

High Porous Alumina Bodies: Production and Properties via Gel-Casting Technique

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Abstract

Porous ceramic materials have found widespread technological and industrial applications from filtration, absorption, catalysts and catalyst supports to lightweight structural components. In the present work, processing is based on the generation of foam from an aqueous suspension of ceramic powder and the subsequent stabilization of the structure by in-situ polymerization of organic monomers. The process offers a number of advantages from other processes. It is shown here, the in-situ polymerization of organic monomers led to a fast solidification and strong, porous bodies. SEM results showed, that the ceramic foams had highly interconnected network of spherical cells with low densities. The cell size distribution was dependent on the density of the samples as well as the polymerization onset time. Good correlations were found between the green microstructure, rheology of the suspensions and the particle interaction forces.

Keywords: *Dispersant, Gel casting, Organic monomers, Porous body, Rheology, Slurry*

1. Introduction

Although alumina has been used in different industries for different applications for a long time ago, yet improving its specific surface area is a challenging research area [1]. In the past few years, the gel-casting technique has caught the attention of many researchers all over the world for its simplicity and the advantages it offers over other ceramic manufacturing techniques [2, 3].

A general classification of porous ceramics, a number of innovative processing routes developed for critical control of pores are described, along with some important properties. The processes are divided into four categories including (i) partial sintering, (ii) sacrificial fugitives, (iii) replica templates and (iv) direct foaming. Figure 1 shows this classification along with typical applications and fabrication processes specific to the pore diameters. The partial sintering, the more conventional technique for making porous ceramics, has been substantially sophisticated in recent years. Very homogeneous porous ceramics with the extremely narrow size distribution have been successfully prepared through sintering combined with in-situ chemical synthesis [4, 5]. In the initial period after its invention, the process did not appear very attractive from an industrial viewpoint due to its use of toxic organic additives. A recent study reported that methacrylamide (MAM) with methylene bisacrylamide (MBAM) as a monomer and cross-linker were suitable for aqueous gel-casting and were much lower in toxicity as compared to the previously used acrylamides [2, 3-7]. For

aqueous slurries made using MAM–MBAM, ammonium per-sulphate (APS) and tetra-methylethylenediamine (TEMED) serve as the initiator and catalyst, respectively. Besides the simplicity and capability of forming near net complex shapes, a number of studies have demonstrated the large number of advantages for conventional gel-casting based on the MAM–MBAM system.

Although, the gel-cast ceramic samples have low binder content (3–4 wt%), they possess sufficient strength to permit machining in the green state [8, 9]. Gel-casting has been used for a wide variety of materials including metals, ceramics, alloys and composites. Gel-casting has also been successfully used in making highly porous ceramics by direct foaming techniques [10, 11]. The foamed gel-casting suspensions are cast to form net shape porous ceramic shapes.

In this work, high porous Alumina bodies successfully prepared via gel-Casting technique. Gel-casting was done by using Methaacrylamide as a monomer, N, N-Methylenbisacrylamide (MBAm) as a cross linker, N,N,N,N-tetramethylendiamine as a catalyst and ammonium presulphate as an initiator. Sodium dodecyl sulfate (SDS) was added as a surfactant to the alumina suspensions and vigorous stirring was applied in order to generate the foam. This procedure was performed in a sealed vessel under a controlled nitrogen atmosphere.

