

PROPERTIES OF Al_2O_3 FOAMS OPTIMIZED BY FACTORIAL DESIGN

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Alumina foam was prepared by the direct foaming method. The foam was stabilized by in situ partially hydrophobized particles of Al_2O_3 . Dodecylbenzenesulphonic acid was used for hydrophobization and it also acted as a foaming agent. The composition of the starting suspensions (Al_2O_3 , boehmite, dodecylbenzenesulphonic acid and water) were varied according to factorial design. The resulting properties observed were: foam ratio, foam shrinkage on drying and sintering, bulk density and porosity of ceramic foams, average pore size and compressive strength. The final properties of foams dependent on statistically significant factors (boehmite, dodecylbenzenesulphonic acid) were evaluated by common software. The foam ratio decreased and the bulk density of the alumina foams increased with increasing quantity of the dodecylbenzenesulphonic acid (0.1-0.2 wt.%). Bulk density of alumina foams ranged from 88 to 155 kg/m^3 and average pore size reached 111 μm to 215 μm depending on the quantity of the dodecylbenzenesulphonic acid. The microstructure of ceramic foams reached high porosities ranging from 96 to 98 %. The compressive strength of the alumina foams increased with increasing quantity of boehmite (1-3 wt.%) and it reached values of 333 kPa.

INTRODUCTION

The increasing interest in ceramic foams is mainly been associated with their properties, such as high porosity, high surface area, high permeability, low mass, low specific heat, low thermal conductivity, etc. These properties are suitable for some technological applications, such as catalyst supports, filters for molten metals and hot gases, refractory linings for furnace [1, 2, 3].

Alumina foams are usually produced by the polymeric sponge method which involves the impregnation of polyurethane sponges with slurries containing ceramic particles followed by pyrolysis and sintering for solidification of the foam [4, 5]. This method allows to prepare ceramic foams with pore sizes ranging from 200 μm to 3 mm and porosity levels between 40 % and 95 % [6]. The bulk density of alumina foams prepared by this technique ranges from 314 kg/m^3 to 1370 kg/m^3 [7].

An alternative method for obtaining a ceramic foam is the direct foaming method. This method is suitable for the fabrication of porous structures with porosities ranging from 45 % to 97 %, cell sizes being between 30 μm and 1 mm and bulk densities being between 156 kg/m^3 to 1560 kg/m^3 [7]. Direct-foaming methods involve incorporation of a gaseous phase into a ceramic suspension consisting of ceramic powder, solvent, dispersants, surfactants, polymeric binder and gelling agents.

Wet foams are thermodynamically unstable systems which undergo continuous disproportionation and coalescence processes in order to decrease the foam overall free energy [6]. A surfactant is necessary to stabilize the foams for a longer time prior to solidification by reducing the surface tension of the gas-liquid interfaces. Colloidal particles adsorbed on the gas-liquid interface were observed to impede the destabilization mechanisms for several days, as opposed to a few minutes typically required for the collapse of foams prepared with surfactant. The foam formation is therefore based on the adsorption of partially hydrophobic particles into the air-water interface. Ultra-stable foams can be produced by using these particles [6]. Partially hydrophobic particles with wetting angle close to 70° are the most effective stabilizing agent [8, 9].

Liquid shells of wet foam are created by suspension of particles. For this reason the foam stability is influenced by the stability of the suspension. When particles are dispersed in an aqueous medium, the surface charges on the particles influence the state of dispersion or aggregation. The particles undergo either dispersion or aggregation depending on the polarity and the extent of surface charge developed by the particles [10]. Modification of the particle charge can be achieved by different ways, such as - variation of pH, using polyelectrolyte surfactants (dispersants), or addition of potential-determining ions.

