New gel-casting process for alumina ceramics based on gelation of alginate

Yu Jia[a,*], Yoshinori Kanno[a], Zhi-peng Xie[b]

[a]*Department of Mechanical System Engineering, Yamanashi University, Takeda, Kofu-city 400, Japan*
[b]*Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China*

Abstract

Sodium alginate—a natural innoxious polymer, which can be dissolved in cold water by mechanical stirring and in which irreversible gelation takes place when enough calcium ions are added—is applied for in situ forming process of ceramics by using chelator to control its gelling behavior. In the present work, the viscosity of sodium alginate solution and factors influencing on it were analyzed. How to control the gelation behavior was discussed. The rheology property of the slurry was examined. An appropriate method to apply the gelation of sodium alginate in order to fabricate alumina ceramic green body was systematically investigated. The viscosity of alumina slurry with 50 vol.% Al_2O_3 and 1.8 vol.% $Ca_3(PO_4)_2$ dispersed by 1 wt.% sodium alginate solution is less than 400 MPa s when the shear rate is higher than 50 s^{-1}. The green body has uniform structure and smooth surface, and bending strength is about 8 MPa. After being sintered at 1550 °C for 2 h the linear shrinkage of ceramics composed of 95% alumina is about 15.7% during firing and the relative density of the final product is about 98.7%. Bending strength reaches 320 MPa. SEM images show compact and uniform microstructure. © 2002 Published by Elsevier Science Ltd.

Keywords: Al_2O_3; Forming; Gelcasting; Sodium alginate; Solidification

1. Introduction

Gelcasting is a novel forming process of ceramic, which achieves in situ solidification of ceramic slurry by the polymerization of monomers.[1,2] According to this process, ceramic powder was first dispersed into a water-based monomer solution forming uniform slurry and then, after adding catalyst and initiator into the slurry, it was poured into a mould. The remarkable advantage of this process is that the strength of the green body is high enough to be machined. However, the monomer commonly used is acrylamide with neural toxicity. In view of this point, many new gel-casting processes possessing reduced toxicity have been investigated.

In fact, there are a lot of natural polymers in which the solution can gelate under suitable conditions, such as agarose, gelatin, sodium alginate and so on. In food industry the application of gel is so common that ice cream, jelly, bean jelly, pudding and jam are all based on the gelation.[3,8] Besides these, there are some reports about utilizing natural polymer in ceramic forming process.

Agar and agarose have been used in water-based injection molding;[4,5] gelatine and agarose have been used in gel casting.[6,7] In the present paper a natural innoxious polymer, sodium alginate, was used to coagulate ceramic suspensions.

Alginate is a type of gelling polysaccharide which can be dissolved in water at room temperature and then gelled after reacting with divalent metal ions.[8,9] It has been widely used in the food industry, and in traditional ceramic forming processes which has been used in the injection process.[9] In the last few years, some researchers have utilized it in the fabrication of silicon nitride beads[10] and in freeform fabrication of alumina ceramics.[11] In the present research, we apply sodium alginate in in situ forming processes of ceramics by controlling its gelling behavior.

2. Experimental procedures

2.1. Raw materials and preparation

Alumina powders were produced by Henan Xinyuan Aluminum Industry Co. Ltd in China. The particle size

---

* Corresponding author.
  E-mail address: yjia73@sina.com (Y. Jia).

distribution is shown in Fig. 1 and chemical composition is shown in Table 1.

Sodium alginate (NaAlg), calcium phosphate ($Ca_3(PO_4)_2$), ammonium citrate tribasic–$(NH_4)_3C_6H_5O_7$), hexandioic acid ($C_6H_{10}O_4$) and sodium hexa metaphosphate ($NaPO_3)_6$ used in the present research are commercially available fine powder supplied by Beijing Chemical Reagents Company.

The forming process is described in Fig. 2. First, sodium alginate solution was prepared by dissolving sodium alginate in deionized water; then alumina powder, dispersant (ammonium citrate tribasic–$(NH_4)_3C_6H_5O_7$), calcium salt ($Ca_3(PO_4)_2$) and chelator (sodium hexa metaphosphate–$(NaPO_3)_6$) were added into the solution; after that the mixture was ball milled to break down the agglomerate and, finally, uniform slurry was made. After degassing and adding hexandioic acid, the resulting slurry was cast into a nonporous mould. The gelled wet green body will be moved from the mould and then dried at room temperature.

