Preparation of $MgAl_2O_4$ Nanopowder using Combustion Synthesis Method and Its Properties

Tổng hợp bột nano $MgAl_2O_4$ bằng phương pháp đốt cháy và khảo sát tính chất

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Received: June 14, 2018; Accepted: August 29, 2018

Abstract

Preparation of a high purity powder is one of the most important steps in producting transparent $MgAl_2O_4$ ceramic. Additionally, the particles are required to have nanoscale scale, uniform size and least agglomeration, which make diffusion enhanced at grain boundary during sintering process, promote densification to achieve full dense bulk material. In present work, solution combustion synthesis was carried out to prepare $MgAl_2O_4$ nanopowder from magnesium nitrate hydrate ($Mg(NO_3)_2.6H_2O$) and aluminum nitrate hydrate ($Al(NO_3)_3.9H_2O$) as oxidizers and urea CH_4N_2O as a fuel. The obtained products present large agglomerates of nanoscale particles with average size of about 20 nm. Investigation into the influence of the milling processing on deagglomeration efficiency and properties of sintered samples showed that increasing milling time and ball-to-weight ratio led to reduce agglomerate size and fraction, consequently, enhanced significantly shrinkage value, relative density and compressive strength of sintered $MgAl_2O_4$ samples. The relative density and the compressive strength achieved highest values of 98% and 155 MPa, respectively, regarding to the powder with milling condition of 48h milling time and 30/1 ball-to-powder ratio.

Keywords: $MgAl_2O_4$, combustion synthesis, ball milling, nanoparticle, agglomerate

Tóm tắt

Tổng hợp bột với độ sạch cao là một trong những bước quan trong nhất trong quy trình chế tạo gốm trong suốt $MgAl_2O_4$. Bên cạnh đó, bột được yêu cầu phải có kích thước nanomét, đồng đều và hạn chế các khối tích tụ nhằm mục đích tăng cường khả năng khuếch tán ở biên giới hạt trong quá trình thiêu kết để thu được sản phẩm có tỷ trọng gần đặc. Trong nghiên cứu này, phương pháp đốt cháy được sử dụng để tổng hợp bột MgAl2O4 kích thước nanomét sử dụng các muối ($Mg(NO_3)_2.6H_2O$) và ($Al(NO_3)_3.9H_2O$) làm chất oxy hóa và urea làm nhiên liệu. Sản phẩm nhận được có dạng các khối tích tụ lớn của các hạt bột nhỏ với kích thước hạt trung bình là 20 nm. Nghiên cứu ảnh hưởng của quá trình nghiền đến khả năng tách rời các hạt và tính chất của sản phẩm sau thiêu kết cho thấy kéo dài thời gian nghiền và tỷ lệ bi/bột giúp làm giảm kích thước và tỷ phần của các đám bột tích tụ; do đó làm tăng khả năng co ngót, tỷ trọng và độ bền nén của mẫu sau thiêu kết. Tỷ trọng tương đối và độ bền nén của mẫu đạt giá trị cao nhất tương ứng là 98% và 155 MPa.

Từ khóa: $MgAl_2O_4$, phương pháp đốt cháy, nghiền cơ học, hạt nanô, sự tích tụ

1. Introduction

Recently, $MgAl_2O_4$ Spinel has received a great deal of attention from academia and the industry sector on account of its best combination of several important properties, such as high melting point, hardness, mechanical strength both at room and elevated temperatures, resistance against chemical attack, electrical resistivity, thermal shock resistance; and relatively low density, and thermal expansion coefficient[1,2]. Furthermore, fully dense, polycrystalline $MgAl_2O_4$ spinel is transparent to electromagnetic radiation from ultraviolet through mid-infrared range (0.2 – 5.5 μm). Applications of these materials have been found in a wide range such as solid – state lasers, lighting, scintillators, optical devices, electro-optical devices and biomaterials[3–5].

