + e\ C_{(soot)} + f\ H_2 \xrightarrow{air} a–d\ MgO_{(s)} + e\ CO_2 + f\ H_2O_{(g)} + q_{aerobic}.^{[6a]} \quad (2)$$

Δ_cH is a key figure in describing the performance of a payload as it is directly related to the spectral efficiency, E_λ /$J{\cdot}g^{-1}{\cdot}sr^{-1}$ of a composition via the following equation

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$$E_\lambda = (4\pi)^{-1} \cdot \Delta_c H \cdot F_\lambda\,(T) \qquad (3)$$

F_λ is the fraction of radiation emitted in the band of interest accounting for both the temperature and the temperature dependent emissivity ε_λ of the combustion products.

The radiance L_λ /W·sr^{-1}·cm^{-2} is the product of mass consumption rate, dm/dt /g·s^{-1}·cm^{-2} and the spectral efficiency within the band of interest, E_λ /J·g^{-1}·sr^{-1}.

$$L_\lambda = E_\lambda \cdot \mathrm{d}m/\mathrm{d}t \qquad (4)$$

The composition, the experimental and theoretical maximum density (TMD) of a baseline flare composition Mg/PTFE/Viton® (**MTV**) and three ytterbium based formulations (**YTV**) are given in Table 1. The stoichiometry of the ytterbium based compositions was adjusted to a similar volumetric metal/fluorocarbon ratio as the baseline **MTV** formulation. Preliminary experiments have shown that pyrolants at these stoichiometries yield extended combustion plumes required to obtain a high radiant intensity.[5a,6a]

Table 1. Composition by weight and *volume*, experimental and *TMD* of baseline **MTV** (60/35/5) and three experimental ytterbium based formulations (**YTV**).

Composition	Density Exp. *TMD* /g·cm^{-3}	Mg /wt.-% */vol-%*	Yb /wt.-% */vol-%*	PTFE /wt.-% */vol-%*	Viton® /wt.-% */vol-%*
MTV	1.790	60	–	35	5
	1.832	*67.4*	–	*27.3*	*5.3*
YTV-1	4.690	–	77	18	5
	4.771	–	*52.7*	*34.4*	*12.9*
YTV-2	4.990	–	82	13	5
	5.082		*59.8*	*26.4*	*13.7*
YTV-3	5.230	–	87	8	5
	5.307		*67.9*	*17.4*	*14.7*

The gravimetric and volumetric reaction energies for MTV have been calculated based on the Equation (1) and Equation (2) and are displayed in Table 2. Likewise for the YTV formulations the reaction energies have been calculated based on the assumed simplified Equation (5) and Equation (6) given below:

Table 2. Gravimetric and volumetric anaerobic and aerobic reaction energies of baseline **MTV** (60/35/5) and three **YTV** formulations.

Composition	Q_{anerobic} /kJ·g^{-1}	Q_{aerobic} /kJ·g^{-1}	Q_{anerobic} /kJ·cm^{-3}	Q_{aerobic} /kJ·cm^{-3}	Q_{total} /kJ·cm^{-3}
MTV	–3.14	–16.00	–5.62	–28.64	–34.26
YTV-1	–2.30	–3.63	–10.79	–17.02	–27.81
YTV-2	–1.58	–4.24	–7.88	–21.16	–29.04
YTV-3	–0.87	–4.85	–4.63	–25.80	–30.43

$$a\ \mathrm{Yb_{(s)}} + b\ –(\mathrm{C_2F_4})– + c\ –(\mathrm{C_{10}F_{13}H_7})– \rightarrow d\ \mathrm{YbF_{3(s)}} + e\ \mathrm{YbC_{2(s)}} + a–d–e\ \mathrm{Yb_{(g)}} + g\ \mathrm{H_2} + q_{\mathrm{anaerobic}} \qquad (5)$$

$$e\ \mathrm{YbC_{2(s)}} + a–d–e\ \mathrm{Yb_{(g)}} + g\ \mathrm{H_2} \xrightarrow{\mathrm{air}} (a–d)/2\ \mathrm{Yb_2O_{3(s)}} + 2e\ \mathrm{CO_2} + f\ \mathrm{H_2O_{(g)}} + q_{\mathrm{aerobic}} \qquad (6)$$