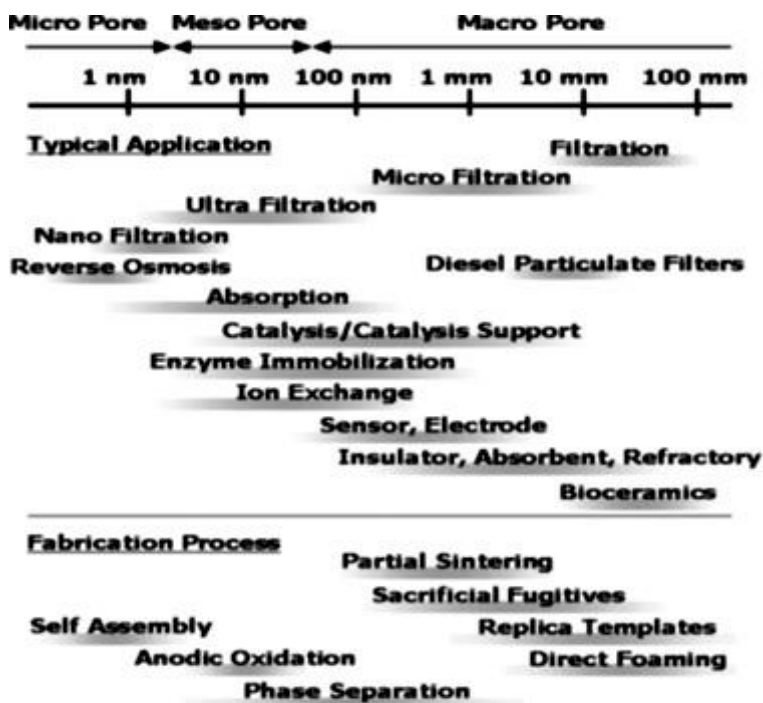


Figure 1. Classification of porous materials by pore size and corresponding typical applications and fabrication processes

2. Experimental Procedure

In the first stage, materials used 70 wt.% of high purity powder of α -Al₂O₃ ~ 99.8 wt.% (d_{50} ~ 0.5-0.8 μ m and the surface area (BET) ~ 6-10 m²/g), a polyacrylic dispersant, Dolapix (CE64 in the range of 0-0.7 on basis of the weight of dry powder) which shows in Figure 2, the molecule structure of its, helps for stabilization of slurry via electro-statically mechanism. A 20 wt% aqueous solution of monomer Methaacrylamide (C₇H₁₀N₂O₂) and cross-linker

N,N-Methylenbisacrylamide ($C_2H_3CONH_2CH_2$)), in 6 : 1 ratio was used as premix for slurry preparation. For polymerization, N,N,N,N- Tetramethylethylenediami with chemically formula $C_6H_{16}N_2$ added as a catalyst and 10 wt% aqueous solution of ammonium pre-sulfate (APS) with chemically formula $H_8N_2O_8S_2$ acted as an initiator. In the second stage, for slurries preparation at first, dolapix, monomer and cross-linker mixed with water for 15 min in ball mill. Then, powder added to them. For better homogenization the mixture mixed again in a satellite blender for 20 min.

In the third stage, Sodium dodecyl sulfate (SDS) in the range of 0.01- 0.05 of the weight of dry powder was added as a surfactant to the alumina suspensions and vigorous stirring was applied in order to generate the foam. Finally, this procedure was performed in a sealed vessel under a controlled nitrogen atmosphere. In Casting, since gel-casting is a low temperature process (ambient, $80^\circ C$) and it needs impermeable molds, a variety of mold materials such as aluminum, stainless steel, plastic, glass and wax molds can be used. Properties of the mold materials coupled with the mold design play a significant role in forming of complex shapes, as it must allow shrinkage to occur and minimize stresses in the cast part during drying. After that, the sample dried for a week in the ambient temperature, then, for 5 hours dried at $120^\circ C$, to avoid the crack formation, because drying is one of the most critical steps in gel-casting. In the final stage, sintering was done at $1400^\circ C$ for 2 hours. The process for fabricating the porous Alumina bodies is given by the flowchart in Figure 3.

