BURNING AND INFRARED EMISSION CHARACTERISTICS OF THE PYROTECHNIC COMPOSITION BASED ON MAGNESIUM-TEFLON-VITON WITH IRON (III) OXIDE NANOPARTICLE AND GRAPHENE

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TÓM TẮT

ĐẶC TÍNH CHÁY VÀ PHÁT XẠ HỒNG NGOẠI CỦA THUỐC HỎA THUẬT TRÊN CƠ SỞ MAGIE-TEFLON-VITON CÓ BỔ SUNG PHỤ GIA SẮT (III) OXIT VÀ GRAPHEN

Bài báo trình bày các nghiên cứu về ảnh hưởng của nano-Fe_2O_3 và graphen đến đặc tính cháy và phát xạ của chế phẩm pháo hoa MTV. Phương pháp phân tích ảnh SEM và EDX được sử dụng để đánh giá hình thái học và sự góp mặt của phụ gia trong vật liệu. Đo quang phổ và sử dụng máy quay phim tốc độ cao để xem xét sự đóng góp của các phụ gia vào tốc độ cháy và phát xạ của vật liệu. Kết quả nghiên cứu đã chỉ ra, so với các mẫu không bổ sung phụ gia, các mẫu chứa Fe_2O_3 nano và graphen có tốc độ cháy tăng lên 1,9 lần, hàm phân bố độ chói theo bước sóng (spectral radiance) tăng lên 1,5 lần. Tuy nhiên, nhiệt độ cháy có xu hướng không thay đổi nhiều khi được bổ sung 2 loại phụ gia Fe_2O_3 nano và graphen. Tỷ lệ hàm lượng Fe_2O_3/graphen được bổ sung để hàm phân bố độ chói theo bước sóng của hỗn hợp MTV ở các bước sóng khác nhau đạt giá trị lớn nhất là 4/8.

Từ khóa: *Hàm phân bố độ chói theo bước sóng, xúc tác cháy, MTV, Fe_2O_3 nano, graphen.*

1. INTRODUCTION

Infrared decoy flares are one of the effective measures used to protect aircraft against current infrared-guided missiles. The requirements of pyrotechnic composition used in decoy flares are as follows: the radiant intensity must exceed that of aircraft within the missile's search wavelength band; the time to reach peak intensity should usually be less than one second; the burning time must be long enough, approximately four seconds, to prevent the missile reaching the target after the pyrotechnic mixture is extinguished [1, 2]. The ability to emit in a specified wavelength band of the pyrotechnic composition is mainly expressed (measured) in the following parameters: spectral intensity I_λ, spectral radiance L_λ, and spectral efficiency E_λ. These parameters are determined as follows [2-7].

$$I_\lambda = \frac{\Phi_\lambda}{\omega} \quad (\mathrm{W.sr^{-1}.\mu m^{-1}}) \quad (1)$$

$$L_\lambda = \frac{\Phi_\lambda}{\Omega.\cos\theta.\omega} \quad (\mathrm{W.sr^{-1}.m^{-2}.\mu m^{-1}}) \quad (2)$$

$$E_\lambda = \Delta_c H.\frac{1}{4.\pi}.F_\lambda.\delta_w.\delta_a \quad (\mathrm{J.g^{-1}.sr^{-1}.\mu m^{-1}}) \quad (3)$$

$$I_\lambda = E_\lambda.\dot{m} \quad (\mathrm{W.sr^{-1}.\mu m^{-1}}) \quad (4)$$

where, Φ_λ (W) is the spectral flux of the emission source; ω (steradian) and Ω (m^2) are the solid angle and projected area of the emitting surface, respectively; θ (radian) is the angle between the direction perpendicular to the emitting surface and the viewing direction; $\Delta_c H$ ($J.g^{-1}$) is the enthalpy of combustion of the payload; F_λ is the reaction enthalpy that contributes to the radiant energy in the band of interest; δ_w is the windstream degradation factor; δ_a is the aspect angle factor; $\dot{m}$ (g.s^{-1}) is the mass consumption rate; The quantities I_λ, L_λ, E_λ are written with the subscript λ to indicate that their values must be integrated to specify the amount of radiation in a particular spectral band [6].

