CERAMIC FOAMS PROCESSING INNOVATION FOR HIGH TEMPERATURE APPLICATION

Vânia Regina Salvini [1,2*], José de Anchieta Rodrigues [1], Victor Carlos Pandolfelli [1]

[1] UFSCar-DEMa, GEMM, São Carlos, Brazil.

[2] SOLVE High Temperature Ceramics

* vr.salvini@gmail.com

Abstract

There has been wide interest in ceramic foams because of their properties, which comprise high volumetric porosity, with open and interconnected or closed and isolated pores, and a broad range of pore size. These properties have uses as filters for castings, catalytic supports, bioceramics and thermal insulating ceramics. However, a common issue of filters made by replica templates is their low mechanical strength due to the hollow struts and microcracking generated during the thermal decomposition of the polymer. In turn, the insulating foams used as hot face lining of furnaces are subjected to chemical attack by alkaline vapors, which reduce their durability due to cracking and/or infiltration of substances. In this context, this work presents innovative processing routes for ceramic foams, such as vacuum infiltration process of colloidal sols (Al_2O_3 and SiO_2) for filters and surface deposition of refractory powders (Al_2O_3) by the fiber laser process on insulating foams.

Introduction

Given the importance of energy costs and environmental concerns, foamed ceramics have received much attention in recent years. This group of porous materials presents key properties such as high porosity, open and interconnected or closed and isolated pores, and a broad range of sizes (micropores: d<2nm; mesopores: 50nm>d>2nm; macropores: d>50nm) which are useful for several applications.

Ceramic foam filters are open-pores materials (porosity level in the range of 70-95%), formed by a three-dimensional network of struts that are connected to each other [1, 2]. This web-like structure generates tortuous flow paths that favor fluid mixing and improve contact between solid particles and the internal filter surface, enhancing trapping and conversion efficiencies. Due to this interesting feature, the range of application of these porous materials has spread to several solid-fluid contact processes [1, 3-5].

Patented in 1963 by Schwartzwalder and Somers [6], the polymeric sponge replica method is amply used for production of reticulated ceramic foams. This method involves coating a polymeric sponge by dipping it into a shear-thinning ceramic suspension. The impregnated sponge is then compressed by rollers to ensure filling of void cells with suspension and to remove the excess of slurry. After that, the coated sponge is dried to remove liquids, and then is fired slowly to pyrolysis of polymeric sponge and to sinter the ceramic material.
Therefore, independently of ceramic composition and cell size of sponge, the common issue of foam filters is the low strength due to the hollow struts and cracks generated at the thermal decomposition of polymeric foam, as shown at Zr_2SiO_4, and SiC filters (Figure 1). Brown and Green [7] identified that the thermal expansion differences between the polymeric sponge and the ceramic coating is the primary cause of the cracking of filter struts.

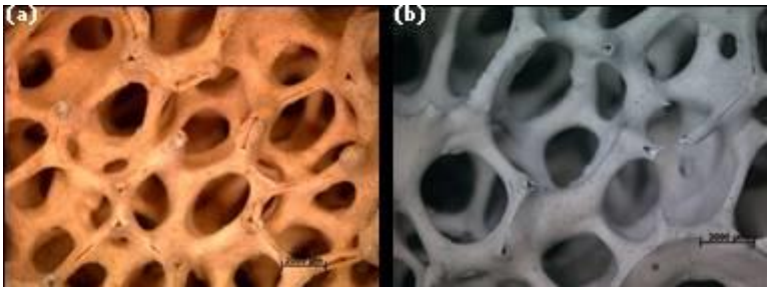

Figure 1: Hollow struts and cracks at (a) Zr_2SiO_4 and (b) SiC filters [1]