Transparent ceramics in general and transparent $MgAl_2O_4$ in particular have an amount of sites influencing on transparency including pores, impurities, secondary phase, crystalline structure, grain boundary, surface roughness and thickness[6–9]. Consequently, each step of processing plays a vital

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role in performance of final ceramics products, especially powder fabrication and sintering. The transparency of ceramic is very sensitive to impurities, hence powder must have high purity (> 99.5%) and homogeneous phase. Additionally, the particles have nanoscale scale, large specific surface area, uniform particle size and least agglomeration, since nanoscale particles make diffusion enhanced at grain boundary during sintering process, promote densification to achieve full dense bulk material. Thus selection of synthesis methods is directly responsible for transparency and mechanical properties of transparent ceramics.

Numerous methods have been adapted to synthesize nanoscale $MgAl_2O_4$ powders, including physical[10] and chemical methods[11]. Recently, chemical synthesis methods have been received increasing attention due to their ability to produce a large variety of composition and assurance of homogeneous mixing of the constituent particles at atomic level. Some chemical methods that have been widely used to synthesize $MgAl_2O_4$ nanopowders are such as sol-gel method[12], hydrothermal[13], chemical precipitation[14], and combustion synthesis. Among chemical synthesis methods, solution combustion synthesis is a sophisticated approach to synthesize nanoparticles due to low temperature requirement, homogeneous products, and low-cost precursors[15–19]. Variety of researches reported that solution combustion synthesis have been effective for preparation of ultrafine $MgAl_2O_4$ powders[20–25]. However, powders prepared from solution combustion synthesis route present agglomerates, which considerably influences on their performances. Deagglomeration nanoparticle step was often required to isolate the particles.

In the present study, solution combustion synthesis was carried out to prepare $MgAl_2O_4$ nanopowder from magnesium nitrate hydrate ($Mg(NO_3)_2.6H_2O$) and aluminum nitrate hydrate ($Al(NO_3)_3.9H_2O$) as oxidizers and urea CH_4N_2O as fuel. Influence of milling processing on deagglomeration efficiency and properties of sintered samples was investigated

2. Experimental procedure

The starting materials were aluminum nitrate hydrate ($Al(NO_3)_3.9H_2O$) (99%, Xilong Scientific Co. Ltd., China) and magnesium nitrate hydrate ($Mg(NO_3)_2.6H_2O$) (99%, Xilong Scientific Co. Ltd., China) as oxidizers, and urea (CH_4N_2O) (99%, Xilong Scientific Co. Ltd., China) as a fuel. Precursor mixture was stoichiometrically balanced by a molar ratio of 3:6:20, and then dissolved in distilled water. Subsequently, the solution was placed in an electric resistance furnace (Linn HT1300, Germany) which preheated at 500ºC. The combustion reaction occurred according to the following reaction to form a voluminous product:

$$3Mg(NO_3)_2\,(aq) + 6Al(NO_3)_3\,(aq) + 20CH_4N_2O\,(aq) \rightarrow 3MgAl_2O_4(s) + 20CO_2(g) + 40H_2O(g) + 32N_2(g)$$

The synthesized product was milled for 24, and 48 hours in a highly pure ethanol solution using alumina balls with ball – powder mass ratios of 20/1 and 30/1. The milled powder was dried at 120ºC for 24 hours and then calcined at 1100ºC for 2 hours. The green compacts were formed by uniaxial pressing in a 15 mm inner diameter cylindrical steel die with a uniaxial applied pressure of 550 MPa. The compacted samples were then sintered by an electrical resistance heating furnace (Linn HT1600, Germany) at 1550ºC for 4 hours in argon atmosphere.

The phase analysis was carried out by X-ray diffraction (D5000 Siemens) using Cu Kα radiation. The average crystallite sizes of $MgAl_2O_4$ spinel were determined by Scherrer method. Morphology of synthesized powders and sintered samples was characterized by a field-emitting scanning electron microscope (FE-SEM Hitachi S4800, Japan). Particle size and size distribution were evaluated by ImageJ software through SEM images. In addition, energy dispersive analysis (EDX) was performed to identify the elements that present in synthesized powders. The compressive strength was tested on MTS 300 machine (USA). Relative density was calculated by Archimedes method in water.

