Factors affecting the microstructure of porous ceramics

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Abstract: In this study, porous ceramics were produced by using two methods: the polymeric sponge and foam method. A study of the effect of viscosity on the characteristics of the final product produced using the polymeric sponge method revealed that the microstructure of porous ceramics is highly affected by the viscosity of the slurry. The optimal ratio between porosity and the strength of the porous material was achieved by subsequently repeating the immersing and drying processes. A study of the porous material obtained using the foam method revealed that the pore size and foam volume can be controlled by varying the amounts of anhydride and thermal blowing agent. The problem related to foam collapsing was solved by using a thermal blowing agent. The microstructure of the samples was characterized by SEM.

Keywords: porous ceramics, polymeric sponge method, foam method, microstructure characterization.

INTRODUCTION

Several methods for the production of porous ceramics have been proposed. The most commonly used methods are the polymeric sponge method, which involves the impregnation of a polymeric sponge with slurries containing ceramics particles and appropriate additives, and the foam method, where a porous material is produced by foaming the solution containing the ceramic material. Reticulated porous ceramics produced by the polymeric sponge method are highly porous ceramics with an open, three-dimensional network structure. The foaming method produces fine open-cell porous ceramics. The data reported so far were based on patents[1–3] and dealt with the modification of the production procedure with the aim of improving the microstructure of the ceramic materials.[4–20]

This work is based on the production of porous ceramic using the polymeric sponge and foam method. The possibility of the control of the micro structure of ceramic foams by varying the starting material, the processing parameters and the

experimental procedure is shown. The microstructure of the samples was characterized by SEM.

EXPERIMENTAL

The production of porous ceramics by the polymeric sponge method

Two different types of slurries were prepared depending on the binder used, *i.e.*, aluminum phosphate (made using phosphoric acid, BASF AG, and alumina powder, Alcoa) or acrylic ester in the form of a dispersion having a solid content of 50 % (Acronal S360D, BASF AG). Both slurries were water based containing particles of alumina (Al_2O_3 consisting of two components "MA2" and A16", in the ratio 70:30), with a particle size of 0.5 μm and 8 μm, respectively, (Alcoa Industrial Chemicals, Pittsburgh, PA), Fig. 1. All the components were mixed and left in a milling machine for several hours.

A polymeric sponge with an average porosity of 2 – 5 pores/cm was impregnated with the slurry. The sponge was compressed to remove air, immersed into slurry and then allowed to expand. This compression-expansion step was repeated to achieve the desired density. The next step was the removal of the excess slurry from the sponge (25 % – 75 %) to provide a satisfactory porosity. The infiltrated sponge was dried under microwave radiation to deposit the ceramic particles on the sponge. The dried structure was heated in air at 350 – 800 ºC for 2 h to remove of the organics from the slurry and to volatilize the polymeric sponge. Slow controlled heating was desirable to avoid blowing the ceramic structure apart.
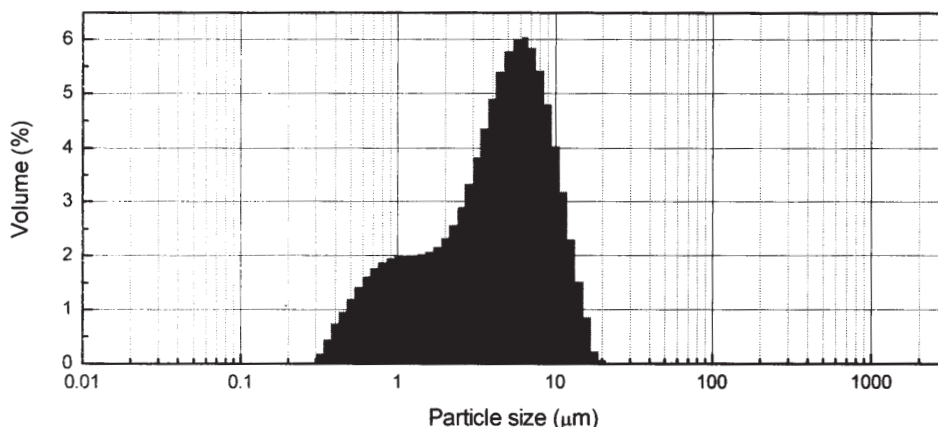

Fig. 1. Particle size distribution of the ceramic powder.

