MgAl$_2$O$_4$ Foams Obtained by Combustion Synthesis

Graziela G. Moraes[a], Ida E.F. Pozzobom[a], Celso P. Fernandes[a], Antonio P. Novaes de Oliveira[a*]

[a]Graduate Program in Materials Science and Engineering – PGMAT, Laboratory of Glass-Ceramic Materials – VITROCER, Federal University of Santa Catarina - UFSC, 88040 900Florianópolis - SC, Brazil.
antonio.pedro@ufsc.br

This work aims to study magnesium aluminate (MgAl$_2$O$_4$) ceramic foams obtained by combustion synthesis in solution without the need of surfactants to stabilize bubbles.The ceramic suspension containing acetone (75 wt%), calcined powder (25 wt%) and a mixture of glycerine (80 % blonde glycerine and 20 % crude glycerine) in the fraction of 100 % with respect to solids was prepared in an alumina ball mill, for 60 min. Subsequently, the suspension was heated at 40 °C, for 30 min, until it became rigid. In order to promote foaming, the suspension was heated to 70 °C and then the following substances were added to it: 2.5 wt% distilled water, 25 wt% Al(NO$_3$)$_3$.9H$_2$O), 12.5 wt% (Mg(NO$_3$)$_2$.6H$_2$O) and 0.625 wt% of a glycerine mixture (80 % blonde glycerine and 20% crude glycerine). After additions the suspension was stirred for 5 min at 950 rpm in a mixer. The resulting foams were dried at 40 °C, for 24 h, in a muffle and fired in two steps, i.e., heating at 0.5 °C/min up to 600 °C/120 min and at 5 °C/min up to 1600 °C/120 min.The obtained materials were characterized by SEM,TEM and from tomographic images. The results showed that the obtained magnesium aluminate foams have a high porosity (97 %), a high connectivity and pore sizes (diameters) between 30 and 1200 µm.

1. Introduction

The cellular ceramics are increasingly used in various applications such as filtration of molten metals, catalytic supports, thermal insulation, biomedical implants, etc. (Green and Colombo, 2011). They are generally prepared by the replication method or by the foaming of ceramic suspensions. In the replication method a polymeric foam is impregnated with a suspension of a ceramic powder, followed by drying and firing (Studart et al., 2006). In the foaming method, gas bubbles are stabilized in suspensions of ceramic powders by using surfactants and then the foam suspensions are gelled. After drying and heat treatment, ceramic foams are produced with approximately spherical and interconnected cells (Mao et al., 2008). The present processing methods for the preparation of ceramic foams use synthetic organic polymers and monomers, surfactants and solvents, which are produced from petroleum as processing additives. Recently, many investigations of alternative materials to these additives with natural and renewable molecules such as proteins and polysaccharides are studied for the formation of foams from suspensions of ceramic powders for the preparation of cellular ceramics, as gelatine (Ortega et al., 2003), as ovalbumin (Dhara and Bharagava, 2003), as albumin (Garnn et al., 2004) and sucrose, which is a renewable natural molecule, which was used by Vijayan et al. (2014) to produced ceramic foams with different porosities, using the thermal foaming of aqueous suspensions of alumina powders.An alternative could be the use of residual blond glycerin as foaming agent. The residual blond glycerin comes from the biodiesel production from vegetable oils and fats, i.e., from a renewable resource. However, with the growth in biodiesel production the problem of disposal of the residual glycerin continues and it may thus represent an economic and environmental problem (Nicolò et al., 2014).

Thus, this work considers the thermal foaming route for the production of magnesium aluminate (MgAl$_2$O$_4$) ceramic foams, making the reuse of glycerin from biodiesel as an activating agent of the foaming reaction.

2. Methodology

2.1 Materials

In this work, aluminium nitrate nanohydrated, $Al(NO_3)_3.9H_2O$, magnesium nitrate hexahydrated, $Mg(NO_3)_2.6H_2O$ (both as foaming agents and $MgAl_2O_4$ precursors), crude glycerine (50 % glycerol) and blonde glycerine (glycerol 76.5 %) provided by the company BioPar - Bioenergy (Paraná-Brazil) and particulate magnesium aluminate were used as raw materials.