The pyrotechnic composition based on Magnesium-Teflon-Viton (MTV) was commonly used in infrared decoy flares as the main infrared emitter [4, 8, 9]. Meanwhile, Fe_2O_3 nanoparticle and graphene were capable nanomaterials of increasing the spectral radiance of MTV composition [4, 10]. Fe_2O_3 (hematite) was known as an important additive that acted as a combustion catalyst to rise the burning rate of high-energy materials [11]. The catalytic efficiency of Fe_2O_3 nanoparticle compared to their micro-sized was also proven in the study of Joshi and colleagues (2008) [12]. The redox reaction of Fe_2O_3 with metallic Mg also created a significant heat source for the emission of combustion products of the MTV composition [10]. In addition, graphene had the ability to emit like a black body, receiving heat from the combustion reaction and the thermite Mg/Fe_2O_3 mixture [8], which would increase the spectral radiance of MTV composition.

This article presents studies of the effects of nano-Fe_2O_3 and graphene on the burning and radiance characteristics of the MTV pyrotechnic compositions.

2. EXPERIMENTAL

2.1. Materials

The pyrotechnic composition was prepared from magnesium powder with a particle size ≤ 63 µm, teflon micro powder (polytetrafluoroethylene) with a particle size ≤ 10 µm (molecular weight $10^4 \div 10^5$ g.mol^{-1}), viton (vinylidene fluoride/hexafluoropropylene copolymer) with 66% fluorine content (density 1.81 g.cm^{-3}), Fe_2O_3 with particle size 50 ÷ 200 nm, graphene with a thickness of 10 ÷ 50 nm (length 200 ÷ 5000 nm), pure acetone. These chemicals originated in Xilong company, China.

2.2. Preparation of samples

Viton binder was dissolved in acetone at concentration of 0.05 g/mL for at least 8 hours. Fe_2O_3, graphene was added into the viton/acetone solution, which was stirred for 30 minutes with a sample homogenizer. The magnesium/teflon mixture was dryly prepared before adding it to the viton/acetone/Fe_2O_3/ graphene solution. The resulting mixture was granulated through a 0.8 mm sieve after being air-dried for about 1 hour. Finally, they were dried for 2 hours and preserved. The studied pyrotechnic compositions were presented in Table 1. M0 with the component content selected according to references [13, 14] was the sample with outstanding spectral efficiency. SEM images were captured at varying magnifications ($5.10^2 \div 10^5$ nm) and different locations, elucidating the distinct surface morphology of Fe_2O_3 nanoparticles (Fig 1a) and graphene (Fig 1b). Figures 1c, 1d depicted the presence of Fe_2O_3 nanoparticles and graphene, encapsulated by viton and evenly dispersed on the Mg/teflon surface.

Table 1. The compossition of pyrotechnic samples

Material	Particle size (µm)	Content (% wt)										
		M0	M10	M11	M12	M13	M14	M20	M21	M22	M23	M24
Mg	≤ 63	65	65	65	65	65	65	65	65	65	65	65
Teflon (PTFE)	10-200	30	30	30	30	30	30	30	30	30	30	30
Viton A		5	5	5	5	5	5	5	5	5	5	5
Nano-Fe_2O_3 (external content)	0.05-0.20	0	10	10	10	10	10	0	2	4	8	12
Graphene (external content)	0.01-0.05 (thickness)	0	0	2	4	8	12	8	8	8	8	8