The primary property of the dispersant is its ability to disperse particles to stabilize the dispersion. For electrostatic stabilization, iso-electric point (IEP) is a crucial parameter in preventing the nanomaterials from aggregation, especially for those prepared from aqueous dispersions of nanoparticles [11]. The foam stability can thus increase by the gelation suspension near the IEP of the powder [12]. If the suspension is stable at low pH (commonly pH~4), the system is gelling at high pH and vice versa. The two most important systems are urea/urease for shifting the pH from acidic to an alkaline regime and glucose/glucose oxidase, which enables an internal pH change from alkaline to acidic regime [12].

An alternative method for achieving gelling is a gelcasting process. The gelcasting process consists of stirring a colloidal ceramic suspension containing water-soluble monomers and a foaming agent. After foam formation the suspension is rapidly gelled by means of the polymerisation of the monomers [13, 14]. The gelation must be sufficiently fast to prevent the foam from collapsing which occurs due to liquid drainage by capillary and gravitation forces. The green body is then dried and sintered. The in situ polymerisation of the organic monomer led to fast solidification resulting in strong porous bodies. The cell size ranges from approximately 30 to 800 µm and the bulk density ranges from 390 kg/m³ to 1170 kg/m³ [1, 15]. Compared to the polymeric sponge method the foaming method allows to produce small-pore-sized closed-cell foams which cannot be made by an impregnation technique [16].

The aim of this work was to quantify the influence the composition of a suspension on the resulting parameters of the alumina foams by factorial design. The foam is stabilized by in situ partially hydrophobized particles of Al₂O₃. Dodecylbenzenesulphonic acid was used for hydrophobization and it also acted as a foaming agent.

EXPERIMENTAL

Materials and suspension preparation

Aqueous suspensions were prepared using deionized water, boehmite (Condea Pural SB-1), with a specific surface area of 250 m²/g (primary particle size ~4 nm [17]), α-Al₂O₃ (Martoxid MR 70, Martinswerk Bergheim, Germany) with an average particle diameter (d₅₀) of 500 nm and a specific surface area of 10 m²/g and anionic surfactant – dodecylbenzenesulfonic acid (DBSA).

The suspension was prepared in the amount of 200 g. The suspension composition of the zero experiment was determined by preliminary tests by try and error method (30 wt.% Al₂O₃, 2 wt.% boehmite, 0.15 wt.% DBSA). The composition of suspension (Al₂O₃, boehmite and DBSA) varied according to the factorial design 2³ [18], i.e. with every factor having

two levels (Table 1). The use of factorial design helps to determine the minimum number of experiments needed in order to produce relevant information for given set of factors. The advantage of this method is its quick evaluation. Composition of the suspensions is given in Table 2.

Table 1. Factors of factorial design.

	Factor	Level 1	Level 2
A (wt.%)	Al ₂ O ₃	25	35
B (wt.%)	Boehmite	1	3
C (wt.%)	DBSA	0.1	0.2

Table 2. Composition of the suspensions (wt. %) of the factorial design.

Number of samples	Factor			Factor (wt.%)		
	A	B	C	Al ₂ O ₃	Boehmite	DBSA
1	1	1	1	25	1	0.1
2	2	1	1	35	1	0.1
3	1	2	1	25	3	0.1
4	2	2	1	35	3	0.1
5	1	1	2	25	1	0.2
6	2	1	2	35	1	0.2
7	1	2	2	25	3	0.2
8	2	2	2	35	3	0.2

Foam and its characterization

All components were thoroughly stirred for 3 min. Foaming of suspensions was carried out using a laboratory mixer at a mixing velocity of cca. 800 rpm for 30 s. The foam volume was measured and later on it was used to calculate the foam ratio (foam volume / initial volume of the system). All experiments were performed at the laboratory temperature of 22 ± 1°C. The resulting wet foams were put into forms. All foams were initially dried at laboratory temperature for 48-72 h.

Sintering of the foams

Sintering of the dried foams was performed in an electrical furnace in two stages:

1. for 30 min at 900°C using heating rates of 5°C/min
2. for 1 h at 1400°C using heating rates of 10°C/min.