Aiming to improve the Al_2O_3-based filters mechanical properties (strength, friability, thermal shock) and keeping their high level of permeability by the vacuum infiltration process, this work evaluated the influence of the processing parameters as solids concentration (15 to 40 wt%) and particle size (nano to micrometric) of suspensions, and infiltration time (1 to 5min).
In turn, alumina ceramic foams are materials with high porosity (70 to 85%-Vol.), low density (0.7 to 1.1 g/cm3), low thermal conductivity (< 2 W/mK) and free from of carcinogenic and/or toxic ceramic fibers. Due to these characteristics, their use as hot face lining of furnaces and industrial equipment that operate at high temperatures (1200 to 1800^{o}C) has increased.
At high temperatures the main heat transfer mechanism is the thermal radiation. Thus, ceramic foams with good thermal insulation must be able to reduce the intensity of radiation emitted outside the system within the temperature range of interest. Additionally, in use, the surfaces of insulating ceramic foams are subjected to chemical attack by alkaline vapors (Potassium, K, Sodium, Na), corrosion and erosion by contact with liquid metals (steel, aluminum), which decrease the structural durability of the material due to the appearance of cracks and/or infiltration of substances as shown at Figure 2.

Figure 2: Typical cracking on hot face insulating lining of furnaces.

Considering these aspects, surface modification of insulating ceramic foams by the fiber laser deposition of alumina powder process was evaluated considering the advantages, the key issues to be solved and the trend of developments.

Materials and Methods

Initially we will present the experimental procedure given to ceramic filters, and then, the one applied for the insulating foams.

- ***Ceramic filters***

Al_2O_3-based filters were produced by the replica method using 10ppi (pores per inch) polyurethane sponge of (Heisgiess, Germany) of 50mm x 50mm x 25mm as the template material. The ceramic suspension was comprised by fine aluminas (CL370C and CT3000SG, Almatis, Germany), colloidal silica (Bindzil 1440, Eka Chemicals, Sweden) as sintering additive, Castament® FS20 (Basf, Germany) as dispersant, Rhodopol® 23 (Rhodia, USA) as thickener, Polyvinyl alcohol (0.2 wt%) as binding additive and distilled water (Table 1). All raw materials were firstly homogenized in a high shear mixer for 1h at room temperature before the slurry’s contact with the polymeric foam.

Table 1 – Raw materials used for the preparation of the ceramic suspension.

Raw materials	Ceramic suspension (wt.%)
Calcined alumina (CL370C)	73.1
Reactive alumina (CT3000SG)	6.0
Colloidal silica (Bindzil 1440)	10.0
Dispersant (Castament® FS20)	0.2
Rhodopol 23	0.3
Polyvinyl alcohol (sol. 0.2%)	0.2
Distilled water	10.0
Silicone	0.2

Figure 3 presents step by step detail of the conventional process and the proposed one for producing foam ceramics by the replica sponge method.

By the conventional process, after impregnated and compressed by rollers, the samples received a thin coating layer of low viscosity suspension. After that, they were dried at 110ºC per 15 min and then, are fired to pyrolysis of polymeric sponge and to sinter the ceramic material.

According to the proposed process, after impregnated and compressed by rollers, samples were initially heated up to 600°C per 1h (heating rate=1°C/min) to burnout the sponge. Because of high reactivity of colloidal silica in composition, the skeleton showed good strength for further steps. Then, samples were placed in vacuum infiltration chamber for filling in the generated hollow struts and flaws due to sponge burnout. This step was carried out considering different solids concentration of fine Al_2O_3 suspensions (15 wt% and 30 wt%, <10μm), distinct sol size of colloidal suspensions (SiO_2 sol – 40 wt%, 14nm and Al_2O_3 sol – 40 wt%, 80nm), and infiltration time ranging from 1 to 5 minutes.

After vacuum infiltration, samples were dried at 110ºC per 15 min and then, are fired at 1150ºC for 1h (heating rate=2ºC/min).

