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Research Article

Comparative Study of Synthesis Approaches for $MgAl_2O_4$ as a Refractory Material

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ABSTRACT

$MgAl_2O_4$ is one of the most concentrated spinels, which possesses many applications as an important refractory compound in the fields of steel-making industries. In this research, $MgAl_2O_4$ refractory materials were synthesized via the employment of combustion and solid-state approaches. To produce this material through combustion synthesis, aniline was used as a fuel. The XRD spectra showed that the synthesized materials via combustion approach include amorphous products while well crystallized cubic phases are formed within solid-state procedure. The SEM images indicated that the utilization of combustion and solid-state approaches leads to the production of $MgAl_2O_4$ materials with the average particle sizes of 40 nm and 70 µm, respectively. The DTA/TGA results of the combustion synthesized $MgAl_2O_4$ confirmed a considerable weight loss of 15.1 % within heating to 550 °C. Additionally, the exothermic peaks at 126 and 380 °C are related to the elimination of the organic compounds of the combustion-synthesized materials. Based on the obtained results, although both combustion and solid-state approaches can successfully synthesize $MgAl_2O_4$ refractory materials, the combustion method is more recommended due to its ability to produce finer, uniform nano-sized particles with higher surface area and reduced agglomeration problems, making it a superior route for refractory applications.

1. Introduction

$MgAl_2O_4$ is a spinel material that exhibits interesting optical, thermal, and mechanical properties [1]. In this regard, this compound has been considered as a refractory material in the steel industry due to its high melting point (2135 °C), good chemical stability, low thermal expansion coefficient, and adequate thermal conductivity. The literature review reveals that $MgAl_2O_4$ possesses many applications in steel-related industries. $MgAl_2O_4$ castables are used in the non-slag-tapping side of refining ladles and lining of steelmaking furnaces. The mentioned refractories have better thermal shock resistance and high temperature strength than traditional MgO-Cr_2O_3 compounds [2-5]. On a large scale, $MgAl_2O_4$ can be synthesized by solid-state reactions between Al_2O_3 and MgO at temperatures greater than 1500 °C [1, 6]. Although this method is cost-effective, the final product may contain impurities due to milling or crushing processes [7], which can affect the properties of the compound. As discussed, the solid-state reaction

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method was selected among various synthesis approaches due to its cost-effectiveness, wide availability, and suitability for large-scale production [6, 7]. Additionally, it has been traditionally employed in the industrial fabrication of $MgAl_2O_4$ refractories, making it a relevant and practical reference for comparison. Incorporating the solid-state procedure in this study provides a meaningful benchmark to evaluate the advantages and limitations of the combustion method, particularly regarding crystallinity, particle size, and agglomeration. By applying other techniques such as sol-gel [8, 9], co-precipitation [10], hydrothermal [11], pyrolysis [12], mechanical alloying [13], and combustion [14-17], the purity of the final product may be enhanced. In the sol-gel process, inorganic salts have been used to produce $MgAl_2O_4$ after calcination at 600-900 °C [8, 9]. Nam et al. [10] used the carbonate precipitation method to fabricate nanostructured $MgAl_2O_4$. In the hydrothermal process, magnesium hydroxide and pseudoboehmite have been used to synthesize magnesium aluminium hydroxide hydrate [11]. Spinel powders were also synthesized by pyrolysis of complex compounds of aluminum and magnesium with triethanolamine (TEA) after heat treatment at 675 °C [12]. Mechanical alloying of γ-Al_2O_3–MgO, AlO(OH)–MgO, and α-Al_2O_3–MgO mixtures at room temperature under an air atmosphere up to 140 h resulted in the formation of $MgAl_2O_4$ [13]. Recent studies have highlighted the potential of nano-sized $MgAl_2O_4$ powders for advanced applications such as additive manufacturing, improved refractory performance, and enhanced corrosion resistance [18-22]. These works suggest that reducing particle size can significantly improve densification, mechanical strength, and chemical stability of the final products. However, despite these promising results, a systematic comparison of nano-sized $MgAl_2O_4$ powders prepared by different synthesis routes is still limited, particularly with respect to combustion methods. Among the mentioned processes, solution combustion is promising because it is cost-effective and fast [14-17]. In this process, different fuels can be used to produce $MgAl_2O_4$ powder. Aniline was selected in this study as the fuel because its high nitrogen and carbon contents ensure a strong exothermic reaction, generating large volumes of gaseous byproducts (CO_2, H_2O, N_2) that favor the formation of foamy, fine powders with uniform morphology and reduced agglomeration. Compared with other fuels such as glycine, urea, or hydrazine, aniline provides higher combustion enthalpy and more effective pore-forming ability, leading to nano-sized particles with narrow size distribution [15-17, 23, 24].