In order to evaluate the feasibility of this forming process, alumina green body (the chemical composition is indicated in Table 2) with agglutinants was sintered at 1550 °C for 2 h.

Table 1
The chemical compositions of α-Al_2O_3

Al_2O_3 (wt.%)	Impurities (wt.%)				True density (g/cm³)	α-Al_2O_3 (wt.%)
	SiO_2	Fe_2O_3	Na_2O	B_2O_3		
> 99.7	0.05	0.03	0.05	0.04	> 3.96	> 95
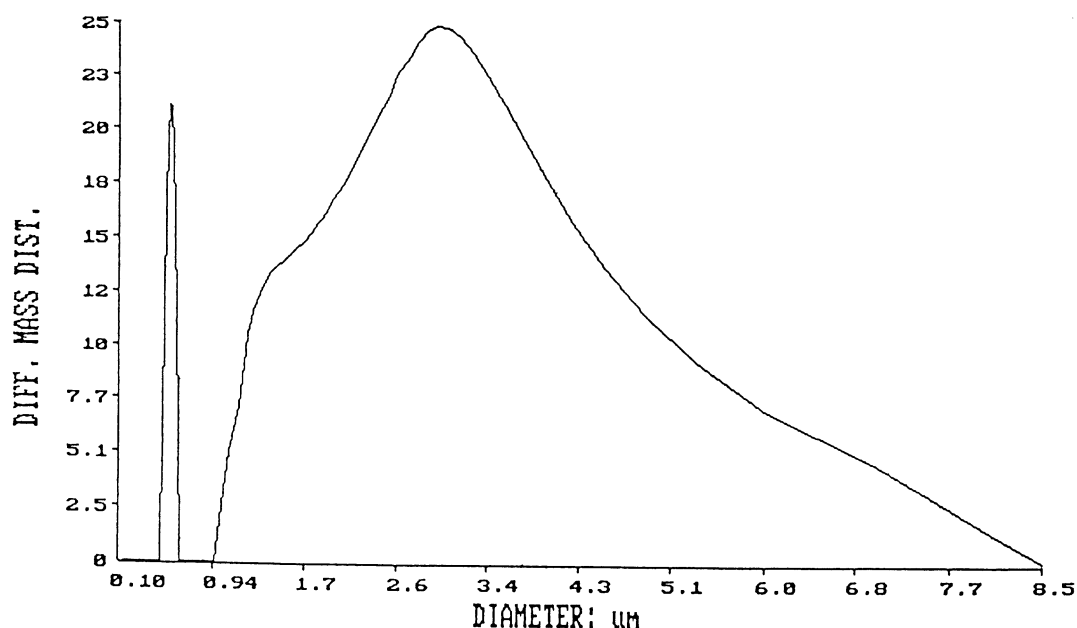
2.2. Measurements

The particle size distribution of alumina powder was measured by BI-XDC of Brookhaven Instruments Co., USA. The apparent viscosity was measured by a rotating viscometer (model NSX-11) of Chengdu Instruments Plant. A dried green body was cut into sample bars of 3×4×36 mm. A sintered plate was cut into samples of 3×4×36 mm and then polished. Flexural strength of both the green bodies and the sintered ones (in the present research, 8 samples have been tested), was determined by three-point flexure test with a span of 30 mm at a loading rate of 0.5 mm/min. The ceramics sample was heated at 1450 °C for 2 h to remove the glass phase from the crystal boundary and then was examined using a scanning electron microscope (SEM, National S-450). The density of samples was measured by the fluid-displacement method with distilled water.

3. Results and discussion

3.1. Controlling the gelation of the sodium alginate solution

When adding divalent metallic salt into the sodium alginate solution, the sodium cation will be replaced by divalent cation, then the viscosity of the solution will increase; irreversible gelation will then take place when enough divalent metallic salt is added. To all the divalent salts, the most commonly used divalent metallic salts are calcium ones.

Fig. 1. The particle size distribution of alumina powders.

But if we add a divalent metallic salt solution into the sodium alginate solution, the irreversible reaction will take place immediately and unevenly. So, if we want to apply sodium alginate in the gel casting process for fine ceramics, the most important thing is to control the gelation behavior. Because the gelation behavior is decided by the calcium cation's solubility in the solution, the present work is to dominate the calcium cation's concentration.