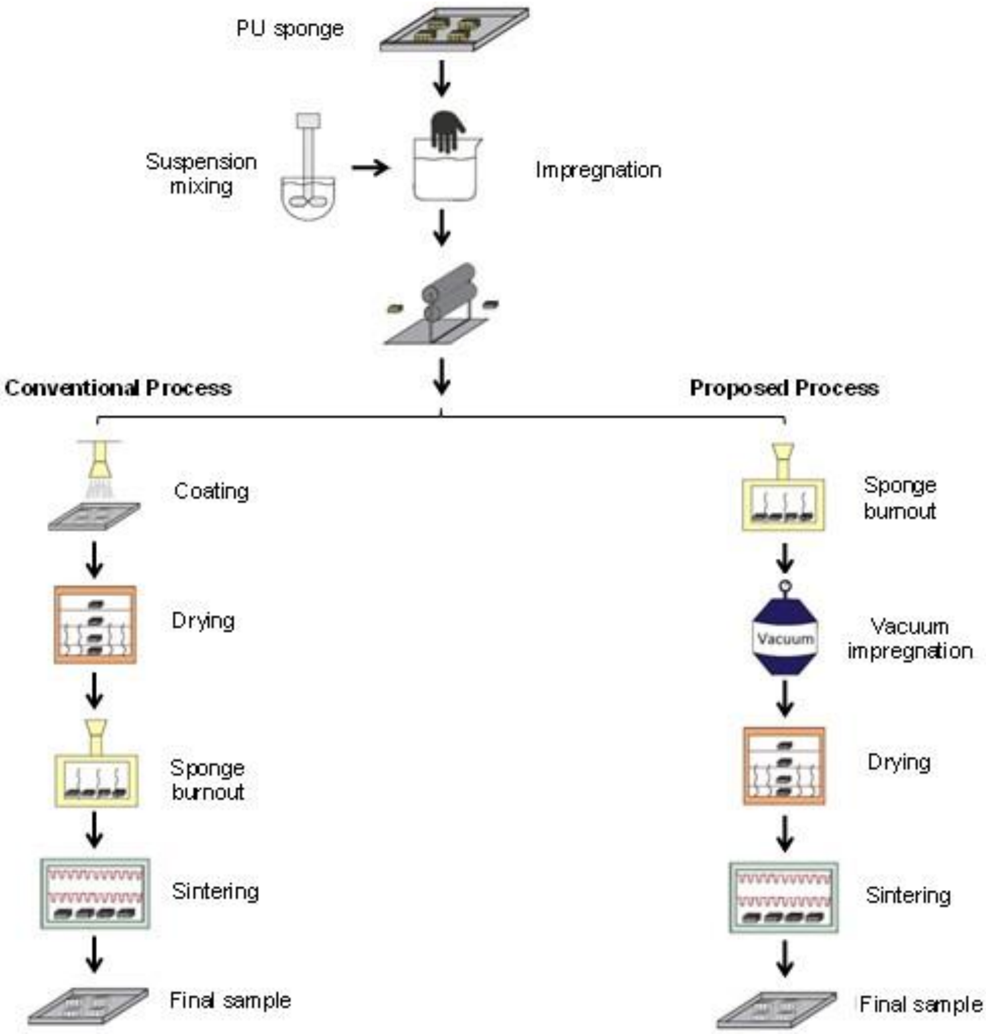

Figure 3: Steps of the conventional and the proposed process for the preparation of porous ceramics by the replica sponge method.

- ***Insulating foams***

The complete Laser Cladding system consists of a medium power laser source, a powder feeder assembly with dispensing nozzle and a software-controlled positioning device, in addition to the equipment control system. The system is illustrated by Figures 4 and 5.

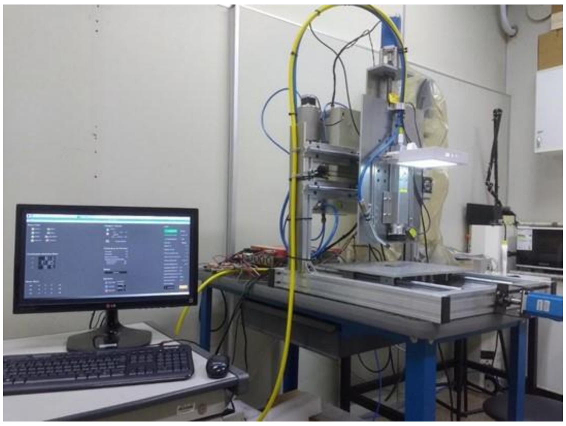

Figure 4: Experimental arrangement of the laser metallic materials deposition system.

