

Fabrication of Highly Porous Alumina Ceramics

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Abstract

Highly porous alumina with perforated pore of 50 μm in average diameter was fabricated. Addition of some organic materials was necessary to exceed 30 % porosity which was a limit attained by ordinary packing of the alumina particles. Potato starch as a natural organic material and benzoguanamic resin as a synthetic one with suitable particle size and sphere shape were successfully examined in this study.

Thickening of the alumina slurries to a limit keeping high organic material contents was important to perforate pores by the contact of the organic particles. It could be attained by the aid of dispersant to fluidize the slurries. Improvement of fluidity was evaluated with the flow point and the wet point values. Lowering of the flow point is the necessary and sufficient condition of the fluidization and thickening. Polyacrylic dispersant or carboxylic co-polymer with a suitable chain length was effective for alumina-organic materials co-dispersion and for the thickening of the slip to attain c.a. 80 % porosity limit.

Binder which was castable in an oligomer or a precursor form and then reacted to bind the thin skeleton of the highly porous body was proposed. Formalization of PVA or polymerization of urea were examined for such kind of binding reactions.

1. Introduction

Highly porous ceramics with perforated pore in pore size more than 50 μm is desirable for an industrialized successive biofermentation process

to keep yeasts in the pore and also to keep a smoothed flow of the fermentated medium. Porous ceramics with fibrous alumina have already been fabricated and examined experimentally for this purpose.¹⁾ Structural, highly porous body from powder forming process has been obtained by dipping ceramic slip into organic porous body and following firing.^{2,3)} It is difficult, however, to reduce the pore size under few hundreds micrometer by this method due to the difficulty of the dipping of the concentrated ceramic slip into such a small pore.

Potato starch works as a good organic material to open pore in normal powder processing technique. PVA sponge has been prepared using potato starch to open pore.⁴⁻⁷⁾ The slip must be thickened to perforate the pore by the contact among the neighbouring organic particles. The thickening can be aided by the dispersant which is effective for fluidization.^{8,9)} Promotion of the fluidization could be evaluated with the lowering of the flow point. Selection of dispersant which is effective for the fluidization in conformity with the alumina powder and potato starch determines the limit of thickening of the slip.⁹⁾ Benzoguanamic resin, Epostar, which has suitable size and uniform sphere shape, is another organic material to open pores. Addition of Epostar necessitates different dispersant other than polyacrylate due to the more hydrophobic surface than that of potato starch.

The use of least amount of binder is necessary to keep the thin skeleton of the highly porous ceramic body. The reaction binder which is castable with the concentrated alumina slurry containing organic material and then polymerizes to bind alumina particles is attractive. Formalization of PVA is one of the candidates. Polymerization of urea is another possibility.^{10,11)}

It is the purpose of this report to evaluate the dispersants for the thickening of alumina-organic materials slurries to a limit, in

conformity with the organic materials to open the pore, such as potato starch and benzoguanamic resin, and also to examine the effect of binders, such as PVA or urea resin, which is castable in a precursor form and then polymerize to work as binder.

2. Experimental

2.1. Materials

Alumina used in this experiments is A-16 SG α -Al₂O₃ from Alcoa Co.. Polymeric dispersant used for alumina-potato starch system is the Seruna D-305 from Chukyo Yushi Co., Nagoya, Japan, which may correspond to the ammonium polyacrylate of the molecular weight around 2000-3000.

Dispersant for alumina-Epostar system is the Seruna D-735 from Chukyo Yushi Co., Nagoya, Japan, which may correspond to the co-polymer of the styrene-maleic acid of the molecular weight around 2000. Potato starch was the commercial reagent and benzoguanamic resin, Epostar, were supplied from Japan Catalyst Co., Osaka, Japan.

2.2. Determination of the Wet Point and the Flow Point.

Wet point and flow point are defined as the least amount of water for an unit amount of alumina powder to make a lump and to start to flow, respectively.^{12,13)} Twenty grams of alumina powder were mixed with 2.5 ml (the amount is below the wet point) dispersant solutions of various concentrations. Then, adding water, the least amount of water to form a lump without pieces was read as wet point and the amount of water at which the slip starts to flow was read as flow point. The suspension at the flow point corresponds to the most concentrated suspension with fluidity.

