Optimizing the gel-casting parameters in synthesis of MgAl_2O_4 spinel

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Abstract

In this paper MgAl_2O_4 spinel powder with average particle size of 90 nm, purity of 99.99%, with stoichiometric ratio $\alpha\text{-Al}_2\text{O}_3$ and MgO and only 0.8 %wt. LiF add-on was solid-state synthesized at a temperature of 1300°C and used in gel suspension with 83% solid load. Using the optimal value of ISOBAM (0.9 %wt.) as both dispersion and gelation factors led to a significant increase in the relative density of green body from 48.5% to 62.2%. Relative density increased after sintering at 1550°C for 1h from 78% to 99.6% and pore size (40 nm) reduced to half the size of powder particles. Also, it resulted in appropriate pore distribution, because of the low number and value of the add-on in the gel system, and also optimization and preparation of nanopowders, as well as preparation and manufacture of suspension. XRD, BET, ICP, FESEM, FTIR analyses were done for synthesis and preparation of powder. Viscometry, Rheometry, Porosimetry, TG-DSC, Zeta potential, and sediment deposition analyses were done in order to optimize the parameters of the casting.

Keywords: MgAl_2O_4 Ceramics, Gel-Casting, Optimization Parameters, Relative Density, Isobam

1. Introduction

Magnesium aluminum spinel, due to the high melting point (2135°C), excellent resistance against chemical attack and thermal shock, and appropriate mechanical strength at room temperature and higher, is one of the most important spinel oxide and ceramic materials that can provide good mechanical properties and can cover a vast range of applications even in high temperatures[1-5]. Moreover, low dielectric constant and unique optical properties have provided special usages for spinel. The existence of any defects and impurities causes sharp drop in throughput of transparent ceramics[3]. Therefore, using cost-effective methods that prevent entry of impurity to ceramic body is vital. Nowadays using wet shaping methods which provide higher density than the ordinary press has increased due to the homogeneity of manufactured pieces. Optical transparent ceramics are thought to allow visible light to pass due to their unique physical properties (electron configurations) [2, 3, 6, 7]. Since the early 1960s, spinel has attracted extensive attention. Spinel has many decent properties which have made it applicable in optical systems, Pressure Vessels, infra-red windows, etc.[2-4, 6, 7]. Synthesis of transparent spinel, using low-pressure sintering and high purity powders, is a challenging process. Hence, hot pressing, hot isostatic press and spark plasma sintering are of great necessity[6-8]. Wet chemical methods are, however, the most recent manufacturing techniques of optical ceramics. Using these methods compared to previous methods such as hot press, hot isostatic press, etc. has advantages such as higher homogeneity and density of green body, the ability to create complex shapes and, finally, lower costs[9]. Gel casting is one of the most widely used methods today due to its high functionality such as casting complex shapes and that there is no need to remove the fluid bed for the piece to take shape

(unlike suspension casting) and also no need for porous molds [10]. Ganesh et al. Have reported a strong green body using sub-micron powders. They followed, gel-casting and more than six additives as dispersal and gelling agents were utilized[11]. Zhang et al. produced an aqueous suspension with 54 %vol. solid loading. They formed a dense green body using commercial sub-micron spinel and only one additive served as both dispersant and a gelling agent which has linear transparency of 85.3% for an 1100 nm wavelength light after HIP sintering in 1 mm thickness[12]. Basically, the majority of wet forming methods utilize sub-micron grains, because, the sub-micron powders are suitable for suspensions hardly stable due to agglomeration[12, 13]. In the study conducted with powder synthesis using solid-state, powder of high purity (99.99%) and nanosized particle (90 nm) was fabricated for the first time and the powder was used in the gel casting method. This led to higher condenses of the green body and relative density of 62.2%. Also, only one additive was used as both a gelling and dispersant agent that caused significant reduction in pores and high density of parts before and after sintering.