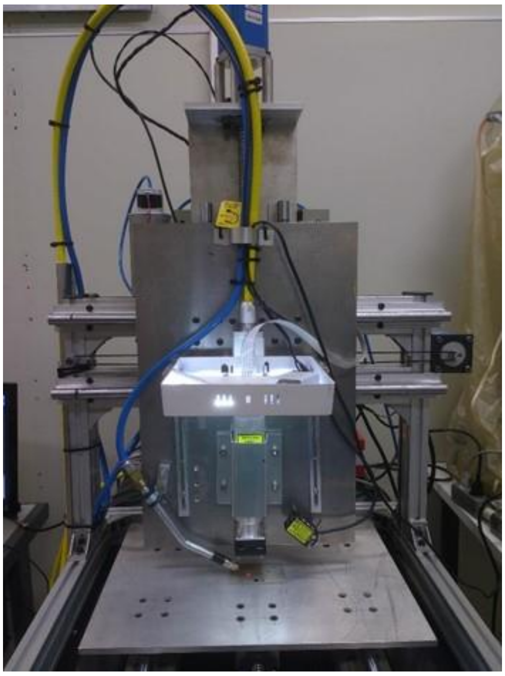

Figure 5: System with intelligent control, based on algorithms of computational vision, able to evaluate the surfaces to be worked for customized applications.

The system consists of a movement platform to control three XYZ axes, using stepper motors and their respective control modules (drivers). This system is robust and can drive stepper motors with a resolution of up to 51,200 steps per revolution. With this precision and the 3 possible degrees of freedom of movement, it allows the deposition of metallic powders on predominantly flat surfaces and with variable heights, satisfying the needs of the project. Figure 5 shows the platform developed at BR Labs Tecnologia Óptica e Fotonica, in which the X axis corresponds to the single movement of the support table where the part to be coated is positioned and the Y axes (together with the X axis make up the movement two-dimensional system) and Z (responsible for the vertical or height movement of the system) dictate the movement of the head where the laser source is installed, whose beam is focused by a lens (radius incident 90° in relation to the XY plane), the camera with its lighting system, laser distance sensor and powder gun. The system has adjustments and calibration of the respective axes to ensure the desired accuracy.

Results and Discussion

This section has been organized into two parts. The first one shows the effect of the particle size and solids concentration of ceramic suspensions on the properties of vacuum infiltrated Al_2O_3-based ceramic filters. The second part presents the results of surface powder deposition on Al_2O_3 foams.

1. *Vacuum infiltration on ceramic filters*

Figure 6 points out some of the main characteristics observed in the dried alumina filters after sponge burnout and the vacuum infiltration with alumina or colloidal silica suspensions. Regarding the samples that were in contact with Al_2O_3 suspensions (Figures 6a and 6b), the triangular hollow channels still remained within the struts and, besides that, the solid particles were preferentiality placed on the external surface of the reticulated structures. Conversely, a more effective filling up the triangular voids and sealing the cracks were observed after vacuum infiltration the filters into the colloidal silica suspension (Figure 6c ad 6d). These results indicate that the reduced size (14 nm) and lower density (1.264 g/cm^3) of the colloidal SiO_2 suspension favored better covering of the flaws/defects before sintering process.

Nevertheless, the coating process by vacuum infiltration may cause the thickening of the struts with significant reduction in permeability of reticulated porous ceramic. Hence, measurements of the total mass and the strut thickness were carried out of vacuum infiltrated filters samples with alumina and colloidal silica suspensions for 1, 2 or 5 minutes, followed by sintering at 1150°C for 1h.

Figure 7 shows that, compared to the reference samples, the Al_2O_3 suspension infiltrated filters (15 wt% and 30 wt% of solids) presented higher mass and thicker struts due to settling of the solid particles on the reticulated structure (Fig. 7a and 7b). Regarding the infiltrated filters with colloidal SiO_2, similar results or just a minor increase in the struts thickness and samples' mass was attained when compared to the reference samples.