The final step was densification of the ceramic network by sintering at 1400 ºC, which was performed by controlled heating to prevent the collapse of the ceramic framework.

Production of porous ceramics by the foam method

The water soluble components: the dispersant, 25 % aqueous solution of tetra methyl ammonium oleate, (BASF AG), blowing agent, ammonium hydrogen carbonate, (Merck) the viscosity modifier, poly(vinyl pyrrolidone), (Luviskol K90, BASF AG), framework former, 50 % aqueous solution of a urea formaldehyde resin, (BASF) and binder, acrylic ester dispersion (Acronal S360D, BASF AG), were mixed at room temperature. The inorganic powder (Al_2O_3, "MA2" with an average particle size of 8 μm) was added under stirring. For the foaming process, maleic anhydride and pyromeltic anhydride (BASF AG) were used.

The composition foams and expands to a volume 2 to 5 times higher than the initial volume. After stabilization (5 – 10 min), the foamed material was removed from the mold, left to dry and then heated slowly in air at 350 to 800 ºC for up to 6 hours to remove the organics and avoid collapsing of the foamed structure. The final step was densification of the ceramic material by sintering at 1400 ºC.

The cell size was controlled by controlling the amount of the evolved gas. An inverse relationship between the pore size and reticulation was found. Foams with finer pores tended to have more open structures. This can be explained by the fact that for a given foam height, the smaller pores have more wall area at a fixed solid volume.

RESULTS AND DISCUSSION

The effect of viscosity

In contrast to the foaming method for the production of porous ceramic, where a change of many parameters leads to different types of product from the same starting materials, in the polymeric sponge method, the final product can be affected only by changing the slurry viscosity.

In this study, the viscosity was varied by adding a viscosity modifier, poly (vinyl pyrrolidone).

When the viscosity is low, the resulting product is a positive replica of the used polymeric sponge. On the other hand, when the viscosity is high, the resulting product is a negative replica of the used polymeric sponge. The viscosity was measured using the rotating plate method, Model 2ARES/3A Rheometer (Rheometrics Scientific Ltd., Surrey Business Park, Surrey, UK).

Two types of experiment were performed with respect to the binder used.

In the experiments where alluminum phosphate was used as the binder, the viscosity of the slurry was low, *i.e.*, 450 mPa s (Fig. 2). The resulting ceramic was very porous, but not strong enough due to the thin walls.

In the second type of experiment, acrylic ester was used as the binder and poly (vinyl pyrrolidone) was a viscosity modifier. In addition, the process of immersing
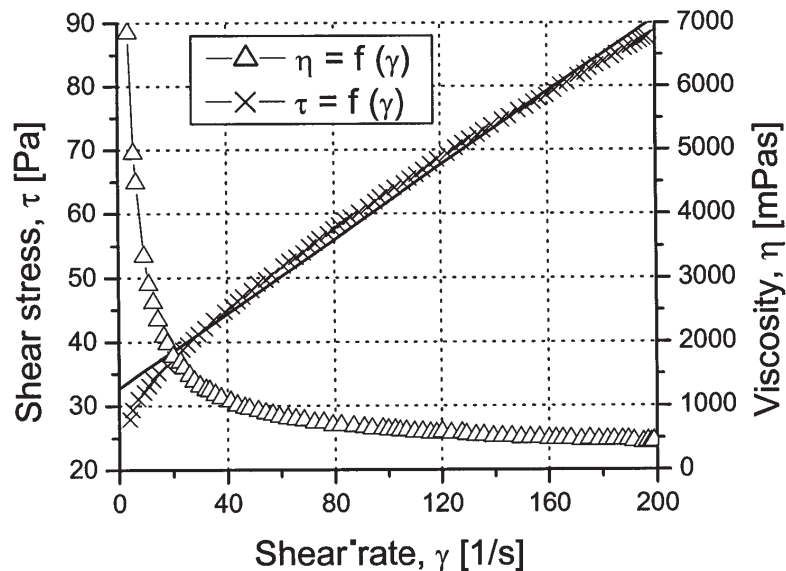