By adding calcium salt and chelator for calcium into the sodium alginate solution simultaneously, the solution will keep stable because of the firm combination of them. At last, we destroyed the combination by adding hexandioic acid into the solution, and calcium ions would be released then gelation took place. Table 3 shows the influence of chelator and calcium and hexandioic acid on gelation of sodium alginate. In this table, the starting time of gelation means the time past from the point acid was added to the point the gelation took place. Because the gelation is an exothermic reaction, by checking the temperature of solution we can decide whether the gelatination has taken place or not.

According to Table 3, by comparing sample 1 with samples 2 and 3 we can know that the starting time of the gelation will be extended when the volume of chelator increases. And the results of samples 1 and 4 tells us that the longer starting time of gelation is in company with smaller volume of acid. The result of samples 4 and 5 indicate that the reaction will speed up if we add more calcium salt. This result is associated with the following mechanism. The chelator is a reagent to limit the content of free calcium ions in solution and acid is a reagent to release free calcium ions. When the amount of usage of chelator increases or the one of acid decreases the volume of free calcium ions in the solution will reduce, which is to slow down the gelation speed. Of course, when using more calcium salt the volume of free calcium ions in the solution increases, which results in high gelation speed.
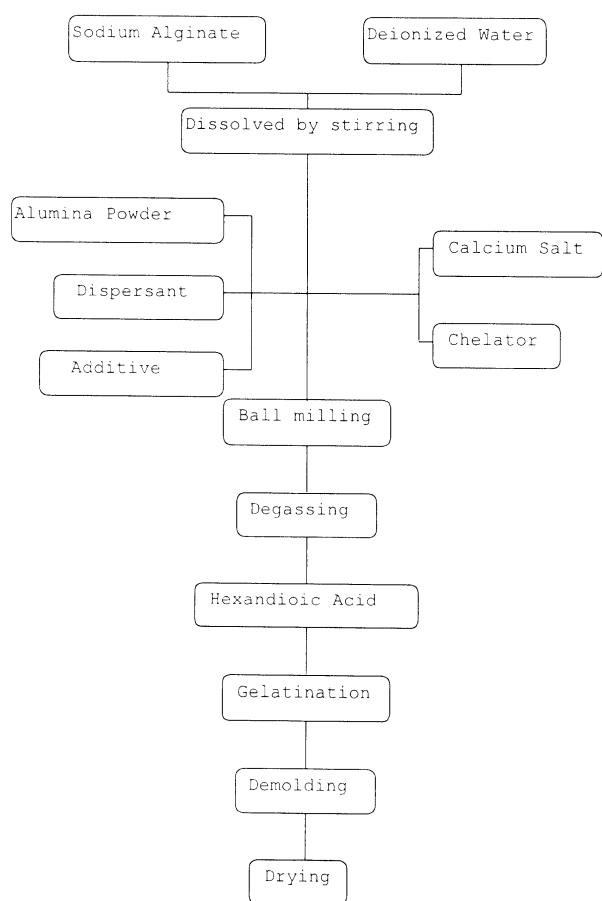
3.2. Rheology property of the slurry

Sodium alginate can be dissolved in water and form a sticky aqueous solution. The viscosity of solution will increase remarkably with increasing the concentration of sodium alginate (Fig. 3 shows the variation of viscosity of

Fig. 2. Flow chart of the forming process.

Table 2
The ingredients of Al_2O_3 ceramic

Ingredients	α-Al_2O_3	CaO	SiO_2
Contents (wt.%)	96	1.8	2.2

CaO is introduced by $Ca_3(PO_4)_2$.

