Superior spectral performance of decoy flares compositions via inclusion of graphite as a black body emitter

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Abstract. Graphite particles can offer high interfacial surface area as well as high emissivity as black body; therefore it can find wide applications in advanced decoy flares. In the current study, graphite particles of 100 µm size, were employed with different reactive metal fuels including Mg, Al, and Mg-Al alloy. Different formulations based on graphite ratio up to 8 wt % were developed via granulation with subsequent pressing. Thermal signature was measured using IR spectrometer (1-6 µm) Arc-Optics. Composite flare based on Mg-Al fuel, and graphite demonstrated superior spectral intensity; this formulation offered an increase in average intensity by 83 % to reference MTV flare. In the mean time, composite flare based on Al and graphite offered the highest relative intensity value $\Theta$ of 0.6. Graphite, as an allotrope of carbon, can act as an excellent source of carbonaceous materials; that can strengthen incandescence emission. Furthermore Mg-Al reactive metal alloy can offer novel synergism as Mg could vaporize at 1000 °C offering efficient combustion process. It can be concluded that tailored flare with customized thermal signature can be developed.

1. Introduction
Decoy flares are effective countermeasures that are ejected from aircraft and separates away to divert away infrared (IR) missile [1]. Decoy flare must provide thermal signature similar to aircraft for effective countermeasure of IR missile. During the last decades, several attempts were directed to enhance performance of traditional Magnesium/Teflon/Viton (MTV) decoy flare, in an attempt to keep up with recent developed IR-missiles. Enhanced decoy flare formulation should secure thermal signature with higher intensity over $\alpha$ band (2-3µm) and $\beta$ band (3-5µm) [2]. Consequently, IR missile could favor the decoy flare over the aircraft. Another vital factor for IR countermeasure is the average intensity over $\alpha$ band / average intensity over $\beta$ band ($\Theta = I_\alpha / I_\beta$). Modern decoy flares should offer thermal signature with high intensity and in the mean time should maintain $\Theta$ value similar to aircraft. It has been reported that recommended $\Theta$ value should be in the range from 0.5 to 0.8 according to the aircraft signature. Tailored spectral performance of the traditional MTV composition can be achieved via introducing novel materials for instance silicon [3-7], phosphorous [8-12], boron[2, 6], ytterbium [13], deuterium [14], ferric oxide [1, 7, 15-18], and graphite [2, 19-20]. Graphite is an attractive material as it can act as black body emitter [2, 15, 19]. Black body radiation is the major source of decoy flare emissivity. According to Plank's law, the emissivity of a radiating body can be described by Equation 1:

$$W_\lambda = \frac{2\pihc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \tag{1}$$
Where: \( W, \lambda, h, k, c, \) and \( T \) are the spectral radiance in \( \text{W cm}^{-2} \text{µm}^{-1} \), wavelength in \( \mu\text{m} \), Planck’s constant \( 6.626 \times 10^{-34} \text{W s}^{2} \), Boltzmann constant, velocity of light \( 2.998 \times 10^{10} \text{cm/s} \), and is absolute temperature in Kelvin respectively. The maximum emission wavelength \( (\lambda_{\text{max}}) \) shifts to shorter wavelengths with increase in radiator temperature equation 2.

\[
\lambda_{\text{max}}T = 2898 \mu\text{m.K}
\]

Traditional metal fuel such Mg can suffer from lack of chemical stability and low heat output. Another metal fuels can offer substantial heat output with an increase in reactive emitting species signature [21-22].

In this study graphite was employed in standard MTV composition with content ranging from 4-8 wt %. Graphite was further employed with different reactive metal fuels such as Al, and Mg-Al alloy. MTV, ATV, and MATV refer to flare based on Mg, Al, Mg-Al alloy respectively. The impact of graphite content on thermal signature was measured using (FT-MIR 1–6 µm) spectrophotometer. Spectral performance was evaluated to standard MTV flare (reference). Whereas MTV based on 4 wt % graphite demonstrated an increase in thermal signature average intensity by 67%; MATV based on 8 wt % graphite offered an increase in average intensity by 83 %. In both cases good average relative intensity ratio \( (\Theta) \) in the order of 0.5 was achieved. Superior performances of MATV flare based on 8 wt % graphite can be ascribed to the synergism between the two components (Mg, Al) of bi-metal alloys. Where Mg could act as tinder; and could combust efficiently with substantial heat output. Surplus magnesium could vaporization at 1000 °C. These features could secure fine environment for efficient combustion of aluminum. High temperature is required for graphite to act as black body emitter; in the mean time the resulted black carbon can further strengthen the developed thermal signature.