2.3. Calcining and Firing

In calcining process, the reduction of weight by thermal decomposition of potato starch starts from 300°C, accelerated around 400°C and completed at 500°C. Epostar decomposed at the higher temperature in

50°C than potato starch. Calcination was conducted in programmed temperature as follows, i.e. the temperature was first slowly raised to 600°C in 12°C/min following keeping the temperature at 600°C for 5hr. Subsequently to the calcining the temperature was raised to the firing temperature at 1200 to 1500°C, in the rate 200°C/min.

2.4. Observation of Microstructure

Microstructure of the fractured surface of the porous body was observed directly with SEM. The dispersion of the organic materials in the microstructure was observed after cutting and polishing the fired body into flat surface to come out the pore dipped with epoxy resin under evacuation.

2.5. Measurement of Porosity

Porosity was calculated from the bulk density determined by the measurement of the weight of the sample in rectangular shape which size was averaged in two sites for length or in five sites for width and thickness.

2.6. Bending test

Three point bending test was conducted with Shimazu Autograph with 30 mm span and 0.5 mm/min. cross head speed.

3. Results and Discussion

3.1. Selection of the dispersant to concentrate the slip containing organic material

Thickening of the slip with a dispersant is the key to obtain high porosity and the perforation of the pore. Measurement of the wet point and the flow point is useful to evaluate the effect of dispersants.^{12,13)} Daniels pointed out that the smaller difference between the flow point and the wet point is an index of better dispersion.¹³⁾ The increase in the fluidity of the slip can be evaluated from the lowering of the flow point. Lower flow point indicates the

possibility of the thickening of the slip. And the limit of thickening corresponds to the state at the flow point. Improvement of dispersion is not sufficient for the concentration of the slip. Fluidization is necessary for the concentration. Some dispersant works for the improvement of the dispersion and of the fluidization simultaneously. Simultaneous attainment of the small difference between the flow point and the wet point and also the lower flow point could be sufficient condition for such a dispersant.

Polyacrylic dispersant lowered the flow point of alumina keeping almost constant low wet point as shown in Fig. 1.

Therefore, at the concentration of the polyacrylic dispersant to give minimum for the flow point, the difference between the flow point and the wet point gives a minimum and the slip can flow with minimum amount of water. Polyacrylate works for the dispersion and also for the fluidization of the slip simultaneously.¹⁴⁻¹⁷⁾

