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

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Abstract

Nano additives are materials that have been widely used to increase the effectiveness of pyrotechnic compositions. This study examines the effects of iron (III) oxide (Fe_2O_3) nanoparticles on the burning characteristics (i.e., the heat of combustion, the burning rate, and the infrared radiance) of the pyrotechnic composition based on Magnesium-Teflon-Viton (MTV). The dispersion of nano additive in the pyrotechnic composition is evaluated using SEM and EDX. The experimental results demonstrate that the heat of combustion and the burning rate are increased while the spectral radiance is shifted to the shorter wavelength area with the complement of the additive Fe_2O_3 nanoparticle to the MTV composition.

Keywords**:** *Additive nanoparticle; burning rate; infrared radiance; Magnesium-Teflon-Viton.*

1. Introduction

Infrared-guided missiles (i.e., also known as heat-seeking missiles) are one of the biggest threats to military aircraft [1-3]. These missiles use infrared detectors to recognize infrared radiation and identify aircraft as a target. Infrared countermeasures using infrared emission pyrotechnics were discovered to counter infrared-guided missiles early in the 1950s [1, 3, 4]. Based on the radiative mechanism a black body of carbon black [1], the pyrotechnic systems that produce large amounts of heat and carbonaceous combustion products have been developed. The pyrotechnic system based on magnesium/fluorocarbon polymer meets these requirements. Decoy flares mainly use the pyrotechnic compositions consisting of Magnesium-Teflon-Viton because their reaction produces high combustion heat and combustion temperature together with high radiation efficiency in the required ranges of wavelength. The MTV pyrotechnic compositions are relatively effective against older heat-seeking missiles. Moreover, the MTV purotechnic composition are safe in preparation and of low cost [1, 3-7].

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At present, the new generation missile has made great strides in the target search system when using two or more spectroscopic probes to distinguish between decoy flares and aircraft [7]. This issue requires finding suitable pyrotechnic systems capable of providing a radiant flame with intensity ratios between different bands (relative radiation intensity [1, 8-10]) that meet similarly to an aircraft to fool the infrared guidance system of the missile. Recent studies have shown the ability to adjust radiation intensity in appropriate wavelength bands of the MTV composition when adding additives and adjusting the technological mode [8, 11-14]. In particular, the addition of nano-additives has changed the burning rate and infrared emission efficiency of the pyrotechnic systems at different wavelength bands [4, 8, 15, 16]. Thermite reaction between Fe_2O_3 and Mg has a high combustion heat [15]. The conventional thermite mixtures have a slow reaction rate due to comparatively slow particle diffusion, but the thermite mixtures containing nano-additives have a higher particle diffusion capacity, resulting in increased efficiency and reaction rate [15, 16]. Nanoscale transition metal oxides such as iron oxide have strong catalytic activity that depends on their particle size and surface area: quantum effects due to particle size reduction and surface effects. The atoms on the surface increase due to the reduced particle size and hence the increased catalytic activity of the metal oxide nanoparticles. Therefore, in the MTV infrared emission composition, an iron oxide nanoparticle is added to form a thermite (with Mg) that has a higher combustion heat than the pyrotechnic which only has Mg. In addition, the combustion reaction rate is higher, which improves the infrared emission efficiency of this pyrotechnic [8]. This article presents the results of an experimental investigation on the effects of Fe_2O_3 nanoparticles on the burning characteristics and infrared emission of the MTV pyrotechnic.

2. Materials and methods

2.1. Materials

Magnesium powder has a particle size ≤ 63 μm (density 1.73 g/cm^3). Teflon powder (PTFE) has a particle size of 5-10 μm (density 2.31 g/cm^3). Viton A rubber has a fluorine content of 66% (density 1.81 g/cm^3). Fe_2O_3 nano-additive has a particle size of 50-200 nm (density 5.24 g/cm^3). Acetone is 99.5% pure. These chemicals belong to Xilong company-China.