2.2 Methods

2.2.1 Preparation of powders

The particulate magnesium aluminate was synthesized from the mixture of their precursors ($Al(NO_3)_3.9H_2O$) and ($Mg(NO_3)_2.6H_2O$) stoichiometrically balanced by a ratio of 2:1 (mol) so that in a subsequent step they were magnetically stirred in aqueous solution (20 wt% distilled water) under heating at 70 °C, for 15 min. The residual blonde glycerine (as fuel) was added (0.71 mol) at the beginning of the reaction, remaining for 60 min. Subsequently, the mixture was placed in a muffle furnace (preheatedat 500 °C) and then calcined at 900 °C, for 120 minat 10 °C/min. The obtained powder was dry milled for 15 min in an alumina ball mill (CT 242 - SERVITECH). Detailed information on the process for synthesis of the magnesium aluminate can be obtained from Moraes et al. (2014).

2.2.2 Preparation of powder compacts

To determine the firing temperature of the produced foams, with high density walls, the calcined powders were uniaxially compacted at 5.4 MPa in a cylindrical steel die by means of a hydraulic press (Bovenau P10 ST).The obtained powder compacts (10 x 10 mm) were dried (110 °C/120 min) and fired at 1450 °C, 1500 °C, 1550 °C, 1600 °C and 1650 °C, for 120 min, respectively so that, in a further step, their densities (real and apparent) were determined.

2.2.3 Preparation of suspensions and ceramic foams

The ceramic suspension containing acetone (75 wt%), calcined powder (25 wt%) and a mixture of glycerine (80 % blonde glycerine and 20 % crude glycerine) in the fraction of 100 % with respect to solids was prepared in an alumina ball mill, for 60 min. Subsequently, the suspension was heated at 40 °C, for 30 min, until it became rigid. In order to promote foaming, the suspension was heated to 70 °C and then the following substances were added to it: 2.5 wt% distilled water, 25 wt% $Al(NO_3)_3.9H_2O$, 12.5 wt% ($Mg(NO_3)_2.6H_2O$) and 0.625 wt% of a glycerine mixture (80 % blonde glycerin and 20 % crude glycerine). After additions the suspension was stirred for 5 min at 950 rpm in a mixer (Philips, Walita, 200 W).
The resulting foams were dried at 40 °C, for 24 h, in a muffle (SP Labor, Model SP 100) and fired in two steps, i.e., heating at 0.5 °C/min up to 600 °C/120 min and at 5 °C/min up to 1600 °C/120 min (best thermal cycle).

2.3 Characterization of materials

The morphology of the powders was investigated by transmission electron microscopy, TEM (JEOL- JEM 1011).The distribution of sizes of agglomerates of the calcined powder was determined using a laser scattering particle size analyser (Malvern, ZEN-3600).The specific surface area was determined by BET method (NOVA 1200e, Quantachrome Instruments).
The apparent density (ρ_{ap}) was determined by applying the Archimedes' principle with immersion in water at 22°C, using a Shimadzu equipment (AX200/401 SMK with accuracy of ± 0.001 g) provided with a density measurement kit SMK 401.The real (ρ_{real}) or true density of the powder was determined by helium pycnometry (AccuPyc1340, Micromeritics, USA). The relative density (ρ_{rel}) was calculated by dividing the apparent density (ρ_{ap}) and the real density (ρ_{real}) (Eq.1).

$$\rho_{rel}\ (\%) = \frac{\rho_{ap}}{\rho_{real}}\ x100 \tag{1}$$

The microstructure of pores could be seen from images of fracture surfaces, obtained in a scanning electron microscope, SEM (JEOL, JSM-6390LV). Through 3-D images reconstructed from the produced ceramic foams, obtained by X-ray microtomography (XRadia, model Versa XRM-500) and with the aid of an image analysis software (IMAGO®), the porosity and connectivity of the pore size distribution were determined.