3. Results and Discussion

X-ray diffraction patterns of combustion-synthesized product before and after annealing at 1100ºC in air for 2 hours are shown in **Figure 1**. XRD pattern of combustion-synthesized product before annealing (red line) showed 4 peaks at 2θ of 36.81º, 44.79º, 59.38º, 65.24°. These peaks and their relative intensities correspond to magnesium aluminate spinel phase as given in the ICDD 01-082-2424 file. Besides, the broaden peaks reveal a poor crystallinity of the combustion-synthesized product. After anealing, almost all of the $MgAl_2O_4$ reflections appeared in the XRD pattern (black line) are detected at 2θ of 31.29º, 36.81º, 38.52º, 44.79º, 56.21º, 59.38º and 65.24º corresponding to (220), (311), (222), (400), (422), (511), and (440) diffraction planes. The peaks of $MgAl_2O_4$ phase are more intense and well-defined. Moreover, the small peak width indicates a good crystallinity with a large crystallite size of the annealed product. In addition, no peaks of impurities observed indicates that the combustion synthesis process was operated in a very well-controlled condition.

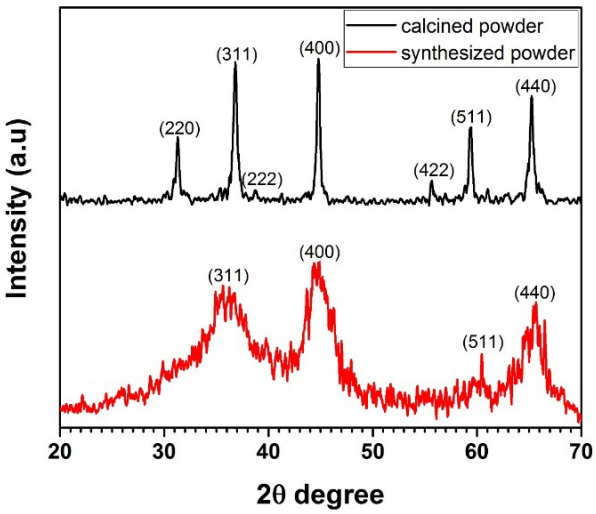

Fig.1 XRD patterns of combustion-synthesized powders before and after annealing at 1100°C in air for 2 hours

The average crystallite sizes of $MgAl_2O_4$ spinel before and after annealing were determined by Scherrer method from the full width at the half maximum (FWHM) of the $MgAl_2O_4$ (311) peak. The crystalline size of combustion-synthesized $MgAl_2O_4$ before and after annealing were approximately 0.54 and 15.61 nm, respectively. This phenomenon revealed that heat treatment recovered considerably internal strains and made the crystallite size increase remarkably.

The combustion-synthesized $MgAl_2O_4$ product before annealing was voluminous white and occupied the entire volume of container (Figure 2).

Fig.2 Photograph of combustion-synthesized $MgAl_2O_4$ product

Due to difficulty of observing morphology from the photograph, morphology of the combustion-synthesized product was further characterized by SEM observation. As expected, SEM images (Figure 3a and Figure 3b) revealed much better local morphology of product. The product was in form of large agglomerates of fine spherical particles. Average sizes of particles and agglomerates were 20 nm and 8 µm, respectively. Energy-dispersive X-ray spectroscopy (EDX) pattern acquired at the agglomerates showed that magnesium, aluminum and oxygen were the only detected elements with an atomic ratio approximately 1:2:4. It implied that combustion-synthesized product possessed a relatively high purity.