2.2. Sample preparation

The binder solution was prepared with Viton A rubber and acetone in a polymer/solvent ratio of 1/20 (g/ml), this solution was covered and soaked for about

6-8 hours for Viton A to completely dissolve. Fe_2O_3 nanoparticles were quantitatively weighed (external content) and added to Viton/Acetone solution, then stirred with a sample homogenizer for about 30 minutes (with a stirring rate of 3400 rpm) (Fig. 1). The Mg and PTFE powder was weighed to a given mass ratio and dry-mixed on a 0.8 mm sieve approximately 5-7 times. Then, the Mg/PTFE mixture was added to the prepared Viton/Acetone/Fe_2O_3 solution and wet-mixed for other 30 minutes. The obtained mixture was dried for 60 minutes at room temperature and then granulated on a sieve of 0.8 mm. The final mixture was dried by convection at 60^{o}C for 3 hours to remove all solvents. The pyrotechnic compositions based on Mg/Teflon/Viton/Fe_2O_3 were presented in Table 1.

Table 1. The compossiton of MTV pyrotechnic samples

Material	**Particle size (μm)**	**Content (% wt)**					
		M0	**M1**	**M2**	**M3**	**M4**	**M5**
Mg	≤ 63	60	60	60	60	60	60
Teflon (PTFE)	10 - 200	35	35	35	35	35	35
Viton A		5	5	5	5	5	5
Fe_2O_3 nanoparticle (external content)	0.05 - 0.2	0	4	6	8	10	12
Oxygen balance, Kb		-75.5	-72.0	-70.4	-68.8	-67.3	-65.8

2.3. Experimental techniques

The distribution of Fe_2O_3 nanoparticles in the MTV composition was determined by SEM imaging and EDX analysis. SEM creates images by scanning a sample with a high-energy electron beam. When the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by one or more detectors to form an image that is then displayed on a computer screen. EDX is an X-ray technique used to determine the elemental composition of materials. EDX systems are an attachment to an Electron Microscopy (SEM or Transmission Electron Microscopy (TEM)) device where the imaging capabilities of the microscope determine the interest sample. The data generated by the EDX analysis includes spectra showing peaks that correspond to the elements that make up the true composition of the sample.

The combustion heat of the pyrotechnic composition was determined on a Parr 6200 device. The pyrotechnic samples before measurement were dried at 60^{o}C for 2 hours; each sample was weighed about 2 g. Each pyrotechnic sample was conducted at least 3 times, and the resulting combustion heat value was determined as the average of the measurements.

To define the linear burning rate of the pyrotechnic sample, the MTV-Fe_2O_3 composition was compressed into an acrylic cylinder (12 mm inner diameter, 30 mm length) by a hydraulic compressor with a compression pressure of 0.5-1.0 tons to reach the required density (≈ 1.6 g/cm^3). The principle of determining the burning rate was based on the determination of the time at which the burning surface moved within the given distance *L* (mm) [17-20]. Burning time *t* (s) was determined using a Handycam FDR-AXP55 high-speed camcorder (Sony, Japan). The schematic diagram of the burning rate measuring device was shown in Fig. 2.

The linear burning rate *u* (mm/s) of the pyrotechnic composition was determined by the following formula:

$$u = \frac{L}{t} \quad \text{(mm/s)} \tag{1}$$

The mixture was ignited with an electric igniter. Each pyrotechnic sample was measured at least 3 times, and the results were determined as the average of the measurements.

Fig. 1. Nano additive is dispersed into the binder solution.

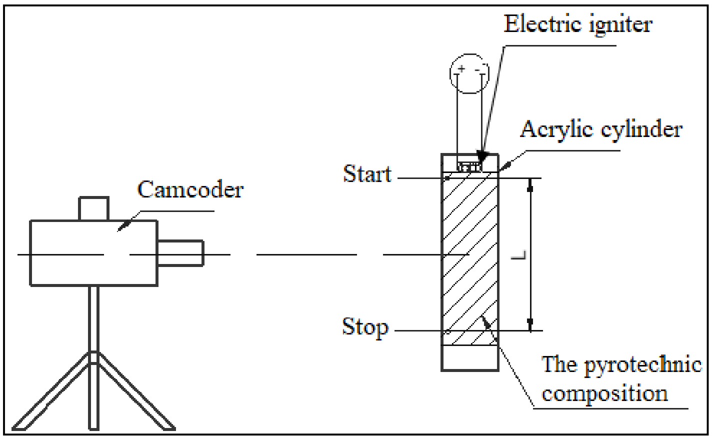


Fig. 2. Experimental determination of burning rate.