The gravimetric energy content is lower for all **YTV** formulations due to the high atomic mass of ytterbium in comparison to magnesium (173.04 vs. 24.305 g·mol^{-1}). The volumetric energy content of **YTV-1** and **YTV-2,** however, supersedes that of **MTV** for the primary reaction by 92 % and 40 %, respectively. The volumetric energy content for the secondary reaction is lower than for baseline **MTV** (59 % and 74 %). For both pyrolants the total volumetric reaction enthalpy, Q_{total}, approaches **MTV** energies (79 % and 87 %).

The spectral efficiencies for **MTV** and **YTV** formulations in two band pass ranges designated α-band (λ = 1.8–2.6 µm) and β-band (λ = 3.5–4.6 µm) derived from radiometric measurements are presented in Table 3. The gravimetric spectral efficiencies in α-band are in the range 25–28 % **MTV** only. In the β-band the spectral efficiencies are in the range 32–42 % **MTV**. However, the volumetric spectral efficiencies are in the range 73–76 % in α-band and either similar (96 % **MTV**) for **YTV-3** or superior to MTV for **YTV-1** and **YTV-2** in β-band (112 and 108 % respectively).

Table 3. Spectral efficiency of **MTV** and **YTV**.

Composition	E_α /J·g^{-1}·sr^{-1}	E_β /J·g^{-1}·sr^{-1}	E_α /J·cm^{-3}·sr^{-1}	E_β /J·cm^{-3}·sr^{-1}
MTV	180	78	322	139
YTV-1	50	33	235	155
YTV-2	49	30	245	150
YTV-3	45	25	239	133

The burn rates of **YTV** were determined to be comparable or superior to that of the baseline **MTV** and allow for high mass consumption rates at the investigated densities. The radiance, L_λ of **YTV** in α-band is slightly inferior to **MTV** (67–94 % MTV) however the radiance is comparable or superior to **MTV** in the important β-band[2b] (102–124 % MTV, Table 4).

Table 4. Radiance, burn rate and mass consumption rate.

Composition	u /mm·s^{-1}	dm/dt /g·s^{-1}·cm^{-2}	L_α /W·cm^{-2}·sr^{-1}	L_β /W·cm^{-2}·sr^{-1}
MTV	2.70	0.48	86	37
YTV-1	2.48	1.16	58	38
YTV-2	3.09	1.54	75	46
YTV-3	3.37	1.79	81	45

The increase in β-band spectral efficiency relative to **MTV** causes a higher spectral ratio $E_\beta/E_\alpha = \theta_{\beta/\alpha}$ for **YTV** in comparison to **MTV**. The fraction of radiation emitted in both α- and β-band for **YTV-2** and **YTV-3** is similar or superior to **MTV** although both Yb-based formulations are energetically inferior to **MTV** (Table 5).

Table 5. Fraction of radiation emitted and band ratio.

Composition	F_α	F_β	$\theta_{\beta/\alpha}$
MTV	0.117	0.051	0.43
YTV-1	0.071	0.047	0.66
YTV-2	0.106	0.065	0.61
YTV-3	0.099	0.055	0.55

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As the combustion temperatures of **YTV** (1975 ± 200 K) are about similar to those of MTV (2000 ± 200 K)[5b] the better combustion energy efficiency is very likely due to the higher emissivity of the **YTV**-flare combustion products. Yb_2O_3 formed through aerobic combustion of ytterbium carbide and excess ytterbium (Equation (6)) has a considerably higher emissivity than MgO in the same band ($\varepsilon_{3.5–4.6\mu m,\ 1850\ K}$ (Yb_2O_3): approx. 0.25–0.35 vs. $\varepsilon_{3.5–4.6\mu m,\ 1850\ K}$(MgO): approx. 0.06.[2a,7] Yb_2O_3 thus allows for more effective conversion of thermal energy into useful radiation and compensates for the lower energy density of **YTV**.