Table 3
The influence of each reagent on the gelatination of sodium alginate solution

Sample	1	2	3	4	5
NaAlg (ml)	20	20	20	20	20
$(NaPO_3)_6$ (µl)	120	240	440	120	120
$C_6H_{10}O_4$ (g)	0.15	0.15	0.15	0.08	0.08
$Ca_3(PO_4)_2$ (g)	0.3	0.3	0.3	0.3	0.1
t (min)	<1	3	18	3	4.5

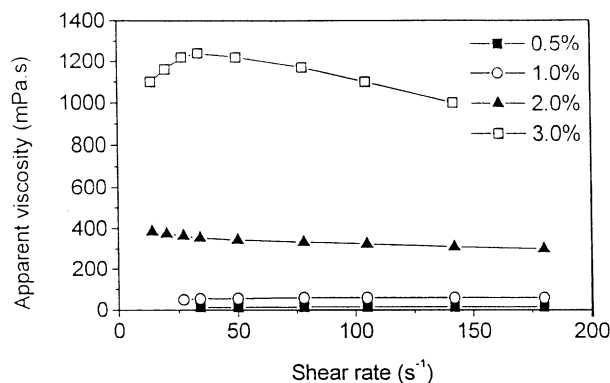The concentration of NaAlg is 1 wt.%; the concentration of $(NaPO_3)_x$ is 20 wt.%.

Fig. 3. Influence of sodium alginate content on solution viscosity at 25 °C.

solution against the concentration of sodium alginate). In order to make slurry possessing high performance we prefer to use sodium alginate solution with low concentration. However, the characteristic of strength of gel is in reverse, which means the high strength is accompanied by high concentration of sodium alginate, therefore in the present research we adopt 1 wt.% sodium alginate solution. (If it has not been specially indicated, the concentration of NaAlg solution used in the present research is 1 wt.%.)

The rheology property of the alumina slurry has been investigated. In Fig. 4, curve A is the slurry which includes chelator and 1.8 vol.% $Ca_3(PO_4)_2$ besides 50 vol.% Al_2O_3; curve B is the slurry with 50 vol.% alumina and curve C represents the fluidity of the slurry which includes 51.8 vol.% Al_2O_3. In comparison with curve A and B, the viscosity of the slurry has been increased a little when calcium salt was added. But curve A and curve C almost has no distinct. So it is clearly that the increasing of the viscosity of slurry A is due to the increasing of solid loading of the slurry. Therefore, we can conclude that the addition of calcium salt will not introduce the gelation of alginate which would result in the apparent increasing of the viscosity of the slurry. It is believed that chelator and calcium react with each other and forms a three-dimensional network structure which results in the stabilization of slurry.

3.3. Forming process of the green body

On the base of controlling of gelation by using chelator, we wonder if there are any differences when we apply this process in the solidification of alumina slurry. Table 4 gives the outcome. In comparison with samples 6 and 7, we can notify that the dispersant has some influence on the gelation, but the inference is not so marked. By comparing sample 7 with sample 8 and/or sample 9 with sample 10 we can find out a little difference between
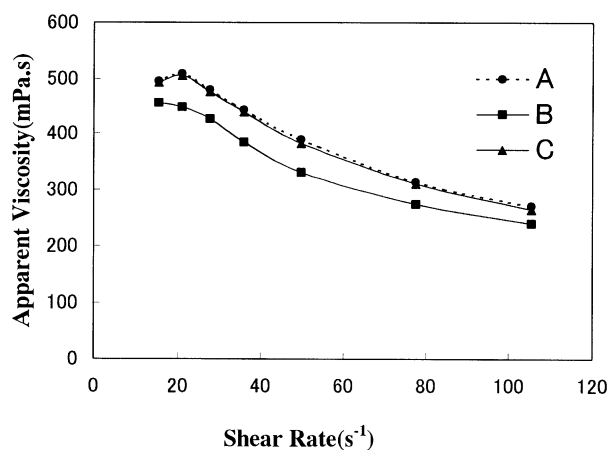
Table 4
The influence of each reagent on the gelatination of alumina slurry

Sample	6	7	8	9	10
NaAlg (ml)	20	20	20	20	20
$(NaPO_3)_6$ (μl)	400	400	400	1000	1000
$C_6H_{10}O_4$ (g)	0.15	0.15	0.15	0.6	0.6
$Ca_3(PO_4)_2$ (g)	0.3	0.3	0.3	2.3	2.3
Dispersant (g)	–	0.2	0.2	0.2	0.2
Al_2O_3 (g)	–	–	72	–	72
t (min)	7	9	13	26	28

them. We suppose that the result will be explained in view of the measurement to define the gelation. In the present research, we decide whether it is gelation or not by tracing the temperature of mixture. After adding alumina powders, the temperature variation of mixture is delayed.