The spectral radiance was determined by Spectroradiometer SR-5000N (CI Systems, Israel 10551) with a spectral band of 2.4-14.3 µm. The pyrotechnic sample was compressed into a cylindrical steel tube (12 mm inner diameter, 75 mm long) by a hydraulic compressor with a compression density of 1.6 g/cm^3. The tube was placed 5 m away from the measuring device; the tube was directed into the receiver so that the center of the lens coincided with the center of the tube burning surface (Fig. 3). The raw data that is collected from the spectrometer is presented in counts and calibrated into units of irradiance. In the case of an extended source (as one that fills the instrument field of view - FOV), W(λ) - the source spectral radiance is measured in units of [Watt/(str.cm^2.μm)]. When a target does not fill the FOV, both it and its background contribute to the detected signal, L(λ) - the radiance contrast is measured in units of [Watt/(str.cm^2.μm)]. The spectral radiance is given by equal below [4]:

$$W_\lambda = \frac{2.\pi.c_1}{\lambda^5.\left(e^{\frac{c_2}{\lambda.T}} - 1\right)} \quad \left[\frac{\text{Watt}}{\text{cm}^2.\text{Str}.\mu\text{m}}\right]$$

where c_1 is first Planck's radiation constant = 1.19104 × 10^4 (Watt.μm^4/Str.cm^2), c_2 is second Planck's radiation constant = 1.4388 × 10^4 (μm.K).

Spectral radiance and emission wavelength were processed by software and exported as graphs with data in an excel file.

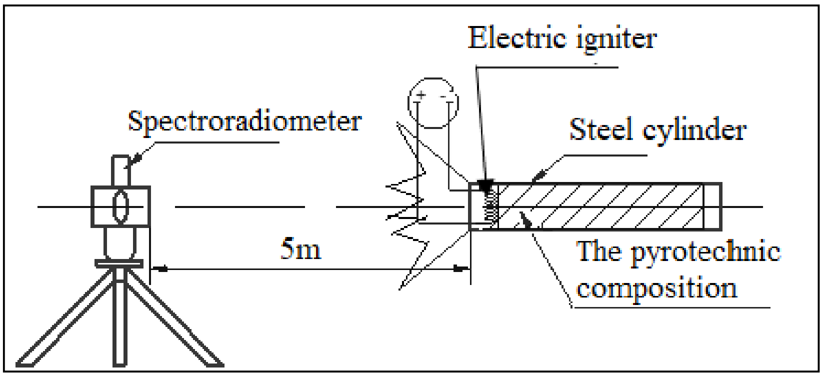


Fig. 3. Experimental determination of spectral radiance.

3. Results and discussions

3.1. The dispersion of nano additive in the MTV pyrotechnic

The Fe_2O_3 with particle size from 50-200 nm (Fig. 4a) was dispersed into the pyrotechnic mixture by sample homogenization method. They were mixed in a Viton/Acetone binder solution. SEM imaging results show that Fe_2O_3 nanoparticles were surrounded by Viton binder and evenly adhered to the surface of Mg particles (Figs. 4b- 4c). EDX analysis results of the M1 sample at three different points on the surface of the pyrotechnic sheet (3 mm thick compression) showed the presence of Fe_2O_3 in the pyrotechnic composition (Table 2, Fig. 5).