2. Experimental

2.1 Materials

Different metal powders including Mg, Al, and Mg-Al alloy were employed as fuels. An energetic fluorocarbon polymer (Teflon) was employed as energetic binder; Viton A was employed as plasticizer. Graphite was employed as black body emitter. The structure, function, and supplier of all employed chemicals are listed in table 1.

| Chemicals | Function | Formula | Grade | Supplier |
|-----------|----------|---------|-------|----------|
| Teflon    | Oxidizer | \([C_2F_4]_n\) | \(n=20000\) Fine powder (Reagent Grade) | Alpha chemika |
| Magnesium | Fuel     | Mg      | 98%, ribbon (Reagent Grade) | Alpha chemika |
| Aluminum  | Fuel     | Al      | 98%, powder (Reagent Grade), Average particle size (4–7 µm) | Alpha chemika |
| Viton A   | Binder   | \(C_5H_2F_9X\) | Fluorine: 65 % (Reagent Grade), 1.85 g/cm³ | Alpha chemika |
| Acetone   | Solvent  | \(C_3H_6O\) | 100% (Reagent Grade) | Sigma Aldrich |
| Graphite  | Enhancer | C       | 99.5%, flakes (Commercial Grade) | NICE (India) |
2.2 Decoy flare formulation

Decoy flare development should secure intimate mixing of different ingredients. Decoy flare grain was developed via granulation and subsequent pressing; this technology includes the following processes.

- Sieving of solid particles to fine powder less than 300 µm
- Teflon as oxidizer and binder along with Viton A® as a plasticizer were dissolved in acetone.
- Granulation was conducted to assure composition homogeneity.
- The final grain was developed by pressing 25 g composition in aluminum mold.

All formulations were developed with the same methodology to avoid any variability that could affect performance. Chemical composition of investigated formulations is tabulated in table 2.

| Sample Number | MTV (Teflon 30%, Viton 5%) | ATV (Teflon 30%, Viton 5%) | MATV (Teflon 30%, Viton 5%) |
|---------------|-----------------------------|-----------------------------|-----------------------------|
|               | Mg | Graphite | Al | Graphite | MA | Graphite |
| 1             | 65 % | --- | 65 % | --- | 65% | --- |
| 2             | 61 % | 4 % | 61 % | 4 % | 61 % | 4 % |
| 3             | 59 % | 6 % | 59 % | 6% | 59 % | 6 % |
| 4             | 57 % | 8 % | 57 % | 8 % | 57 % | 8 % |

2.3 Spectral measurements

Experimental setup for spectral performance measurements includes combustion chamber, optical fibers, IR spectrometer (1-6 µm) Arc-Optics, and data receiving and a recording system (Figure 1).

![Figure 1. Schematic for spectral measurements of decoy flares.](image-url)
IR spectrometer recorded thermal signature with interval time of 6 seconds. The spectrometer response was recorded in counts/s over IR band 1-6 µm. After acquiring the spectral data, the average intensity value was calculated. Additionally the intensity over α and β bands was calculated; consequently the relative intensity ratio $\theta = I_\alpha / I_\beta$ was calculated.

3. Results and discussion

3.1 Characterization of graphite

Graphite was characterized by scanning electron microscopy (SEM) ZEISS, EVO-MA10. Morphological characterization of employed graphite confirms its flake nature figure 2. SEM micrograph demonstrates multiple layers structure; each layer of one µm thickness. Graphite demonstrated flakes of 150 µm lateral dimensions.

![Figure 2. SEM micrograph of the employed graphite.](image)

Graphite powder was examined using X-ray powder diffractometer, Panalytical XPERT PRO MPD. XRD diffractogram of as obtained graphite flakes is presented in figure 3.