Characterization of the ceramic foam

Dimensions of the foams were measured after drying, the first and second sintering. The linear shrinkage (Δl) of foams during the course of sintering was determined.

Cylindrical samples with diameters of 17 mm and lengths of 30 mm were drilled out of the foam with a core drill. The bulk density of the foams was calculated

from the weight-to-volume ratio. The porosity (P) of the foam was calculated using the equation:

$$P = (1 - \rho_R) \times 100 \% = (\rho_t - \rho_b) / \rho_t \times 100 \% \quad (1)$$

where ρ_R is the relative density, ρ_t is the theoretical density (3980 kg/m³) and ρ_b is the bulk density of the alumina foam.

Compressive strength measurements were performed using a universal testing machine (Hegewald & Peschke, Nossen, Germany). Samples were crushed under a compression of 5 mm/min. The compressive strength was evaluated at the strain of 20 %.

Microstructure was observed by scanning electron microscopy (SEM, TESLABS 300). Afterwards, alumina foams were cut and pore size distribution was directly obtained from planar section. Diameters of approx. 100 pores were measured using SEM. The average pore diameter was calculated according the linear intercept method [19] and divided by 0.79 [20].

RESULTS AND DISCUSSION

The measured parameters and values of alumina foams are given in Table 3. The foam ratio is an important parameter in the process of foam stability determination [1]. The foam sample number 2 with the foam ratio = 9.0 was the most affected by the destabilization mechanisms [6] and it collapsed during the drying process.

Factorial design - 2³ [18] was used to determine the statistical significance of input factors (Table 4). The sum of squared deviation is split into its components (each with one degree of freedom), where z_w is an orthogonal comparing function and D_w is the sum of squared

coefficients in this function ($D_w = 8$). Thereafter, we used an F-test with a significance level $\alpha = 0.05$ to determine the statistical significance of the input factors.

The foam shrinkage during the sintering process appeared to be an insignificant parameter. Bigger shrinkage was observed during the drying process. The quantity of dodecylbenzenesulfonic acid was the determining factor for the following parameters: foam ratio, bulk density, porosity and average pore size. The amount of Al₂O₃ seems to be a statistically insignificant factor. The quantity of boehmite is a significant factor for compressive strength of ceramic foams (Table 4).

The final properties of alumina foams dependent on statistically significant factors (boehmite, dodecylbenzenesulfonic acid) were evaluated by software (Scientist). With this software the significant dependences of output parameters on significant input factors using the sum-of-squared deviation criteria were calculated. Figure 1 show the dependences: foam ratio and bulk density of DBSA quantity. The calculations were performed within the range of 0.05 to 0.25 wt.% DBSA and the values for other two factors (Al₂O₃, boehmite) were averaged from both the level 1 and that of level 2. Figure 2 is showing the dependence of compressive strength on the boehmite quantity. The calculations were performed within the range of 0.5 to 3 wt.% boehmite and the values for the other two factors (Al₂O₃, DBSA) were averaged from both the level 1 and 2.

The quantity of DBSA (0.1-0.2 wt.%) affected the foam ratio and the bulk density as shown in Figure 1. On increasing the quantity of DBSA the foam ratio decreases and the bulk density increases. The smaller amount of DBSA leads to a higher foam ratio and lower bulk density. In other words, a greater amount of DBSA does

Table 3. Parameters and values of the alumina foam.

Number of samples	Foam ratio	Foam shrinkage (%)	Bulk density (kg/m ³)	Porosity (%) (equation 1)	Compressive strength (kPa)	Average pore size (µm)
1	5.5	8.6	95 ± 26	98	134	196
2	9.0	–	–	–	–	215
3	6.2	8.7	88 ± 13	98	171	187
4	7.9	9.3	114 ± 7	96	189	194
5	4.9	8.2	107 ± 11	97	155	132
6	5.1	7.5	139 ± 32	96	84	130
7	4.6	9.7	122 ± 26	97	220	139
8	4.6	8.8	155 ± 45	96	333	111

Table 4. Statistical significance of input factors on the parameters of the resulting foam.

