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Ceramics International 34 (2008) 661–667

CERAMICS INTERNATIONAL

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Gelcasting of alumina foams using agarose solutions

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Received 12 December 2006; received in revised form 10 January 2007; accepted 2 February 2007
Available online 6 March 2007

Dedicated to Professor Henryk Galina on the occasion of his 60th birthday.

Abstract

Aqueous gelcasting of dense or cellular ceramics by using biopolymers as gel-formers, instead of monomers, is a promising technology mainly in terms of environmental aspects. The main difficulty of using biopolymer solutions in processing of cellular ceramics by foaming method is their high viscosity, which prevents the foaming capacity of the ceramic suspension. In this work, the procedure for preparing concentrated agarose solutions (4 wt.%) by dissolving under overpressure conditions was evaluated for the gelcasting of alumina foams, and the rheological behaviour of alumina suspensions containing agarose was studied. The viscosity of the gelling solution obtained under overpressure conditions was lower than that prepared by simply heating at 90 °C, thus providing high foaming capacity of the alumina suspensions and consequently manufacturing of highly porous ceramics (86–90%). The microstructure of alumina foams was typically composed of approximately spherical cells interconnected by circular windows. The use of different agarose concentrations in alumina suspensions effected the rheological conditions, which resulted in changes in the pore and window sizes of the resulting ceramics. Depending on agarose concentration (0.50–1.0 wt.% on a dry solids basis) in the starting (35 vol.%) alumina slurry, the mean pore size ranged from 529 to 375 μm, while the mean window size varied from 113 to 77 μm.

Keywords: A. Processing; B. Porosity; Gelcasting; Agarose

1. Introduction

Cellular ceramics are very attractive for a wide range of applications, due to their high porosity, high gas permeability, good mechanical stiffness, and good thermal shock resistance [1,2]. In recent years, a new class of ceramic foams with porosity levels up to 90% has been developed as a result of the association of the gelcasting process and the aeration of the ceramic suspension containing foaming agents and gelling agents [3,4]. The *in situ* polymerisation of organic monomers, as gelling agents, led to fast solidification, resulting in strong, porous bodies, which could withstand machining. The resulting ceramic foams consisted of a highly interconnected porous network of spherical cells. Analogous to the conventional gelcasting procedure for dense components, the main drawback of this process is the toxicity of acrylamide, which is a neurotoxin. Hence, processes of reduced toxicity were searched for, and many alternative gelling systems for the gelcasting of foams based on low-toxicity monomers were demonstrated by Ortega et al. [5]. Alternatively, gelcasting techniques utilizing environmentally friendly biopolymers as gel-formers in manufacturing of ceramic foams are intensively studied. Different biopolymers such as gelatine [6], proteins (ovalbumine and bovine serum albumin) [7–10], sucrose [11], agar [12], starch [13], and wheat particles [14] have recently been applied as non-toxic components for the fabrication of porous ceramics. Apart from the positive environmental aspects, the additional advantage of using biopolymers is that they do not require atmosphere control on the set of foamed suspensions. However, the gel-formers used in gelcasting of foams must fulfil several requirements that are stricter than those found in dense ceramic production. First of all they should not increase the suspension viscosity to a level that would limit the production of low-density foams. The next condition is that gelation has to be completed in a few minutes to prevent foam damage due to liquid drainage and cells coalescence. Moreover, the gel has to be sufficiently strong to withstand the body weight, even at the typically low solids loading used in these

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doi:10.1016/j.ceramint.2007.02.001

suspensions [5]. For these reasons biopolymer solutions should be concentrated and simultaneously their viscosity should be low.

In manufacturing of dense ceramics, agarose is considered as a very promising gelling binder in aqueous gelcasting of ceramic powders, because it forms very strong gel on cooling that allows fast consolidation and enhances green strength [15,16]. To improve green and sintered properties of alumina bodies, a new procedure for the preparation of concentrated agarose solutions following the dissolution of the binder under overpressure conditions at temperature above 110 °C, instead of simply heating at 90 °C, was proposed by Santacruz et al. [17]. This procedure allowed complete dissolution of agarose, providing lower viscosity of the solution and consequently manufacturing of dense alumina bodies with densities near to the theoretical density.