The forming process performed by controlling the gelation of sodium alginate is described in Fig. 2. We add hexandioic acid into the slurry by mechanical stirring after it has been ball milled and degassed. The wet ceramic green body can be demoulded after casting for 6–8 h. The demoulded bodies had precise size reproduction and very smooth surface. After that, the wet green were dried at room temperature for 36 h.

With an aid of proposed forming process, we can make some complicate green parts. Fig. 5 shows some models made by the proposed method.

3.4. Properties of green body and ceramics

During the drying process, the green body has a shrinkage (linear) of 2–3%. Fig. 6 gives the SEM micrograph of a dry body. It can be seen that the green body has homogenous and compact microstructure with no apparent agglomerate or pores. The alumina powders are surrounded by the network of polymer.

Fig. 4. Viscosity of the flurry: A, 50 vol.% Al_2O_3 + 1.8 vol.% $Ca_3(PO_4)_2$; B, 50 vol.% Al_2O_3; C, 51.8 vol.% Al_2O_3.
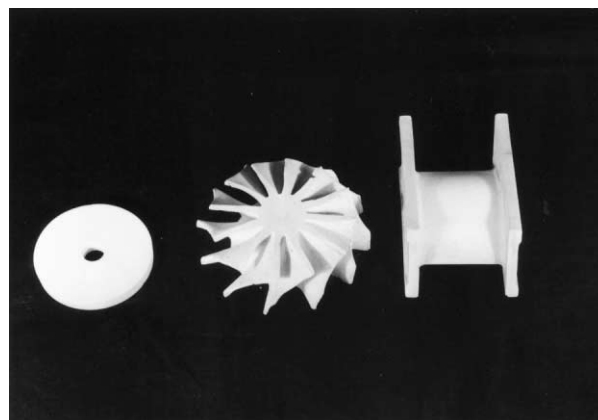

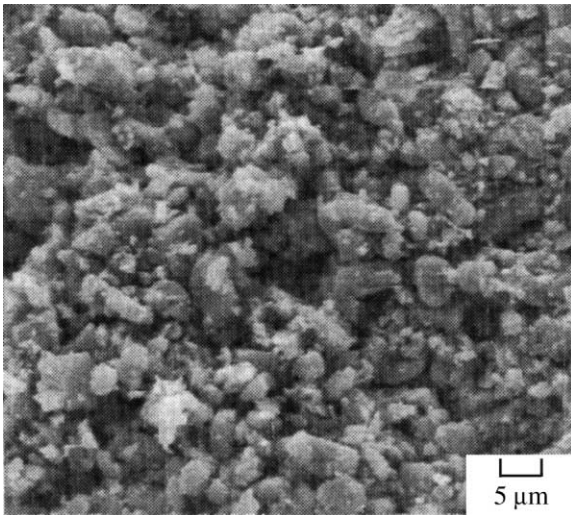Fig. 5. Examples of some green parts made by the proposed forming process.

Fig. 6. SEM micrograph of a dry green body.

The strength of green body is decided by the crosslink of polymer chains owing to the action of calcium ions between two chains. Because the concentration of sodium alginate is limited owing to the requirement of fluidity of slurry, we adjust the amount of calcium salt from 0.24 to 1.8 vol.% to improve the strength of green body. With 1.8 vol.% calcium salt, the bending strength of green body is as high as 8.0 ± 2.4 MPa. (Because the content of NaAlg is lower than 0.3 wt.% of the green body, no plastic deformation was observed.) Of course when we are improving the amount of calcium we should change the amounts of other reagents in order to have a suitable starting time of gelation. At last we settled the composition as sample 10 arranged in Table 2.

Green parts can be sintered directly without special binder removal treatment because the organic binder content of the green body is less than 0.3 wt.%. Ceramics
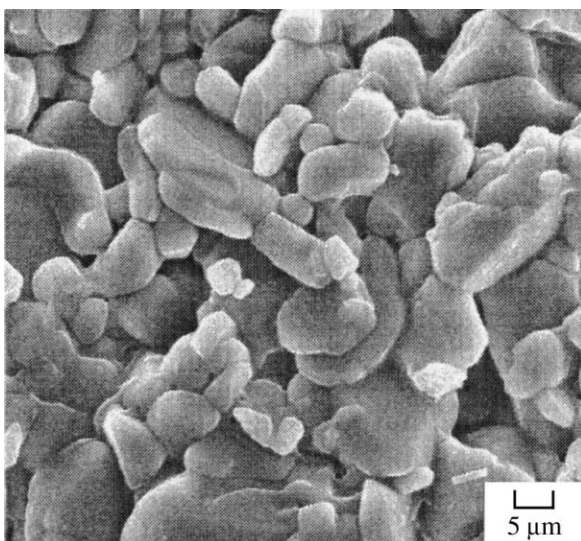
with the formation of 95 wt.% alumina and 5 wt.% clay (the chemical composition is shown in Table 2) made by this method have linear shrinkage of 15.7% during firing. Theoretical density of the final product is 98.7% and bending strength reaches 320.4 ± 27.3 MPa.