Although the combustion process has been used previously, however, a comparison of this method with the conventional solid-state technique was not performed. This comparison is important because each approach has distinct advantages and limitations. The solid-state route is low-cost and well-established for large-scale refractory production, but it requires high temperatures and prolonged processing, often leading to coarse particles and agglomeration. In contrast, the combustion method is a rapid and energy-efficient process that produces fine, uniform powders with high surface area, but it may involve residual organic phases that require post-calcination. Therefore, evaluating both techniques side by side provides a comprehensive understanding of their suitability in terms of cost, energy consumption, scalability, and product quality for refractory applications. The goal of this study is to compare the characteristics and properties of $MgAl_2O_4$ powders synthesized by traditional solid-state and combustion methods.

2. Experimental

2.1. Materials preparation

The $MgAl_2O_4$ particles were synthesized via combustion and solid-state methods. Aluminum nitrate ($Al(NO_3)_3.9H_2O$), magnesium nitrate ($Mg(NO_3)_2.6H_2O$), and aniline ($C_6H_5NH_2$) were used as the starting materials in the combustion synthesis. Accordingly, aluminum and magnesium nitrates were dissolved in a small quantity of de-ionized water under vigorous stirring for about 7 minutes.

Then, aniline was added to the obtained precursor while stirring, serving as the fuel. The resulting mixture was transferred to an electric box furnace set at 500 °C. After about 12-15 minutes, foamy and low-density $MgAl_2O_4$ powders were obtained. To eliminate the organic compounds, the powders were calcined at 800 °C for 1 hour. The overall balanced chemical equation for the combustion process of the mixture is shown in Eq.(1) :

$$31Mg(NO_3)_2 + 62Al(NO_3)_3 + 40C_6H_5NH_2 = 31MgAl_2O_4 + 240CO_2 + 140H_2O + 144N_2 \quad \text{Eq.(1)}$$

This reaction is exothermic and self-sustaining, with the evolved gases (CO_2, H_2O, and N_2) forming a porous, foam-like structure in $MgAl_2O_4$. Thermodynamically, the reaction has a negative ΔH and ΔG, ensuring both the release of energy and the stability of the product.

Additionally, aluminum oxide (Al_2O_3) and magnesium oxide (MgO) were used as the initial materials in solid-state approaches. The mixture of initial materials was heated in a tube furnace fixed at 1300 °C for two h. The attributed reaction in the solid-state procedure can be considered as follows (Eq.(2)):

$$Al_2O_3 + MgO = MgAl_2O_4 \quad \text{Eq.(2)}$$

As discussed, the solid-state synthesis of $MgAl_2O_4$ involves heating a mixture of MgO and Al_2O_3 at 1300 °C for 2 hours, leading to the formation of a stable crystalline spinel. At lower temperatures, the reaction is non-spontaneous ($\Delta G^\circ > 0$) and requires external

thermal energy to enable the migration of Mg^{2+} and Al^{3+} ions within the oxide lattice. The obtained spinel possesses high crystallinity as well as excellent chemical and thermal stability.

2.2. Characterizations

The crystallographic characteristics of materials were studied by X-ray diffraction (XRD, Rigaku, Japan) using a rotating anode and Cu Ka radiation source (k = 0.15418 nm). The microstructure of phosphors was evaluated through the employment of a scanning electron microscope (SEM, JSM 6360, Japan). The thermal gravimetry and differential thermal gravimetry (TG, DTG, SDT Q 600, USA) were employed to investigate the effect of calcination on the surface chemistry and structure of combustion-synthesized phosphors.