Fig 2. The viscosity of the slurry containing alluminum phosphate.
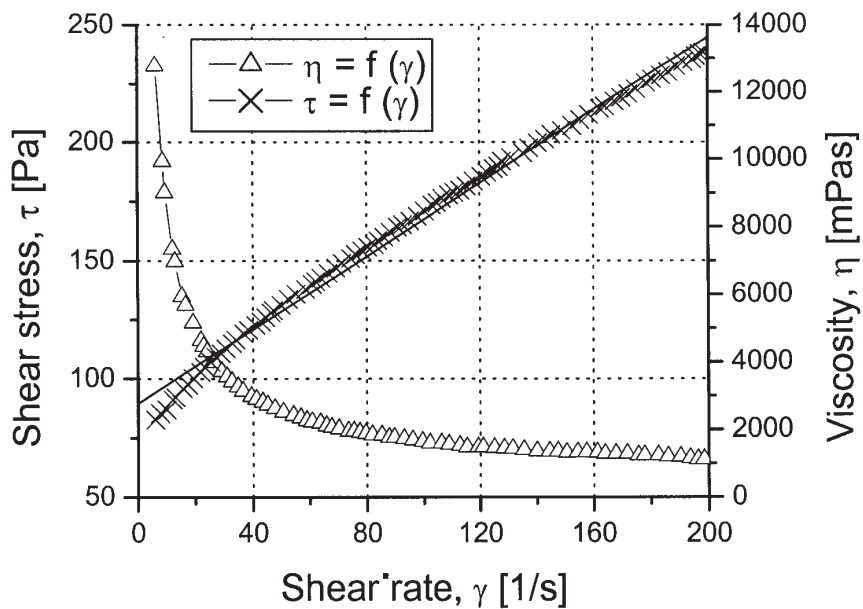
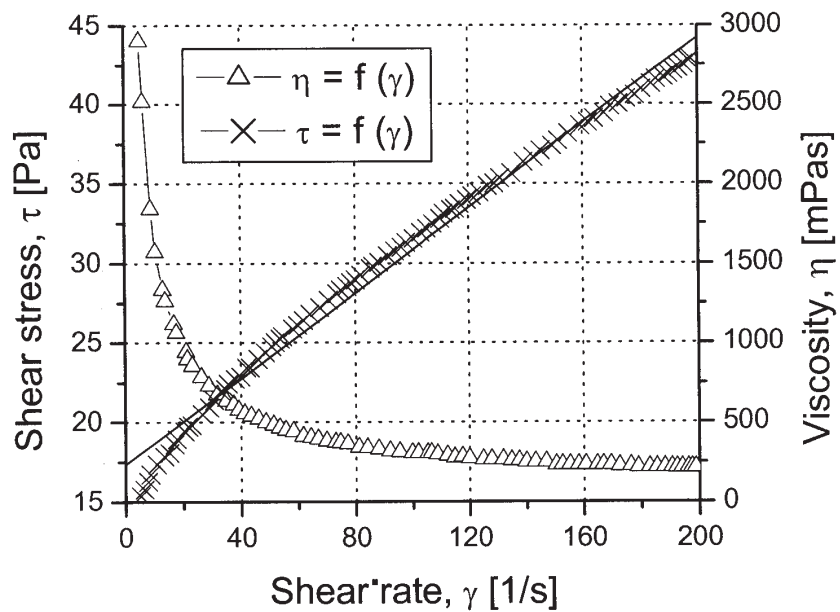Fig. 3. The viscosity of the slurry used for the first immersing.

Fig. 4. The viscosity of the slurry used for the second immersing.

and drying was repeated several times in order to obtain a better ratio between the porosity and the strength of the final porous material.