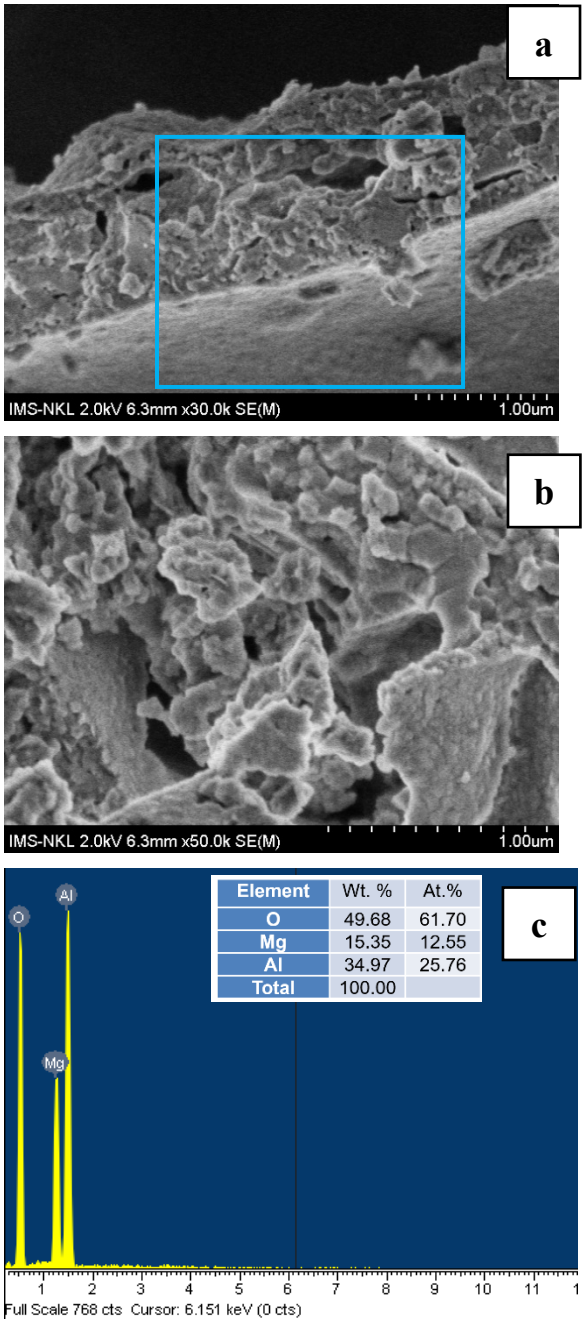

Fig.3 SEM image of combustion-synthesized $MgAl_2O_4$ product before annealing at different magnifications of 50k (a) and 100k (b) and corresponding EDX spectrum (c)

Wet-ball-milling was carried out to isolate the $MgAl_2O_4$ particles. In order to investigate the deagglomeration efficiency, the ball-powder mass ratio was varied from 10/1 to 20/1 and the milling time was varied from 24 to 48 hours. Figure 4 displayed SEM images of $MgAl_2O_4$ powders milled with different milling conditions. It seems that the particle size does not change significantly when changing the milling parameters. However, the milling condition has a great influence on deagglomeration of particles. As can be seen, the agglomerates were still existed as a large particle at lower ball to powder ratio and shorter milling time. Increasing the milling time and ball-to-powder ratio, the amount of particle agglomerates significantly decreases. The agglomerate-size distribution and the percentage of particle volume of $MgAl_2O_4$ powders milled with different milling conditions are presented in Figure 5. Increasing the milling time and ball-to-powder ratio tends to give a narrow size distribution. After 24 hours of milling with ball-to-powder ratio of 20/1, the agglomerate size is up to about 80 nm. Increasing milling time to 48 hours or ball-to-powder ratio to 30/1 leads to a decrease not only in the agglomerate size to about 22 nm but also the agglomerate proportional volume. Moreover, the particle size was homogeneous when the milling time prolonged to 48h with the ball-to-powder ratio of 30/1.

To investigate the influence of agglomerate state on sintering ability and microstructure of sintered samples, Figure 6 depicts microstructure of fractured surface of $MgAl_2O_4$ samples with different milling conditions corresponding to no-milled powder (Figure 6a) and powder milled in 48 hours with ball-to-powder ratio of 30/1 (Figure 6b).