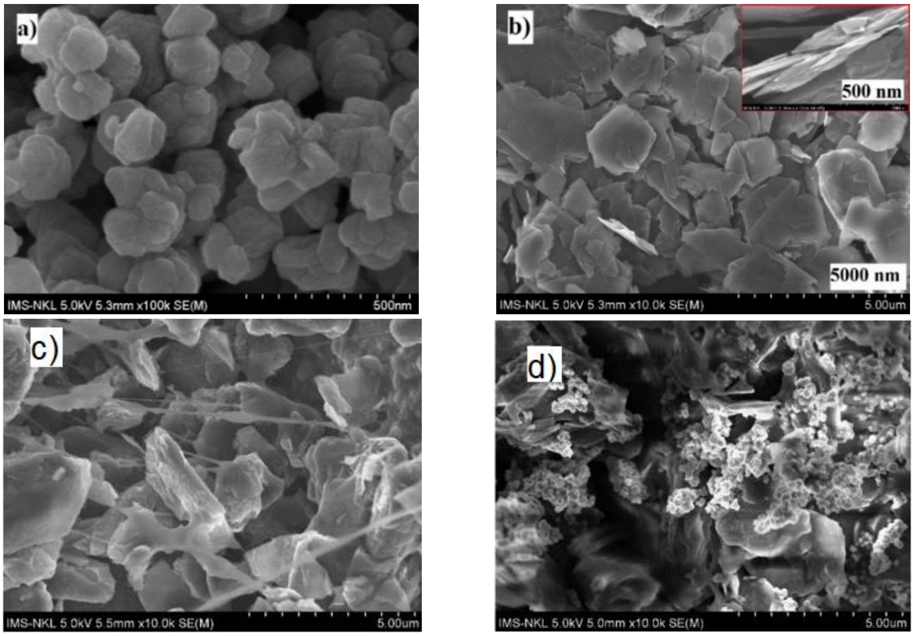

Figure 1. SEM images of Fe_2O_3 nanoparticles (a), Graphene (b), MTV-Graphene (c), MTV-Fe_2O_3/Graphene (d).

2.3. Experimental Techniques

The composition of MTV/Fe_2O_3/graphene pyrotechnic was analyzed by SEM imaging (FESEM S-4800, Hitachi-Japan) and EDX technique (Horiba-7593H, Japan) was used to determine the distribution of nano additives in the mixture. The linear burning rate of the pyrotechnic composition which was compressed into a cylindrical acrylic tube (h1 = 25 mm, ϕ = 12 mm) with a compressed density of 1.6 g/cm^3 was measured using high-speed camcorder (Handycam FDR-AXP55, Sony-Japan). The combustion temperature of the mixture was defined by the thermocouple method (Multichannel ADC B-480, Russia) (using tungsten-rhenium thermocouples 50 μm thick on the pyrotechnic composition pressed in an acrylic tube) (Fig. 2a). The Spectroradiometer SR-5000N (CI System, Israel) was used to determine spectral radiance of the pyrotechnic samples which was compressed into a steel cylinder (h2 = 65 mm, ϕ = 12 mm) with 5-10 MPa pressure (Fig. 2b).

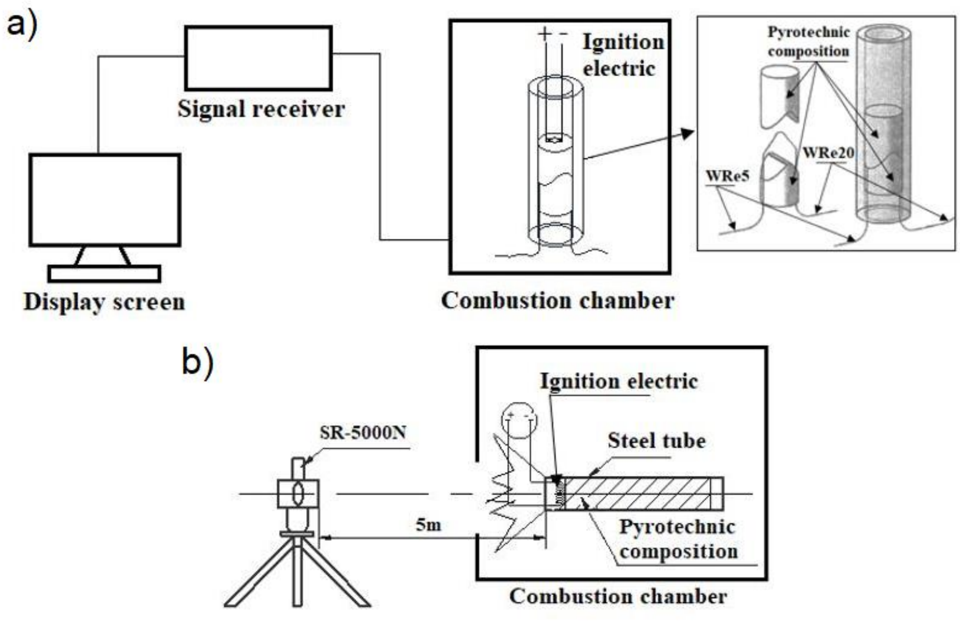

Figure 2. The experimental setup for determining the combustion temperature (a) and spectral radiance (b).

3. RESULTS AND DISCUSSION

3.1. Effect of nano-Fe_2O_3 and graphene additives on the combustion characteristics of the MTV pyrotechnic composition

The burning rate was specified for the MTV composition with various additive contents. The results were presented in Figure 3.