3. Results and discussion

Figure1 refers to a sample of the produced powder which was calcined at 900 °C/120 min in which one can observe an image of an agglomerated powder containing particles having sizes smaller than 100 nm.
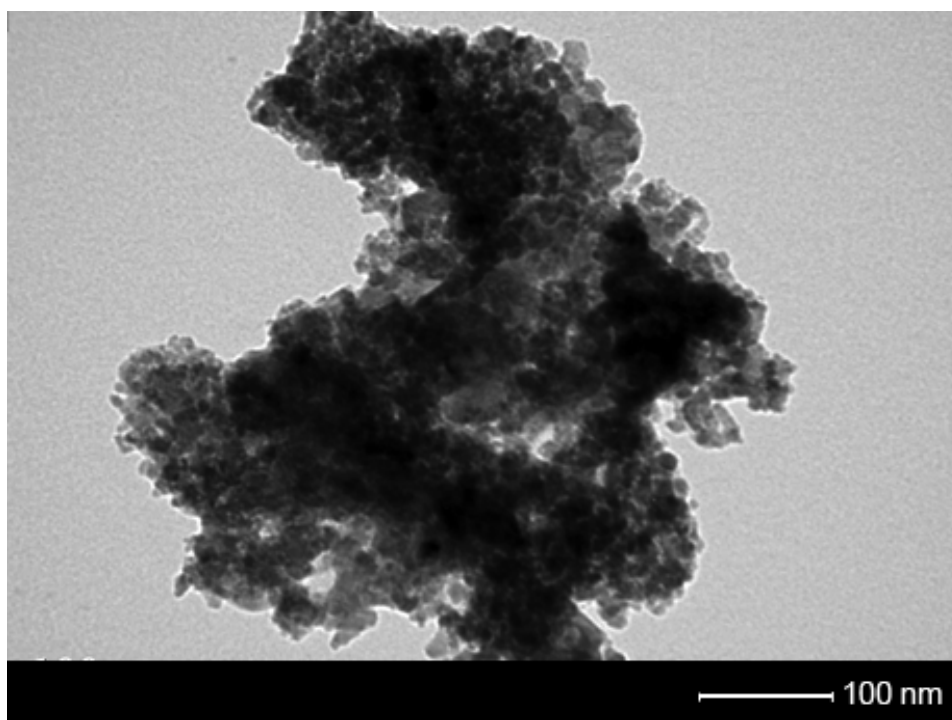

Figure 1: TEM micrograph related to a sample of the produced powder (calcined at 900 °C/120 min)

The real density, obtained with aid of a pycnometer, for powders calcined at 900 °C/120 min, was 3.24 g/cm^3 and the specific surface area obtained by BET method was 111.50 m^2/g which is greater than that of powders produced with the most widely used fuel, 32m^2/g (mixture of urea and glycine) (Baiet al, 2011). The size distribution of the agglomerates of the calcined powder showed that 50 % of the particles have sizes of about 0.33 µm (330 nm). Ceramic particles of this size are appropriated for obtaining powder compacts with good sinterability since, according to Chen et al. (2002), the sintering time and temperature can be significantly reduced for powders having narrow distribution and small particle sizes.

Figure 2shows relative densities for compact powders fired at different temperatures for 120 min. The relative density as shown in Figure 2 increases as the firing temperature increases, reaching maximum densification (89 %) at 1600 °C and remained constant up to 1650 °C.
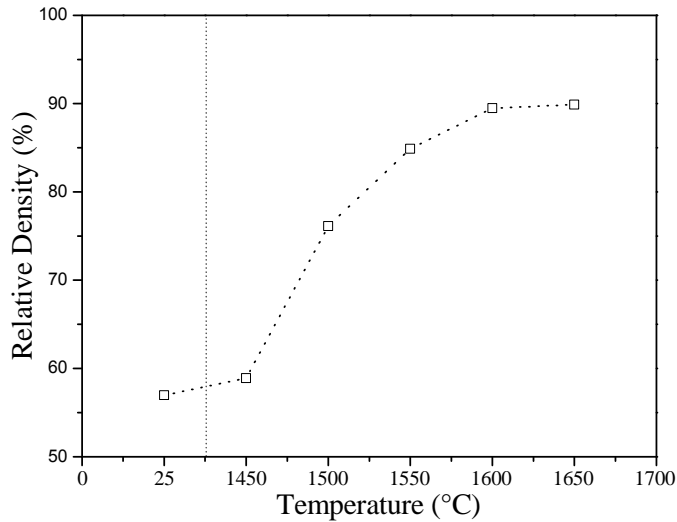
Figure 2: Relative density of powder compacts fired at different temperatures for 120 min