3. Results and Discussion

Fig. 1 (a). shows the XRD spectra of combustion-synthesized $MgAl_2O_4$ nano-powders. The broad peaks indicate that the as-synthesized materials are not well crystallized, and the main parts of combustion-synthesized $MgAl_2O_4$ include amorphous compounds. In other words, through the employment of the short combustion approach, the synthesized compounds possess weak crystallinity. It is observed that the calcination of these materials at 800 °C converts the amorphous phases into crystalline material. It was found that the XRD results of the produced $MgAl_2O_4$ spinels completely match with JCPDS 01-073-1959. The most powerful diffraction peaks have occurred at 2θ of 18.9, 31.25, 36.8, 45.1, 55.9, 59.92, and 65.05, which are respectively attributed to (111), (220), (311), (400), (422), (511), and (440) planes [23-27]. Fig. 1 (b). indicates that the produced $MgAl_2O_4$ via solid-state possesses proper crystallinity. This issue originates from high temperature and sufficient diffusion in this procedure. Fig. 1 (c). presents the XRD spectra of the combustion/solid-state synthesized $MgAl_2O_4$. It is seen that the XRD peaks of the solid-state related materials are slightly sharper and narrower than those of the combustion one.

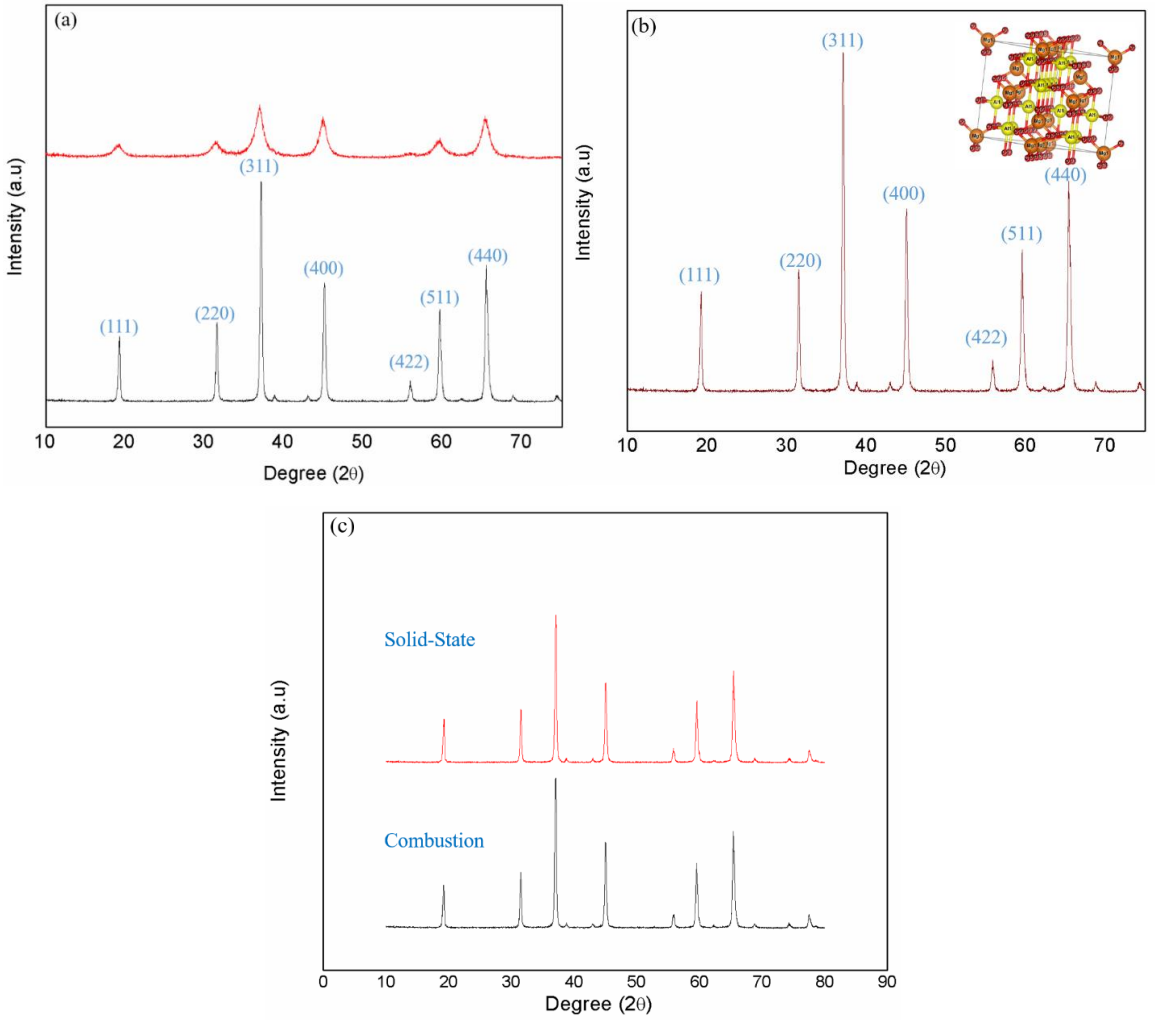