Fig. 7 gives the SEM micrographs of Al_2O_3 ceramics. It should be noted that the ceramics have a high density and uniform microstructure without developing a huge grain growth.

4. Conclusions

1. Sodium alginate—a natural innoxious polymer which is used instead of the commonly used monomer acrylamide with neural toxicity—was successfully used in a gelcasting forming process for alumina ceramics.
2. We can control the gelation successfully by using chelator, which is very easy to operate. When adding each reagent in the ratio of sample 3 (in Table 3), we can lengthen the gelation from instantly to after 18 min.
3. After dispersing 50 vol.% alumina by 1 wt.% sodium alginate solution, we get slurry with a high rheology property in which the viscosity is less than 400 MPa s when the shear rate is higher than 50 s^{-1}. Because of the function of chelator, addition of calcium salt did not introduce the gelation of alginate which would result in the apparent increasing of the viscosity of the slurry.
4. Via the present forming process, we can fabricate alumina ceramic green body with precise size and smooth surface. SEM shows that the microstructure of the green body is homogenous and compact with no apparent agglomerate or pores. This forming process can also be utilized in fabricating complicate alumina ceramic green body.
5. The linear drying shrinkage of green body is 2–3%; the strength of dry body is 8 MPa. Sintered samples have shrinkage of 15.7%; theoretical density of final product is 98.7% and bending strength is 320.4 MPa. The ceramics have high density and uniform microstructure.

Acknowledgements

Fig. 7. SEM micograph of alumina ceramics.

References

1. Baskin, D. M., Zimmeran, M. H. and Faber, K. T., Forming single-phase laminate via the gelcasting technique. *J. Am. Ceram. Soc.*, 1997, **80**(111), 2929–2932.

2. Omatete, O. O., Janney, M. A. and Strehlow, R., A, Gelcasting— a new ceramic forming process. *Am. Ceram. Soc. Bull.*, 1991, **70**(10), 1641–1649.

3. Whistler, R. L. and Bemiller, J. N., *Industry Gums: Polysaccharids and Their Derivations*, 3rd ed. Academic Press, Inc, London, 1993.

4. Fanelli, A. J., Silvers, R. D., Frei, W. S., Burlew, J. V. and Marsch, G. B., New aqueous injection molding process for ceramic powders. *J. Am. Ceram. Soc.*, 1989, **72**(10), 1833–1836.

5. Zhang, T., Blackburm, S. and Birdgwater, J., Properties of ceramic suspension for injection moulding based on agar binders. *Brit. Ceram. Trans.*, 1994, **93**(6), 229–233.

6. Chen, Y. L., Xie, Z. P. and Huang, Y., Alumina casting based on gelation of gelatine. *J. Eur. Ceram. Soc.*, 1999, **19**, 271–275.

7. Xie, Z. P., Yang, J. L., Chen, Y. L. and Huang, Y., Gelation forming of ceramic compacts using agarose. *Brit. Ceram. Trans.*, 1999, **98**, 58.

8. Ji, M. H., *Marine Alga Chemistry*. Academic Press, Beijing, 1997.

9. Jin, J. and Lin, M. J., *The Application and Processing of Marine Alga*. Academic Press, Beijing, 1993.

10. Ross, H., Fathi, Z. and Kiggans, J. O. Jr., Low-density silicon nitride beads as high-temperature microwave furnace insulation. *MRS Bull.*, 1997, **32**(6), 749–754.

11. Baskaran, S., Maupin, G. D. and Graff, G. L., Freeform fabrication of ceramics. *Am. Ceram. Soc. Bull.*, 1998, **July**, 53–58.