Conclusions

Three ytterbium/PTFE/Viton® pyrolants although having lower calculated combustion enthalpies than baseline MTV show increased radiance in β-band. This is most likely due to the formation of highly emissive Yb_2O_3 which increases the radiant yield in the λ = 3–5 µm-range.

As a result of their higher mass densities flares based on Yb/PTFE/Viton® formulations will separate faster and yield higher radiant intensity in β-band than standard MTV. These formulations qualify as such for further investigation under dynamic conditions as combustible nose cones for kinematic decoy flares.

Experimental Section

Raw materials were purchased from: ALFA AESAR ytterbium (mean particle size: 10 µm), DuPont: DLX-6000 PTFE Micropowder (primary particle size: 200 nm); MACH I Inc.: 3M Fluorel FC-2175; Merck KG: Acetone; Henkel AG: Macroplast 2168 (29 wt.-% solid content) and ECKART Metallwerke: LNR 61 Mg (mechanically ground magnesium, mean particle size: 45 µm). All chemicals were used as received. The compositions were mixed in 50 g batch sizes. The dry components (PTFE and metal powder) together with five 1 cm^3 conductive rubber cubes were loaded into a 250 mL spherical mixing vessel made of electrically conductive polypropylene and tumbled for 2 h at 120 rpm in a WAB TURBULA mixer. The dry premix was manually kneaded with a 15 wt.-% solution of Fluorel FC-2175 in acetone in a stainless steel bowl with a stainless steel spatula until the mass broke into a granulate, when acetone evaporated during the kneading. The bowl was placed in a vacuum oven at 50 °C and 0.05 MPa and dried overnight.

Warning:

Metal-Fluorocarbon pyrolants are explosive materials inherently sensitive to electrostatic discharge, heat, flame, friction and impact. When alight these materials yield intense flame and thermal radiation sufficient to cause severe skin burns. In the unconsolidated state the material can undergo deflagration and even transition to a low order detonation in larger amounts (> 1 kg). The baseline MTV and all the ytterbium based compositions tested in this investigation require a friction force > 120 N to yield a reaction and thus are considered safe to handle.[8]

All preparations were carried out in accordance to German regulations BGV 55k and BGV B5 of Verband der chemischen Industrie.[9] In particular, the personnel involved must wear flame-resistant personal protection equipment such as an overall, and a balaclava made from NOMEX®-III or aluminized PBI® with a facial heat shield and leather gloves. The personnel must be grounded by conductive protective shoes and a wristband, all equipment and tooling must be grounded as well.[6b]

All the YTV pellets were pressed under safety at 150 MPa pressure – applied for 10 s – in a 9.9 mm diameter cylindrical die. The MTV pellets were pressed under the same conditions using a 16.8 mm diameter cylindrical die. All pellets had a length to diameter ratio of approximately 2:1. Each pellet weighed nominally 10 g. After pressing the lateral faces were lacquered with Macroplast 2168 to assure terminal burning only. The terminal face of the pellet was ignited with a small external pyrotechnic charge not causing detectable levels of radiation. No ignition paste was applied on the pellets in order to be able to evaluate the ignitability of the compositions. The coated pellets were glued with Macroplast 2168 on 100 × 100 × 5 mm mild steel plates and dried overnight at 50 °C and ambient pressure.

The burn rate was measured with a video camera at 30 Hz frame rate from the first appearance of light up to the point, where no more pyrotechnic flame was visible ignoring any afterglow of the combustion products. The video recordings were considered more accurate than the radiometric signal for the burn rate determination, because the radiometer time constant is approximately 1 second vs. 1/30 s for the video camera.

The radiometric performance was determined in two bands designated α: 1.8–2.6 µm and β: 3.5–4.6 µm with an IR radiometric system (RM 6600) having two non-cooled silicon-based pyroelectric detectors RkP-575 (both of Laserprobe Inc.) with a large 28° view angle. The analogue signal from the radiometer was recorded with a Nicolet 60 data logger. The radiometer was calibrated against a blackbody source (SR-32, CI Electro-Optical Systems) set to T = 1273 K. The measurement distance was 1.5 m and the calibration distance 0.5 m. No correction for atmospheric absorption was made.

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