

## DEVELOPMENT OF A NOVEL HYBRID METHOD FOR THE PRODUCTION OF MACROPOROUS FOAM CERAMICS

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### ABSTRACT

Macroporous ceramics with a porosity in the range of 10% to 90% have been produced for a number of applications, such as molten metal filtration, catalysis, refractory insulation, and hot gas filtration. With macroporous foam ceramics it was possible to achieve a porosity of more than 90%. The main processing routes that can be used for the fabrication of macroporous foam ceramics with tailored microstructure and chemical composition are replica, sacrificial template, and direct foaming techniques. These technologies are well described in the literature and did not lead to a large technically feasible, cost-effective production process. To accomplish a simple and inexpensive manufacturing process, a novel hybrid method of direct foaming and replica technique was developed. In this new process, a suspension is made of a first ceramic raw material, which is primarily foamed with air, and then mixed with a second suspension or a ceramic powder. Consequently it is a staged mixing process. The foam of the first raw material serves as a template for the second suspension or the ceramic powder. To meet different requirements the ceramic foam can be adjusted concerning pore size and porosity over a wide range by varying the raw materials, the foaming process, the foaming agent and the binder. The ceramic foam produced has a low density and low thermal conductivity and is suitable as thermal insulation in high temperature applications up to 1800°C.

### INTRODUCTION

The production of Ceramic bodies with a low density and low thermal conductivity dates back to the early 30<sup>th</sup> of the last century. The first approaches for the production of porous ceramic bodies' used combustible materials like wood chips or other organic materials [1]. This technique is well known as "sacrificial template".

Later unstructured organic materials (like wood chips) were replaced with structured combustible materials. The structure of these materials (i.e. plastic foams) can be replicated by ceramic materials. This led to the "replica technique" for production of high porous ceramic (Schwartzwalder et.al.)[2].

Stuart et.al. [3] showed different types of possible templates the "replica technique". These templates can be distinguished in "artificial" and "natural" templates. Artificial templates are usually polymeric foams, natural templates like coral skeleton or wood can be also used.

Another kind of "replica technique" uses wet foams as a template. Usually a ceramic suspension is mixed with prefabricated wet foam. Fujii et.al. [4] showed this approach in 1960 for porous refractory materials. Using this method suspensions of fine grinded raw materials are mixed with soapy foam and a binder.

A newer approach for the production of ceramic foams is the method of "direct foaming". In the "direct foaming" approach the pores/bubbles are produced directly inside the ceramic body.

Opposite to the methods of "sacrificial template" or "replica technique" there are neither combustible materials nor templates necessary. With the "direct foaming" methods it is possible to produce closed pores ceramic foams.

The generation of bubbles in a body can be achieved with different methods. These methods are [3,4,5]:

- Direct introduction of air in a raw material suspension.
- Development of gases in a raw material suspension due to a chemical reaction ("chemical blowing").
- Development of gases due to evaporation of a liquid ("physical blowing").

The direct introduction of air into a water based suspension leads to "wet foams". Wet foams are in principle thermodynamically instable. Therefore it is necessary to stabilize the wet foams to reach a sufficient structure in the dry foam.

For the stabilization of the wet/liquid foam two different approaches can be used. These are [3]:

- stabilization due to surfactants
- stabilization due to particles

For the stabilization due to surfactants lauryl sulfates or proteins can be used. Particle stabilization can be performed by very small (surface reactive) particles.

One critical aspect by the "direct foaming" approach is the time dependency of the foam stability of the water based foams. To achieve a stable dry foam in the green body it is necessary to use a binder (i.e. cement) or to remove the water very quickly (drying process) [3,6,7].

### METHODS, EXPERIMENTAL SECTION

#### Process

The new approach bases upon recent findings and well known advantages and disadvantages of current methods of ceramic foam production. Goal of the research is the development of an inexpensive, simplified, general method for production of ceramic foam for a wide range of materials and properties.

The new hybrid method combines the "direct foaming" and the "replica technique". Fig. 1 shows the schematic process of the method.