2. Materials and method

Highly pure powder of alpha-alumina (99.999%, average particle size= 50 nm and BET SSA= 30 m²/g, JCPDS file 01-078-2426, US-Nano, USA), highly pure powder of magnesia (99.999%, average particle size= 50 nm and BET SSA= 43 m²/g, JCPDS file 00-001-1235, Sigma-Aldrich, Ordered by Serva Co., USA), highly pure powder of Lithium Fluoride (99.99%, average size= 100 nm, Sigma-Aldrich, USA), and deionized water (18 MΩ) were used as the starting materials and suspension preparation, respectively. A binary copolymer PIBM (Isobam104AF (Ib104), Kuraray, Osaka, Japan) served as both gelling and

dispersant agents. Alumina milling balls (diameter 10mm, Tosoh, Tokyo, Japan) were used for 24h milling and the weight ratio of powder to balls was 1:6. Ultrasonic (probe ultrasonic, 20 kHz, 400w, Topsonics, Iran) wave was used in order to homogenize the suspension. Rheological properties of the slurries were conducted with a rotary viscometer (LV DV-II +PRO CP, Brookfield, MA, USA) with a CP40 spindle at a constant temperature of 25°C. The purity of the powder was determined by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Optima-4300 DV, PerkinElmer Inc., MA, USA) analysis (see Table1). Surface area measurements were investigated by Brunauer-Emmett-Teller (BET) analysis. Phase composition of commercial spinel powder was carried out by X-Ray Diffraction (XRD). The microstructure of spinel powder before and after milling was studied by Field Emission Scanning Electron Microscope (FE-SEM) (MIRA3, TE-SCAN, Czech Republic). In order to investigate the behavior of gels and downtime, Rheometer Anton Paar (Austria), Physica MCR301 model with the ability to measure the frequency range 4-10 to 100 Hz, torque of 0.0001-200 mNm and vertical forces of N50-(-50) is used. Distribution of porosity was studied using Thermo Finigan, Pascal 440. Zeta potential and isoelectric point were measured by means of particle measurement Metrix Report, Germany. Thermal characteristics, Thermogravimetry and Differential Scanning Calorimetry (TG-DSC; Model STA 409 PC Luxx, Netzsch, Selb, Germany).

2.1. Synthesis of MgAl_2O_4 powder

To synthesize the solid-state magnesium aluminate spinel, alumina and magnesia powders with molar ratio of 1:1 were mixed and placed at temperatures of 1300,

1400, 1500, 1600°C in a furnace for 1 hour[13]. As shown in Figure 1, at temperatures of 1300, 1400 and 1500°C initial magnesia and alumina peaks are observed and it is only at 1600°C that spinel is fully formed. To reduce synthesized temperature, alumina and magnesia powders with molar ratio of 1:1 with 0, 0.5, 0.8, and 1 %wt. LiF powder were mixed with jar-mill for 12 hours and put in a furnace with an air atmosphere at 1300 °C for 1 hour. As specified in Figure 2, at 0.8 and 1 wt.% of LiF spinel was fully formed, so the optimal LiF value for the solid-state synthesis at 1300 °C was 0.8 wt.%. Because the high amount of LiF makes creating additional phases at grain boundaries possible according to the following reaction, the least amount of LiF powder in which spinel is fully formed is chosen as an optimal amount. In solid state sintering, essentially LiF doesn't diffuse into the lattice, thus, the lattice constant doesn't change and remains 0.8085 nm (00-002-1084 JCPDS file). By changing the stoichiometric ratio and also chemical synthesis methods, lattice constant can be changed. After melting at 850 °C, LiF becomes as liquid phase and stay between Al₂O₃ and MgO particles. By reducing the activation energy, diffusion increases and Spinel phase formation is done at lower temperatures.

LiF reaction with spinel initiates before reaching the melting point of LiF, through which LiAlO₂ and MgF₂ or LiF mix to form a eutectic fluoride molten. As temperature rises LiAlO₂ changes to Li₂Al₄O₇ which as a derivative of spinel, has intrinsic oxygen vacancies and is expected to increase penetration, and make grains coarse if it is formed in Spinel grain boundaries. Thus, the least amount of LiF where spinel formation was complete was 0.8 %wt. Ganesh in their review

article noted that solid-state synthesis of spinel is used in the refractory industry, and not in transparent ceramics, which require high purity and particle size is roughly spherical[14]. But in this study for the first time we reached spinel powder of high purity and nearly spherical particle size through solid state synthesis method. Figure 3A shows the field emission scanning electron microscope image from the powder particles synthesized. According to the figure, the powder has appropriate morphology. Figure 4 shows the Fourier Transform Infrared Spectroscopy (FTIR) spectra of the synthesized powders gained through the solid-state method. As illustrated, the broad peak in the region 3500 cm^{-1} and peak at 1624 cm^{-1} corresponded to the OH stretching and H-O-H banding of the water adsorbed, which shows high surface area of the powder[15]. The spinel type structure is proved by the bands at (532cm^{-1} and 699cm^{-1}), which are associated with lattice vibrations of tetra and octahedrally coordinated metal ions[16]. The IR spectral regions ($700\text{-}500\text{ cm}^{-1}$) result from the bending mode of Al^{3+} which is octahedrally occupied in normal spinel.