![Figure 3. XRD diffractogram of graphite.](image)

The prominent peak at ~ 26°, was attributed to the (002) plane of ordered hexagonal graphite structure. This is an evident of crystalline carbon structure. Raman spectra were acquired using dispersive
Raman microscope (model Sentera, Bruker, Germany). A Nikon 20x objective was used to focus the Raman excitation source (10 mW, 532 nm neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. The most prominent features in the Raman spectra of graphitic materials are G band appearing at 1582 cm$^{-1}$ (graphite), the D band at about 1350 cm$^{-1}$, and the $G'$-band at about 2700 cm$^{-1}$ figure 4.

![Raman spectra of graphite.](image)

The integrated intensity ratio D band and G band is widely used for characterizing the defect quantity in graphitic materials. It is obvious the employed graphite has relatively low D-band defect intensity, which is localized where the crystalline structure is not perfect, mostly at the edges of the crystallite. Raman results confirmed high crystalline structure of employed graphite material.

3.2 Impact of graphite on spectral performance of MTV flare
Graphite was found to improve total ignition time (TIT) of standard MTV flare. The optimum wt % of graphite was found to be 4 wt %. This ratio offered an increase in TIT by 75 % to reference formulation figure 5.

![Impact of graphite content on total ignition time of MTV flare.](image)
The impact of graphite content on spectral performance of MTV flare was conducted. Graphite content of 4 wt % offered the highest intensity to reference MTV flare figure 6.

![Figure 6. Impact of graphite content of spectral performance of standard MTV flare.](image)

The received thermal signature was transformed into EXCEL data. Average total intensity was calculated using matlab software. Average intensity over α (2-3 µm) and β (3-5 µm) bands were calculated; consequently Θ value was retrieved. The impact of graphite content on average intensity and Θ value is demonstrated in Figure 7.

![Figure 7. Impact of graphite content of spectral performance of standard MTV flare.](image)

Figure 8 confirmed that graphite content 4 wt % offered superior spectral performance compared to reference formulation. This ratio offered the highest average total intensity as well as low Θ value. This enhanced spectral performance can be ascribed to graphite as an effective source of carbon particles which absorbs heat and emits nearly as a black body emitter offering enhanced total emission. Also evolved carbon at high temperature would combust with atmospheric oxygen at the tertiary zone producing CO₂ which results in further increase in overall intensity.
3.3 Impact of graphite on spectral performance of ATV flare
ATV with 6 wt % graphite content secured optimum performance; this formulation offered an increase in TIT by 100 % figure 8. 6 wt % graphite offered dramatic increase in ATV thermal signature average intensity figure 9.

![Figure 8](image1.png)

**Figure 8.** Impact of graphite content on total ignition time of ATV flare.

![Figure 9](image2.png)

**Figure 9.** Impact of graphite content of spectral performance of standard ATV flare.

It is undeniable that the inclusion of 6 wt % graphite greatly enhanced the spectral performance to reference formulation. The impact of graphite content on both average intensity and Θ value is represented in figure 10.
It is obvious that a sample containing 6 wt % graphite offered enhanced spectral performance compared to the reference ATV formulation. It offered a dramatic increase in average total intensity by 590 %. Additionally, Θ value was found to be within the accepted range. This can only be credited to the graphite role in amplifying the spectral output.

### 3.4 Impact of graphite on spectral performance of MATV flare

Graphite improved TIT of standard MATV flare. 6 wt % graphite was reported to be the optimum loading level. This ratio offered an increase in TIT by 20 % figure 11.

Spectral performance of MATV formulations with different graphite content revealed that 8 wt % graphite offered the highest spectral performance figure 12.
Figure 12. Impact of graphite content of spectral performance of standard MATV flare.

The impact of graphite content on average intensity and $\theta$ value for MATV flare is represented in figure 13. MATV demonstrated an increase in average intensity with graphite content.

Figure 13. Impact of graphite content of spectral performance of standard MTV flare.

Optimum graphite content (8 wt %), demonstrated the highest average intensity. In the mean time, $\theta$ value was almost constant.

3.5 Comparative spectral performance assessment

Comparative investigation for graphite impact on spectral performance of different flare formulations (based on different metal fuels) were conducted to reference ATV flare figure 14.
Figure 14. Comparison between average intensity values for all formulations.

Whereas MTV flare with 4 wt % graphite offered an increase in average intensity by 67%; MATV flare with 8 wt % graphite offered an increase in average intensity by 83%. The explanation to graphite’s impact on spectral performance can be further clarified through understanding the combustion reaction mechanisms within each of the three flame zones separately.

