DESIGN AND FABRICATION OF CELLULAR GLASS CERAMIC STRUCTURES FOR FILTERING COMBUSTION GASES OF DIESEL ENGINES

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Abstract

An exploratory study was developed to determine the potential use of glass ceramic materials in the manufacture of an open pore foam catalytic support for diesel soot filtration. This project determines the behavior of some mechanical and morphological properties of a cellular glass ceramic structure according to three different variables of analysis: pore density, type of ceramic suspension, and percentage of compression during the excess material removal stage. The replication method was used based on polyurethane (PU) foam templates of 45 and 60 pores per inch (ppi). The parent glass used corresponds to a system called LZSA (Li2O – ZrO2 – SiO2 – Al2O3). Best fabrication parameters were determined to obtain LZSA foams with properties similar to those of commercial foams used for this application.

Keywords: Cellular structures, Glass ceramic, Replication method

Resumen

Se desarrolló un estudio exploratorio para determinar el potencial del material vitrocerámico en la fabricación de una estructura celular porosa apta como soporte de catalizador para la filtración de material particulado en los gases de combustión de motores diesel. Este proyecto determina el comportamiento de algunas propiedades mecánicas y morfológicas de una estructura celular vitrocerámica de acuerdo a tres diferentes variables de análisis: densidad de poros, tipo de suspensión cerámica y porcentaje de compresión en la etapa de remoción de material en exceso. El método de réplica se implementó basado en espumas de poliuretano (PU) de 45 y 60 poros por pulgada (ppi). El material vitreo utilizado corresponde al sistema llamado LZSA (Li2O – ZrO2 – SiO2 – Al2O3). Los mejores parámetros de fabricación se determinaron para obtener espumas de LZSA con propiedades similares a esas de las espumas comerciales utilizadas en esta aplicación.

Palabras Claves: Estructuras celulares, Vitrocerámico, Método de réplica

1. INTRODUCTION

The diesel engine is becoming nowadays one of the most popular vehicle engines due to developments that have achieved high energetic efficiency levels with limited pollutant emissions. However, diesel emissions have specific pollutants such as NOx and soot that can be very hazardous not only to human life but also to the environment (1). Cancer, cardiovascular, and respiratory problems as well as water, air, and soil contamination, are some of the effects of these toxic emissions (2).

In order to reduce soot emissions form diesel engines several techniques are being developed. Among these, fuel modification or fuel alternatives, engine modification, and after-treatment technologies (3). The after-treatment technique consists on filtering the soot with specially designed ceramic traps that can be catalytic or non-catalytic and honeycomb type or foam type. Catalytic foam traps present an advantage over other types of filtering systems since they are self-regenerating (4). The morphology of this filter allows the soot to make close contact with the catalyst, allowing its combustion without any additional regenerating equipment (1; 3; 4; 5).

Ceramic foams can be produced by several techniques including the replication method, direct foaming or the use of a sacrifice material. However
the replication method is the most known and used in industry as well as investigation. The replication method consists on impregnating polymeric foams with a ceramic suspension followed by a thermal cycle. This thermal cycle has to main functions: it degrades the polymeric foam and consolidates the ceramic material, generating a replica of the original structure.

Generally, ceramic materials are used in the fabrication of catalytic traps because of their high thermal stability and good chemical compatibility with most of the reactive material used for the catalytic activation. Alumina (Al₂O₃) or ZTA (zirconia-toughened-alumina) foams with pore densities from 55 to 65 ppi are commonly used for this specific application. However, these materials require high temperature cycles (up to 1600°C), making the production more expensive and complex (6). In this work, glass ceramic is introduced as an alternative material for the fabrication of catalytic foam traps given that it requires a less demanding heat treatment cycle.

A glass ceramic is a polycrystalline solid with a residual vitreous phase. This material can be considered as a non porous compound formed by nanometric crystals randomly arranged on a vitreous matrix (7). The glass material is transformed to glass ceramic by a process of crystallization during an applied thermal cycle. The number, kinetics, and final size of crystals depend on the temperatures reached (8). Since crystallization temperatures of a glass ceramic do not exceed 900°C, the use of this material reduces the end cost of the final product. This would be an affordable alternative for third world countries in their search for a better environment.