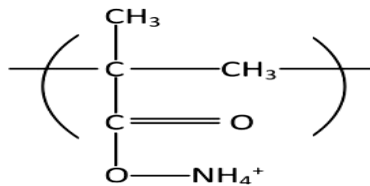


Figure 2. The molecule structure of Dolapix CE64

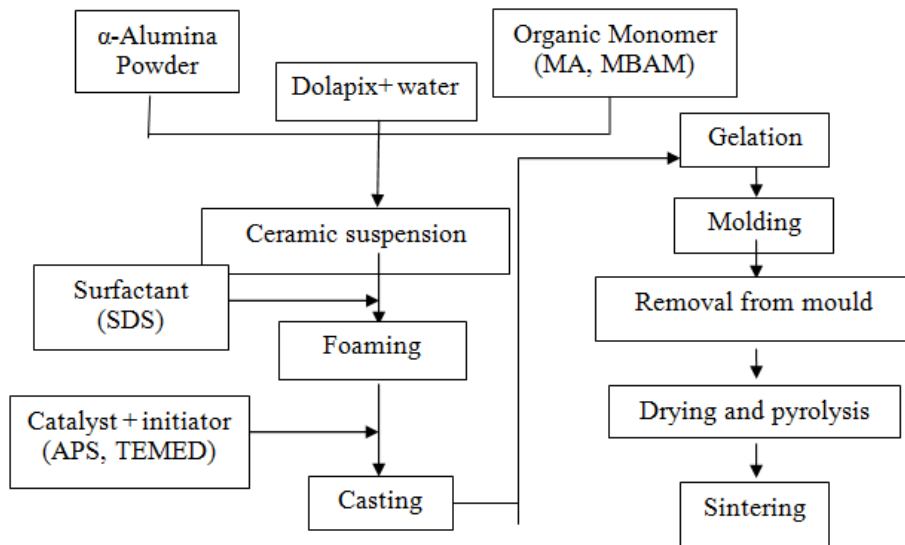


Figure 3. Gel-casting process for production of porous bodies

3. Result and Discussion

3.1. Rheology behavior study on suspensions

The foam rheology is important because the process involves casting. In common with other casting operations, very fluid systems are required in order to enable easy filling of small detail sin molds to allow production of high complexity shapes. The high viscosity characteristics of foamed systems at low shear rates can thus be a critical factor for the production of complex shaped foamed bodies. The gel-casting slurry is a vehicle for the ceramic powder and facilitates homogenous mixing and enables casting of the components. Low viscosity slurry is beneficial for both mixing and casting in slurry processing and needs to be combined with high solids loading to reduce shrinking and the risk of crack formation during drying [12, 13]. The suspensions rheology was evaluated through measurements of shear stress and viscosity at increasing shear rates, from 0.1 to 1000 S^{-1} . The gravitational force between alumina particles in the aqueous cause's alumina particles to stick together and form of structures in the slurry that with increasing shear rate, these structures are destroyed and viscosity decreases. As far as the shear rate is so high that no internal structure form in the slurry. Then, slurry shows Newtonian behavior [14]. Figure 4, shows the effect of shear rate on the viscosity of suspensions at various loadings of dispersant concentration.

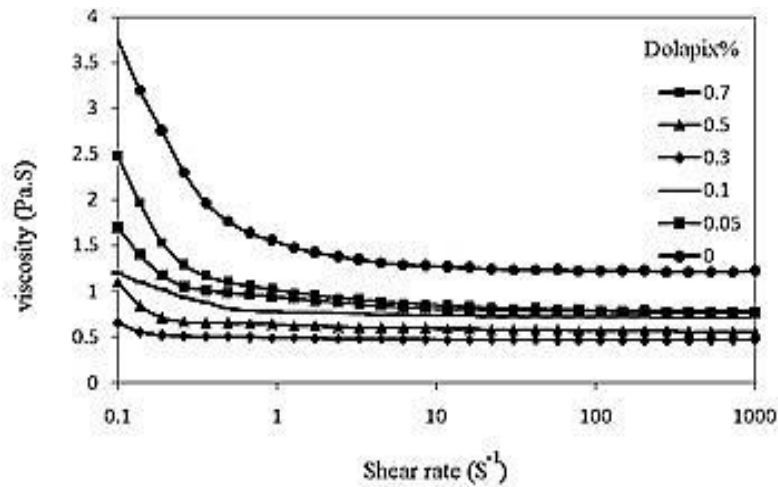


Figure 4. the effect of shear rate on the viscosity of suspensions at various loadings of dispersant concentration

3.2. The effect of various loadings of alumina powder on rheology behavior

All the slips prepared in this work revealed a shear thinning or pseudo-plastic behavior. This behavior is characterized by the decrease in viscosity at increasing shear rates and is typically found in the dispersion of alumina suspensions containing a high percentage of solids. In the fabrication of ceramic foams, a slight pseudo-plasticity can favors the generation of the foam since lower viscosities are obtained under shearing, and, under static conditions, can significantly improve the foam stability since the viscosity increase delays the collapse of fluid films around the bubbles. As shown in Figure 5, shows the effect of shear rate on the viscosity of suspensions at various loadings of alumina powder. It is observed, viscosity increases with increasing the amount of solid percent. That's why, suspension

indicating more resistant to shear force. The suspension shows Pseudo-plastic behavior at low shear rates which is the best behavior for foaming.

