MECHANICAL STRENGTH ENHANCEMENT OF OPEN-CELL ALUMINA FOAMS USING OPTIMUM CONCENTRATION OF DEFLOCCULANT

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Submitted September 29, 2014; accepted June 27, 2015

Keywords: Mechanical strength, Open-cell foam, Tiron, Alumina

Open-cell alumina foams were prepared using the appropriate alumina slurry and polyurethane sponge with linear pore density of approximately 14 pores per inch (ppi) as a template by the replica method. The rheological studies showed that the optimum solid content for the slurries without deflocculants was 60 wt. %. In order to increase the slurry solid content, Tiron (1,2-dihydroxy-3,5-benzene disulfonic acid disodium salt) was used as dispersant. To determine the optimum concentration of dispersant, the viscosity curves of alumina slurries containing different values of Tiron from 0 to 1.2 wt. % (based on dry material weight) were studied. The optimum concentration of Tiron obtained for lowest viscosity was 0.8 wt. %. Thus, the solid content in the slurry could be increased from 60 to 66 wt. %. The effect of increase in the slurry solid content and the way it affects the foam structure and the mechanical strength were investigated. Microstructural observations of the foams show a significant reduction in macroscopic and microscopic defects in the foam struts when the slurry solid content is increased. Total porosity of the produced alumina foams prepared using slurries containing 60 and 66 wt. % solid are 83.3 and 80.4 %, respectively, while the compressive strength of the foams has increased from 1.33 to 3.24 MPa.

INTRODUCTION

Open-cell ceramic foams have special properties that make their use inevitable in many industrial applications. These structures have a high volume of porosity (> 70 %) and include a network of interconnected hollow polygonal cells which leads to their high permeability [1, 2]. In addition to high porosity and permeability, high chemical stability, high thermal resistance, low density and high surface area make open-cell ceramic foams suitable to be used in special applications such as molten metals and hot gas filters, catalyst supports, heat exchangers, bioimplants and metal matrix composites [2-4].

The first report about production of open-cell ceramic foams dates back to 1963, when Schwartzwalder and Somers prepared these foams by replication of the reticulated polymeric sponge [5, 6]. Since then, this technique (replica method) is being adopted as the most common method for production of open-cell ceramic foams [7, 8]. This method is generally based on the impregnation of a flexible polymeric sponge with ceramic slurry and then squeeze to remove the excess slurry, followed by drying and sintering [9]. Cracks and fine pores in the structure of sintered foam are the main defects of the foams derived trough the replica method that lead to reduction in mechanical strength [7]. In order to diminish the defects and improve the mechanical strength of open-cell ceramics many attempts have been made like:

- using of the ceramic fibers in the ceramic slurry for reinforcing the sintered foam [10],
- repeating the impregnating of the polymeric template and drying steps for several times [11, 12],
- recoating the sintered foam by a low viscosity slurry [13, 14].

These techniques often lead to additional expenses and more time consumption in terms of manufacturing process that limit their industrial application.

The use of a sufficient and useful dispersant for increasing the solid content in the slurry and the study of its effect on the mechanical strength of the open-cell ceramic foams have not been addressed properly in the literature. Tiron (1,2-dihydroxy-3,5-benzene disulfonic acid disodium salt) is an anionic dispersant that its characteristics have been investigated by many researchers and it is found to have a good effect on the dispersion of alumina particles in aqueous suspensions and their stabilization [15-17].

Applying the optimum concentration of Tiron in order to increase the solid content in the slurry is investigated in this work. Mechanical strength of two classes of the foams prepared by slurries containing Tiron and without Tiron are compared with each other and outcomes are discussed. The effect of addition of Tiron in slurry and increase the solid content on improvement the mechanical strength of the alumina foams is studied as well.