The consolidation of ceramic foams implies dense struts since the increase of the porosity of the cell structure results in decreased mechanical strength. Thus, in this work, the temperature of 1600 °C has been found suitable for the production of ceramic foams.

Figure 3 shows a SEM micrograph of the obtained ceramic foams (fired at 1600 °C for 120 min). Figure 3 shows that the pores have different sizes, i.e., a fraction of pores sizes (diameters) between 30 and 300 µm and another fraction with pore size of approximately 1200 µm.
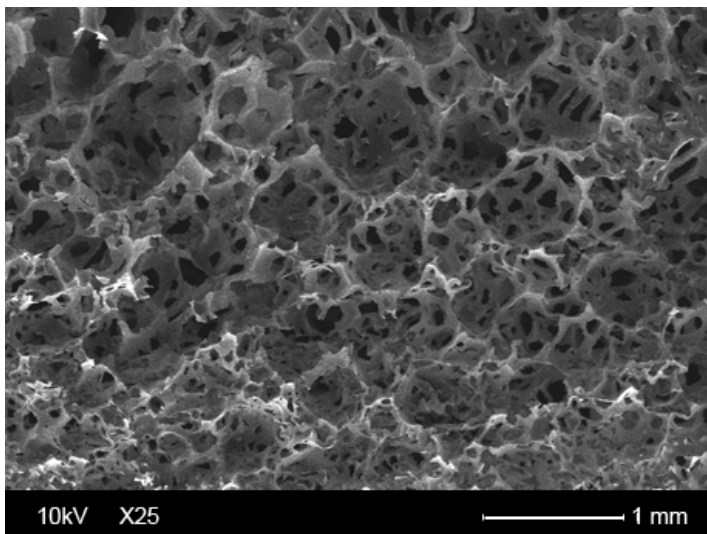

Figure 3: SEM micrograph of a produced ceramic foam fired at 1600 °C for 120 min

Figure 4 shows that the cell walls (struts) are very dense (substantially free of pores) and are composed of relatively small grains well defined and well evidenced by their boundaries. This result may be related to a better packing of the nanoparticles occurred in the colloidal processing of the synthetic precursors, i.e., better dispersion of the particles and formation of a film of glycerine around them. In addition, the cell walls are thinner which also favours a better packing of the particles. On the other hand, the produced compacts from the synthesized powders form strongly linked agglomerates, as evidenced in Figure 1, resulted in materials with some residual porosity, i.e., 22 % for powder compacts fired at 1600 °C for 120 min. For the production of ceramic foams, the cell walls with high densities are important because they can resist higher mechanical stresses compared to the same material (with same porosity), but with less dense walls.
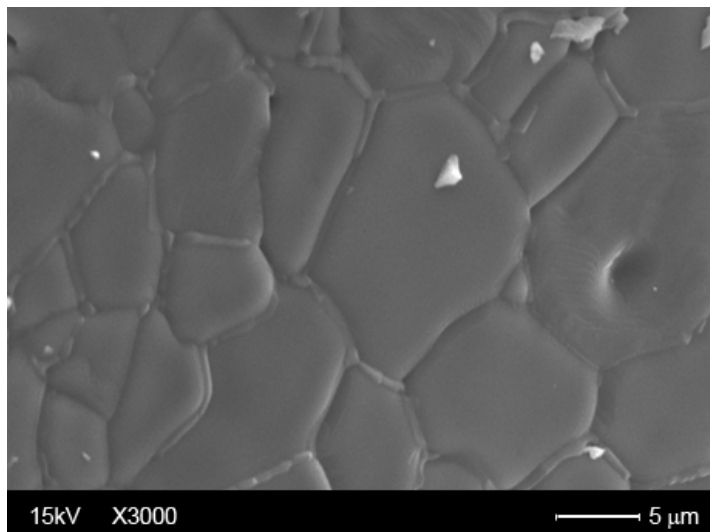
Figure 4: SEM micrograph of the cell walls microstructure of a ceramic foam fired at 1600 °C for 120 min