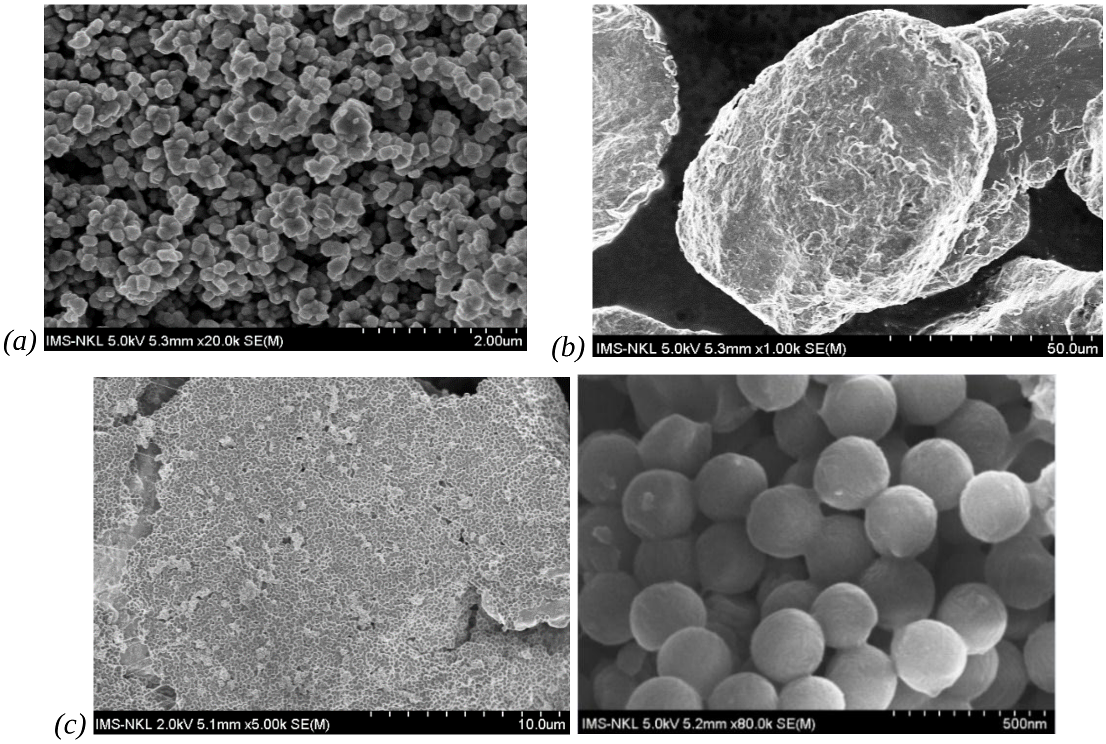


Fig. 4. (a) SEM image of Fe_2O_3 nanoparticles, (b) SEM image of Mg particles, and (c) SEM image of Fe_2O_3/Viton rubber nanoparticles on Mg/PTFE particles.

Table 2. EDX analysis results of Fe_2O_3 nanoparticles distribution

Element	**M1_1**		**M1_2**		**M1_3**	
	Weight%	**Atomic%**	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**
C	26.00	37.73	27.17	38.87	26.46	38.17
O	10.96	11.94	10.96	11.77	10.69	11.58
F	31.27	28.69	33.53	30.33	32.85	29.97
Mg	28.96	20.76	25.83	18.26	27.26	19.43
Fe	2.80	0.87	2.51	0.77	2.74	0.85

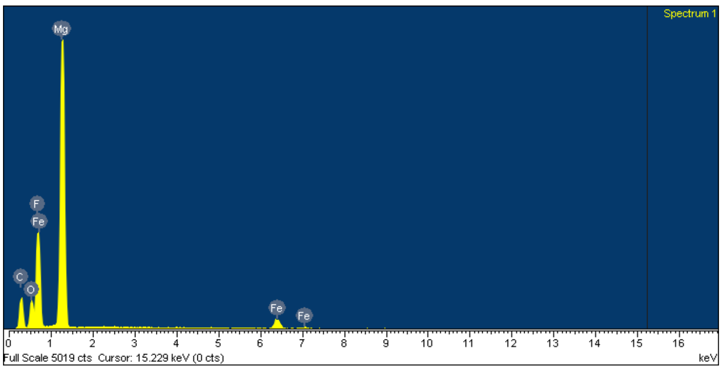


Fig. 5. EDX analysis results of M1_1 sample.

The results of EDX analysis at 3 points and SEM images showed the presence and fairly even distribution of Fe_2O_3 nanoparticles in the MTV pyrotechnic. The combustion and emission of pyrotechnic will be stable if the additive is evenly distributed in the mixture.

3.2. Effect of nano-Fe_2O_3 admixture on the combustion characteristics of the MTV pyrotechnic

The combustion heat and the linear burning rate were determined for the MTV pyrotechnic samples with different admixture content. The results were presented in Table 3 and Fig. 6. The relative burning rate Z was the ratio of the burning rate of the admixture-containing pyrotechnic to that of the non-admixture pyrotechnic.