In this work, the procedure of dissolving of agarose under overpressure conditions was applied to manufacturing of highly porous alumina foams. It was expected that lowering the viscosity of agarose solutions might provide the high foaming capacity of the ceramic suspensions. Particular attention was paid to the effect of agarose concentration in starting slurry on the rheology, which resulted in changes in the cell and window sizes of the alumina foams after sintering process.

2. Materials and methods

2.1. Solution preparation

Agarose (POCH, Gliwice, Poland, Cat. No. 111720491) was used as gelling additive. 4 wt.% agarose solutions were prepared by mixing the gel-former with de-mineralised water followed by heating using two different procedures. One way involved heating at temperature of 121 °C under overpressure of 1.4 bar in an autoclave during 11 min. Afterwards the solutions were kept at 60–65 °C. The second way was simply heating up to 90 °C in a flask during 120 min. The solution prepared by simply heating was not used for slurry preparation but only for comparison of viscosity results.

2.2. Slurry preparation

The alumina powder CT 3000 SG with a specific surface area of 7.0 $m^2 g^{-1}$ (Alcoa Chemie, Ludwigshafen, Germany) was used as the ceramic raw material. Ceramic suspensions were always prepared to a solids loading of 55 vol.% dispersing with ammonium polyacrylate (40 wt.% solution) (Darvan 821A, R.T. Vanderbilt Company Inc., U.S.A.) at a fixed concentration of 0.5 wt.%, on a dry solids basis. Homogenisation was carried out by mechanical mixing, followed by ball milling for 6 h using alumina balls and jar.

The 4 wt.% agarose solution and water was added in different quantities to the 55 vol.% alumina slurries maintaining the temperature of all constituents at 60–65 °C. The final alumina content was always fixed at 35 vol.% (68 wt.%) in order to determine the effect of agarose concentration on rheological behaviour of the ceramic slurry. The total concentrations of active gelling matter in final slurries were 0.25, 0.50, 0.75 and 1.00 wt.% with regard to dry alumina, which corresponded to: 0.47, 0.96, 1.44 and 1.94 wt.% of agarose with regard to water.

2.3. Gelling behaviour and rheological analysis

The gelation of agarose solutions was monitored by measuring the raise in viscosity on cooling from 65 to 25 °C. For this purpose, a Brookfield (RVDII+, Brookfield Eng. Labs. Inc., U.S.A.) viscometer equipped with the small sample adapter was used. The suspensions were subjected to a constant 60 s^{-1} shear rate and the viscosity value was registered as a function of temperature.

The rheological behaviour of the suspensions above the gelling point of agarose was determined using rotary rheometrer (Rheotest R.V.2, Rheotest Messgerate Medingem, Germany) fitted with double concentric cylinder geometry. All rheological measurements were conducted at shear rates from 5 to 1310 s^{-1} at temperature of 60 °C. A solvent trap was coupled to the measuring unit to reduce evaporation. Pre-sharing was carried out at 437 s^{-1} for 1 min before measurements followed by an equilibration time of 1 min. The viscosity values were fitted with a power law model as per the following equation:

$$\eta = k\gamma^{n-1} \tag{1}$$

where η is the viscosity of the slurry, γ the applied shear rate, and k and n are the consistency factor and non-Newtonian index, respectively [18–20].

2.4. Foaming process and fabrication of porous ceramics

The applied foaming agents were non-ionic surfactants, Tergitol TMN-10 (Aldrich, Germany) and Simulsol SL-26 (Seppic, France). At first, the saturation limit of each surfactant and their combination at 1:1 weight ratio was evaluated on the base the foam volume generated as a function of surfactant concentration during mixing by double shear mixer during 5 min. This procedure was done at temperature of 60 °C for 35 vol.% alumina slurry without agarose. Next, the cylinders containing foams with surfactant concentration corresponding to saturation limit were transported to water bath with temperature of 15 °C and foam stability was visually observed. Taking into account maximum foam volume and maximum foam stability an effective foaming agent was chosen for later studies.

The foamed suspension containing agarose was poured into a mould and the mould was cooled down using flowing cold water at 15 °C to transform the slurry from a liquid state to a gelled state. The green body was then de-moulded and left in room conditions to dry for 48 h. Sintering was performed for 2 h at 1575 °C using heating rate of 2 °C min^{-1} to 600 °C and then 4 °C min^{-1} up to sintering temperature.