This project determines the behavior of some mechanical and morphological properties according to three different variables of analysis: pore density, type of ceramic suspension, and percentage of compression during excess material removal stage. Porosity, permeability, mechanical resistance, and form retention were measured and compared to a commonly used alumina foam trap. Best fabrication parameters were determined to obtain LZSA foams with properties similar to those of commercial foams used for this application.

2. EXPERIMENTAL PROCEDURE

2.1 Foam Fabrication

The experimental procedure is presented based on the different stages of the replication method shown on the diagram in Figure 1.

A – Raw Material:
The glass ceramic system used in this work corresponds to a LZSA (Li₂O – ZrO₂ – SiO₂ – Al₂O₃) system. This system was developed by the Federal University of Santa Catarina, Brazil (9) where several studies have been made concerning foam replication based on this material (10; 11). The raw material to produce the parent glass powder was melted at ~1500±5°C for 7 hours on a gas furnace. Then it was quenched in water generating glass frits (9). These were reduced to d₅₀=4.26x10⁻⁶ m by mechanical milling. Commercial additives such as a binder and dispersant were used. These were bentonite (Colorminas - Brazil) and sodium silicate (Merck) respectively.

B – Polymeric Foam:
The polymeric foams used correspond to polyurethane (PU) reticulated foams with open cells. Two different cell densities were used: 45 and 60 pores per inch (ppi).

C – Ceramic Suspension:
The ceramic suspension was prepared using a planetary ball mill with a mixing time of 5 minutes. The solid phase corresponds to 95 wt% of LZSA.
parent glass powder and 5 wt% of bentonite. The liquid phase corresponds to 1 wt% sodium silicate and 99 wt% alcohol-isopropyl as aqueous medium. The use of this medium helps promote a thixotropic behavior of the vitreous suspension, which improves the impregnation of the polymeric foam (10). The solid/liquid phase ratio in wt% was varied between 50/50, 55/45, and 60/40.

D – Impregnation and removal of excess material:
The PU foam samples were immersed on the parent glass suspension and the excess slurry was removed using controlled compression with roller equipment. Each sample was passed four times through the rollers and was rotated after each pass in order to improve the distribution of the remaining slurry. The compression percentage of the foam corresponds to a variable in this project, and was controlled with different roller separation. The compression percentages used correspond to 35%, 50%, 60% and 70%. Samples were left to dry at room temperature for 24 hours.

E – Thermal cycle:
Heat treatment of the samples was performed in a three stage process in an electric furnace in air. The first stage at 450°C holding for 1 hour at a heating rate of 1°C/min is for the PU foam decomposition. The second stage at 650°C holding for 10 min at a heating rate of 5°C/min is for the densification and sintering of the parent glass. The third stage at 800°C holding for 10 min at a heating rate of 5°C/min for the crystallization of the glass (9; 12).

2.2 Characterization techniques
A morphological characterization of the cellular structures is done using SEM images. Samples were prepared using and isometric cutter with a diamond blade to obtain sectional views.
Permeability measurements were performed on an air flow apparatus (Amscor Air Flow). Samples were prepared in order to leave only the front and back face permeable. Direct airflow measurements were taken. Permeability was calculated according to Forchheimer’s equation,

$$\Delta P / L = (\mu / k_1) V + (\rho / k_2) V^2$$  \hspace{1cm} (1)

where $\Delta P$ [Pa] corresponds to the pressure drop, $L$ [m] the sample thickness, $\mu$ [Pa s] the viscosity of the fluid (in this case air), $\rho$ [kg m$^{-3}$] the density of the fluid, and $V$ [m/s] the volumetric flow rate per unit of cross sectional area measured from airflow data (13). The constants $k_1$ (Darcyan) and $k_2$ (non-Darcyan) include the structural properties of the porous medium and are used to compare the permeability between different media (14). The first term of the right side of equation 1 is attributed to laminar flow and the second term to turbulent flow. Since we are working with Re below ~150 we can drop the term associated with turbulent flow and then the Darcyan permeability can be defined as

$$k_1 = (\mu V) / (\Delta P / L).$$  \hspace{1cm} (2)

Figure 2. (a) Sketch of the assembly used during compression tests (b) Form retention (sample 45ppi, 50/50 and 50% compression).