3.6 Combustion wave of decoy flare
It is widely accepted that combustion wave of decoy flare consists mainly of three reaction zones. These zones can be varied in size and associated chemical reactions according to chemical composition.

Primary Combustion Zone
Magnesium and Teflon react within the primary anaerobic zone close to the pyrolant surface to yield condensed magnesium fluoride, carbon (soot), excess vaporized magnesium and heat as in eq. (3) [23].

\[ m \text{Mg} + (C_2F_4) \rightarrow 2 \text{MgF}_2 + m\text{Mg} + 2 \text{C} + \text{h}\nu \]  

ATV follows the same trend as MTV, and yield aluminum products instead of magnesium (Equation 4). At high temperature, the formed AlF$_3$ reacts with metallic aluminum to produce AlF (active transient species) equation 5 [24-26].

\[ n \text{Al} + 3 \text{C}_2\text{F}_4 \rightarrow 4 \text{AlF}_3 + n\text{Al} + 6 \text{C} + \text{h}\nu \]  

For MATV, magnesium could acts as a tender for aluminum. Aluminum would react with teflon to yield aluminum fluoride. Bimetal fuel (Mg & Al) would induce exothermic reactions via oxidation with teflon equation 5

\[ m \text{Mg} + n \text{Al} + 10 \text{C}_2\text{F}_4 \rightarrow 8 \text{MgF}_2 + 8 \text{AlF}_3 + m\text{Mg} + n\text{Al} + 20 \text{C} + \text{h}\nu \]
Secondary combustion zone
Oxidation of primary products will occur in this zone. Excess metal fuel will be combusted in secondary reaction zone, according to the type of employed metal (Equations 6-8).

\[
\begin{align*}
\text{Mg} + \text{O}_2 & \rightarrow \text{MgO} + \text{h} \text{u} \\
4 \text{Al} + 3 \text{O}_2 & \rightarrow 2 \text{Al}_2\text{O}_3 \\
\text{Mg} + 2 \text{Al} + 2 \text{O}_2 & \rightarrow \text{MgO} + \text{Al}_2\text{O}_3 + \text{h} \text{u}
\end{align*}
\] (6-8)

MATV formulation, surplus magnesium could vaporize and oxidized with air oxygen offering substantial heat output; as it has low boiling point of 1000 °C. Therefore excess Al could combust more efficiently with additional heat. This action could stimulate the active emitting species in the primary reaction zone offering extended primary reaction zone at higher temperature.

Tertiary combustion zone
Upon mixing with air in the outer boundaries of the third zone, the remaining carbon would be oxidized with air developing \( \text{CO}_2 \) (selective radiator) offering enhanced flare intensity equation 9 \[6\].

\[
2 \text{C} + 2 \text{O}_2 \rightarrow 2 \text{CO}_2 + \text{h} \text{u}
\] (10)

The enhanced average intensity for all formulations can be attributed to the fact that graphite, is a carbonaceous material, supplies the flame with carbon particles which absorbs heat and emit in IR region. The impact of graphite content of \( \Theta \) value for investigated flare formulations based on different metal fuels was evaluated figure 15.

![Graphite % vs Theta Ratio](image)

**Figure 15.** Comparison between theta ratio behaviors for all formulations.

Graphite content did not significantly impact \( \Theta \) value for different flare formulation. It is apparent that MTV flare with 8 wt % graphite offered enhanced \( \Theta \) value of 0.6. It can be concluded that customized flare can be developed according to spectral intensity as well as relative intensity ratio.

4. Conclusion
Graphite can find an application in decoy flares field as it improved thermal signature overall intensity. MATV as multi-component flares based on 8 wt % graphite demonstrated superior spectral intensity. This flare formulation offered an increase in average intensity by 83 % to reference MTV
formulation. In the meantime MTV flare based on 8 wt% offered the highest relative intensity value $\Theta$ of 0.6. Graphite, as an allotrope of carbon, can act as an excellent source of carbonaceous materials. That can strengthen incandescence emission as ideal black body. Mg-Al alloy can offer novel synergism as Mg can act as tinder for Al offering efficient combustion process. Mg could vaporize at 1000 °C offering efficient combustion process. It can be concluded that tailored flare can be developed according to the required spectral data.

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