Fig. 1. XRD spectra of $MgAl_2O_4$ synthesized via (a) combustion, (b) solid-state, and (c) combustion/solid-state approaches.

Table 1. presents the crystallographic characterizations of the synthesized $MgAl_2O_4$. Accordingly, the synthesized spinel possesses a cubic crystal structure with an Fd-3m space group. Meanwhile, the lattice parameter of this cubic crystal structure is 8.05 Å.

Figs. 2 (a-c). show the SEM microstructures of solid-state synthesized $MgAl_2O_4$ in different magnifications. It is seen that the particle size of the synthesized materials is mainly in the range of 50-90 μm. Additionally, the formed particles do not possess any geometrical shape. It should be noted that the employment of a solid-state approach may result in severe agglomeration. Fig. 2 (c). reveals that the size of agglomerated particles can reach more than 200 μm. The EDX data of this material shows that the obtained purity is acceptable and no impurity can be traced (see Fig. 2 (d)).

Table 1. Crystallographic characterizations of the synthesized $MgAl_2O_4$.

Items	**$MgAl_2O_4$**
Reference Code	01-073-1959
ICSD Name	Magnesium Aluminum Oxide
Chemical Formula	$MgAl_2O_4$
Crystal System	Cubic
Space Group	Fd-3m
Space Group No.	227
a (Å)	8.05
b (Å)	8.05
c (Å)	8.05
Alpha (^{0})	90
Beta (^{0})	90
Gamma (^{0})	90
Calculated density (g/cm^3)	3.62