EXPERIMENTAL

Alumina foams preparation

In order to produce alumina foams, α-alumina powder (99.5 % purity, Inda alumina, India) with mean particle size of 5 μm was used as the main material. 2.5 wt. % titanium dioxide (99 % purity, Merck, Germany), and 5 wt. % clay (Industrial Grade) were used to improve the rheological behavior of slurry and to reduce the sintering temperature. For homogenizing the materials, alumina powder and additives were dispersed in ethanol and mixed by magnetic stirrer for 3 hours. Then the mixture was dried completely and sieved through a 70 mesh screen. Polyvinyl alcohol (PVA, 70 000 average molecular weight, Merck, Germany) and Tiron (332.22 molecular weight, Merck, Germany) were used as organic binder and dispersant in the slurry, respectively. To prepare the slurry, PVA was dissolved in distilled water. Tiron was then added to the solution and stirred for 15 minutes with speed of 500 rpm. Afterwards the homogenized powder of raw materials was added to the solution and was gently stirred to get a uniform slurry. For improving the effect of Tiron and to achieve better equilibrium condition, the slurries were stored in sealed glass container for 48 hours. Polyurethane sponge with linear pore density of approximately 14 ppi was fully immersed in the slurry, until saturated with the suspension. The impregnated sponge was then taken out of the slurry and was compressed between two parallel plates to a specific gap to remove the excess slurry and allow to the formation of open-cells and pores. The samples were aged in air for 48 hours and eventually were dried in an oven at 110°C for 12 hours. Firing of the samples took place in a programmable furnace. To burn out the organic materials without collapsing the deposited ceramic powder, the samples were first heated at a rate of 1.6°C min^{-1} to 600°C and then heated at 3°C min^{-1} to 1600°C. To complete the sintering process, the samples were kept at 1600°C for 2 hours.

Characterization

Flow behavior and viscosity of the slurry were measured using a model Physica MCR 301 rheometer (Anton Paar, Belgium) in the shear rate range of 0 to 1000 s^{-1} at 25°C. Loading mass per unit volume of the foam network was obtained by measuring the mass of 50 cm^3 of sponge before and after the coating process in dry state. The total porosity of the alumina foams was calculated using the following equation:

$$\text{Porosity} = (\rho_r - \rho_b) / \rho_r \quad (1)$$

where ρ_r is the real density of the composition and ρ_b is the bulk density of the foam. Bulk density was calculated from the mass to bulk volume ratio of the foam. To determine the real density, some parts of the sintered foams were pulverized to microsize powder and then the density was measured using a helium pycnometer. The compressive strength of the sintered alumina foams was measured using a universal testing machine (Shirley, UK). The load was applied uniaxially with crosshead speed of 0.5 mm·min^{-1}. In order to provide a more uniform load distribution on the sample surface, a plastic pad was used between platens and sample. Pore morphology and macrostructure of the foams were evaluated using optical stereograph microscope model sz61 (Olympus, Japan). The foam microstructure and the struts were observed by XL 30 (Philips, Netherland) scanning electron microscope (SEM).

RESULTS AND DISCUSSION

In order to produce foam by the replica method, slurry with specific behavior and viscosity is needed. The slurry viscosity should be relatively high, because the high viscosity increases the thickness of the deposited layer on the polymeric sponge ligaments; thus stronger struts in the final foam will be achieved. But, too high viscosity prevents the flowability of the slurry and leads to poor coating and nonuniformity of the foam structure. In addition, it is necessary that the slurry be fluid enough to enter into the sponge network during the immersion and to remove excess part during compression process easily. After final compression, under static conditions, the remaining slurry should be viscous enough to avoid dripping and to keep the thickness around the polymeric ligaments uniform. Therefore, the prepared slurry should have shear thinning behavior and be thixotropic. Thus, based on the above considerations, a slurry with a maximum solid content of 60 wt. % was prepared and used for coating of 14 ppi polymeric templates. Figure 1 shows the viscosity changes versus the shear rate for this slurry.