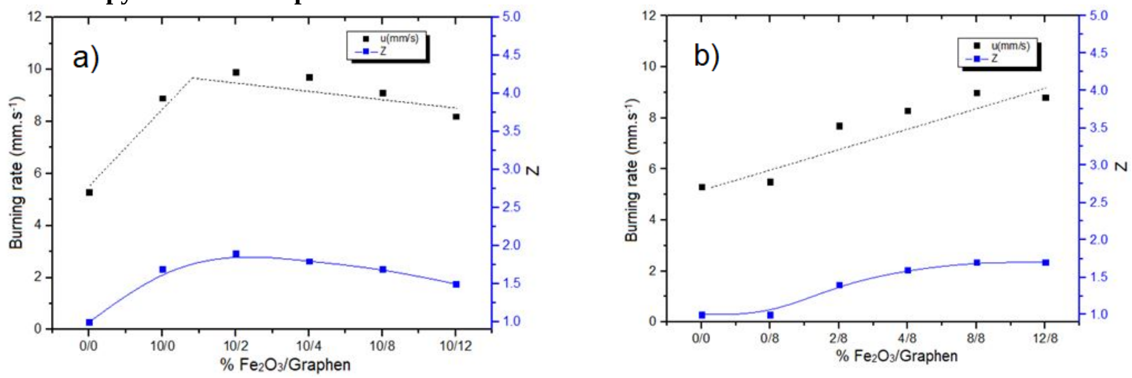

Figure 3. Effect of nano-additive on the burning rate of the MTV pyrotechnic composition: (a) only change the percent of graphene and (b) only change the percent of nano-Fe_2O_3.

With two nano-additives added, Fe_2O_3 nanoparticles had strong catalytic activity on the burning rate. Indeed, the burning rate of the MTV mixture increased significantly when Fe_2O_3 nanoparticle was added, while for graphene the change was very little (samples M10, M20 compared to sample M0). When fixing the Fe_2O_3 content and raising the graphene content, due to the combustion catalytic activity of nanosized Fe_2O_3, the burning rate of the system increased to nearly 10 $mm.s^{-1}$ (sample M11 with Fe_2O_3/graphene content was 10/2 %), nearly double compared to that of sample M0 (5.3 $mm.s^{-1}$) (Figure 3a). Once the graphene content was increased further, there was a slight decrease in the burning rate (Figure 3b). This occurred because graphene absorbed the heat generated during reaction, thereby impeding heat transfer to the system's burning surface. Conversely, maintaining a constant graphene content while increasing the Fe_2O_3 nanoparticle content resulted in a rise in the burning rate.

3.2. Effect of nano-Fe_2O_3 and graphene additives on the combustion temperature and infrared emission of the MTV pyrotechnic composition

The infrared emission ability of MTV samples were determined according to the value of spectral radiance L_λ in different wavelength bands. The influence of nano-additives on the combustion temperature and spectral radiance of MTV composition were presented in Table 2. The MTV samples underwent combustion in the atmosphere, where the reaction with oxygen elevated the combustion temperature of the mixture to approximately 2200 K [15]. When incorporating both types of nano-additives, the combustion temperature of the MTV mixture fluctuated within the range of 2100-2250 K, indicating a minimal alteration in the combustion temperature. Both Fe_2O_3 nanoparticles and graphene were dispersed across the burning surface, exerting a concurrent influence on the combustion process. They had a simultaneous effect on the combustion process of the system. Nanosized Fe_2O_3 was essentially a combustion catalyst, increasing the burning rate of the system, meaning the air content participating in the reaction was reduced. To validate this assertion, the author employed Matlab [16] to compute the combustion temperature of the pyrotechnic mixture under varying levels of air oxygen participation (according to experimental combustion temperature) (refer to Table 2).

Table 2. Effect of nano-additives on the combustion temperature and the spectral radiances of MTV composition

Sample	Content of ingredients, %		Combustion temperature, *K*		$L_{\lambda1-\lambda2}$ ($W.sr^{-1}.cm^{-2}.\mu m^{-1}$)			
	MTV-Fe_2O_3/graphene	Air	Theoretical	Practical	2.5÷3 µm	3÷5 µm	2.5÷5 µm	8÷10 µm
M0	47	53	2376	2380	0.7508	2.4316	3.1823	0.1566
M10	55	45	2116	2100	1.2760	2.8101	4.0861	0.1870