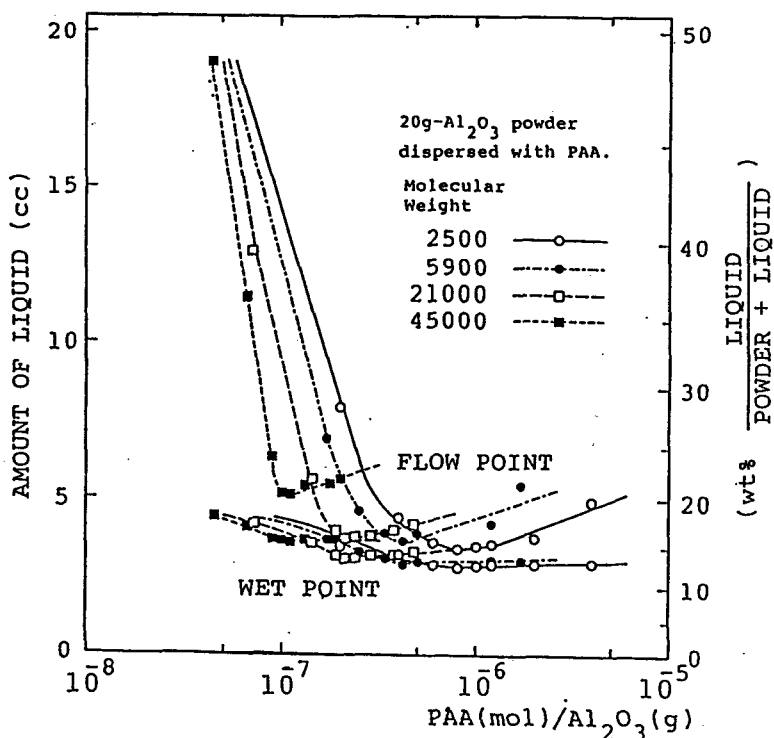


Fig. 1 Flow Point of Alumina

Mixing potato starch to alumina, however, increased the flow point due to the increase in the wet point keeping the difference of the flow point and the wet point in small even in the presence of polyacrylic dispersant as shown in Fig 2. Polyacrylate worked well for dispersion, but lost the effectiveness for the improvement of the fluidity with increase in the potato starch content. High flow point and small difference between the wet point and the flow point mean low fluidity keeping high dispersion. Potato starch inhibited the lowering of the flow point due to the increase in the wet point. The increase in the viscosity with increasing the potato starch limits the maximum fraction of the potato starch to be added keeping fluidity that leads porosity to a certain limit. Polyacrylic dispersant was effective, however, for the thickening of the alumina slurries containing potato starch up to 80 % porosity.

The microstructure of the fired body with maximum porosity showed the good dispersion of the potato starch particles as shown in Fig. 3.

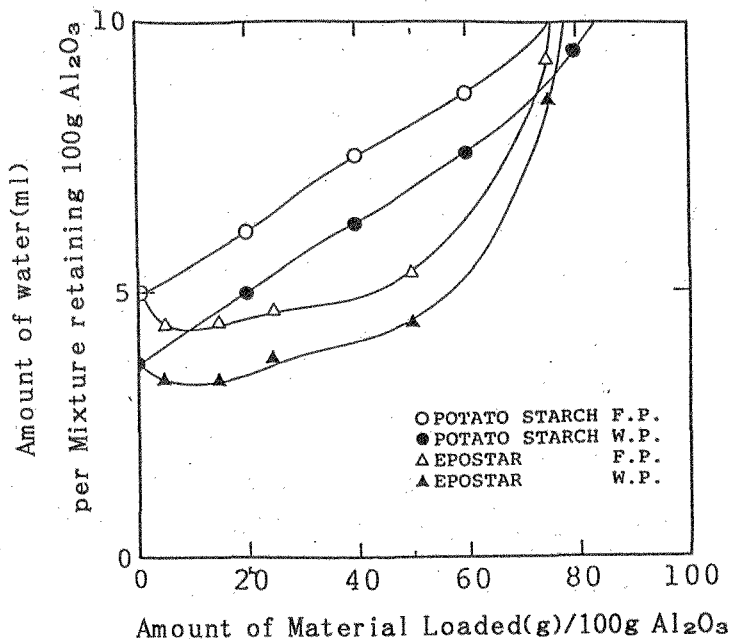


Fig. 2 Flow point of the mixtures of alumina-potato starch and alumina Epostar by the addition of Seruna D-305

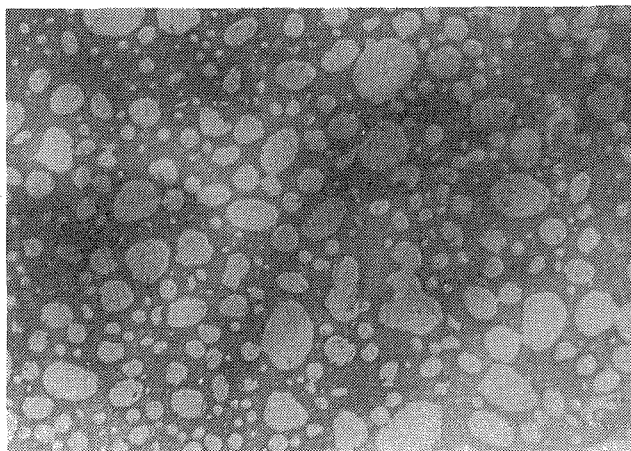


Fig. 3 The microstructure of the porous body fabricated from alumina slip containing maximum fraction of potato starch in presence of polyacrylic dispersant.