As seen in the Figure 1, with increasing shear rate the viscosity has decreased, confirming the shear thinning behavior of the slurry. Also the occurrence of a hysteresis loop between the ascending and descending curves are indication of the thixotropy of the slurry that is provided through the presence of clay in the slurry. Through the network connections (house of cards), clay particles trap part of the water within the slurry and increase the viscosity. By applying shear to the slurry,

network connections have to be broken and that part of the trapped water inside the network is released, resulting in a decrease in the viscosity. The high concentration of solid content in the slurry is another affecting factor on formation of shear thinning behavior.

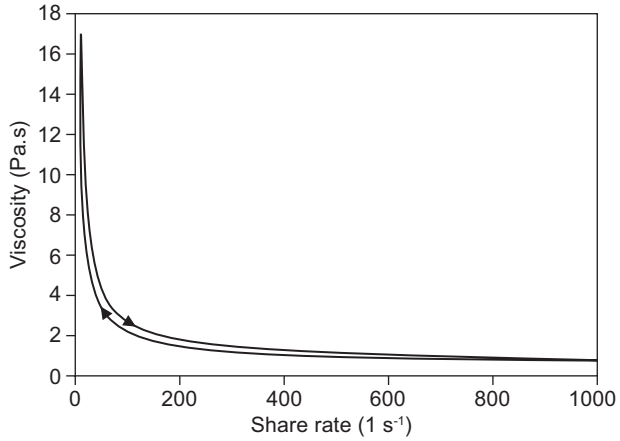


Figure 1. Viscosity curve of 60 wt. % solid content slurry.

The presence of clay in the composition also has a desirable effect on the mechanical strength of the foam. Clay increases the adhesion in slurry and causes the formation of thicker and more efficient coating, especially at the sharp edges of the polymeric struts and thus increases the strength of the produced alumina foam. Using the 60 wt. % solid content slurry, the loading on 14 ppi polyurethane sponge network was measured to be equal to 0.3 g·cm^{-3}.

To provide further increase in the solid content in the slurry in order to achieve further increase in the mechanical strength of the alumina foams, Tiron was used as a dispersant in the slurry. For this purpose, different amounts of Tiron from 0 to 1.2 wt. % were added to the 60 wt. % solid content slurries and their viscosity changes with changing shear rate were studied (Figure 2).

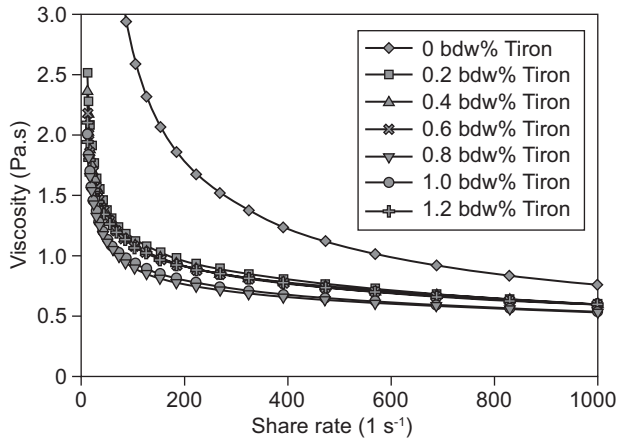


Figure 2. Viscosity curves of 60 wt. % solid content slurries containing different concentration of Tiron from 0 to 1.2 bdw. %.

Figure 2 shows that adding dispersant Tiron has effectively reduced slurry viscosity. Tiron is a low molecular weight weak tetra-protic acid that includes two hydroxyl- and two sulfo- groups attached to a benzene ring. When Tiron is added to the slurry, it adsorbs onto the particles surfaces due to the electrostatic and hydrogen bond interaction [18]. The alcohol groups are very efficient in complexing metallic cations, leading to chemisorption of the molecule onto the metallic oxide surface. Additionally, the ionizable sulfonate groups cause negative charge development [16-18]. Hence, as a result of Tiron molecules adsorption, the particles surface becomes highly charged and electrical double layer repulsion increases, causes a high repulsive potential between the particles and a decrease in slurry viscosity.