2.2. Sample Preparation

The low percentage of solid loading (2 %wt.) was used to perform sedimentation test more accurately, however, results of experiments in higher solid loading were the same. An aqueous suspension with 2 %wt. solids loading was prepared and different amounts of isobam (0.7-1.1 %wt.) was added to the suspension and was taken in 1 min under ultrasonic wave probes to approach homogenize and suitable particle size for gel-casting. Figure 5 shows that increasing the ultrasonic time to one minute, resulted in a more significant change in particle size, and in duration more than 3 minutes, little change in average diameter can be seen. In this case

because of powder severe agglomerates, the slurry is rapidly precipitated on all graded cylinders as shown in Figure 6A. De-agglomeration was done by milling in optimal time, speed and powder to balls weight ratio, 1:6 for 12h, and 216 rpm, respectively. These data were confirmed by BET and FESEM. However, agglomerates can be seen in FESEM images. According to FESEM images before milling (Figure 3A), showed the agglomerates in the slurry are soft. After de-agglomeration (Figure 3B), the deposition sediment test containing 2 %wt. solids loading with the same values of isobam was conducted again and as shown in Figure 6B, this time, there was no rapid sedimentation and stability of the slurry after 36 h were unusual. An issue that requires further consideration is that deposit levels in the cylinder are very close to each other and this makes diagnosis difficult. That's why the viscosity test was carried out to optimize the exact amount of dispersant and also to review and determine the rheological behavior of the slurry.

3. Results and Discussion

3.1. Determining the amount of dispersant

A ceramic slurry consists of solid ceramic particles, polymers, and a liquid medium. Producing a well-dispersed suspension during the colloidal process is crucial for a high solid loading slurry and homogeneous, high-density green bodies for ceramics in order to have a complex shape without cracks during wet-forming techniques. For pure ceramic powders, van der Waals forces agglomerate primary particles easily. Hard agglomerations can be broken down only by colloid milling. Primary powders have to be stabilized, during the milling process, to prevent particles from flocculating again. Several factors affect the stability of a slurry including, the particle size, particle size distribution, the solubility of the solid in

the dispersion medium for the specific ceramic powders, and dispersants (also known as deflocculants), which play an important role in the dispersion by inhibiting the aggregation of the dispersed phase. Dispersants have different kinds like organics (polymers[17-20], surfactants[21, 22], or other small molecules[23, 24]) or inorganics (silicate, phosphate)[17, 21, 25]. Dispersants must have the following properties: **(a)** Provide good wetting with the external surfaces of the ceramics powders. **(b)** Decrease the viscosity of the system when wet milling. **(c)** Stabilize the dispersion. So, the adsorption of the dispersant on the particle surface is essential. At the solid surface, it is associated with a decrease in free energy on the surface, which is charged by the particle-dispersant attraction and the attraction/repulsion between the adjacent dispersant molecules adsorbed on the surface. The former makes dense adlayers or multiple layers, whereas the latter makes saturated monolayers[26]. The dispersant molecule adheres to the particle's surface by ionic, physical, or chemical forces[27], including the following: **(a)** Ionic adsorption between the dispersant ions and the oppositely charged site on the particle's surface. **(b)** Ion exchange between the dispersant ions and similarly charged ions in the particle's surface. **(c)** Hydrogen bonds between the dispersant molecule and the particle. **(d)** Physical adsorption by dispersion forces, dipole-dipole interactions, hydrophobic bonding, or charge transfer forces caused by donor-acceptor interactions[28]. **(e)** Chemisorption from the covalent chemical bond. Nonionic dispersants are absorbed by mechanisms 3, 4, and/or 5 listed above. For ionic dispersants, all these mechanisms are effective in adsorption. The mechanisms of high-molecule polymeric dispersants are more complex than low-molecule dispersants[29]. The three functional groups of its molecular structure: COO-NH_4^+ , -CONH_2 , -CO-O-CO- [30]. Sediment deposition test was used to determine the optimum amount of dispersant and gelling agents. For this test, different amounts of isobam 104 were added to suspension with 2 %wt. solid