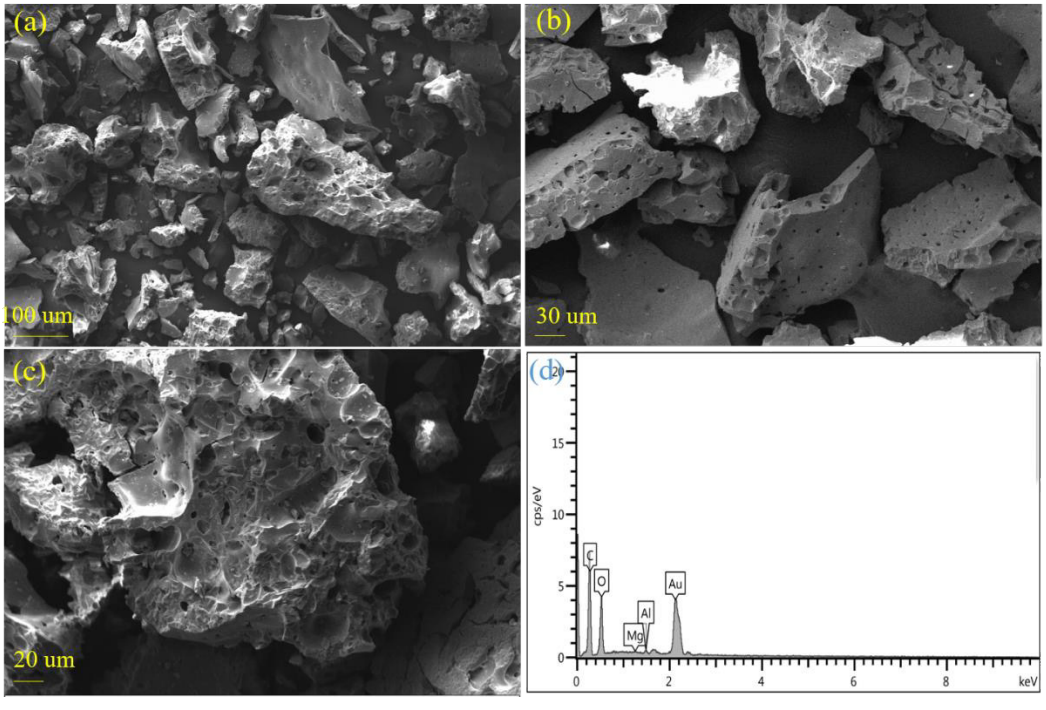

Fig. 2 (a-c). SEM microstructures in different magnifications and (d) EDX data of solid-state synthesized $MgAl_2O_4$.

Figs. 3 (a-d). show the SEM microstructures of combustion-synthesized $MgAl_2O_4$ in different magnifications. Herein, the average particle size of $MgAl_2O_4$ powders is about 40 nm. The large quantity of the produced gas within the combustion procedure leads to the formation of fine particles. Consequently, a high surface area with higher compactability of refractory materials is achieved through the utilization of the combustion approach. Additionally, the formed particles possess semi-spherical morphology. It should be considered that the employment of combustion gives rise to the production of uniform particle size (see Fig. 3 (c,d)). In other words, the combustion technique brings microstructures with a narrow distribution. Similar to the materials synthesized via solid-state, the EDX data reveal that no impurity can be traced and the chemical composition is suitable (see Fig. 3 (e)). The above results show that based on the achieved uniformity and particle sizes, the fabricated $MgAl_2O_4$ spinels via combustion synthesis promise more hopeful benefits for refractory applications than solid-state ones.