Foam collapsing

The problem following all the experiments was the collapse of the obtained material during the foaming process, due to the fact that the urea formaldehyde resin was not able to form an appropriate framework, which could withstand the force of gravity. The curing process of a urea formaldehyde resin can be initiated in two ways. The first one is based on the change of pH value when an anhydride is added and the second one is based on increasing the temperature. In the experiments in which gas was evolved by the reaction of anhydrides with ammonium hydrogen carbonate, the problem of collapsing was the result of the slow curing of the urea formaldehyde resin. To solve this problem, the anhydrides and ammonium hydrogen carbonate were replaced with a thermal blowing agent (azodicarbonamide). When the thermal blowing agent was used, the process of foaming was carried out at an elevated temperature to initiate the urea formaldehyde resin to form a framework and to simultaneously perform the forming. Another advantage of using a thermal blowing agent is that it allows an infinite time for the mixing of all the components, which is not in case when anhydrides are used.

By using the thermal blowing agent, the problem of foam collapse was solved. Pore size analysis of the samples revealed that the average pore size was $350 - 500$ Å.

Characterization of the ceramic structures

The ceramic structures were examined using a scanning electron microscope (SEM, Jeol JX840).

The SEM micrographs of the porous ceramic samples obtained by the polymeric sponge method are shown in Figs. $5 - 8$.

It can be observed in Figs. $5 - 7$ that the ceramic material was comprised of interconnected voids surrounded by a web of ceramic. The cell walls obtained by the deposition of ceramic particles were thin. Traces of polymeric sponge which volatilize in the sintering process can be recognized as holes in the ceramic matrix.
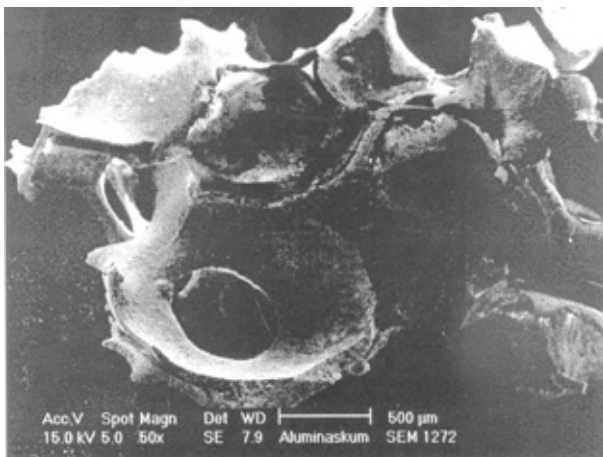

Fig. 5. SEM Micrograph of the porous ceramic obtained by repeated immersion and drying processes.

Fig. 6. SEM Micrograph of the porous ceramic obtained by repeated immersion and drying processes.
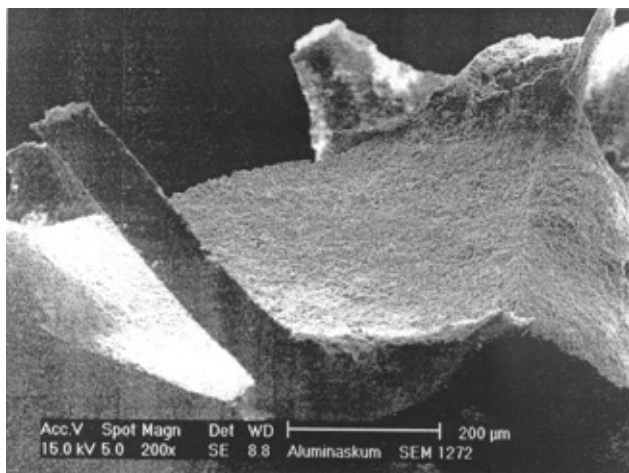