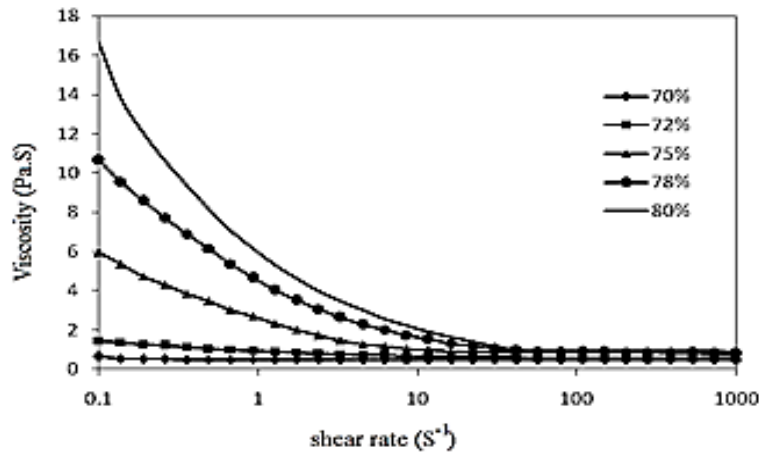


Figure 5. the effect of shear rate on the viscosity of suspensions at various loadings of alumina powder

3.3. The effect of catalyst and initiator at time reaction

Since, polymerization is an exothermic reaction. The time it takes the polymerization is initiated and completed depends to catalyst and initiator percent, PH and temperatures [15]. So, forth different amount of APS and TEMED were tested for polymerization. Catalysts are often added to gel-casting systems to reduce the on-set temperature of polymerization of the monomer and cross-linker. According to Figure 6, with increasing of APS and TEMED, the time for polymerization decreases. On the other hand, the reaction rate increase which is observed in Figure 7.

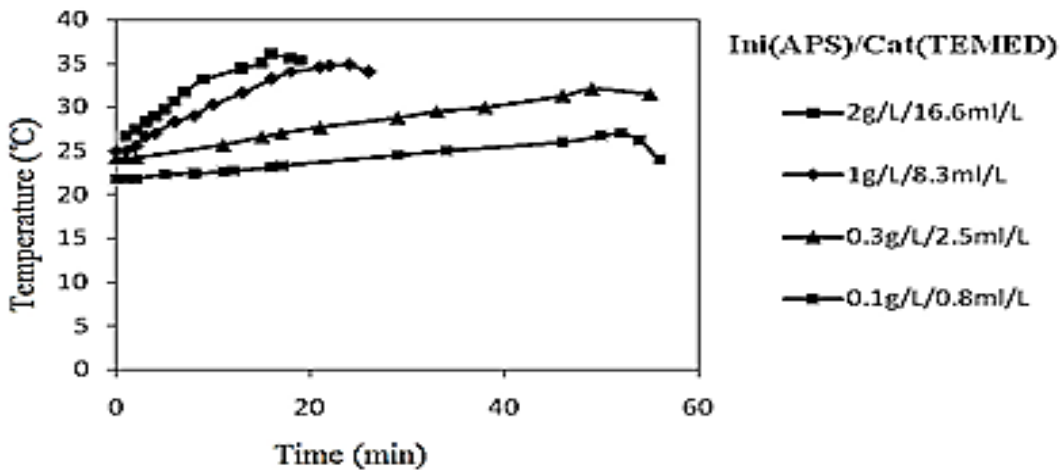


Figure 6. the effect of the optimizing at various loading of catalyze (TEMED) and initiator (APS)

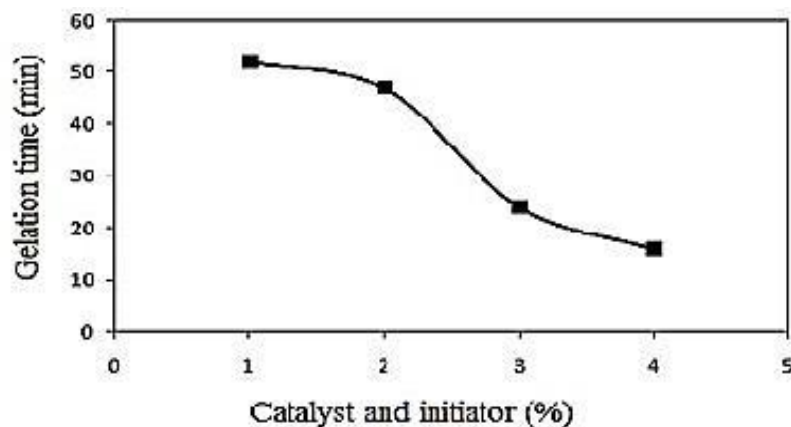


Figure 7. The effect of the optimizing at various loading of catalyst (TEMED) and initiator (APS) on gelation time