Factors	Statistical significance of input factors on the parameters of the resulting foam					
	Foam ratio	Foam shrinkage	Bulk density	Porosity	Compressive strength	Average pore size
Al ₂ O ₃	×	×	×	×	×	×
Boehmite	×	×	×	×	significant	×
DBSA	significant	×	significant	significant	×	significant

× statistically insignificant factors

not create larger amounts of foam but it creates thicker lamellas between bubbles and also thicker surfactant films on the gas-liquid interfacial area. Probably in this case films between bubbles are created by bridging bilayer of the particles. The process also affects the level of particle hydrophobization. More surfactant represents a higher degree of adsorption of DBSA on the particle surface. In summary, this represents a higher wetting angle of Al_2O_3 particles, respectively a larger number of particles wetted by an unsuitable contact angle. Particles with wetting angles greater than 90° cause destabilisation via the so called bridging-dewetting mechanism [8]. In the literature [1, 13, 21], a similar surfactant effect is considered responsible for increasing the suspension viscosity.

The measurement results were supplemented by two other experiments (Figure 1a). The foam ratio increases until it reaches the maximal value and then it slightly decreases. The decrease of the foam ratio is probably above a critical concentration of DBSA. Thus,

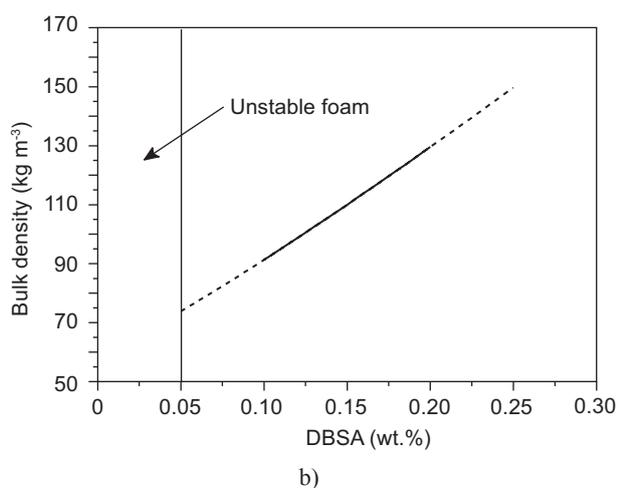
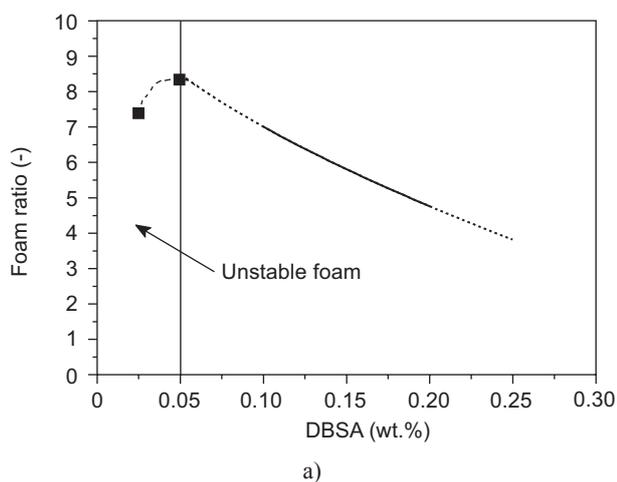


Figure 1. Effect of DBSA quantity on the foam ratio (a), and on the bulk density of alumina foams. The bold line implies the statistically calculated function from the measured values. The dashed line implies the expected tendency. Two marked points on the curve (a) are the results of additional experiments.

the result is a deficit of foaming agent and a deficit of hydrophobic particles necessary to prepare stable foam under the critical concentration of DBSA. Figure 1b presents the statistically calculated function from the measured values of the bulk density data as a function of DBSA quantity. The foams with quantity of DBSA $< 0.05 \pm 0.01$ wt.% are unstable and they collapse.