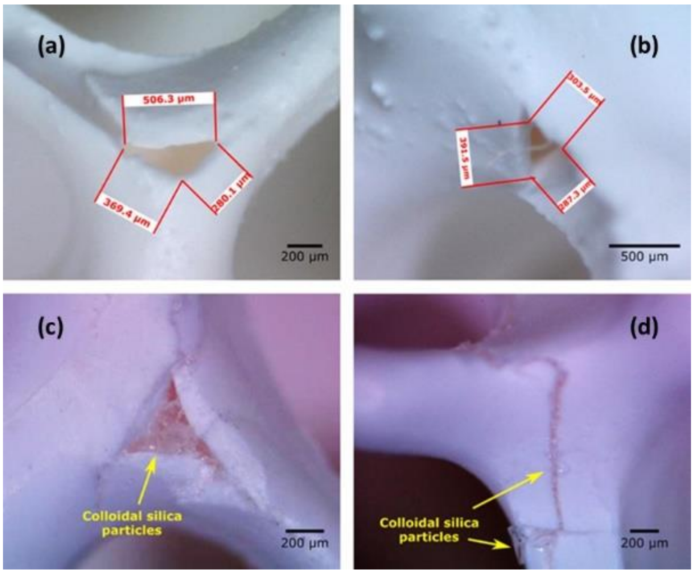

Figure 6: Images of the dried filter samples after sponge burnout and vacuum infiltration with alumina suspensions (< 10µm) with **(a)** 15 wt% and **(b)** 30 wt% of solids, and colloidal silica (<14nm) with 40 wt% of solids **(c and d)** for 5 min.

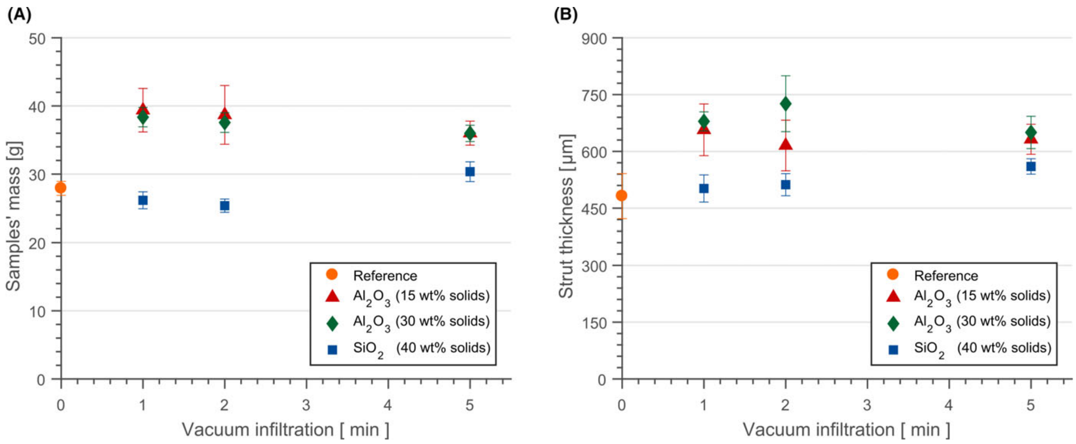

Figure 7: **(A)** Samples' mass and **(B)** strut thickness of the evaluated filters after vacuum infiltration of alumina (< 10µm) and colloidal silica (14 nm) suspensions. All measurements were carried out after firing the materials at 1150ºC for 1h.

As expected, the reinforcement of the struts resulted in higher compressive strength for the filters samples submitted to vacuum infiltration with alumina or colloidal silica suspensions (Figure 8).

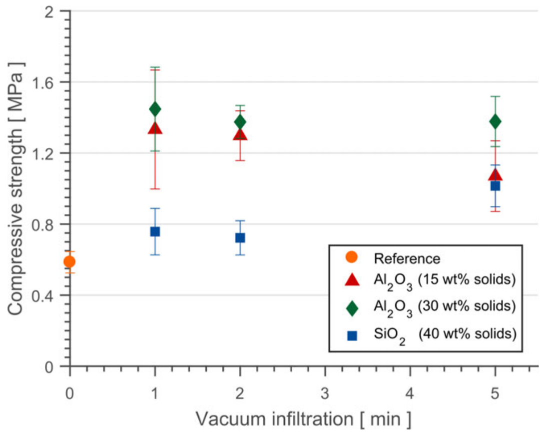

Figure 8: Compressive strength of sintered filters samples after vacuum infiltration by alumina or colloidal silica suspensions.