3.4. Pyrolysis and removal of organic matter study

This stage was investigated by thermo-gravimetric and differential thermal analysis (TG-DTA) which is shown in Figure 8, it is observed that removal of organic matter begins at 400 °C and is completed at 600 °C. In fact, it is the polymerized monomers and cross-linker that constitute the major source of the organic additives in the cast bodies.

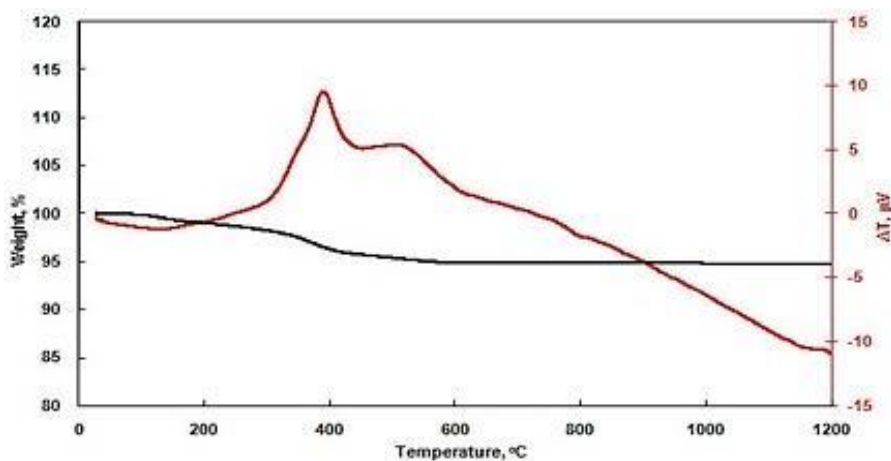


Figure 8. DTA-TG curves of the sample containing 70% solids

3.5. Foam preparation

Figure 9, shows the effect of stirring times on foam volume in suspension at various loadings of SDS as a surfactant ad to it. It is observed; the foam volume increases gradually up to a maximum after reaching to this have steady state behavior. During this initial stirring period gas is entrained into the suspensions and liquid is drawn around each bubble until a thin film is formed. Initially, the ability of a foaming agent to produce large quantities of foam depends on the surfactant's effectiveness in reducing the surface tension of the solution. Subsequently, the surfactant molecules of the foaming agent move from the interior of the slips toward the newly created surfaces, establishing forces to prevent further thinning. When most surfactant molecules have attached themselves to the gas-liquid interfaces, the

stabilization of new films is no longer possible and the volume increase becomes negligible. Hence, the maximum foam volume is associated with a minimum thickness of film that can sustain stable foam. Above this level, stirring may continuously generate bubbles; however, they disintegrate almost instantly preventing an increase in the foam value [16-18]. That's why; SDS is added as a surfactant to reduce the surface tension and to avoid the build-up of internal stresses that can lead to cracking and warping. As shown in Figure 10, the scanning electron microscope (SEM) micrographs of samples with adding different amount of SDS (0.01 %, 0.03 % and 0.05 %) it is observed, with increasing on it, the surface absorbing increase which it causes miss forming.

According to SEM images the pores are homogeneously distributed in the sample which has 0.03 % SDS. Indeed, simple geometric considerations suggest that the (average) wall thickness should be inversely related to the pore size at equal porosities and the pores are heterogeneously distributed in the last one (c).