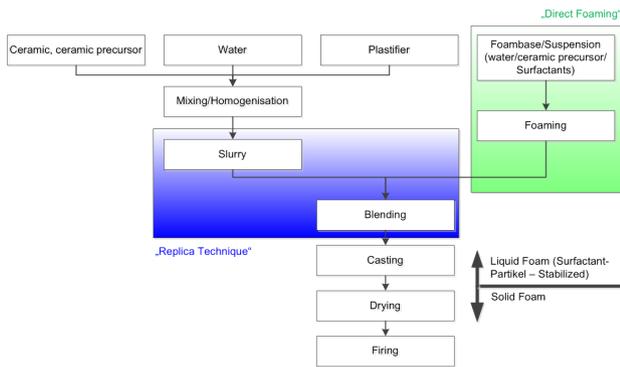


Fig. 1: Process of the hybrid method

The process bases upon two different stages. Stage 1 produces light ceramic foam by “direct foaming”. The stage 1 produces light weight ceramic foam from a foam base and pressurized air. The ceramic foam of stage 1 acts as a template for stage 2. In stage 2 the “template light foam” will be blended/replied with a ceramic suspension (“replica technique”) to achieve foams with the necessary properties (i.e. density). Foaming (stage 1) and blending (stage 2) use static mixer (see Fig. 2).

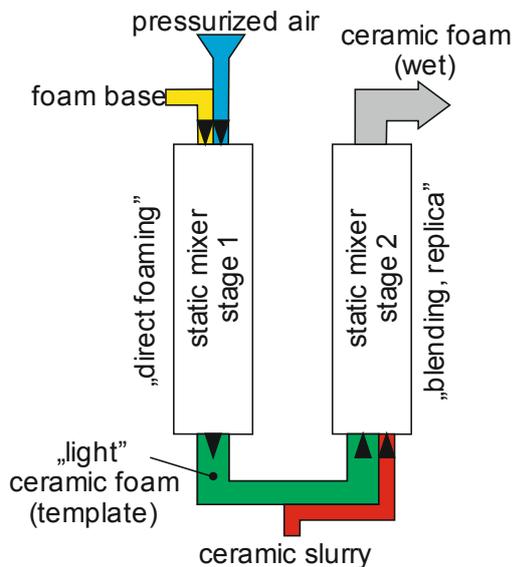


Fig. 2: Two step foam production scheme

The wet foam is casted and dried before firing. The step of drying is a very sensitive process step. Drying must be done very quickly due to the thermodynamically instability of the wet foam. The temperature for drying lies in the range from 40°C up to 100 °C depending on the water content of the wet foam. The quick drying stage avoids the use of binder (i.e. polymeric binder or cement) in the wet foam (see section materials).

After drying the green body is fired to the appropriate temperature (1000°C up to 1750°C). The firing temperature depends on the material. The firing can be done with a fast temperature rise up to 100 K/h due to the absence of (organic) binders or sacrificial templates. This allows a short firing period with low energy consumption.

## Materials

The process uses usually two different bases for the different stages. Stage 1 uses a suspension from:

- a ceramic powder or precursor
- water and
- additives.

Stage 2 uses a (heavy) ceramic slurry mainly based on water, ceramic powder or precursor and plasticizers or liquefier.

The ceramic raw materials depend on the intended use of the ceramic foam. Raw materials for use as refractory materials are:

- Clays, kaolinitic materials (natural Phyllosilicates) up to 1300°C
- Andalusite, kyanite and sillimanite (natural Nesosilicates) up to 1450 °C
- Mullite (artificial) up to 1650 °C
- Alumina (artificial) up to 1850 °C
- Zirkonia up to 2000 °C

All this materials can be used to produce ceramic foam with the hybrid method. For this purpose the main diameter of the materials should be less than 100 micron.

Additives in the foam base are mainly surfactants and substances which stabilize the liquid foams. The described method uses surfactants like lauryl sulfates or proteins. Carboxymethylcellulose is used as stabilizer for the foam and as binder.

The composition of the foam base for stage 1 depends on the ceramic material and the used foaming agent. A generic composition can be described as follows (all weight %):

- Ceramic powder 11 %
- Water 85 %
- Additives (foaming agent, HMZ) 4%

Stage 2 uses for blending usually the same ceramic powder as the foam base of stage 1. A higher concentration of the ceramic powder is used in stage 2. The quantity of ceramic powders in the slurry lies in the range of 55 – 70 %. To achieve this high solid content in the slurry, liquefiers like pyrophosphates or alkalisilicates have to be added.

## RESULTS

### Wet foam stability

The stabilisation of the wet foam is one of the critical points in the production of ceramic foams. In the current approach no binder like cement or organic polymers (polymerisation) are used. The foam stabilisation is based on the surfactants and cellulosic derivatives and a quick drying process. The produced wet ceramic foam is also stabilised true a high content of solid particles. Variation in the expansion ratio of the foam and the solid content shows that a sufficient stability can be achieved within the following ranges (volumetric %):

- Solid contents 23 – 27 %
- Water 75 – 71 %
- Additives 2 %.