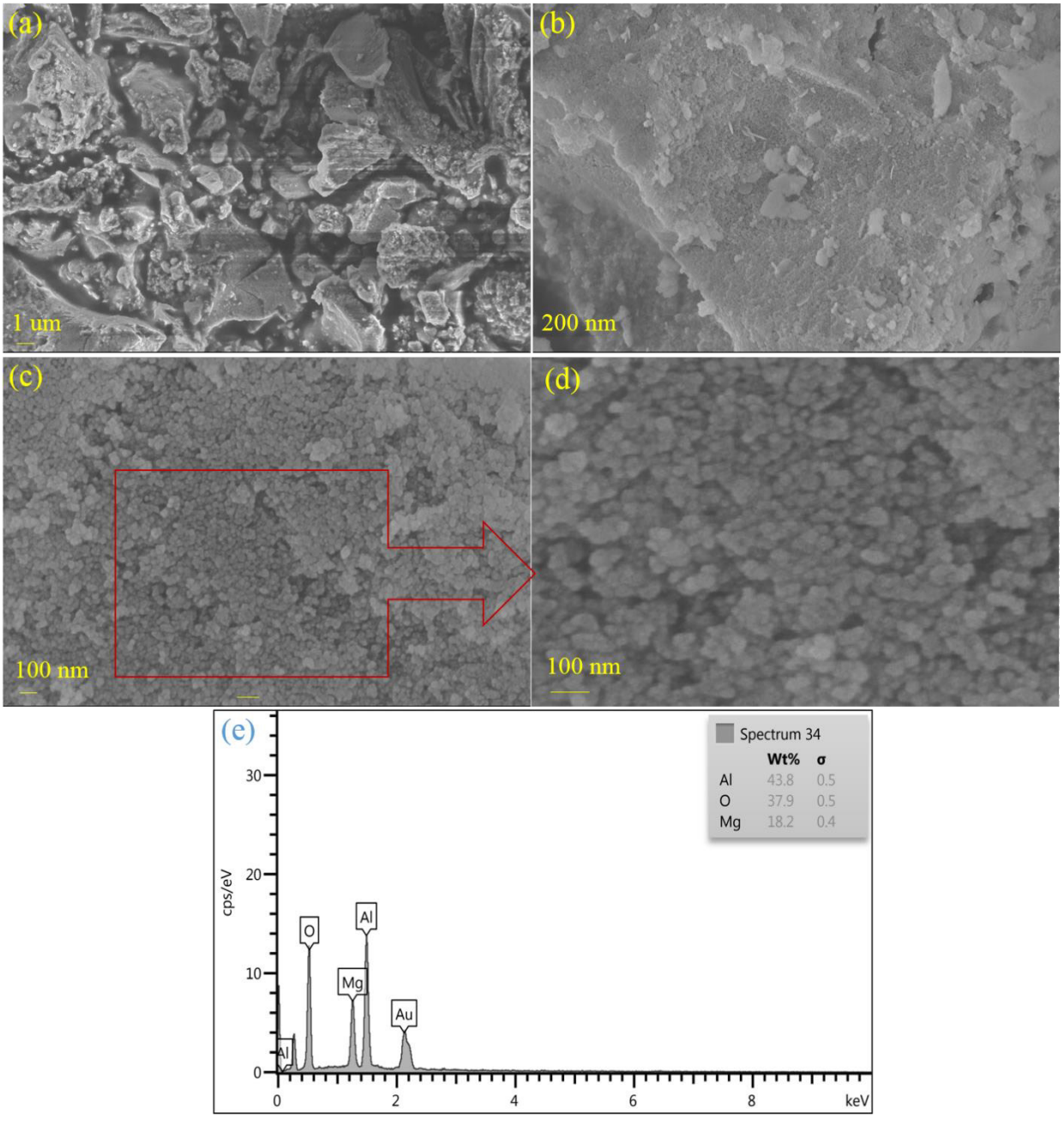

Fig. 3 (a-d). SEM microstructures in different magnifications, (e) EDX data of combustion-synthesized $MgAl_2O_4$.

The DTA/TGA results of the combustion-synthesized $MgAl_2O_4$ materials show the structural transformations through (see Fig. 4). heating from the ambient temperature to 550 °C. Fig. 4 (a). indicates that the occurred weight loss is 15.1 % in the case of using aniline as a fuel within the combustion procedure. It is easily seen that the $MgAl_2O_4$ refractory powder possesses remarkable values of organic phases. This result is in good agreement with the XRD data.

Fig. 4 (b). presents the drive weight of $MgAl_2O_4$ materials versus temperature. It is seen that there are two prominent peaks at 126 and 380 °C. The literature review reveals that these exothermic peaks are related to the elimination of the existing organic compounds in the combustion-synthesized materials [23]. In other words, based on the consumption of remarkable amounts of organic fuels within the combustion approach, the products possess organic phases which are reduced during heating. Notably, the solid-state synthesized materials did not show any similar DTA/TGA results. This phenomenon originates from this fact that, within the solid-state procedure, pure $MgAl_2O_4$ material with a well-crystallized structure has been produced through the application of high temperature.