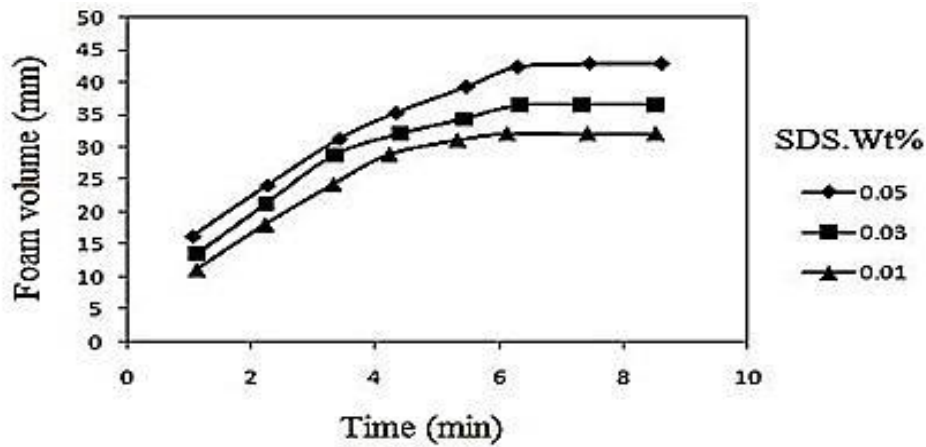
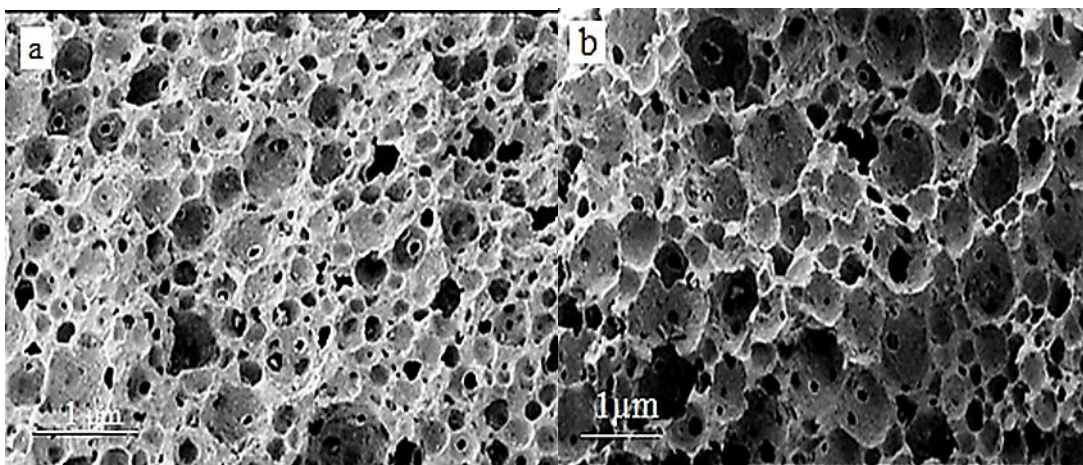


Figure 9. the effect of stirring times on foam volume in suspension at various loadings of surfactant



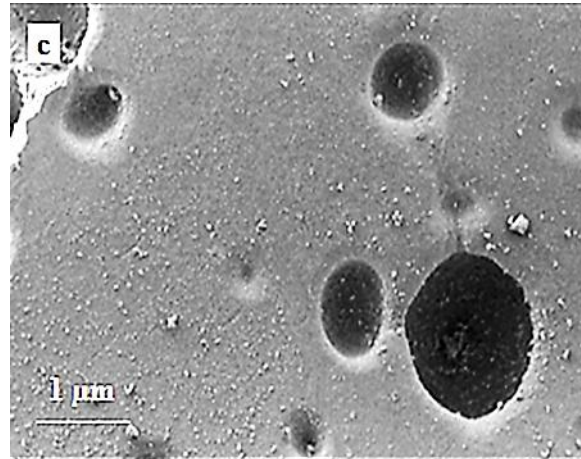


Figure 10. SEM images of samples: a) (0.01 %), b) (0.03 %) and C) (0.05 %) of SDS

3.6. The effect of various loadings of solid powder on foam volume

Figure 11, reveals the maximum foam volume generated with suspensions containing 70 wt% alumina and with each solids content suspension being deliberately formulated to have a range of viscosities. It may be seen that the viscosity had little influence on the final foam volume generated except for the lowest solids content slurry. It should be noted that slips of lower viscosity probably led to smaller foam volumes due to the inferior stability of the liquid films created [19]. Meanwhile, the slight decrease in foam volume generated with slips of higher viscosity and more loadings of solid.