2.5. Characterization of sintered foams

The density of porous bodies was calculated from the mass and dimensions of a minimum of five samples having regular shapes. The theoretical density of fully densified alumina ($3.98\ \mathrm{g\ cm^{-3}}$) was used as a reference to calculate the total volume fraction of porosity.

The microstructure of ceramic foams was observed by scanning electron microscopy (SEM) (Jeol JSM-5500LV). The fractured samples first were coated with thin layer of gold. Pictures for monitoring the cellular structure were taken for estimation of cell and window sizes. This allowed window and cell size to be estimated from cells which presented an equator in the fracture surface and from windows by taking the major axis of oblique windows as the true diameter. The diameter of minimum 150 cells and 350 windows were measured for each sample and the pore and window size distributions were calculated.

The flexural strength of sintered bodies was determined from three point bending. The bars with dimensions of 70 mm × 15 mm × 8 mm were used and the span was 40 mm. The crosshead speed was $0.5\ \mathrm{mm\ min^{-1}}$ for all samples. A universal testing machine (FP100, Tira) Rauenstein, Germany was used.

The compressive strength was measured on unaxial compression, using $0.5\ \mathrm{mm\ min^{-1}}$ crosshead speed. The samples consisted of rectangular bars with dimensions of 15 mm × 15 mm × 20 mm. The loaded surfaces were covered with a thin sponge layer to obtain uniform load distribution throughout the faces. In all mechanical determinations results were based on average of five samples for each density.

3. Results and discussion

3.1. Gelling behaviour and slurry rheology

Fig. 1 is the evolution of viscosity during cooling of 4 wt.% agarose solutions prepared by simply dissolution in water at 90 °C and in an autoclave at 121 °C. From Fig. 1 it is seen that above gelling temperature, the solution prepared under overpressure conditions shows lower viscosity than that prepared at 90 °C, although the agarose concentration in liquid phase is the same. This means that total dissolution of agarose is only reached under overpressure conditions. During cooling the viscosity of both solutions slightly increases with decreasing temperature until they reach the gelling temperature (~37 °C), where the viscosity sharply increases. Taking into account the solution viscosity at 60 °C, we use 4 wt.% agarose solution prepared under overpressure conditions in further studies.

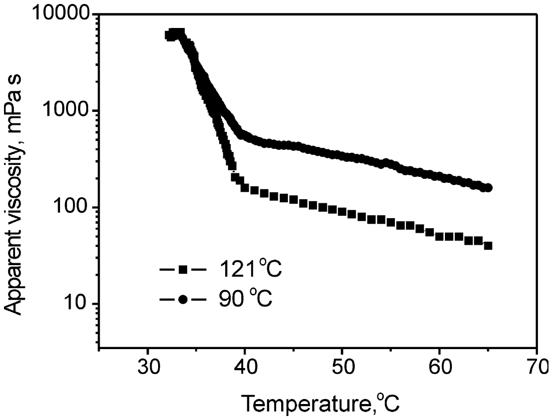

Fig. 1. The apparent viscosity of 4 wt.% agarose solutions vs. temperature.

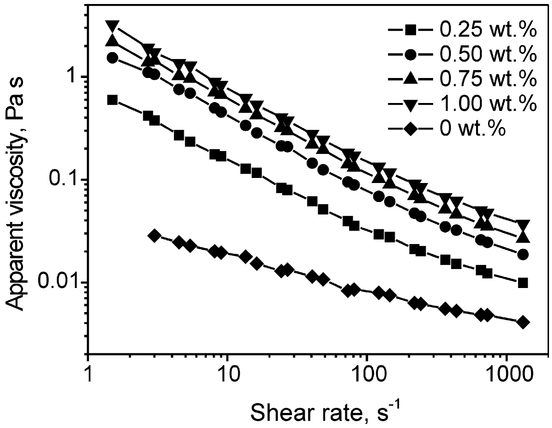

Fig. 2. The apparent viscosity of alumina suspensions at 60 °C with the fixed solids loading of 35 vol.% and varied agarose contents.