loading. Isobam with electrostatic performance caused particles stabilize in suspension, also due to the stability of nanoparticles, the pH was adjusted to 11.38. Figure 7 illustrates the chemical compound and electrostatic performance of isobam that is caused by absorption of charged polymer on the particle surfaces[31]. Figure 8 shows the results of tests conducted. Here the order of deposit height is the sedimentation height at the bottom of the test tube[32]. As it is clear from Figure 8, by increasing the amount of isobam, first deposit height is reduced and then it is increased; the optimum amount of dispersant is queenside by the less sediment. According to Figure 8, the optimum amount of dispersant (isobam 104) is 0.9 %wt. and this result can be seen from the deposition test chart, in which we have the least sediment deposits in the amount of 0.9 %wt.

3.2. Rheological behavior of suspensions

The exact control process of particles dispersing, achieving a suspension with good rheological behavior and enough sustainability is very crucial in gel-casting [12, 31, 33]. Ceramic powders dispersing in aqueous solutions are one of the key points in understanding the fine particle behavior[34]. This property is very important in concentrated colloidal systems that are used for manufactured pieces[34, 35]. Particles in the fluid have surface charge and it is evident that the concentration of ions, the charges of which are opposite to the surface of particles, increases. Therefore, an extra layer of these ions covers surface particle creating an extra layer on it. When a particle moves in a fluid, its surrounding layer displaces. It's supposed that there is a hypothetical distance between fluid environment and

particle. This distance is a layer the similar double layer which has surrounded particle. This distance is called hydrodynamic distance[36, 37]. Figure 9 shows the rheological behavior of suspensions containing 83% wt. solid loading in the presence of optimal amounts of dispersant and gelling agents. As it can be seen, rheological behavior of suspension exhibits semi-plastic behavior. Also, due to more ionic impact and longer cross-linking in the presence of optimal dispersant that was previously specified from deposition sediment test, the lowest viscosity has been seen, that is also a proof for the accuracy of the test sediment. Figure 10 shows the effect of Isobam on the zeta potential of MgAl_2O_4 spinel suspension. As it is clear, the suspension isoelectric point (iep) without Isobam dispersion is at the $\text{pH}=11.2$. After adding Isobam to the suspension, the zeta potential at $\text{pH}=7$ greatly increases from $\text{mV}46$ to $\text{mV}58$. This shows the role of dispersion Isobam MgAl_2O_4 in spinel suspension. Figure 11 shows idle time of magnesium aluminate spinel suspension gel with 0.9 %wt. of Isobam 104, as is evident on the point where the two curves intersect, idle time has started and suspension began to gel, so we have only 300 seconds to cast after preparing the suspension.

3.3. Effect of solid loading

Solid loading is one of the effective and important factors to achieve a dense green body, whenever it is higher there will be more dense green body along with better voids distribution. But the excessive increase in solid loading causes raise in suspension viscosity which can cause a problem for suspension sustainability and gel-casting[12]. Depending on the particle size, gel-casting fundamentally is performed in solid loadings around 75 to 85 (%wt.), in which powders with micron sub-dimensions are mainly used. Nevertheless, the nanosized powder has been used for the first time in this study. A favorable sustainability has been provided by parameters optimization and using the best way to prepare a suspension. Figure 12

illustrates the rheological behavior of the suspension with different solid loadings. It can be concluded that as the solid loading increases the viscosity enhances. Figure 13 depicts the density variation with solid loading. From this figure, it is clear that as the solid loading increases the relative density grows because of the porosity reduction. Moreover, as it is clear from this figure, increasing the solid loading and also using nanosized powder spinel MgAl_2O_4 has increased the relative density of green body from 48.5% to 62.5%. But after sintering without pressure at 1550 °C for 1h, the relative density of green body raised from 78% to 99.6%. Figure 14 shows the sample shrinkage as a function of the solid loading. As the solid loading increases, the shrinkage decreases. Green strength of the bodies is shown in Table 2. MgAl_2O_4 slurries higher solid loading led to stronger green bodies. The green bodies highest bending strength, which prepared from slurry with 83 %wt. solid loading and 0.9 %wt. Isobam104 and was found to reach 11.63 MPa.