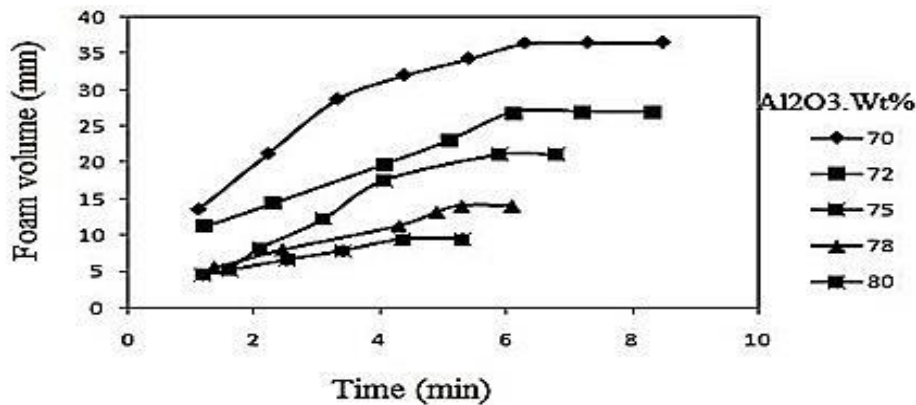


Figure 11. The effect of time on foam volume at various loadings of solid powder on suspension

3.7. Physical and mechanical properties of bodies after sintering

All the green bodies after drying are sintered at 1400 °C for 2 hours. The density plays an important role in the determining the microstructure of the sintered foams. The level of shrinkage after sintering is shown in Figure 12, which indicates by loading solids the sintering

shrinkage decreased. Table 1, indicates the effect of various loading solids on the bulk density and porosity as expected, density increased as the solids content increased. According to SEM micrographs of sintered bodies, it is observed; as density increased the cell size decreased which are shown in Figure 13. Figure 14, shows the effect of various loading solids on cell size distribution as expected, the cell size distribution of foams could be varied independently of the sample density by expanding fluid foam up to a higher final volume by reducing the pressure present prior to polymerization.

Figure 15 depicts the cold crushing strength of alumina foams as a function of the density. As expected, the strength decreases proportionally to the decrease in density owing to the smaller bulk area that is actually submitted to loading in lower density specimens.

Table 1. The effect of loading solid on density and porosity on sintered bodies

Solid content (wt.%)	Bulk Density (g.cm ⁻³)	Porosity (%)
70	0.85	78.75
72	1.12	72
75	1.32	67
78	1.56	61
80	1.98	50.50