As seen in Figure 2 at the concentration of 0.8 wt. %, the lowest viscosity was obtained for the slurry, because here the amount of dispersant is sufficient for covering all particle surfaces. At concentrations below the optimum value, the number of molecules has not been enough for complete surface coverage of all particles, so the viscosity decreases with increase in the Tiron concentration. When Tiron is added in amounts exceeding the optimum concentration value, the excess amount of dispersant which is not adsorbed onto the particles remains in the aqueous phase and acts as an electrolyte. Hence the range of electrical double layer repulsion decreases and this leads to an increase in the viscosity. So, the concentration of 0.8 wt. % of Tiron as the best value was used in reducing the slurry viscosity.

By using Tiron as a dispersant, a slurry with maximum solid content of 66 wt. % was prepared. The viscosity curve for this slurry is presented in Figure 3. As seen, the curve is in a good agreement with that of the 60 wt. % solid content slurry and the slurry possesses the required rheological behavior for coating the applied polymeric sponge.

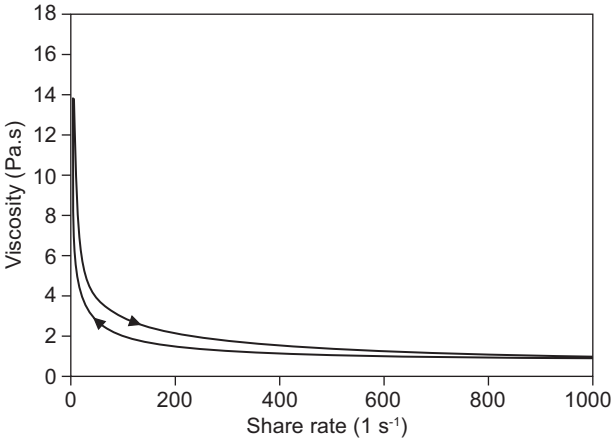


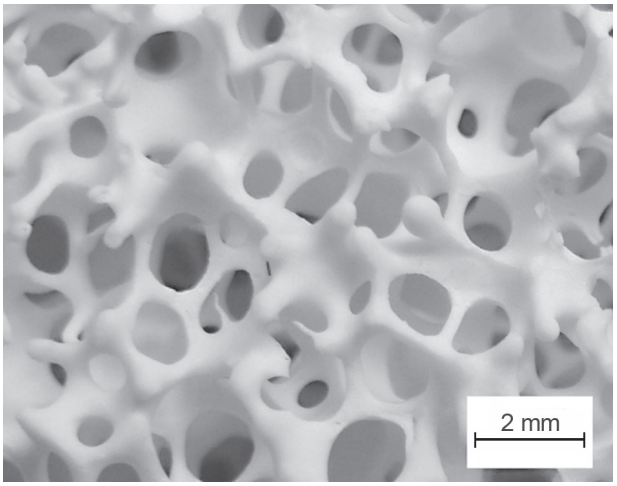
Figure 3. Viscosity curve of 66 wt. % solid content slurry.

By using the 66 wt. % solid content slurry, the value of slurry loading on unit volume of the foam network increased to 0.35 g·cm^{-3}. Table 1 presents the