The stability of the foam also depends on the concentration of the cellulosic materials. These foams are stable for more than 24 h at

room temperature. This means there is no significant evidence of drainage (creaming), coalescence (film rupture), or Ostwald ripening (disproportionation). Foams with lower contents of solids (below 20 %) tend to creaming. The long term wet foam stability and a quick drying process lead to homogeneous dry foam (green body). There is a small evidence that the viscosity of the foam or the rheological behaviour of the foam itself has also an impact on the wet foam stability.

### Foam density

For refractory use the resulting foam density is an essential property of the material. The two-stage process allows the production of different foam densities. Due to the blending stage the ratio between the light foam and the slurry determines the resulting porosity. For the prediction of the resulting foam density (after firing) a raw estimation (1) can be given as:

$$\rho_{\text{foam}} = \frac{\rho_{\text{foam,wet}} * c_{\text{solid}}}{(1 - f_{\text{shrinkage,linear}})^3} \quad (1)$$

where:

$\rho_{\text{foam}}$	estimated foam density [kg/m <sup>3</sup> ]
$\rho_{\text{foam,wet}}$	wet foam density [kg/m <sup>3</sup> ]
$c_{\text{solid}}$	solid mass content of the wet foam [1]
$f_{\text{shrinkage, linear}}$	factor linear shrinkage [1]

The current compositions (see materials) and the described process (see process) allows the production of wet foams with a density in the range of 250 to 500 kg/m<sup>3</sup>. These wet foam densities leads according to (1) to a final foam density in the range of 150 to 350 kg/m<sup>3</sup> (solid content approx. 50%, linear shrinkage 10%). Due to a higher shrinkage during firing compositions with clays or kaolinitic minerals lead to a little bit higher densities as artificial materials like synthetic mullite. The porosity itself depends on the density of the ceramic materials. Usually open porosities in the range of 88 up to 93 % can be achieved.

### Foam structure

With the two-stage process open porous foams can be processed. The structure of the foam depends on the type of surfactant which is used to form the wet foam. The differences are caused by the different size of the membrane thickness of the bubbles and the size and form of the ceramic particles. Principal investigations show, that surfactants foam (lauryl sulfates) forms a skeleton structure. This is caused by the thinner membrane of surfactants foams. Only the gaps between the bubbles can be filled with particles. On the other hand it is possible to fill especially with Phyllosilicates (i.e. mica) also the membranes in protein based forms (see Fig. 3).

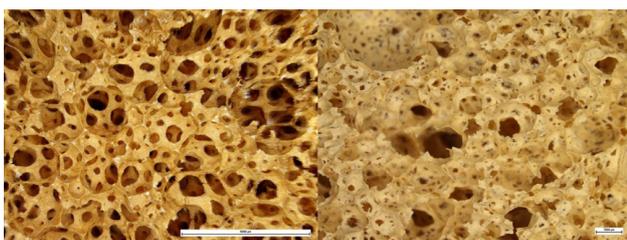


Fig. 3: Foam structures from lauryl sulfates (left) and protein based (right) ceramic foams.

The size of the pores lies between a few micrometres up to 1000 micrometres

### Refractory range

With the new approach it is possible to make refractory ceramic foams for different temperature ranges. The refractoriness depends on the type of the material, which is used for the foam. For low temperature applications materials like Muscovite can be used. With kaolin or andalusite refractory foams can be produced up to a classification temperature of 1450°C. For the high temperature range (more than 1500°C) foams on the basis of mullite and alumina can be produced.

### Discussion, Outlook

The novel hybrid method for the production of macroporous foam ceramics allows the production of ceramic foams in a broad range. The described process has the following main advantages:

- production of stable wet foams due to a twostage process,
- simple compositions of materials,
- usability for a broad range of ceramic raw materials,
- no need for a special treatment of particles for stabilisation,
- custom-made foam densities in one process,
- low apparatus costs (i.e. use of static mixing system).

The foam density can be varied between 150 kg/m<sup>3</sup> and 450 kg/m<sup>3</sup>, the application temperature lies between 1000°C and 1800°C. The thermal conductivity depends strongly on the foam density. In low density products a thermal conductivity of 0.05 W/mK can be achieved.

There is a need to carry out further investigations concerning the influence of the viscosity of the foam or the rheological behaviour of the foam itself on the wet foam stability.

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