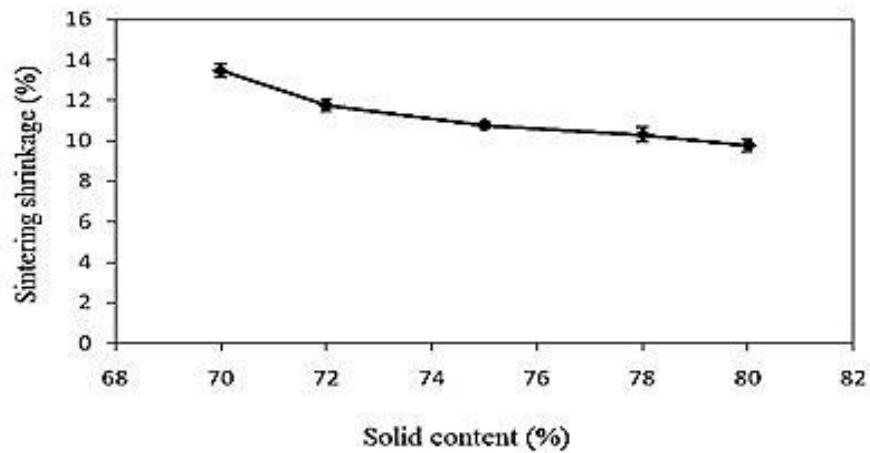


Figure 12. the effect of loading solids on sintering shrinkage

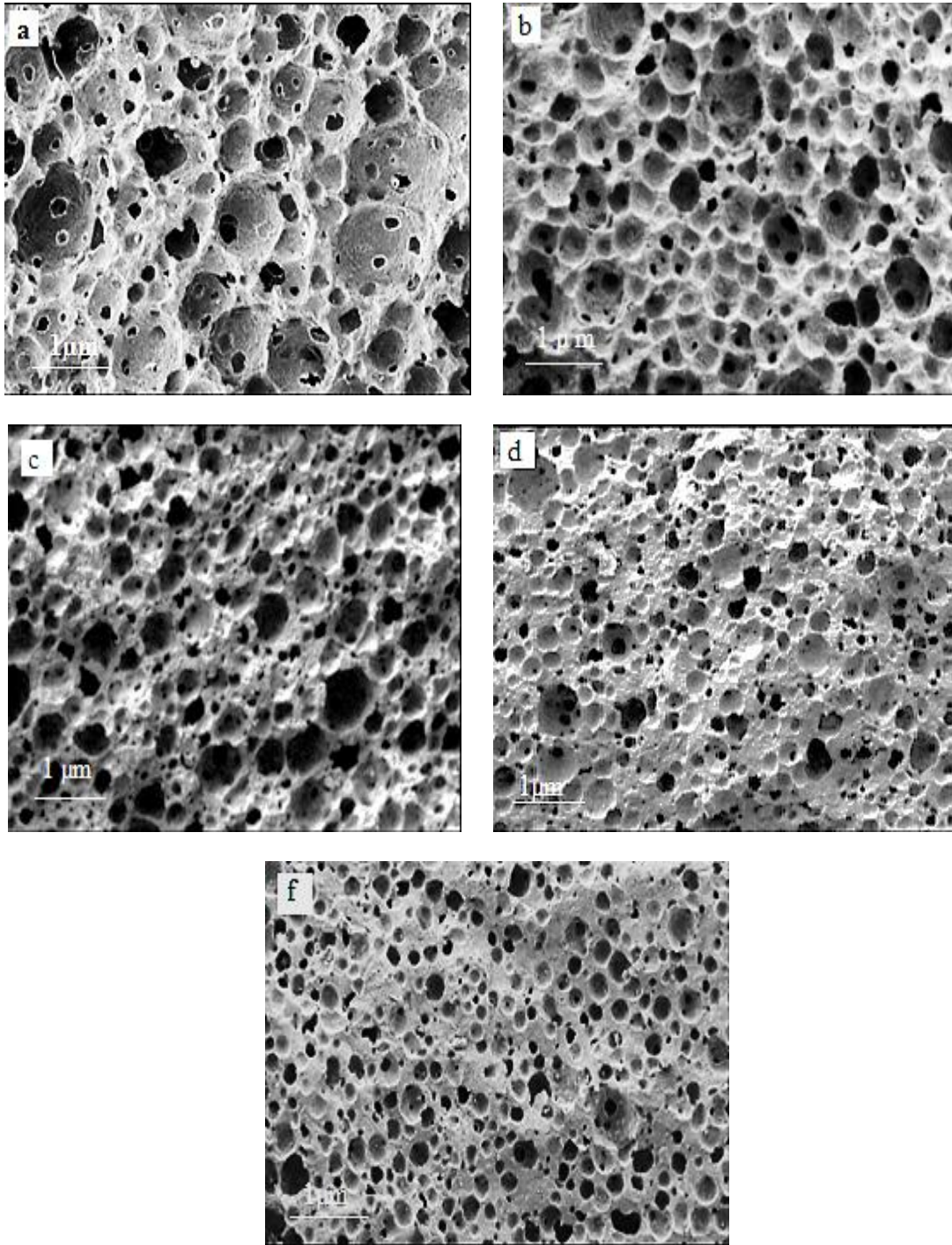


Figure 13. SEM micrographs of effect at various loading of solids on cell size (porosity); a) 70 % solid content, b) 72%, c) 75 %, d) 78 % and f) 80 %

4. Conclusions

The direct foaming technique offers low-cost and easy production of highly porous ceramic materials. In order to suppress coalescence of gas bubbles in ceramic suspension that result in

large pores in the final porous bodies by including the use of effective surfactants, dispersant, catalyst and initiator. The method of foaming followed by polymerization studied in the present paper shows high versatility and the ability to produce highly porous green bodies that are comparatively strong.

The cells showed smaller interconnecting windows and larger strut thickness when the density of the specimens was increased. The induction time for polymerization onset also influenced the cell size distribution since it allowed time for bubble enlargement. The higher strength magnitudes obtained from this material, compared to other conventional methods, are due to the less flawed structure and dense strut sand walls produced.

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