Co-polymer of styrene and maleic acid worked as a good dispersant the mixture of alumina and benzoguanamic resin, Epostar. Figure shows the wet point and the flow point for the mixtures of the alumina and Epostar with various composition. Addition of 40 wt% Epostar Al_2O_3 gave a minimum for the flow point keeping the small difference between the flow point and the wet point. And excess Epostar abruptly increases the flow point due to the increase in the wet point even in presence of the co-polymer dispersant as shown in Fig.4. The addition of 40 wt% Epostar to alumina made possible 80 % porosity. The microstructure of the porous body fired with the maximum fraction of Epostar also showed the good dispersion of the Epostar particles shown in Fig. 5. The small difference of the flow point and the wet point worked as an index of good dispersion for both cases.

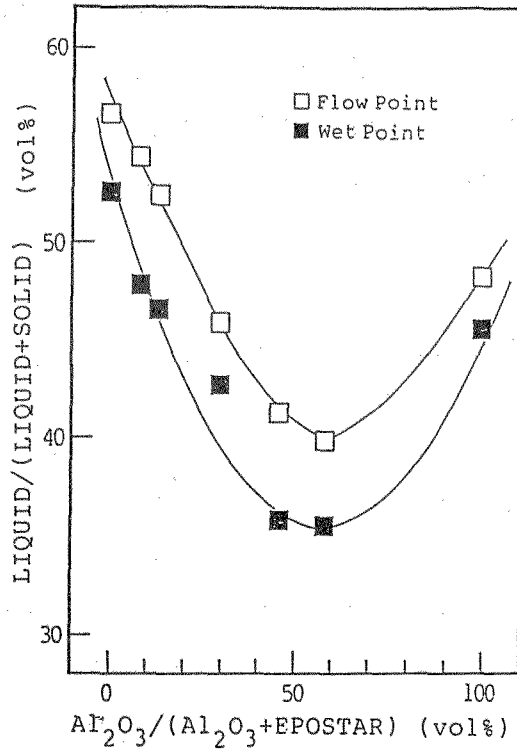


Fig. 4 Flow point of the mixture of alumina and Epostar in the presence of co-polymeric dispersant Seruna D-735

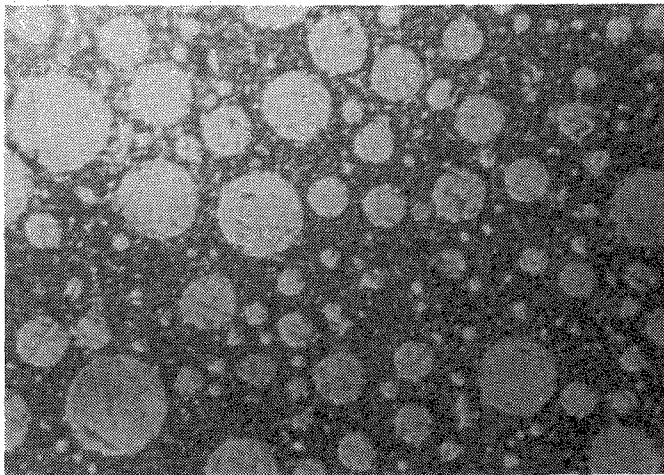


Fig. 5 The microstructure of the porous body fabricated from the alumina slip containing maximum fraction of Epostar in the presence of the co-polymer of stylen and maleic acid.

Excess addition of the organic material inhibited the improvement of the fluidity in spite of keeping dispersion. Therefore, it can be concluded that only promotion of dispersion is not sufficient to increase organic material content, but the improvement of the fluidity is the key and sufficient.

3.2. Binders to keep the thin skeleton of the ceramics of the porous body formed at the thickening limit

Formalization of PVA and polymerization of urea were examined for binders which were castable and bind the thin skeleton of the highly porous body by bridging or polymerization reaction.