The results of tomography analyses of a ceramic foam sample can be seen in Figure 5 (a) and (b).
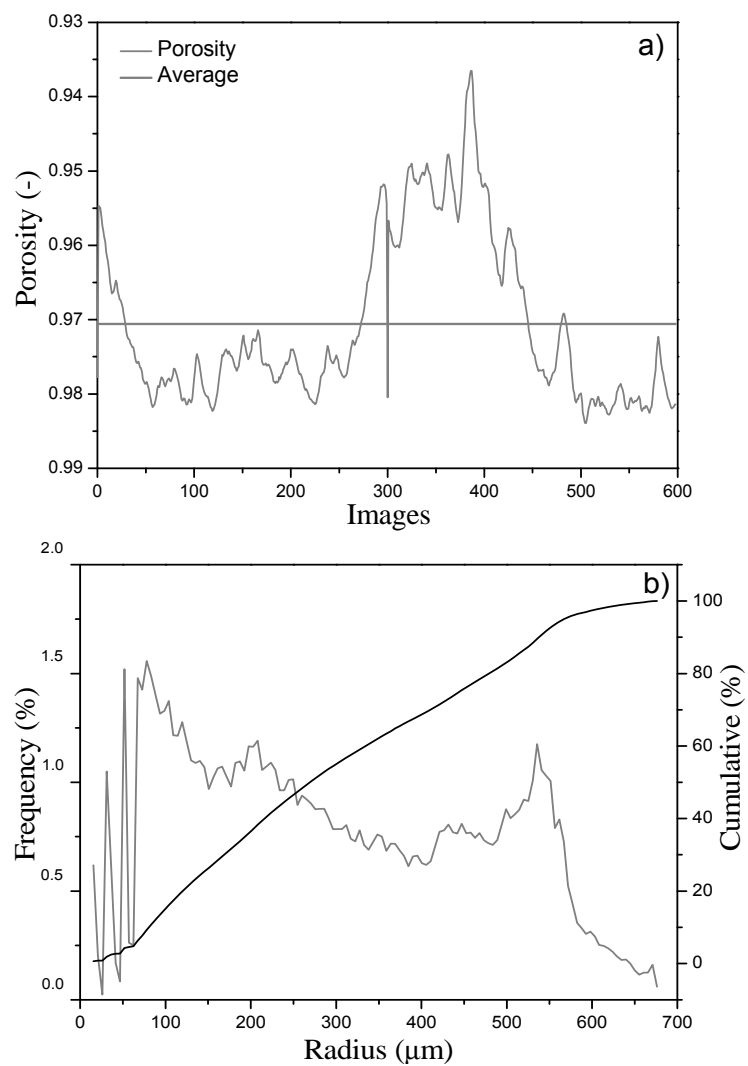

Figure 5: Porosity curve (a) and pore size distribution for a ceramic foam sample fired at 1600 °C/120 min (b)

Figure 5 (a) shows the average porosity (97 %) calculated from 600 images of a ceramic foam sample. The connectivity function gives the probability that two voxels (elementary volume - the smallest element of a three-dimensional digital image) separated by a given distance belong to the same porous phase (Gonzalez and Woods, 2008).Thus, was possible to identify a high connectivity of the produced porous foams (the value where the curve tends to be nearly constant connectivity), i.e., between 94 and 95 %.

Figure 5 (b) shows the pore size distribution for the analysed sample. The distribution curve is bimodal with pore sizes (diameters) ranging from 30 to 1200 µm.