3.4. Investigation of suspension preparation

The method of suspension preparation is one of the key elements in gel-casting because preparation method in gel casting includes the time of suspension making and pouring in the form, hence, gel time must be noticed in addition to factors such as dispersion and particle stability [12, 31, 32]. This means that suspension must be cast before gelation. Moreover, that's why a method must be chosen for suspension production that requires less time, provides sustainability and dispersion of particles in suspension and lowers viscosity. Figure 15 shows the rheological behavior of the obtained suspensions. It is clear that the lowest viscosity is related to the ultrasonic technique since probe ultrasonic breaks soft agglomeration and homogenizes slurry through high vibration in the shortest period before the idle

time. The bulk density including 83 %wt. of the solid fraction was determined by Archimedes' method (Table 3). The highest density ($62.2\% \text{ g/cm}^3$) is associated with the ultrasonic method.

3.5. Typical thermal behavior

Figure 16 shows the Isobam 104 thermal behavior. In all casting methods, the most important issue is removing the additives from casting body. The greater the number and amounts of additives, the more the pores, and porosity during additive releasing and calcination step. However, the goal here is achieving a dense body. There were more than 10 additives in previous works for gel-casting, which made us far from a fully dense body [12, 31, 32, 35]. In this study, only one additive is used as both dispersant and gelling agent, thermal behavior of which is shown in Figure 16. From this figure, several thermal events can be seen, in the range of 377 to 574°C, in the thermogravimetry and differential scanning calorimetry (TG-DSC) graph. There is one isothermal Peak due to decomposition and combustion of isobam. Also, TG graph from the temperature ranges 450 to 600 °C shows a weight loss about 16 percent.

3.6 Porosimetry of green body

This analysis shows some of the most important properties of porous materials such as pore size, pore volume and the volume of material. This method

not only can determine the amount of pores, but also the porosity distribution based on the applied pressure. Gel-casting method is used to prepare a homogeneous body. If the suspension manufacturing process and vacuumed process are done appropriately, grain size distribution and pore size distribution in green sample, are expected to be ideal. In the case of appropriate body for transparent spinel the pore size distribution curve must have a short sharp peak in the range where the size of porosity is less than half the size of spinel powder particles used. As is evident in Figure 17, the pore size is about 40 nm which is less than half the size of primary powder particles. The sharp peak indicates a homogenous distribution of porosity which shows that the cumulative intrusion in gel-casting of green body was 150 mm³/g. High density and suitable porosity distribution and low pore size in the green body of spinel ceramic are advantages of transparency. Figure 18 shows microstructures of the fracture surfaces of the MgAl₂O₄ green bodies with different solid loadings (0.9 %wt. Isobam 104 used). Results showed the MgAl₂O₄ powders were dispersed homogeneously through the interspaces, and the green body became denser at greater solid loading.

4. Conclusions

MgAl₂O₄ spinel with a purity of 99.99% with stoichiometric ratio of α -Al₂O₃ and MgO, and 0.8 %wt. LiF were mixed for 12h and the synthesized at 1300 °C for 1h. Isobam was used as a gelation and a dispersion factor at the same time in the novel gel casting system, and led to suspension sustainability with solid loading of 83 %wt. at the lowest viscosity (6.5 mPa.s). Using Spinel nanopowders and only 0.9 %wt. of isobam increased relative density of green body to 62.2% and relative density of the final body to 99.6% after sintering with no pressure at 1550°C for

1h. The green strength of green body with 83%wt solid loading was 11.63 MPa. The best and fastest way to prepare and homogenize gel suspension was using ultrasound probe, optimized for 1min and 100W of power.

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Figures caption

Figure. 1. X-ray diffraction patterns of alumina and magnesia mixed powder after heating at different temperatures for 1 hour.

Figure. 2. X-ray diffraction pattern of alumina and magnesia mixed powder with molar ratio of 1:1 with 0, 0.5, 0.8, and 1 wt% LiF powder after heating for 1 hour at a temperature of 1300°C.

Figure. 3. FESEM images of MgAl_2O_4 nanopowder, (A) before milling, (B) after milling.

Figure. 4. FTIR graph of the synthesized spinel powder and the spinel structure in fingerprint area.

Figure. 5. Effect of ultrasonic time on the dispersion of agglomerated particles.