The reaction of PVA with formaldehyde produces formal network between oligomers. One gram of the mixture with composition described in Table 1 was added to the concentrated alumina slip as a binder solution after dispersion of alumina-potato starch slip by 3hr milling with dispersant. In this preparation, the amount of water was

Table 1. The composition of the precursor of PVA binder

10 wt% PVA solution	75 wt%
35 wt% Formaldehyde solution	10 wt%
50 wt% Sulfuric acid solution	15 wt%

important to obtain green body without strain. Suitable composition is as follows; Hundred grams of alumina was mixed with various amount of potato starch up to 80g and with water in the equal amount of potato starch in the presence of 1g of polyacrylic dispersant solution. Water in equal amount to potato starch is needed. Insufficient water caused an increase in viscosity of the slip to inhibit the forming and also caused inhomogeneous formalization to result partial strain in formed

body. On the other hand, excess water caused delay of the formalization. The slip added binder solution was casted into mold and kept at 50°C in water bath for 24 hr for the polymerization.

Polymerization of urea has also been applied as a castable binder for alumina-Epostar system. Urea reacts with formaldehyde to form dimethylol urea in neutral to weak acidic medium which could be castable precursor. Adding the pretreated binder solution, the alumina-Epostar slip was brought into acidic condition to start to polymerize the dimethylol urea to work as a binder. Procedures to obtain green body is as follows; Hundred grams of alumina was mixed with various amount of Epostar up to 80g adding the almost equal amount of water as shown in Table 2 in the presence of hydrochloric acid to adjust the pH of the solution to 4.0 for good dispersion.

Table 2. The suitable composition for mixing of the slips at the mixing step containing various amount of Epostar

	Alumina	Epostar	Water	HCl Soln.	pH
Slip No.1	100 g	35 g	32 g	1.1 g	4.3
Slip No.2	100 g	50 g	40 g	1.3 g	4.2
Slip No.3	100 g	80 g	70 g	1.6 g	4.0
Slip No.4	100 g	100 g	95 g	1.7 g	3.9

After 3hr milling, 5 wt% of the pretreated dimethylol urea solution was added. And then the pH of the mixture was brought to 2.0 with hydrochloric acid and kept at 55°C in water bath for 24 hr to accelerate the polymerization. It was necessary to cover the sample vessel with polyfilm to avoid the vaporization of water. Excess addition of binder resulted macrocracks in the green body as shown in Fig. 6.

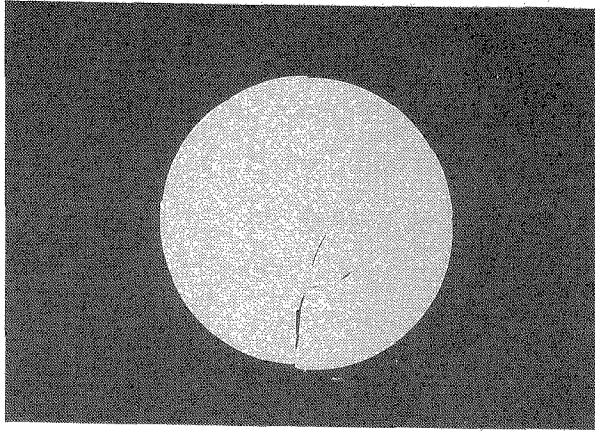


Fig. 6 Green body formed with strain in the presence of excess amount of urea resin

The microstructures of the fractured surface of the fired body processed with PVA and potato starch and with Epostar and urea resin were indicated in Fig. 7.

In the body of c.a. 80 % porosity, perforated pores could be observed. The perforation of the pore could be possible by the contact of the neighbouring organic particles. Simultaneous attaining of the increase in the contents of the organic materials up to 80 vol% and of the thickening of the slip to the limit was important for it.