Table 3. The combustion heat, and burning rate of the MTV pyrotechnic samples

Sample	% Fe_2O_3 (external content)	Combustion heat (cal/g)	Density (g/cm^3)	Burning rate, u (mm/s)	Relative burning rate, Z
M0	0	1445.3	1.62	4.75	1
M1	4	1776.7	1.63	5.58	1.2
M2	6	1807.7	1.61	6.31	1.3
M3	8	1872.4	1.61	6.89	1.4
M4	10	1890.6	1.60	5.89	1.2
M5	12	1830.0	1.64	4.60	1

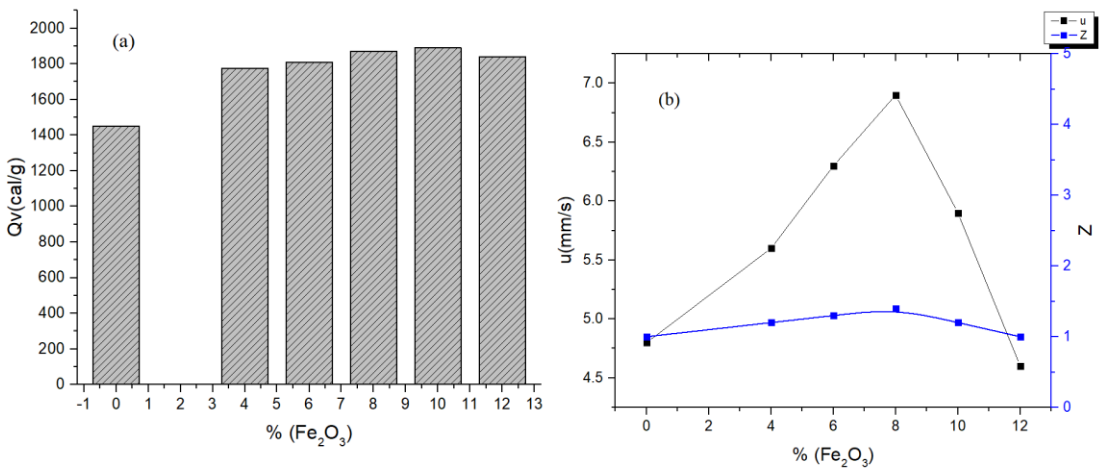


Fig. 6. Effect of nano-Fe_2O_3 additive on the combustion heat (a) and the burning rate (b) of the MTV pyrotechnic composition.

From Table 3 and Fig. 6a, it can be seen that with increased content of Fe_2O_3 nanoparticle additive, the combustion heat of the MTV pyrotechnic increases markedly compared to the sample without the additive. However, with the same samples containing these nano-admixtures, the combustion heat does not change significantly. The reason is that the thermite of Mg/Fe_2O_3 has a high combustion heat, but the amount of oxygen in nano-Fe_2O_3 added to the pyrotechnic composition is not large, so the oxygen balance of the system does not change appreciably, resulting in a negligible change in the heat of combustion between samples containing the additive.