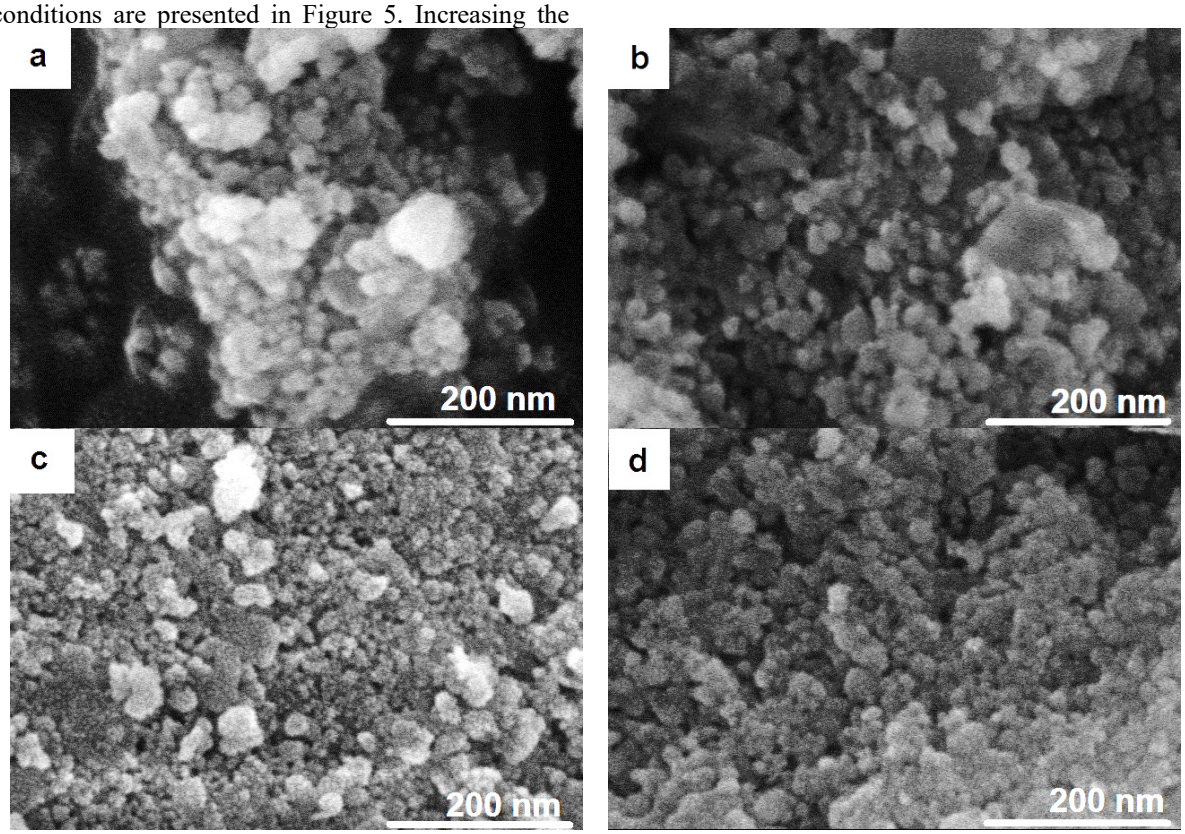

Fig.4 SEM image of $MgAl_2O_4$ powders milled for 24 hours with ball/powder ratio of 20/1 (a); for 24 hours with ball/powder ratio of 30/1 (b); for 48 hours with ball/powder ratio of 20/1 (c); for 48 hours with ball/powder ratio of 30/1 (d)

Tab.1 Shrinkage value, relative density and compressive strength of sintered $MgAl_2O_4$ samples regarding to powders milled at different milling conditions

Milling mode		Shrinkage (%)	Relative density (%)	Compressive strength (MPa)
Milling time	Ball – Powder ratio			
24 hours	20:1	30.35	85.79	136.8
	30:1	32.07	87.79	140.7
48 hours	20:1	38.84	92.78	150.9
	30:1	44.97	97.77	154.4
Without milling		18.05	80.2	65.3