As shown in Figure 2, the compressive strength increases with increasing amount of boehmite, which is confirmed by other authors [12]. The influence of the boehmite quantity on the compressive strength is an interesting fact. Therefore the boehmite addition was increased. Figure 2 shows that the greater addition of boehmite (10 wt.%) did not show any significant influence on the compressive strength. Figure 3 shows the microstructure of the alumina foams obtained after sintering at $1400^\circ C$ with porosities ranging from 96 % to 98 % and the average pore size between $111 \mu m$ and $215 \mu m$ (Table 3). Statistical evaluation showed that the quantity of DBSA affects the average pore size. On increasing the quantity of DBSA the foam ratio decreases (the bulk density increases) and the average pore size decreases too. This result agrees with the mentioned influence of DBSA on the foam ratio.

The relative density plays an important role in determining the properties of porous ceramics. The porosity and grain contacting area are two key factors affecting the strength of alumina foams [4]. Figure 4 presents the compressive strength data as a function of the relative density. As expected [22], there is an increase of the compressive strength with increasing relative density. Relative densities of all samples are below 0.04. Relative densities of alumina foams published by other authors [1, 16, 23] are above 0.1 except for one [7]. According to this article [7] the relative densities of alumina foams are in the range from 0.04 to 0.6. The compressive strength for the value 0.04 is 300 kPa. Our material with the same relative density shows a compressive strength of 333 kPa.

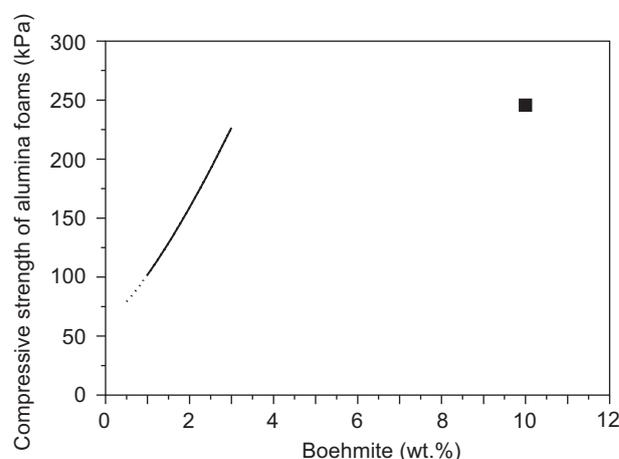


Figure 2. Compressive strength of alumina foams as a function of the boehmite quantity. The point indicated for 10 wt.% boehmite is an additional experimental point.