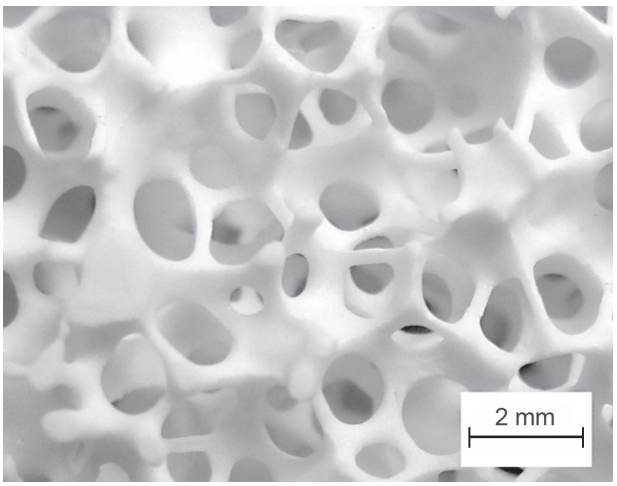
effect of increase the solid content in the slurry on the properties of sintered alumina foams. The bulk density has increased from 0.63 to 0.73 g·cm^{-3} that is a result of increasing the loading of slurry in the sponge network. Also the compressive strength of the alumina foams has enhanced from 1.33 to 3.24 MPa, which is desirable.

Table 1. Properties of the sintered alumina foams prepared using different solid content slurries.

Solid concentration in the slurry (wt. %)	60	66
Bulk density (g cm^{-3})	0.63 ± 0.03	0.73 ± 0.03
Total porosity (vol. %)	83.3 ± 1.0	80.4 ± 0.9
Compressive strength (MPa)	1.33 ± 0.15	3.24 ± 0.30



a) 60 wt. %



b) 66 wt. %

Figure 4. Optical photograph of the structure of the sintered alumina foams prepared using a) 60 wt. % and b) 66 wt. % solid content slurries.

Figure 4 shows the optical photographs of the foams structure prepared using 60 and 66 wt. % solid content slurries. It is evident from the pictures that foams are reticular and have open interconnected cells.

Detail results related to the compressive strength of sintered alumina foams prepared using slurries with and without Tiron, respectively containing 60 and 66 wt. % solid material, are plotted in the diagrams of Figure 5 separately.

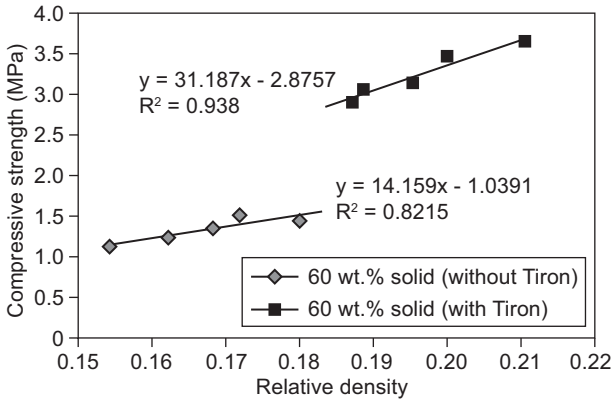


Figure 5. Compressive strength versus the relative density of the alumina foams prepared using 60 and 66 wt. % solid content slurries.

As expected, the compressive strength increases with increasing relative density and reduction of porosity in both classes of the foams. Gibson and Ashby [19] proposed a model to describe the mechanical behavior of open-cell materials. According to this model the dependence of compressive strength of open-cell ceramics on relative density is expressed by:

$$\sigma_{fc} = C\sigma_{fs}(\rho/\rho_s)^{3/2} \quad (2)$$

where σ_{fc} is the compressive strength of the open-cell ceramic, C is a geometric constant characteristic of the unit cell shape, σ_{fs} is the fracture strength of the dense parent material, ρ is the bulk density and ρ_s is the real density of the composition.

For the alumina foams prepared in this work, the geometric characteristic and thus constant C for both classes of the foams is the same. On the other hand, due to the similarity of the ceramic composition of foams prepared with both types of slurries, the σ_{fs} is the same for both the foams, as well. Now when comparing the two plots for a given relative density (e.g. 0.185) it is evident that foams prepared using the slurry containing 66 wt. % solid content have much higher compressive strength value than that of the other class, while Equation 2 does not show this difference. The reason is that the model is based on a defect free and idealized unit cell, and the effect of micro-defects and imperfections in the microstructure and struts have been ignored in that model.