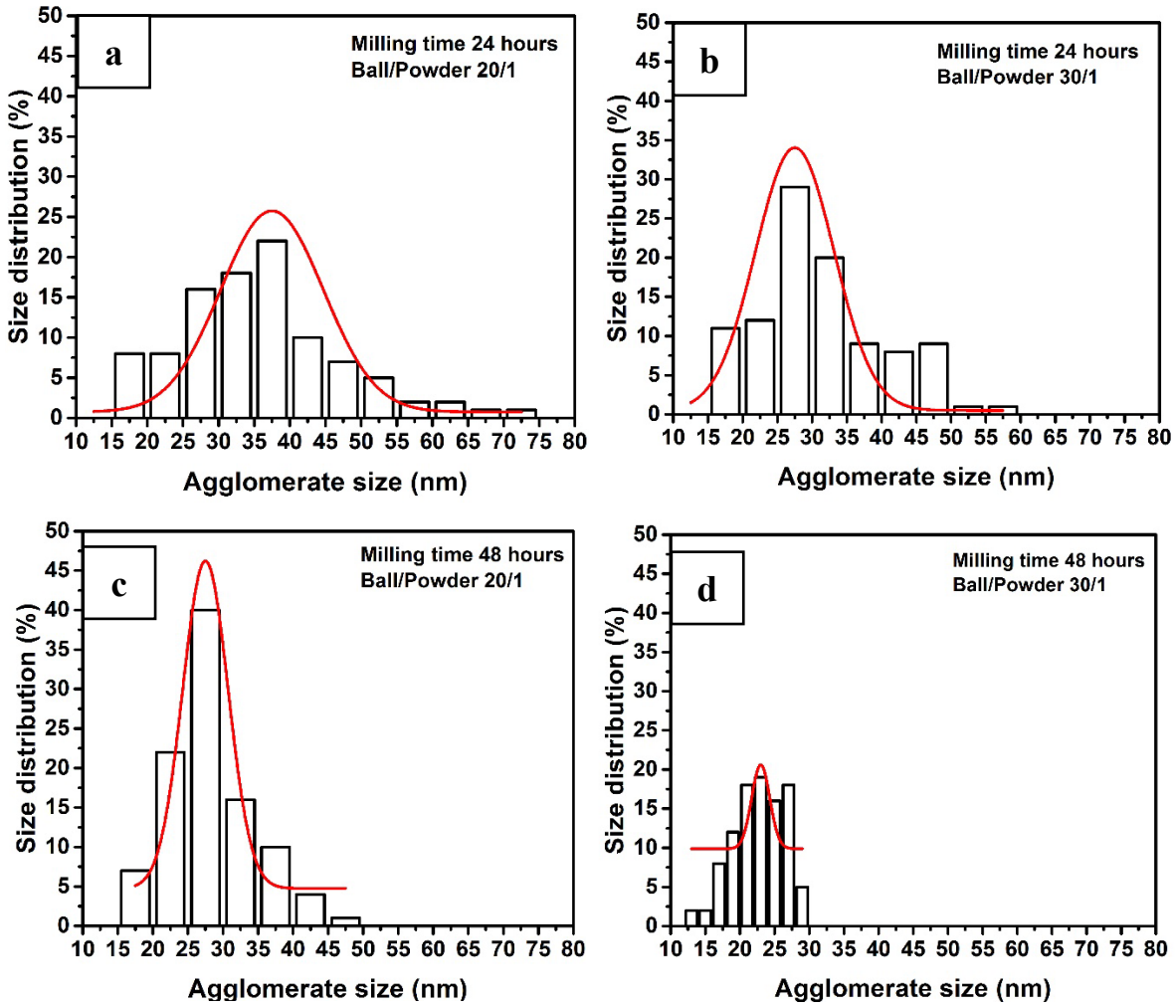

Fig.5 Agglomerate-size distribution of the $MgAl_2O_4$ powders milled for 24 hours with ball/powder ratio of 20/1 (a); for 24 hours with ball/powder ratio of 30/1 (b); for 48 hours with ball/powder ratio of 20/1 (c); for 48 hours with ball/powder ratio of 30/1 (d)