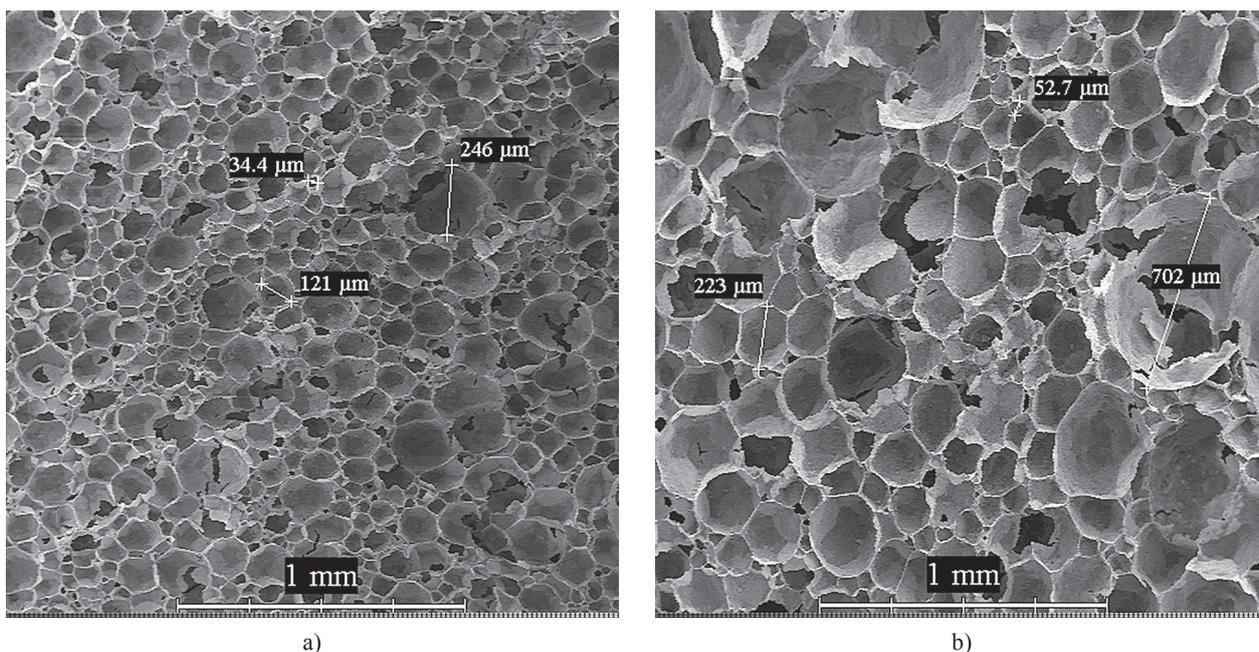


Figure 3. Microstructures of the alumina foams: sample number 8: relative density ~ 4.0 %, average pore size ~ 111 µm (a); sample number 1: relative density ~ 2.4 %, average pore size ~ 196 µm (b).

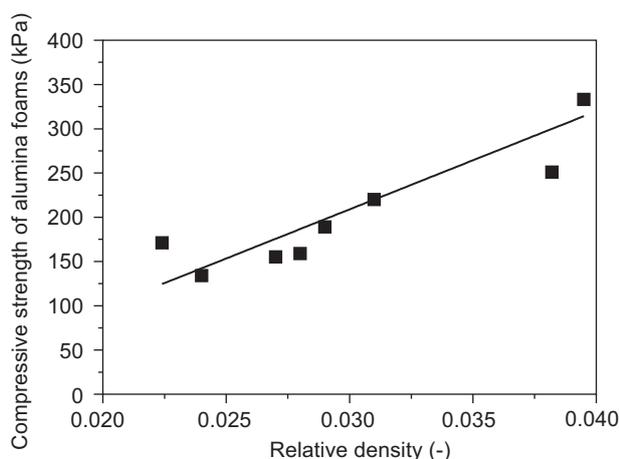


Figure 4. Compressive strength of alumina foams as a function of relative density.

CONCLUSION

Alumina foams were prepared with average pore size varying from 111 to 215 µm and porosities up to 96 %. The compressive strength of the ceramic foams obtained after sintering at 1400°C ranged from 84 to 333 kPa. The relation between the composition of suspension (wt % - Al₂O₃, boehmite, dodecylbenzenesulfonic acid) and the final properties of alumina foams (foam ratio, bulk density, porosity and average pore size) was determined by factorial design. The result is that dodecylbenzenesulfonic acid is a significant factor for all parameters - final properties except for the compressive

strength. Quantity of boehmite is a significant factor for compressive strength. Optimal content of dodecylbenzenesulfonic acid is 0.1 ± 0.01 wt.% and for boehmite it is 3 wt.%.

Properties of foams are dominantly affected by the quantity of dodecylbenzenesulfonic acid. DBSA acts as a dispersant, a foaming agent and it is used to hydrophobize in situ the alumina particles.

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