Fig. 2 shows the influence of agarose concentration (wt.% on a dry solids basis) on the viscosity of 35 vol.% alumina slurries at 60 °C. The viscosity of 35 vol.% alumina suspension without agarose is also plotted in Fig. 2, for comparison. It can be seen clearly that addition of agarose resulted in a significant increase in viscosity over the shear rate considered in the present study. This effect was expected, since the biopolymer solution has generally higher viscosity than pure solvent. Nevertheless, the viscosity of suspension containing 1.0 wt.% of agarose is less than 0.5 Pa s at high shear rate of $100\ \mathrm{s^{-1}}$. This value should not exert an influence on the ability of the slurry to form foam. As can be seen from Fig. 2, all the slurries were pseudoplastic in behaviour. Pseudoplasticity in ceramic slurries usually arises because of the existence of an inter-particle network, which undergoes a gradual breakdown with increasing shear rate, causing the typically observed decrease in viscosity of slurries. The pseudoplasticity of slurries can be characterized by non-Newtonian index n calculated according to the power law model (Eq. (1)). Highly shear thinning slurries, with a strong inter-particle network, show a rapid decrease in viscosity with an increase in shear rate, corresponding to a lower value of the non-Newtonian index, n, and slurries with weak or no inter-particle network become closer to the Newtonian behaviour with n values approaching 1.0 [18–20]. However, in suspensions containing agarose the pseudoplasticity arises not only from a gradual breakdown of inter-particle network of ceramic grains but also from the alignment of the agarose molecules at high shear rates. The calculated n index for the 35 vol.% pure alumina suspension is 0.65 indicating the behaviour closer to Newtonian (Fig. 3). In Fig. 3 one can observe a drastic change in n value between pure alumina suspension and alumina suspension containing small

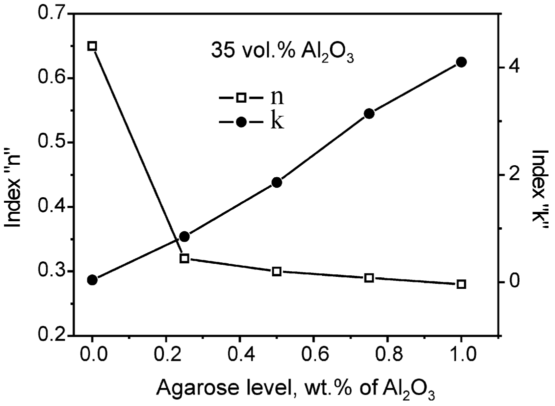

Fig. 3. The parameters n and k as a function of agarose concentration in 35 vol.% alumina suspensions.

amount of agarose about 0.25 wt.% for which the calculated n exponent reaches 0.32. Further addition of agarose up to 1.0 wt.% results in no significant changes in n index, which reaches 0.29 for alumina suspension containing 1.0 wt.% of agarose. On the other hand, the calculated k parameter, which is a consistency factor in the power law model, increases nearly linearly with increasing agarose concentration in the ceramic suspension (Fig. 3).

3.2. Foaming, gelation and drying

Because the foaming process of ceramic suspensions containing agarose is performed at 60–65 °C, the surfactant should show maximum foaming ability at this temperature range. On the other hand, the gelation of foams containing agarose is usually performed at ~15 °C in moulds cooled with cold water, therefore the created foam should be stable during temperature changes for a certain period of time required for cooling and gelation. The surfactants used in this work were Tergitol TMN-10, Simulsol SL-26 and the combination of Tergitol TMN-10 and Similsol SL-26 at 1:1 weight ratio. Fig. 4 presents a comparison of the foaming capacity of 35 vol.% alumina slurry without agarose at 60 °C as a function of surfactant concentrations. The saturation limits of Tergitol TMN-10, Simulsol SL-26 and their 1:1 weight ratio combination were 3.6, 8.2 and 6.9 g/100 ml slurry, respectively. At 60 °C the volumes of alumina foam foamed with Teritol TMN-10 and the combination of Tergitol TMN-10 and Simulsol SL-26 were nearly 8 and 7 times greater than their original volumes, respectively. Fig. 5 shows the time of the beginning of volume loss of alumina suspensions foamed at 60 °C and immediately transformed to water bath with temperature of 15 °C. From Fig. 5 it is seen that the time of the beginning of volume loss shows a tendency opposite to maximum foam volume. Only the combination of Tergitol TMN-10 and Simulsol SL-26 at 1:1 weight ratio gives simultaneously the maximum foam volume and maximum time before the foam starts to collapse. Taking into account maximum foam volume and maximum foam stability, the 1:1 weight ratio combination of Tergitol TMN-10 and Simulsol SL-26 was selected for foaming of alumina suspensions containing agarose.