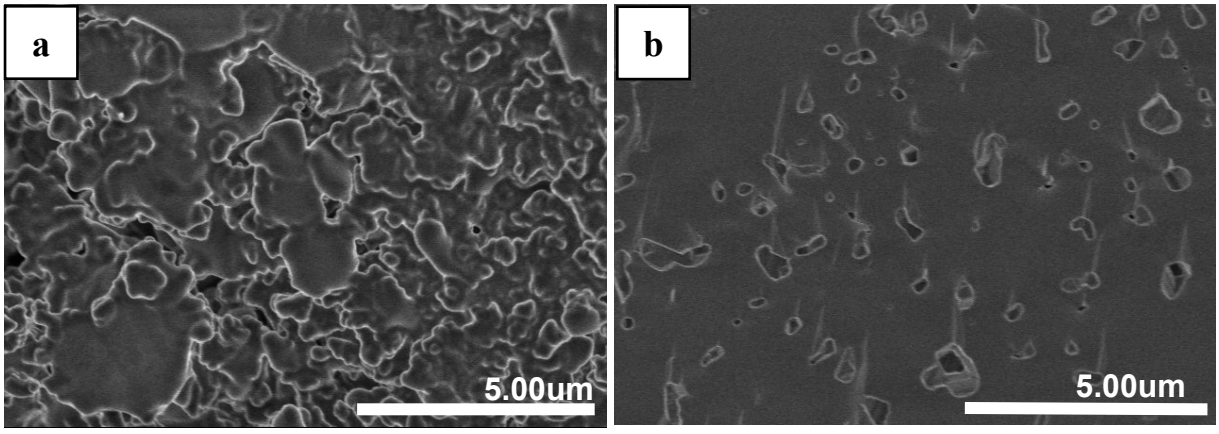

Fig.6 SEM image of fracture surface of sintered samples regarding to no - milled powder (a) and powder milled for 48 hours with ball-to-powder ratio of 30/1 (b)

The shrinkage value, relative density and compressive strength of $MgAl_2O_4$ sintered samples regarding to powders milled at different milling conditions are presented in **Table 1**. The shrinkage values were calculated from the change of sample volume before and after sintering in percent. Increasing milling time and ball-to-weight ratio led to lower agglomerate size and fraction, consequently, higher shrinkage value, relative density and compressive strength of the sintered $MgAl_2O_4$ samples. The shrinkage values of sintered $MgAl_2O_4$ samples changed from 30% to 45%. The relative density and the compressive strength achieved highest values of 98% and 155 MPa, respectively, regarding to powder with milling condition of 48h milling time and 30/1 ball-to-powder ratio.

It can be summarized that more uniform particle size distribution and less agglomerate proportion the milled powder is, the higher shrinkage value and density the sintered samples achieve. This phenomenon might be explained that agglomerates shrink at different rates and pull the compact apart, hence inhomogeneous movements in the green compact prevent during sintering.

4. Conclusions

$MgAl_2O_4$ powder was successfully prepare using solution combustion synthesis. XRD and EDX results indicated that the relatively high purity of combustion – synthesized product. Microstructure was in the form of large agglomerates of fine spherical particles. After milled for 48 hours with ball – powder mass ratio of 30/1, $MgAl_2O_4$ powder had homogeneous distribution with nanoscale average size of 22 nm. The sizes of particle agglomerates strongly influence on the sintering ability and the microstructure of sintered samples. Increasing milling time and ball-to-weight ratio led to reduce agglomerate size and fraction, consequently, higher shrinkage value, relative density and compressive strength of sintered $MgAl_2O_4$ samples. The relative density and the compressive strength achieved highest values of 98% and 155 MPa, respectively, regarding to powder with milling condition of 48 hour milling time and 30/1 ball-to-powder ratio.

5. Acknowledgement

This research is funded by Vietnam Ministry of Education and Training through the project number B2018-BKA-63. The authors also sincerely thank to Dr. Do Minh Duc for the generous help in testing mechanical strength.

References

[1]. Mukasyan, A. S., Epstein, P. & Dinka, P. Solution combustion synthesis of nanomaterials. Proc. Combust. Inst. **31,** 1789–1795 (2007).

[2]. Ganesh, I. A review on magnesium aluminate (MgAl2O4) spinel: synthesis, processing and applications. Int. Mater. Rev. **58,** 63–112 (2013).

[3]. Rubat du Merac, M., Kleebe, H.-J., Müller, M. M. & Reimanis, I. E. Fifty Years of Research and Development Coming to Fruition; Unraveling the Complex Interactions during Processing of Transparent Magnesium Aluminate (MgAl2O4) Spinel. J. Am. Ceram. Soc. **96,** 3341–3365 (2013).

[4]. Patterson, M. C. L., DiGiovanni, A. A., Fehrenbacher, L. & Roy, D. W. Spinel: gaining momentum in optical applications. in Window and Dome Technologies VIII **5078,** 71–80 (International Society for Optics and Photonics, 2003).

[5]. Bayya, S. S., Chin, G. D., Villalobos, G., Sanghera, J. S. & Aggarwal, I. D. VIS-IR transmitting windows. in Window and Dome Technologies and Materials IX **5786,** 262–272 (International Society for Optics and Photonics, 2005).