Sample	Content of ingredients, %		Combustion temperature, *K*		$L_{\lambda1\text{-}\lambda2}$ (W.sr^{-1}.cm^{-2}.µm^{-1})			
	MTV-Fe_2O_3/graphene	Air	Theoretical	Practical	2.5÷3 µm	3÷5 µm	2.5÷5 µm	8÷10 µm
M11	47	53	2212	2205	1.0842	2.3152	3.3994	0.1544
M12	45	55	2136	2156	1.1957	2.4739	3.6696	0.1714
M13	38	62	2252	2231	1.2781	2.8722	4.1503	0.1650
M14	34	66	2238	2237	1.4563	3.1807	4.6370	0.1922
M20	37	63	2237	2276	1.2429	2.9142	4.1570	0.1869
M21	37	63	2248	2234	1.4011	2.7807	4.1818	0.1774
M22	37	63	2267	2211	1.5150	3.2095	4.7245	0.1975
M23	38	62	2224	2201	1.3176	2.9012	4.2188	0.1835
M24	40	60	2117	2130	1.1275	2.2640	3.3915	0.1403

The amount of air participating in the reaction with the MTV mixture was about 45-66% depending on the burning rate of the mixture (Table 2). At that time, the combustion temperature of the MTV mixture did not change much.

The Fe_2O_3 nanoparticles and graphene significantly enhanced the spectral radiance of MTV composition across diverse wavelength ranges. When maintaining the Fe_2O_3 content at 10% and increasing the graphene content, the infrared emission capability of the MTV samples exhibited a clear escalation, peaking at 12% graphene content with $L_{2.5\text{-}3.0}$ = 1.45628, $L_{3\text{-}5}$ = 3,1807, $L_{2.5\text{-}5.0}$ = 4.6370, $L_{8\text{-}10}$ = 0.1922 (W.sr^{-1}.cm^{-2}.µm^{-1}). This phenomenon arised because the blackbody emission of carbon, which amplified with rising carbon content, absorbed the heat from both the combustion reaction and the thermite mixture (Mg/Fe_2O_3) within MTV sample containing 10% Fe_2O_3 nanoparticles.

Conversely, with the graphene content fixed at 8% and the Fe_2O_3 nanoparticle content increased, the emission capability initially ascended, reaching its zenith at 4% Fe_2O_3 content with $L_{2.5\text{-}3.0}$ = 1.5150, $L_{3\text{-}5}$ = 3.2095, $L_{2.5\text{-}5.0}$ = 4.7245, $L_{8\text{-}10}$ = 0.1975 (W.sr^{-1}.cm^{-2}.µm^{-1}), before declining as the iron (III) oxide nano-additives were further augmented. This trend indicated an excess of heat from the thermite reaction compared to the surplus graphene (at an additional graphene content of 8%). The heat source resulting from the reaction between Fe_2O_3 nanoparticles and Mg became ineffectual. Consequently, the thermite mixture of Fe_2O_3 and Mg substantially bolstered the heat source for the MTV system. Moreover, graphene, with its expansive surface area, exhibited black body-like radiant emission when heated by the reaction of MTV/Fe_2O_3 mixture. Measurement results underscored this, revealing that the M22 sample with a nano-Fe_2O_3 content of 4% and graphene content of 8% (externally applied) boasted the highest spectral radiance.

4. CONCLUSION

Research results showed that nano-additives Fe_2O_3 and graphene were added together which increased the burning rate of MTV composition. On the one hand, the burning rate of the MTV samples were increased due to the effective combustion catalytic activity of Fe_2O_3 nanoparticles. On the other hand, with the very good thermal conductivity of graphene, the heat release of the mixture occured faster, causing the burning rate of the system to decrease. The burning rate of the sample with Fe_2O_3/graphene content of 10/2 was increased by up to 1.9 times compared to samples without additives. During the reaction content of air oxygen depending on the combustion speed, the combustion temperature of the system tended to remain unchanged when adding both nano-Fe_2O_3 and graphene. The spectral radiance of MTV pyrotechnic composition increased significantly when adding two nano-additives, showing the heating effect of the Mg/Fe_2O_3 thermite mixture on the black body-like emission of graphene. The largest spectral radiance value in the wavelength range 2.5-5 µm was $L_{2.5\text{-}5}$ = 4.7245 (W.sr^{-1}.cm^{-2}.µm^{-1}), achieved at a Fe_2O_3/graphene content ratio of 4/8. This result was the initial basis for manufacturing decoy flares for aircraft against new generation missiles.

Declaration: The authors declare that this is our work of us, and this content has not been submitted to any journal.

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