Mechanical measurements were performed under compressive force. To ensure a uniform distribution of the load, samples were mounted over epoxy putty that was flattened and left to harden. To ensure the alignment of the sample with the applied force, a steel ball was used between the upper end cap and the flat head of the equipment as seen in Figure 2a. Tests were performed using a standard uniaxial testing apparatus (Instron Model 5586) at a crosshead speed of 0.5 mm/min (15).

After the applied thermal cycle, a volumetric contraction is evident. The homogeneity of this contraction depends on several fabrication parameters. In order to characterize this phenomenon, form retention was measured as a percentage of the side view angles average as seen in Figure 2b. An angle of 90° corresponds to 100% form retention.

Porosity measurements were taken via image analysis. Samples were mounted in a black pigmented polyester resin used as contrast material to fill all the open cells. A porous face was exposed and polished. Images were taken and analyzed using the freeware ImageJ. Only one plane was analyzed by sample.
3. RESULTS AND DISCUSSION OF THE FABRICATION OF GLASS CERAMIC FILTERS

3.1 Morphological characterization of LZSA replicas

A first approach allows identifying a morphological difference between the internal structure and the external structure of the glass ceramic replicas.

Figure 3 shows a better replication process on the external surface compared to the internal section of the foams. A better replication process can be established based on the following observations:

- Fewer closed porosity.
- Cell type structure can be identified such as windows and strut configuration.
- Fewer collapsed areas and clogged areas can be identified.

A possible hypothesis for this behavior is found on the stage of extraction of excess material. Once the foam is impregnated with the slurry, it is passed through a set of rollers with a controlled gap distance. The foam is compressed four times through the rollers with rotation after every pass to promote the homogeneity of the remaining suspension. The first compression eliminates most part of the suspension. The after compressions help distribute the remaining slurry inside the foam, but part of the superficial slurry remains on the surface of the roller. This behavior generates a gradient of ceramic material concentration, creating a different morphology on the surface and the inside of the foams.

Morphological images of the internal sections of the 45 and 60 ppi replicas are shown in Figure 4 and Figure 5 respectively. Areas of excessive clogging and areas with no cell definition can be seen. This behavior is more evident in foams with low compression percentage and more viscous suspension. As seen in Figure 4, no combination of parameters shows a better replication process. On the other hand, for the 60 ppi foams shown in Figure 5, samples (f) and (g) correspond to better morphological replicas of the PU foam.
Figure 4. Morphological comparison of the glass ceramic replicas. 45 ppi foam. Suspension type Vs compression percentage.
3.2 Permeability of the LZSA replicas

Figure 5. Morphological comparison of the glass ceramic replicas. 60 ppi foam. Suspension type Vs compression percentage.

A relationship between the permeability and the type of ceramic suspension can also be observed. Higher permeability values can be obtained with less viscous suspensions. However, less viscous suspensions sacrifice the morphological replication of the polyurethane foam. This phenomenon can be explained based on the morphological results discussed previously. The fluid suspensions are not capable of covering polymeric struts on the impregnation stage, causing partial collapse and generating permeability paths with less fluid energy loss.
3.3 Mechanical characterization of the LZSA replicas

![Figure 6. Permeability results for the 45 and 60 ppi foams.](image)

Mechanical characterization results for the 45 and 60 ppi foams.