Figure. 6. The effect of ball-milling on the perception of MgAl_2O_4 , (A) before ball-mill, (B) after ball-mill.

Figure. 7. Chemical formulas and schematics isobam performance.

Figure. 8. The effect of isobam content (% wt.) on the amount of precipitation.

Figure. 9. Rheological behavior of suspension with different isobam content.

Figure. 10. Effect of Isobam on magnesium aluminate spinel zeta potential.

Figure. 11. Magnesium aluminate spinel suspension rheology behavior and idle time of the suspension gels in 1.1 wt% of Isobam 104.

Figure. 12. Rheological behavior of the different solid loading.

Figure. 13. Density variation with solid loading. Before sintering at 600 °C and after sintering at 1550 °C.

Figure. 14. The samples shrinkage as a function of the solid loading at 600 °C.

Figure. 15. Rheological behavior of the suspensions.

Figure. 16. TG-DSC curves of isobam (Ib104).

Figure. 17. Distribution and pore size in the green examples of spinel MgAl_2O_4 .

Figure. 18. Fracture surfaces of the MgAl_2O_4 green bodies prepared from slurries with different solid loadings. (a) 65 wt%, (b) 70 wt%, (c) 75 wt%, (d) 83 wt%.

Table caption

Table 1. Chemical analysis of MgAl_2O_4 nanopowder

Table 2. Relative density by Archimedes' method

Table 3. Green strength of the bodies at the solid loadings.

Table 1. Chemical analysis of MgAl₂O₄ nanopowder

Element	As	Ba	Ti	Cd	Zr	Zn	S	Li	Pb	Ni	Mo	Ca	Al	K	Fe
ppm	17.9	387	22	0.2	33	21	98	5	5	3	24.3	345	21	242	189
Element	Be	Ce	Co	Cr	Cu	U	La	Sb	Sc	Sr	Th	Ti	V	Y	Yb
ppm	0.7	11	1	5	7	5	1	19	0.5	5	7.6	22	36	8	0.2

Table 2. Green strength of the bodies at the solid loadings.

Solid loading (%wt.)	Green strength (MPa)
40	6.38
50	6.97
60	7.76
75	9.11
78	9.89
83	11.63

Table 3. **Relative density by Archimedes' method**

Method of making suspensions	Ultrasonic	Ball-mill	Jar-mill
Relative density%	62.2	56	54.2

Fig. 1. X-ray diffraction patterns of alumina and magnesia mixed powder after heating at different temperatures for 1 hour.

Fig. 2. X-ray diffraction pattern of alumina and magnesia mixed powder with molar ratio of 1:1 with 0, 0.5, 0.8, and 1 wt.% LiF powder after heating for 1 hour at a temperature of 1300°C.

Fig. 3. FESEM images of MgAl₂O₄ nanopowder, (A) before milling, (B) after milling.

Fig. 4. FTIR graph of the synthesized spinel powder and the spinel structure in fingerprint area.

Fig. 5. Effect of ultrasonic time on the dispersion of agglomerated particles.

Fig. 6. The effect of ball-milling on the perception of MgAl_2O_4 , (A) before ball-mill, (B) after ball-mill.

Isobutylene and maleic anhydride (Isobom)

Fig. 7. Chemical formulas and schematics isobam performance.

Fig. 8. The effect of isobam content (% wt.) on the amount of precipitation.

Fig. 9. Rheological behavior of suspension with different isobam content.

Fig. 10. Effect of Isobam on magnesium aluminate spinel zeta potential.

Fig. 11. Magnesium aluminate spinel suspension rheology behavior and idle time of the suspension gels in 1.1 wt% of Isobam 104. G'' (Loss modulus), G' (Storage modulus).

Fig. 12. Rheological behavior of the different solid loading.

Fig. 13. Density variation with solid loading. Before sintering at 600 °C and after sintering at 1550 °C.

Fig. 14. The samples shrinkage as a function of the solid loading at 600 °C.

Fig. 15. Rheological behavior of the suspensions.

Fig. 16. TG-DSC curves of isobam (Ib104).

Fig. 17. Distribution and pore size in the green examples of spinel MgAl_2O_4 .

Fig. 18. Fracture surfaces of the MgAl_2O_4 green bodies prepared from slurries with different solid loadings. (a) 65 %wt., (b) 70 %wt., (c) 75 %wt., (d) 83 %wt.