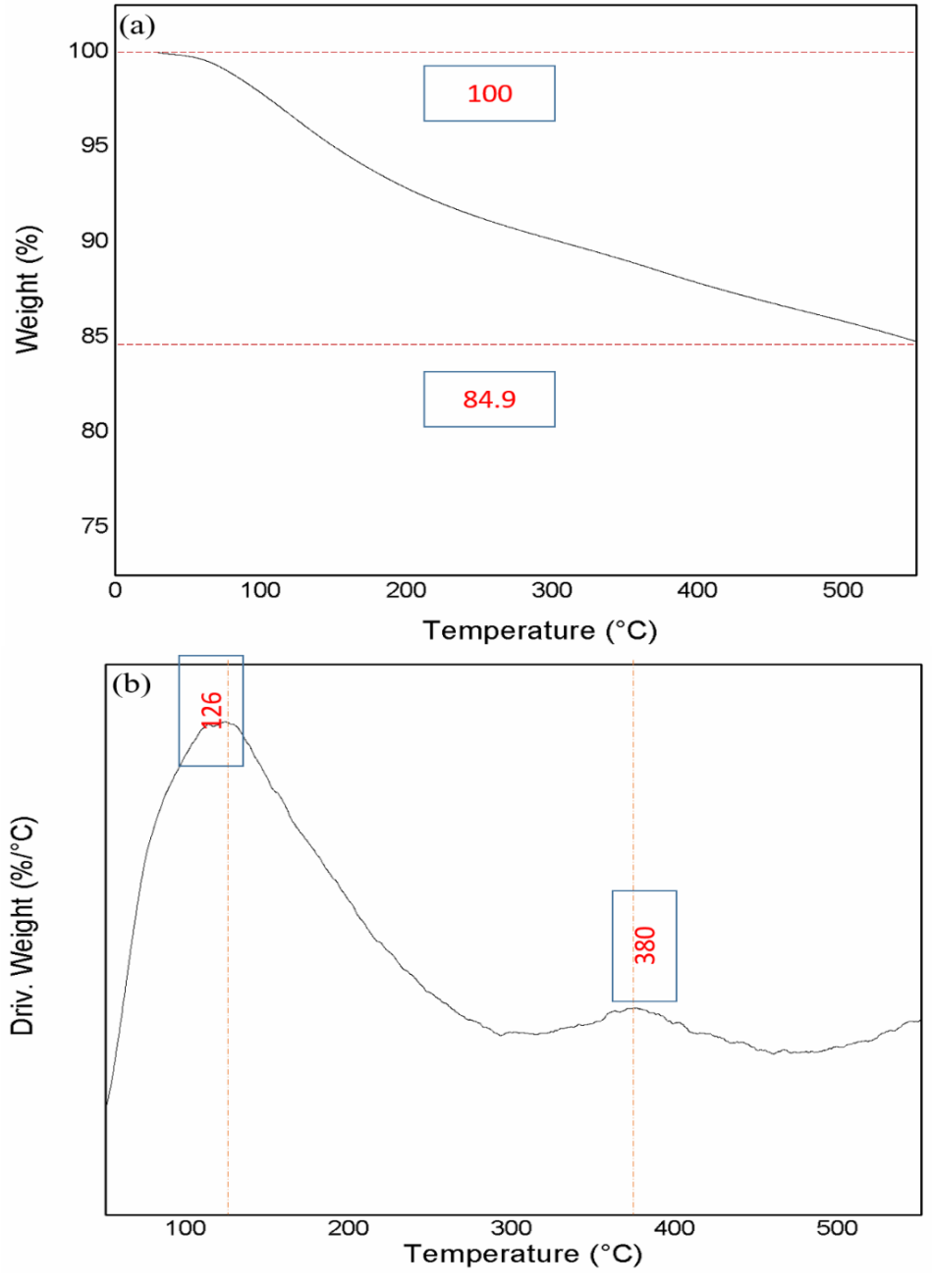

Fig. 4. DTA/TGA spectra of $MgAl_2O_4$ synthesized via combustion approach (a) loss of weight and (b) gain of weight during the increase of temperature.

4. Conclusions

In this work, $MgAl_2O_4$ powders were synthesized through solid-state and combustion approaches for refractory applications. The XRD spectra clarified that the FWHM of the materials synthesized via the combustion technique is remarkably larger than that of the solid-state synthesized products. The SEM images revealed that the employment of combustion and solid-state approaches has given rise to the formation of materials with the average particle sizes of 40 nm and 70 μm, respectively. Additionally, given that the use of solid-state procedure leads to an agglomeration problem, the combustion method can be known as the more proper approach for the production of $MgAl_2O_4$ refractory materials. The DTA/TGA spectra of the combustion synthesized $MgAl_2O_4$ revealed that through the heat treatment of materials from the ambient temperature to 550 °C a considerable weight loss occurs while an exothermic peak of driving weight originates from the evaporation of the organic compounds.

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