Fig. 7. SEM Micrograph of the porous ceramic obtained by repeated immersion and drying processes.
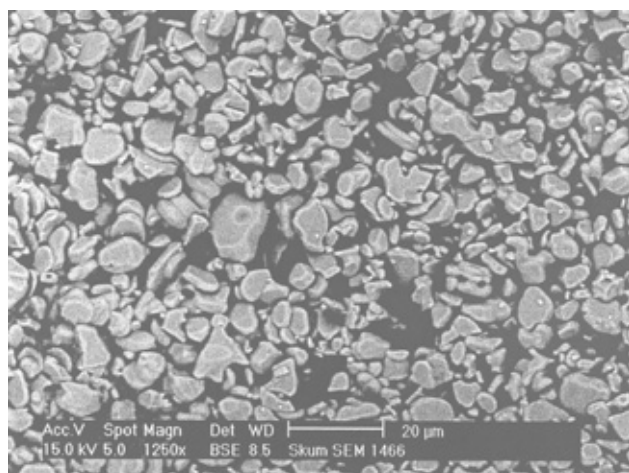

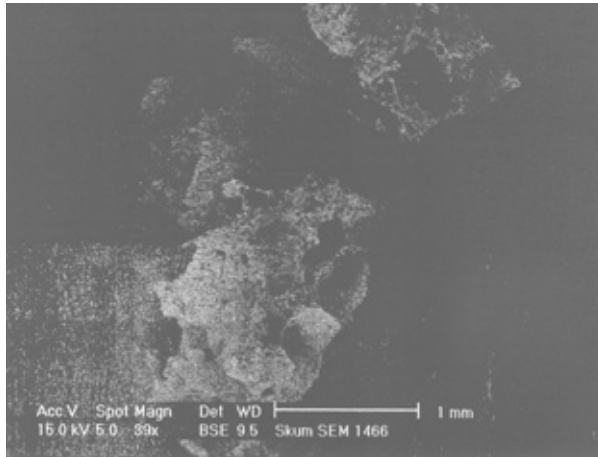Fig. 8. SEM Micrograph of the porous ceramic.

Fig. 9. SEM Micrograph of the porous ceramic obtained by the foam method.

Figure 8 shows that the porous ceramic consisted of two different types of ceramic powder, which differed in particle size.

From Fig. 9, it can be observed that the ceramic material obtained by the foam method consisted of pores with different sizes, caused by the non-uniform size of the bubbles produced in the reaction. The average size of the pores was smaller than in a case of the material produced using the polymeric sponge method. This can be explained by the fact that during impregnation of the sponge, the ceramic slurry fills the whole sponge and on compressing, the sponge slurry leaves only the big pores while the smaller ones are left filled.

The SEM analysis showed that the structure of porous ceramics depends on the production procedure. The material obtained by the polymeric sponge method was macroporous, while the material produced by the foam method was microporous.

CONCLUSIONS

Porous ceramics were produced using two different techniques: the polymeric sponge method and the foam method.

The micorstructure of porous ceramics obtained by the polymeric sponge method were highly affected by the viscosity of the slurry. The samples from a more viscous slurry were stronger but less porous compared with the samples obtained from a slurry having a lower viscosity. The optimal ratio between the porosity and the strength of the porous material was achieved by subsequently repeating the immersing and drying processes.

The problem of foam collapse occurring during the production of porous ceramics by the foam method was prevented by using a thermal blowing agent. Pore size analysis of the samples revealed that the average pore size was 350 – 500 Å.

SEM Micrographs of the samples showed a structure typical of reticulated ceramics. The ceramics obtained by the polymeric sponge method were macroporous, while the structure of the ceramics produced by the foam method were microporous.

И З В О Д

ФАКТОРИ КОЈИ УТИЧУ НА МИКРОСТРУКТУРУ ПОРОЗНЕ КЕРАМИКЕ

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У овом раду је порозна керамика добијена на два начина: методом полимерног сунђера и методом пене. Показано је да микроструктура финалног производа зависи од начина извођења процеса и узајамног односа компонената у керамичкој смеши. Оптимални однос између порозности и јачине керамичког материјала добијеног методом полимерног сунђера је постигнут варирањем вискозности смеше и понављањем ступњева потапања и сушења сунђера. Стабилност пене у процесу добијања порозне керамике методом пене је постигнута варирањем супстанци које узрокују стварање пене. Микроструктура узорака је окарактерисана SEM-ом.

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