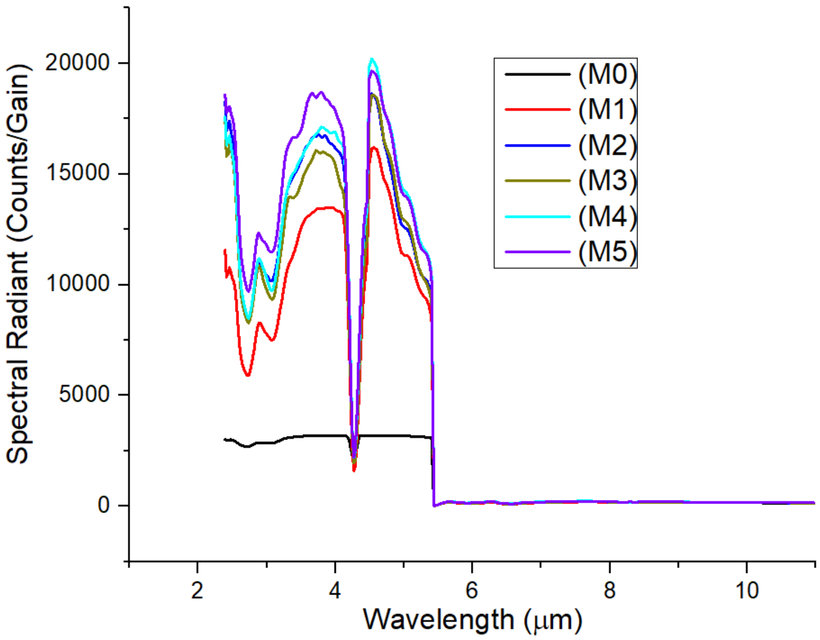
Regarding the combustion process, the pyrotechnic composition for infrared emission works more effectively when the burning rate (equivalent to the mass consumption rate of pyrotechnic composition) is higher [5, 21]. The linear burning rate of MTV pyrotechnic composition with additives is higher than without additives and this value increases with increased content of nano-Fe_2O_3 and reaches the maximum value at the Fe_2O_3 content of 8%, then decreases gradually (Fig. 6b). The thermite of Mg and nano-Fe_2O_3 has a higher reaction rate due to the fast particle diffusion process [15]. However, it only increases to a certain value - reaching the optimal value of combustion catalytic efficiency, then if the additive continues to increase, the burning rate decreases. This can be explained by the catalytic mechanism of metal oxide combustion catalysts [22]. In the process of burning composition, nano-Fe_2O_3 plays the role of both a catalyst to accelerate combustion and an oxidizing agent that oxidizes intermediate compounds, which causes nano-Fe_2O_3 to be reduced. When Fe_2O_3 is reduced to a certain extent, their combustion catalytic effect will decrease, leading to a decrease in the burning rate of the pyrotechnic composition.

3.3. Infrared emission characteristics of the MTV pyrotechnics containing Fe_2O_3 nanoparticles

The infrared emission characteristics of the MTV pyrotechnic composition were determined based on their spectral radiance value at different ranges of wavelength (λ = 2.4-3 μm; 3-5 μm; 8-10 μm). The effect of nano-Fe_2O_3 additive on the spectral radiances of the MTV pyrotechnic composition is given in Table 4. Fig. 7 presents the results of spectral radiance measurement *L* of the MTV pyrotechnic composition with 2 units of measurement: the spectral signal in counts per gain (gain is the gain value used for the detector) (counts/gain) and unites of irradiance after calibrated (W/sr/cm^2/μm).

Table 4. Effect of nano-Fe_2O_3 additive on the spectral radiances of the MTV pyrotechnic

Sample	% Fe_2O_3 (external content)	Spectral radiance, *L* (W/sr/cm^2/μm)			
		λ = 2.4-3 μm	λ = 3-5 μm	λ = 2.4-5 μm	λ = 8-10 μm
M0	0	0.411	0.447	0.867	0.126
M1	4	1.025	1.455	2.506	0.127
M2	6	1.457	1.820	3.312	0.130
M3	8	1.430	1.725	3.188	0.133
M4	10	1.476	1.863	3.373	0.143
M5	12	1.675	2.009	3.723	0.141