Nevertheless, despite the improved mechanical behavior, a drawback associated to infiltration with the Al_2O_3 suspensions was the high pressure drop ($\Delta P/L$) detected during the permeability measurements (Figure 9), due to the buildup of solid particles at the original struts and, consequently, the formation of thicker walls that reduced and/or blocked the pore channels. Permeability is an important aspect for reticulated porous ceramics application. For instance, molten metal filters with reduced permeability might lead to freezing of liquid metal, increasing its viscosity, the mold fulfilling time and, consequently, damaging the metallurgical production conditions.

One of the more significant findings to emerge from Figure 9 is that filters infiltrated with colloidal SiO_2 present similar pressure drop ($\Delta P/L$) values to the commercial filters produced by the conventional replica sponge method with different coating layer. This indicates that the SiO_2 sol placed on the struts did not affect the permeability of filters.

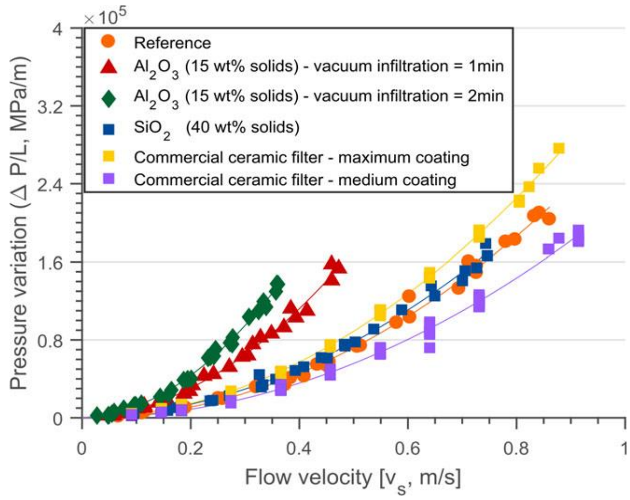

Figure 9: Effect of vacuum infiltration of alumina (10µm, 15 wt%) or colloidal silica (14nm, 40 wt%) suspensions on the permeability of sintered filters samples.

2. *Surface powder deposition on insulating foams*

As a rapid solidification process, cracks induced by large thermal gradient are prone to form during laser power deposition on insulating foam surface, as depicted on Figure 10.

Figure 10: Photo of cross-section of insulating foam with 2.5mm Al_2O_3 layer deposited by laser. Note the cracking perpendicular to the Al_2O_3 layer.

The exhibition of cracks leads to weakened mechanical properties and shortened lifetime of deposited ceramic materials. In addition, the presence of cracks will easily cause the failure of ceramic components.

According to Hu and Cong [8] by optimizing process parameters, such as adding ultrasonic vibration, adjusting laser powder and layer thickness, the cracking problem can be reduced but cannot be eliminated. According to them, methods of pre-heating the substrate prior to laser process, post-heating the deposited materials to heal existed cracks, adding additive materials as Al_2O_3-ZrO_2 proved to be successful in suppressing cracks.

In order to deal with such demand, alternative routes of alumina layer deposition methods and sintering conditions are being studied, such as solid-state sintering of the layer at electric or microwave furnaces.

Conclusions

According to the results presented in this work, a suitable alternative to enhance the mechanical strength, thermal shock resistance and friability of alumina-based ceramic filters consist in infiltrate the reticulated structure with colloidal suspensions via vacuum infiltration technique. The best processing was attained when the filters were vacuum infiltrated with colloidal silica of 40 wt% of solids per 1 min. Moreover, the nanoparticles' infiltrated promoted denser and thin cell walls, the first contributed to reducing the friability, and the later provided high permeability level of the ceramic filters.

The laser deposition of Al_2O_3 in insulating foams induced the formation of cracks due to the large thermal gradient associated with the rapid solidification process. According to the literature, by optimizing process parameters, such as adding ultrasonic vibration, adjusting laser powder and layer thickness, the cracking problem can be reduced but cannot be eliminated. alternative routes of alumina layer deposition methods and sintering conditions are being studied

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