[6]. Kong, L. B. et al. Transparent Ceramics. (Springer International Publishing, 2015). doi:10.1007/978-3-319-18956-7

[7]. Apetz, R. & Bruggen, M. P. Transparent alumina: a light-scattering model. J. Am. Ceram. Soc. **86,** 480–486 (2003).

[8]. Krell, A., Hutzler, T. & Klimke, J. Physics and Technology of Transparent Ceramic Armor: Sintered Al2O3 vs Cubic Materials. (DTIC Document, 2006).

[9]. Krell, A., Klimke, J. & Hutzler, T. Advanced spinel and sub-µm Al2O3 for transparent armour applications. J. Eur. Ceram. Soc. **29,** 275–281 (2009).

[10]. Bafrooei, H. B. & Ebadzadeh, T. MgAl2O4 nanopowder synthesis by microwave assisted high energy ball-milling. Ceram. Int. **39,** 8933–8940 (2013).

[11]. Guo, J.-K., Li, J. & Kou, H.-M. Advanced Ceramic Materials. in Modern Inorganic Synthetic Chemistry 463–492 (Elsevier, 2017). doi:10.1016/B978-0-444-63591-4.00017-3

[12]. Sanjabi, S. & Obeydavi, A. Synthesis and characterization of nanocrystalline MgAl2O4 spinel via modified sol–gel method. J. Alloys Compd. **645,** 535–540 (2015).

[13]. Duan, J. et al. Synthesis and characterization of porous magnesium aluminate spinel by hydrothermal process. IOP Conf. Ser. Earth Environ. Sci. **81,** 012028 (2017).

[14]. Li, H., Liu, Y. Q., Liu, H. & Yang, Z. J. Synthesis of magnesium aluminate spinel nano-powders by co-precipitation method. Mater. Res. Innov. **19,** S9-20-S9-23 (2015).

[15]. Mazzoni, A. D., Sainz, M. A., Caballero, A. & Aglietti, E. F. Formation and sintering of spinels (MgAl2O4) in reducing atmospheres. Mater. Chem. Phys. **78,** 30–37 (2003).

[16]. Munir, Z. A. & Anselmi-Tamburini, U. Self-propagating exothermic reactions: The synthesis of high-temperature materials by combustion. Mater. Sci. Rep. **3,** 277–365 (1989).

[17]. Mimani, T. & Patil, K. C. Solution combustion synthesis of nanoscale oxides and their composites. Mater. Phys. Mech. **4,** 134–137 (2001).

[18]. Li, F., Ran, J., Jaroniec, M. & Qiao, S. Z. Solution combustion synthesis of metal oxide nanomaterials for energy storage and conversion. Nanoscale **7,** 17590–17610 (2015).

[19]. Varma, A., Mukasyan, A. S., Rogachev, A. S. & Manukyan, K. V. Solution Combustion Synthesis of Nanoscale Materials. Chem. Rev. **116,** 14493–14586 (2016).

[20]. Moraes, G. G., Pozzobom, I. E. F., Fernandes, C. P. & De Oliveira, A. P. N. MgAl 2 O 4 foams obtained by combustion synthesis. Chem Eng Trans **43,** 1801–1806 (2015).

[21]. Bai, J. H. & Liu, J. C. Solution combustion synthesis and sintering behavior of porous MgAl2O4 powders. Sci. Sinter. **42,** 133–141 (2010).

[22]. Ianoş, R., Lazău, I., Păcurariu, C. & Barvinschi, P. Solution combustion synthesis of MgAl2O4 using fuel mixtures. Mater. Res. Bull. **43,** 3408–3415 (2008).

[23]. Carvalho, L. S. et al. Effect of Urea Excess on the Properties of the MgAl2O4 Obtained by Microwave-Assisted Combustion. Mater. Res. 0–0 (2017). doi:10.1590/1980-5373-mr-2017-0189

[24]. Ianoş, R. & Lazău, R. Combustion synthesis, characterization and sintering behavior of magnesium aluminate (MgAl2O4) powders. Mater. Chem. Phys. **115,** 645–648 (2009).

[25]. Choudhary, A., Rajeswari, K., Rao, Y. S. & Johnson, R. Effect of Fuel Concentration on the Properties of Combustion Synthesized $MgAl_2O_4$ Spinel Powders. Trans. Indian Ceram. Soc. **73,** 303–306 (2014).