Due to the similar macroscopic characteristics such as shape and size of the cells and pores in both classes of the foams, these two different behaviors relate to their microscopic characteristics. Microscopic observations showed the existence of different defects in the foam structures. In general, these defects can be divided into three groups. The first group includes the pores of a few micrometers in size (about 10 to 80 μm) in the struts formed due to presence of small bubbles in the slurry, removal of water during the drying stage and removal of gases produced by pyrolysis of the organic materials. Figures 6 and 7 show this group of defects clearly. The second group includes cracks in the foam struts. In Figure 7 cracks in the structure of the foam prepared using 60 wt. % solid content slurry are shown with arrows. The presence of cracks can be attributed to stresses caused essentially by thermal expansion mismatch between alumina coating and polyurethane substrate. Brown and Green [12] showed that the thermal expansion difference between the polymeric substrate and alumina coating near the melting point of the polymer leads to accumulation of thermal strains or volumetric expansion in the polymeric substrate, resulting in crack formation. It is worth mentioning that the differential drying between polyurethane substrate and alumina coating, the gas pressure produced by pyrolysis of the organic material and the anisotropic shrinkage of the foam network during the sintering process or a combination of these factors create stresses in the alumina coating that increase the probability of crack formation.

The third group of defects relates to the triangular voids inside the foam struts (Figure 8). These voids are produced due to the pyrolysis of polyurethane struts in the center of alumina struts. In fact, the triangular shape is the result of triangular cross section of the polymeric struts.

As seen clearly in Figure 9, the amount of defects in the structure of the foam prepared using the slurry containing 66 wt. % solid has been considerably reduced. Comparison of the SEM photographs in Figure 9 and Figure 7 indicates a reduced occurrence of pores and cracks in the struts. Since the formation of bubbles in the slurry is accomplished by liquid phase, therefore with increase the solid concentration and reduction in liquid phase (water), the formation of micro-size bubbles in the slurry and thus the amount of micro pores produced at

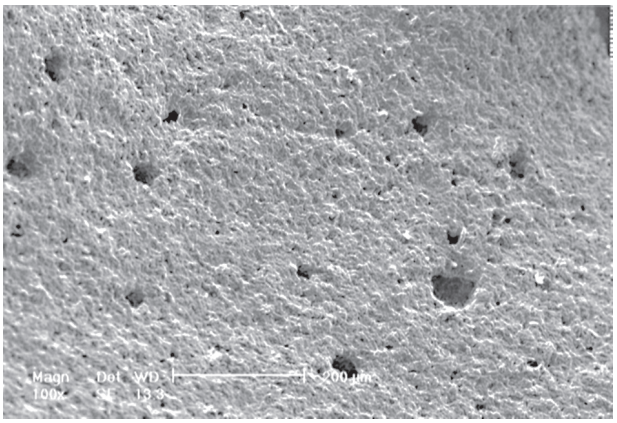


Figure 6. Micro pores in the strut of the alumina foam prepared using 60 wt. % solid content slurry.

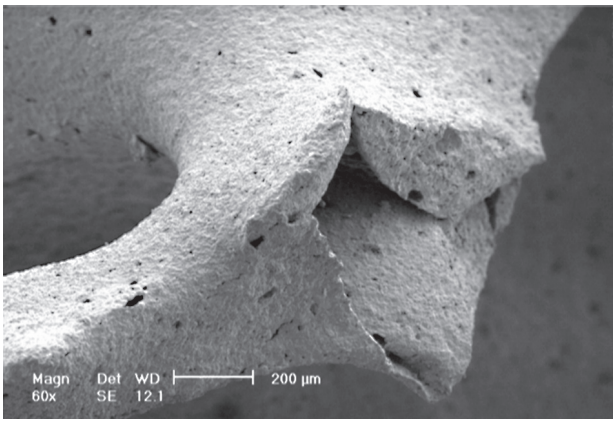


Figure 8. SEM photograph of triangular void inside the alumina foam strut.