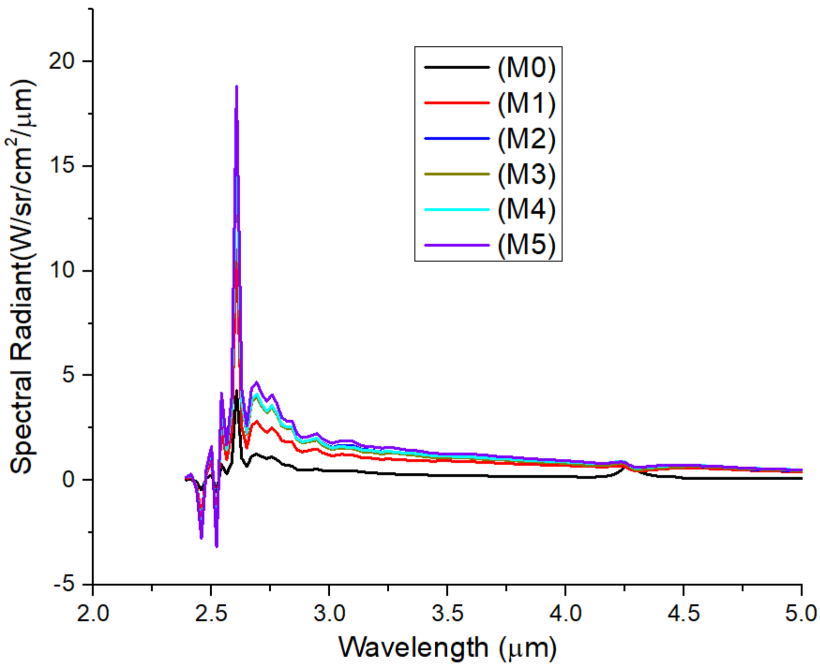


Fig. 7. Effect of nano-Fe_2O_3 additive on the spectral radiances of the MTV pyrotechnic.

As shown in Table 4 and Fig. 7, the nano-Fe_2O_3 additive increased the spectral radiance of the MTV pyrotechnic at different wavelength ranges. The infrared emission spectra increased as the nano-Fe_2O_3 admixture content was elevated. On the one hand, the spectral radiance of the MTV pyrotechnic composition was shifted to the wavelengths of 3-5 μm (increased more than 3 times) more than in the wavelengths of 2.4-3 μm (increased more than 2 times). On the other hand, at the wavelengths of 8-10 μm, the spectral radiance did not change much when adding admixtures with different content. Because the thermite of Mg/Fe_2O_3 produced a higher combustion heat and combustion temperature when reacting, the infrared spectra shifted to a shorter wavelength range (Wien's displacement law). Therefore, it can be confirmed that the added nano-Fe_2O_3 admixtures increased the infrared emission efficiency and shifted the radiation spectra of the MTV pyrotechnic composition mainly to the shorter wavelength area. This result has important significance for tuning the infrared emission spectra of the pyrotechnic composition in different wavelengths.

4. Conclusions

This article presents an experimental investigation on the effect of Fe_2O_3 nanoparticle admixture on some energy characteristics of the pyrotechnic composition for infrared emission based on MTV. The results of SEM and EDX analysis show a fairly even distribution of nano-admixtures in the pyrotechnic samples when using a sample homogenizer to disperse nano-Fe_2O_3 into the binder solution. The combustion heat and burning rate of samples containing additives were increased by nearly 1.3 times compared with those of the samples without additives. The spectral radiance of the pyrotechnic had also increased more than 3 times (in the 2.4-5 μm wavelength band). In addition, the shift of infrared emission to the ranges of the wavelength of 3-5 μm and 2.4-3 μm changed the relative intensity of the MTV composition. This result is the initial basis for assessing the influence of Fe_2O_3 nanoparticles on the infrared emission of the MTV pyrotechnic composition at a shorter wavelength area.

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ẢNH HƯỞNG CỦA PHỤ GIA Fe_2O_3 NANO LÊN MỘT SỐ ĐẶC TRƯNG NĂNG LƯỢNG CỦA THUỐC HỎA THUẬT PHÁT XẠ HỒNG NGOẠI TRÊN CƠ SỞ MAGIE-TEFLON-VITON

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Tóm tắt: Phụ gia nano là loại vật liệu được ứng dụng nhiều hiện nay để làm tăng hiệu quả hoạt động của các loại thuốc hỏa thuật (THT). Bài báo này trình bày các nghiên cứu về sự ảnh hưởng của phụ gia Fe_2O_3 nano lên một số đặc trưng năng lượng của THT phát xạ hồng ngoại trên cơ sở Magie-Teflon-Viton (MTV). Sự phân tán của phụ gia nano trong hỗn hợp THT được đánh giá bằng SEM và EDX. Kết quả nghiên cứu đã chỉ ra rằng phụ gia Fe_2O_3 nano được bổ sung vào hỗn hợp MTV đã làm tăng nhiệt lượng cháy, tăng tốc độ cháy và điều chỉnh khả năng phát xạ hồng ngoại của THT.

Từ khóa: *Phụ gia nano; tốc độ cháy; phát xạ hồng ngoại; Magie-Teflon-Viton.*

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