Porosity of the fired body depends on the firing temperature as shown in Fig. 8. Eighty percent maximum porosity was attained at the firing temperature of 1200°C for each processed bodies which contained an excess pores than the pore expected from the volume of potato starch and Epostar. The excess amount was reduced by raising the firing

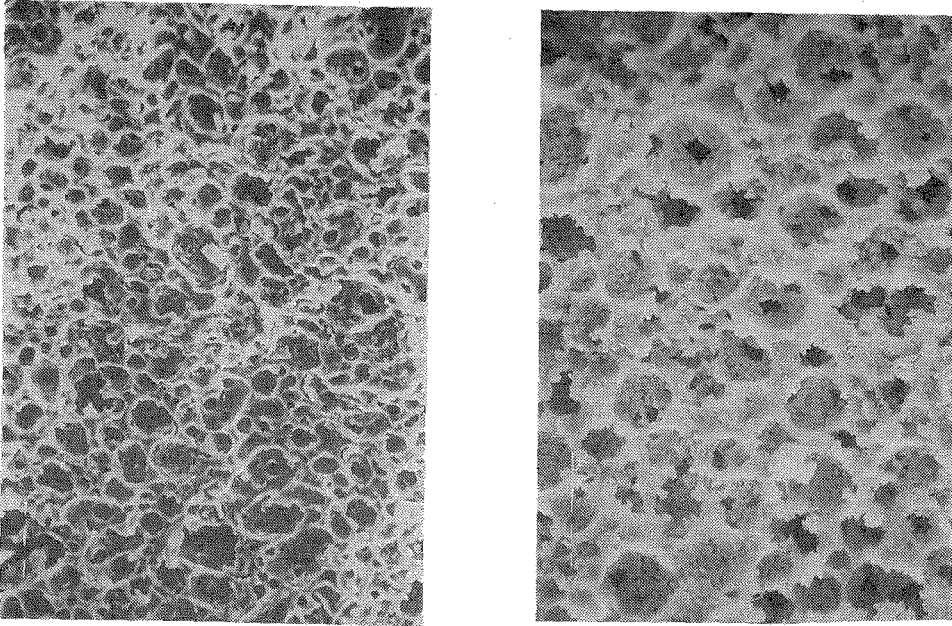


Fig. 7 Microstructure of the fractured surface of the porous body obtained from the described two process

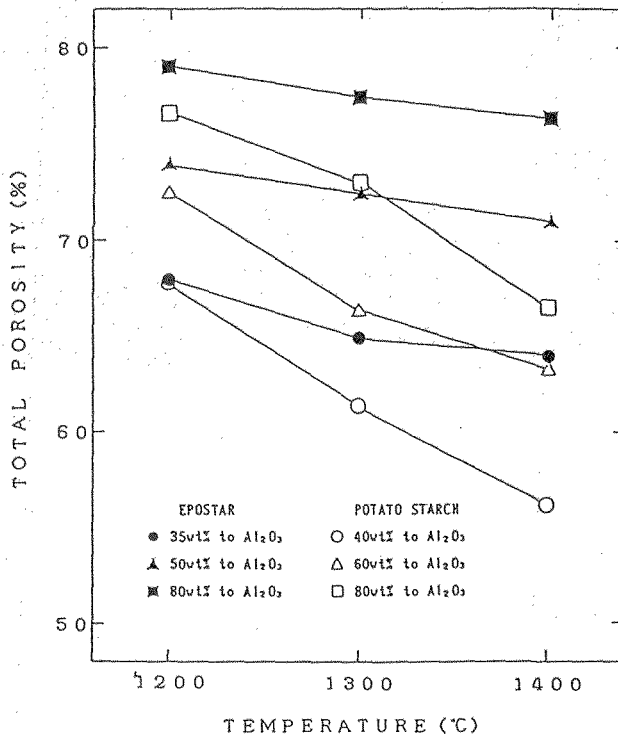


Fig. 8 Porosity of the fired bodies obtained from the described two processes

temperature than 1500°C . The cause of the excess pore might be due to the incomplete sintering between ceramic powder particles. The porous body obtained by described method would, therefore, retain two kind of pore, the one in large size is from added organic material and the other in small size would be from the pore remained between alumina particles by incomplete sintering.