4. Conclusions

Magnesium aluminate ceramic foams were successfully obtained after firing process at 1600 °C for 120 min. TEM micrographs showed that the synthesized magnesium aluminate powders showed particle sizes smaller than 100 nm and agglomerates (50 % of them have sizes of about 0.33 µm). The real density of calcined powders at 900 °C/120min was 3.24 g/cm^3 and the specific surface area was 111.50 m^2/g. The SEM micrographs and the tomographic analysis of the produced ceramic foams (fired at 1600°C/120 min) showed that the pores have different sizes (bimodal distribution), i.e., a fraction of the pore size between 30 and 300 µm and another fraction with pore size of approximately 1200 µm. The results of the tomography analyses of the produced ceramic foams showed a porosity of 97% with high connectivity. The cell walls (struts) are dense (practically free of pores) and consist of relatively small grains well delimited by their boundaries.

Acknowledgements

References

Bai, J.; Liu, J.; Li, C.; Li, G.; Du, Q., 2011, Mixture of fuels approach for solution combustion synthesis of nanoscale MgAl$_2$O$_4$ powders, Advanced Powder Technology, 22, 72-76, DOI:10.1016/j.apt.2010.03.013.

Chen, Z.; Shi, E.; Zheng, Y.; Li, W.; Wu, N. and Zhong W., 2002, Synthesis of mono dispersed ZnAl2O4 powders under hydrothermal conditions, Materials Letters, 56,601-605,DOI:10.1016/S0167-577X(02)00561-X

Dhara S.,Bharagava P., 2003,A simple direct casting route to ceramic foams, Journal of the European Ceramic Society, 86, 1645–50, DOI: 10.1111/j.1151-2916.2003.tb03534.

Garrn I.,Reetz C.,Brandes N.,Krohb L.W.,Schubert H., 2004, Clot-forming: the use of proteins as binders for producing ceramic foams, Journal of the European Ceramic Society,24, 579–87, DOI: 10.1016/S0955-2219(03)00259-0.

Gonzalez R. C., Woods R. E., 2008, Digital Image Processing. 3 ed. Prentice Hall: New Jersey, 2008.

Green D.J. and Colombo P., 2011, Cellular Ceramics: Intriguing Structures, Novel Properties, and Innovative Applications, Materials Research Society, 28, 296-300, DOI: http://dx.doi.org/10.1557/mrs2003.84.

Mao X.,Shimai S.,Wang S., 2008,Gelcasting of alumina foams consolidated by epoxy resin, Journal of the European Ceramic Society, 28, 217–22, DOI: 10.1016/j.jeurceramsoc.2007.06.006.

Moraes G.G., Bonin L.,Moraes E.G.,Donadel K., Barp K., Oliveira A.P.N., 2014, Combustion synthesis of the MgAl2O4 using glycerin from the production of biodiesel, Materials Science Forum, 775 - 76, 682-86, DOI: 10.4028/www.scientific.net/MSF.775-776.682.

Nicolò,M.S.; Franco,D.; Camarda,V.; Gullace,R.; Rizzo,M.G. Fragalà,M., Licciardello, G., Catara, A.F.; Guglielmino, S.P.P., 2014, Integrated Microbial Process for Bioconversion of Crude Glycerol from Biodiesel into Biosurfactants and PHAs. Chemical Engineering Transactions, 38,187-192, DOI: DOI: 10.3303/CET1438032.

Ortega F.S.,Valenzuela F.A.O.,Scuracchio C.H.,Pandolfelli V.C., 2003, Alternative gelling agents for the gelcasting of ceramic foams, Journal of the European Ceramic Society, 23, 75–80, DOI: 10.1016/S0955-2219(02)00075-4.

Studart A.R., GonzenbachU. T., Tervoort E., andGauckler L.J., 2006, Processing Routes to Macroporous Ceramics: A Review, Journal of the American Ceramic Society, 89, 1771–1789, DOI: 10.1111/j.1551-2916.2006.01044

VijayanS.,Narasimman R.,Prudvi C.,Prabhakaran K., 2014, Preparation of alumina foams by the thermo-foaming of powder dispersions in molten sucrose, Journal of the European Ceramic Society,34, 425–433, DOI: 10.1016/j.jeurceramsoc.2013.08.023.