A bad quality impregnation can be caused by high compression percentages or low viscosities of the ceramic suspension, causing cell collapses and the reduction of the mechanical resistance of the ceramic replicas. The mechanical resistance of a cellular structure is related with the longitude and thickness of the cell struts. If the ceramic material is reduced, then the mechanical resistance suffers a reduction as well. A variation in compression percentage from 70% to 35% can increase the compressive mechanical resistance from ~1 MPa to ~7 MPa. Analyzing the morphological results for the LZSA replicas, a hypothesis can be established showing the incidence of the clogged cells on the mechanical resistance of the porous structure. A low compression percentage generates highly clogged cell areas. These clogged cells are interconnected forming a cellular structure with struts equivalent to the size of filled cells. This allows the distribution of the force, thus increasing its mechanical resistance.

3.4 Porosity of the LZSA replicas

Porosity corresponds to another variable to be considered in the characterization of the structures. This property is mostly a function of the compression percentage. The behavior is very similar to the one of permeability; it increases with an increase in compression percentage. The variation of porosity can be significant, from ~65% to ~95% with an increase in compression percentage from 35% to 90%.

The influence of the pore density and viscosity of the ceramic suspension on porosity is not concluding from the samples obtained, as seen in Figure 8.

![Figure 7. Mechanical characterization results for the 45 and 60 ppi foams.](image)
3.5 Form retention of the LZSA replicas

Form retention becomes a problem when enlarging the size of the samples. For catalytic trap application it is important to have larger samples (minimum frontal area ~2.3x10-3 m²) in order to test them on real engine exhaust gases (1; 3; 16; 17). As seen in Figure 9, form retention tends to worsen with an increase in compression percentage during the slurry removal stage. This can be attributed to the lack of parent glass over the PU foam and the sintering mechanism. This mechanism corresponds to viscous flow. In the early stage of sintering, before the glass transition temperature of the parent glass, the microstructure of the material covering the polymeric struts corresponds to a random arrange of packed particles. After the glass temperature is reached, a continuum viscous matrix is formed which defines the densification stage. A lack of parent glass in the foam would cause a severe uncontrolled retraction during the densification stage (8; 18).

3.6 Comparison with commercial ceramic foams used as filtering devices

Figure 10 and Figure 11 show some characteristics of the LZSA replicas (red markers) in comparison with other ceramic foams reported in literature (4). It can be observed that the values obtained with this material follow the generalized trend of other ceramic cellular structures. Mechanical resistance values obtained are in the upper range but permeability and porosity values enter the lower range. However, the values obtained prove the LZSA material as a viable option in the fabrication of ceramic filters.
Figure 10. Comparison of LZSA foam characterization results (red markers) and other ceramic foams (4). The variable of analysis corresponds to the cell density (ppi).

Figure 11. Comparison of LZSA results (red markers) and other ceramic foams (4). The variable of analysis corresponds to compression of the foam during the excess slurry removal stage.
4. CONCLUSIONS
Porous structures were obtained from a glass ceramic material for diesel engine particulate filtering applications. In order to obtain properties similar to those of commercial cellular structures of alumina (Al₂O₃) or zirconia toughened alumina (ZTA) (porosities between 80% and 90% and mechanical resistance between 1 and 7 MPa (1; 15; 19; 20; 21)), the fabrication parameters were chosen as follows: a ceramic suspension of 50/50 (solid/liquid phase ratio) and a compression percentage of 50% during the excess removal stage. Although this combination of parameter does not result on the best ceramic replicas based on morphological analysis, it results on a porous material with good mechanical properties for this specific application. Form retention with these parameters for both types of foams, 45 and 60 ppi, is superior to 90%, having a geometrical tolerance of ±2 mm.

The morphology of the ceramic replicas is influenced by the process variables in a way that it can generate a porous structure but without replicating the polymeric structure. The best replicas were found with the most viscous ceramic suspension and the highest compression percentage. This does not necessarily mean the best mechanical properties.

On the replication method, the compression percentage on the stage of extraction of excess material affects in a very significant way the mechanical properties of the resulting structure. Therefore this must be considered one of the most important variables to be controlled during the replication process. High compression percentages correspond to high porosity and permeability values, with a reduction in mechanical resistance.

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6. REFERENCES
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