3.4. Mechanical finishing of the fired porous body

Mecahnical finishing was possible by machining. Fig. 9 shows the finished bodies into column, plate and cylinder.

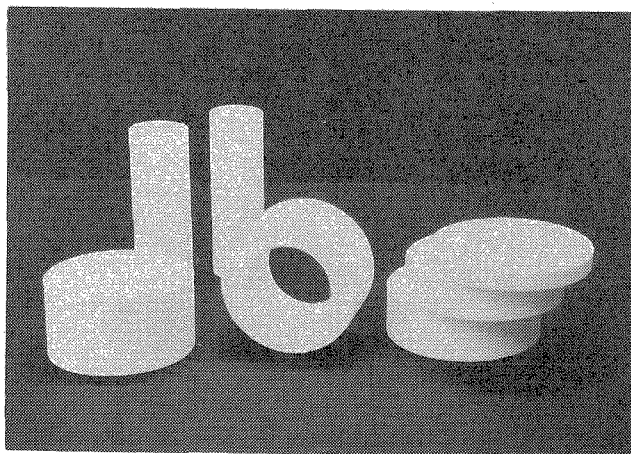


Fig. 9. Mecahnically finished porous bodies obtained from the PVA-potato starch process

Benbnding strength of the body fired at 1200 to 1500°C was in 150 to $400\text{kg}/\text{cm}^2$ as indicated in Fig. 10.

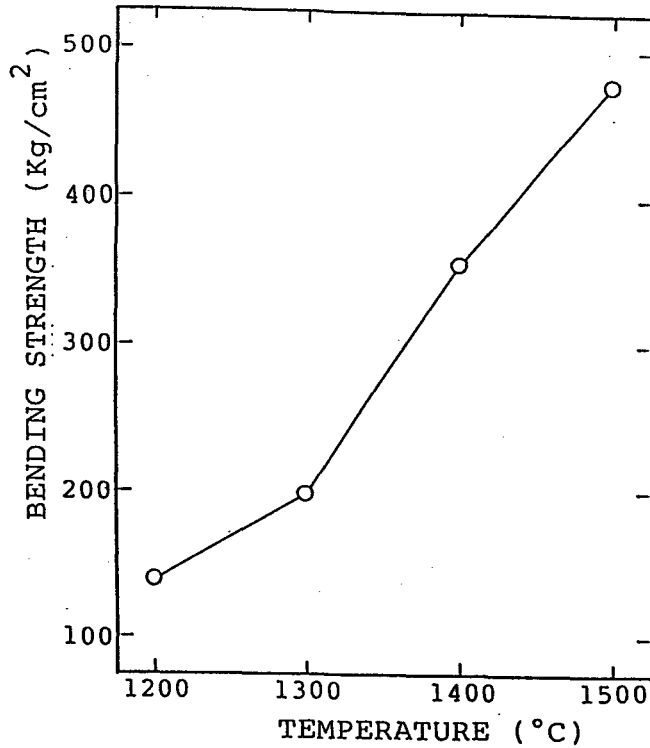


Fig. 10 Bending strength of the porous body obtained by PVA-potato starch process

4. Conclusion

Highly porous alumina body with perforated pore of 50 μ m in average diameter was fabricated by casting the slip retaining potato starch or benzoguanamic resin.

Polyacrylate and co-polymer of styrene and maleic acid were examined as suitable dispersant to increase the organic materials content and to concentrate the slip using the flow point as an index for the fluidization. Addition of the organic materials inhibited the fluidization increasing the wet point. The attainment of low flow point overcoming the increase in the wet point by using the dispersant was sufficient for the simultaneous achievement of the good dispersion and high fluidity of the slip.

Binders which were castable with the concentrated slip and reacted or

polymerized to bind the thin skeleton of the highly porous body were proposed and formalization of PVA and polymerization of urea were successfully examined for the purpose.

5. References

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