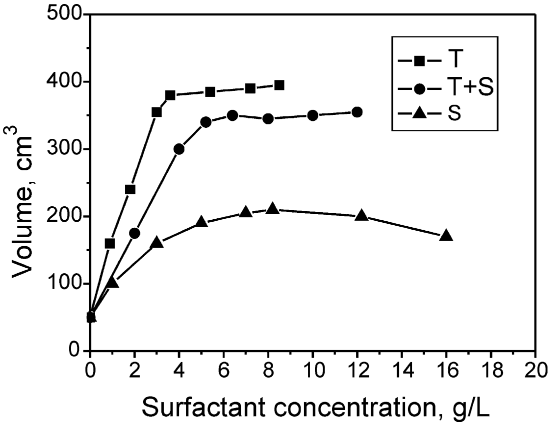

Fig. 4. Evolution of the foaming capacity at 60 °C vs. surfactant concentration in 35 vol.% alumina slurry (T, Tergitol TMN-10; S, Simulsol SL-26; T + S, combination of Tergitol TMN-10 and Simulsol SL-26).

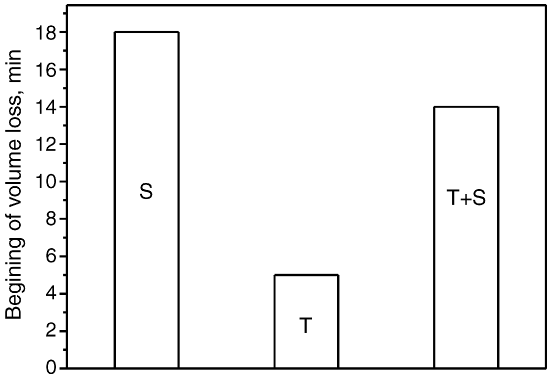

Fig. 5. The time of the beginning of volume loss of the alumina foams prepared with different surfactants at the concentration providing maximum foam volume (T, Tergitol TMN-10; S, Simulsol SL-26; T + S, combination of Tergitol TMN-10 and Simulsol SL-26).

The foaming experiments involving 35 vol.% alumina suspensions containing agarose showed that the foam volume decreased with increasing agarose concentration in the slurry and it was in the range of 0.8–0.9 of the volume obtained for the suspension prepared without agarose. This was due to lower foaming capacity of alumina suspensions containing agarose. Foams prepared with the slurries containing 0.25 of agarose showed cracks and dimensional deformation after drying. Therefore, 0.5 wt.% of agarose was established as the minimum concentration for alumina foams.

The linear shrinkage of the foams ranged between 2.2 and 4.1% during drying. The highest value was observed for foams containing the lowest amount of agarose, e.g. 0.50 wt.%.

3.3. Characterization of ceramic foams after sintering

The sintering shrinkage was in the range 13–14%. The densities of porous bodies increased with increasing agarose concentration in the starting slurry due to lower foaming capacity of alumina suspensions containing more agarose and