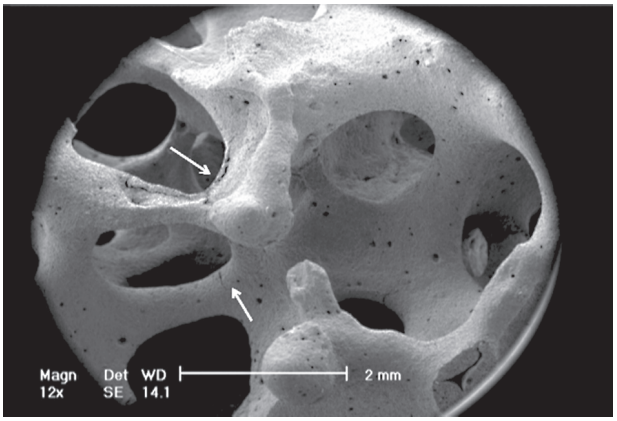


Figure 7. Cracks (noted by arrows) and micro pores in the structure of the alumina foam prepared using 60 wt. % solid content slurry.

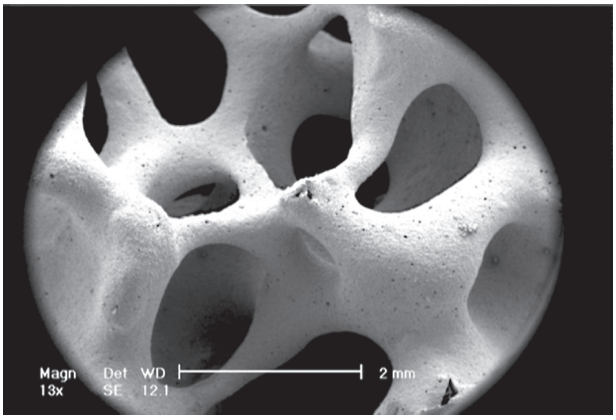


Figure 9. SEM photograph of the structure of alumina foam prepared using 66 wt. % solid content slurry.

the final foam structure has decreased significantly. By a simple calculation, it is found that the amount of water used in the 66 wt. % solid content slurry has decreased 22.7 % by weight in comparison with 60 wt. % solid content slurry. Reduction in the water consumption also causes lower stress on the alumina coating due to lower shrinkage of the coating during the drying stage. On the other hand, increasing the solid content in the slurry allows for more alumina composition to be deposited on the sharp edges of polymeric struts that reduces the formation of cracks in these positions effectively.

Therefore, with increasing solid content in the slurry, a significant reduction of defects in the struts has been occurred. Thus, quality and strength of the struts, which play essential role in the mechanical behavior of the foams, have considerably improved, leading to strength enhancement of the alumina foams. Increase of the relative density and decrease of porosity also have contributed to the increase in strength (Table 1).

CONCLUSIONS

In this study open-cell alumina foams with desirable mechanical strength were prepared by the replica method. For coating the 14 ppi polymeric sponge, the rheological behavior of the slurry was optimized based on a slurry with maximum solid content of 60 wt. %. In order to increase the solid content in the slurry, Tiron was used as dispersant. Tiron had beneficial effect on the reduction of slurry viscosity and with using the optimum concentration (0.8 wt. %), increasing the solid content in the slurry became possible from 60 to 66 wt. %. Thus, the amount of defects in struts and structure of sintered alumina foam were significantly reduced and the compressive strength enhanced to the considerable value of 3.24 MPa. In addition to the reduction of defects, the small increase in the relative density had a positive effect on the increase of strength. Microscopic observations and compression test results of the open-cell alumina foams confirmed that the amount of defects in the struts and foam structure have a significant effect on the mechanical behavior.

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