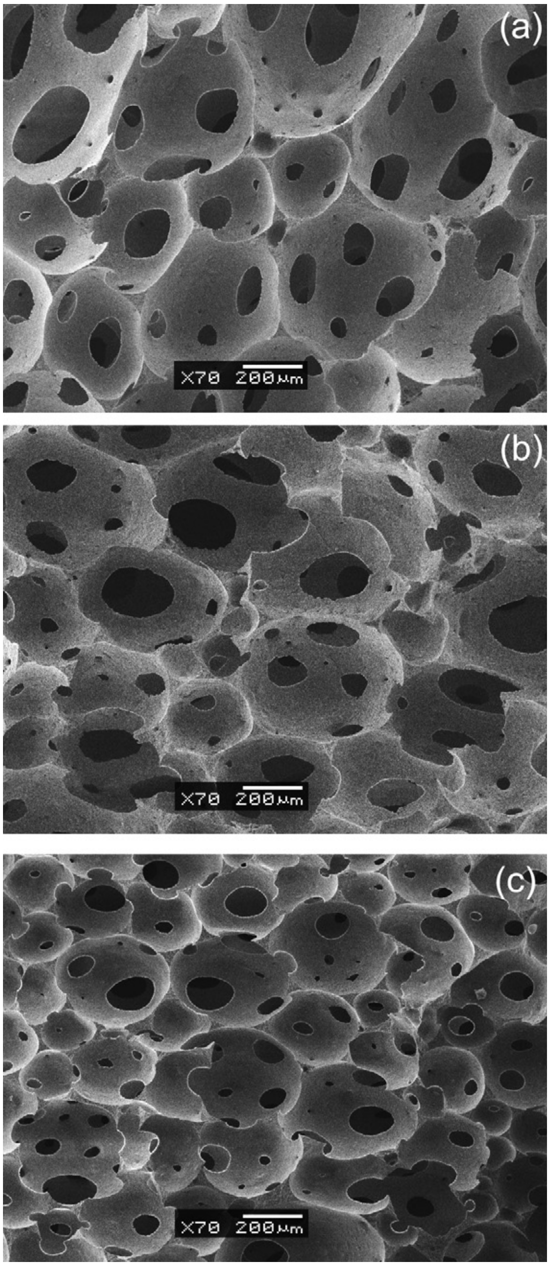

Fig. 6. SEM cross-section of alumina foams prepared with 35 vol.% suspensions and agarose contents of: (a) 0.50 wt.%, (b) 0.75 wt.% and (c) 1.0 wt.%.

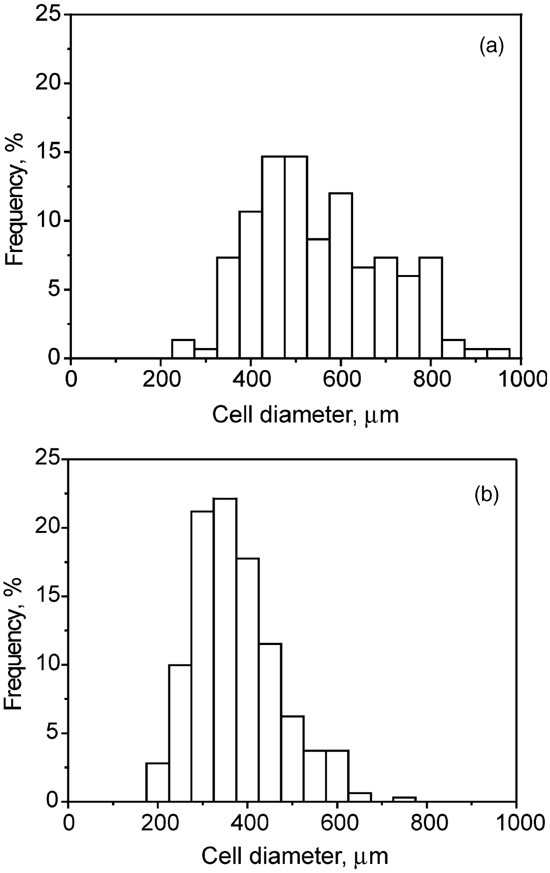

Fig. 7. Cell size distribution for foams prepared with 35 vol.% suspensions and agarose contents of: (a) 0.50 wt.% and (b) 1.0 wt.%.

were found to be between 0.40 and 0.57 g cm^{-3}. The calculated total porosity varied between 89.9 and 85.7%.

The microstructure of the sintered foams is presented in Fig. 6. The alumina foams were typically composed of approximately spherical cells interconnected by circular windows. The cell size and the window size decreased with increasing agarose concentration in the starting slurry. This is illustrated in Figs. 7 and 8 by histograms obtained from the results of image analysis. The foams prepared with suspensions containing 0.50 wt.% of agarose on Al_2O_3 base were characterized by the mean cell size of 529 µm and mean window size of 113 µm. On the other hand, the foams prepared with slurry containing 1.0 wt.% of agarose had the mean cell size and the mean window size of 375 and 77 µm, respectively. From Figs. 7 and 8 it can be seen that increasing of agarose concentration in the starting slurry narrows the cell and window sizes distribution. Two factors are probably responsible for this behaviour. First, the higher viscosity of the suspension containing high agarose level increases the foam stability. Second, the increasing agarose concentration accelerates gelation rate. These two factors slow down the bubbles

Table 1
Microstructural parameters and mechanical characterization of the porous ceramics

Agarose content in alumina slurry (wt.% of Al_2O_3)	Total porosity (%)	Flexural strength (MPa)	Compressive strength (MPa)	Mean cell size (µm)	Mean window size (µm)
0.50	89.9 ± 0.3	2.71 ± 0.43	4.01 ± 0.67	529	113
0.75	88.2 ± 0.2	3.68 ± 0.49	5.23 ± 0.81	482	98
1.00	85.7 ± 0.4	5.50 ± 0.53	8.18 ± 0.96	375	77

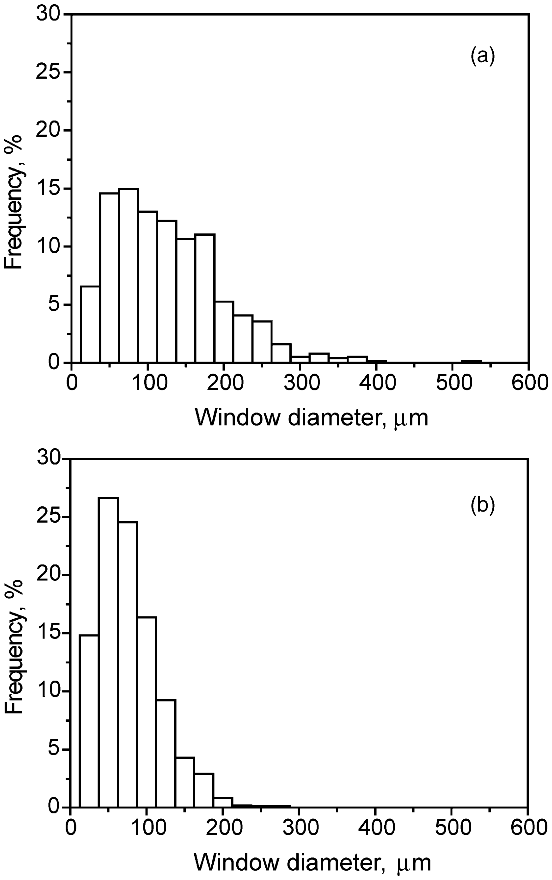

Fig. 8. Window size distribution for foams prepared with 35 vol.% suspensions and agarose contents of: (a) 0.50 wt.% and (b) 1.0 wt.%.

drainage and coalescence before gelling process and therefore the cell and windows size distribution is narrower.

The mechanical properties of alumina foams were characterized by their flexural and compressive strengths. These strengths in relation to the microstructural parameters of alumina foams are shown in Table 1. Depending on the agarose concentration in the staring slurry, a degree of variation in flexural and compressive strengths was observed between the sintered foams. This was caused by different porosity and different cell and window sizes in the resulted ceramics. These results indicated that the agarose concentration in the starting slip with a fixed ceramic powder level is extremely important in determining the structure of the resulting porous body and the mechanical strength. In the porosity range obtained in this work (90–86%), the values of the flexural and compressive strengths were in good agreement with those reported in literature [3,21] for alumina foams obtained by the use of an acrylamide-*N*,*N*′-methylenebisacrylamide gelling system.

4. Conclusions

The procedure for preparing concentrated agarose solutions (4 wt.%) by dissolving under overpressure conditions was applied to gelcasting of alumina foams. The viscosity of the gelling solution prepared by this manner was lower than that prepared by simply heating, thus providing high foaming capacity of ceramic suspensions and consequently manufacturing of highly porous ceramics (86–90%). The morphology of alumina foams was composed of approximately spherical cells interconnected through windows.

The use of different agarose concentrations in 35 vol.% alumina slips effected the rheological conditions, which resulted in changes in the cell and windows sizes of the resulting ceramics. Depending on agarose concentration (0.50–1.00 wt.% on a dry solids basis) in the alumina slurry, the mean pore size ranged from 529 to 375 μm, while the mean window size varied from 113 to 77 μm.

Depending on the porosity level (86–90%) and related with that parameter the mean pore and window size, the flexural and compressive strengths of alumina foams were measured to be between 2.71–5.50 and 4.01–8.18 MPa, respectively.

Acknowledgements

The author wishes to thank Drs. M. Czygier, M. Oleksy, J. Konkol and M. Motyka for their help in rheological and morphological measurements. R.T. Vanderbilt Company Inc. for providing free samples of Darvan 821A is gratefully acknowledged. This work was supported by Grant No. 3 T09B 048 28 of Polish Ministry of Higher Education and Science.

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