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Gelcasting of a rutile mixture applied to extrusion forming

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Abstract

To improve sintering and forming behaviors, many additives are normally included in the rutile powder during extrusion forming. Hence, this complex rutile mixture is difficult to be dispersed into an aqueous solution of acrylamide monomers for gelcasting. In this work, with the aid of a dispersant, the mixture is easy to be dispersed by calcining at high temperature and then ball-milling, and a concentrated rutile suspension with low viscosity was successfully obtained. The suspension can be used to form in-situ a ceramic green body. After sintering the green body, the microstructure and performance of the product are both improved. For example, breakdown strength improved from 12.6 kV/mm to more than 23.6 kV/mm. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Breakdown strength; Calcination; Extrusion; Gelcasting; TiO_2; Rutile

1. Introduction

Gelcasting is a near-net-shape method combining physical chemistry for polymer, colloidal chemistry and ceramic technology.[1,2] The main steps[3–5] of gelcasting are as follows: First, the ceramic powder (e.g. alumina or silicon nitride) together with small quantities of gel initiators, catalyst, monomers, crosslinker, and sintering aids is thoroughly mixed to form the homogeneous suspension with high solid volume loading and low viscosity. Second, Gelation is initiated after the suspension is cast into a non-pore mold and the temperature elevated. Thus the three-dimension network structure resulting from this in situ polymerization holds the ceramic particles together. Finally, After unmolded and dried the green body possesses high homogeneity and high strength, and after sintered such bodies have good mechanical property.[6,7] As a promising colloidal in-situ forming technique, it has been highly concerned and utilized in the forming of many sorts of ceramic material systems.[8–10]

Rutile possess an excellent mechanical and electrical performance, a high dielectric constant, a low loss angle and a large breakdown strength. It is an important material especially applied as a high power capacitor. It has been widely used in high frequency appliances, such as broadcast emitters, radar, high frequency welding machines, smelting furnaces etc. For these applications the properties of most concern are dielectric constant, loss angel and breakdown strength.[11,12] Usually, the dielectric constant of rutile ceramic is $60\sim80$ ranging from 0.5 Hz to 5 MHz at room temperature. For rutile ceramic the tangent of loss angle under 1 MHz is about $4\sim5\times10^{-4}$ (testing temperature is 20 ± 5 °C), such low loss angle is benefit to decrease the energy loss of the rutile ceramic under high frequency. Another important property of dielectric materials is the ability to withstand large field strengths without electrical breakdown. According to the national standard of the People's Republic of China, the breakdown strength of the rutile ceramic applied under DC field should be above 10 kV/mm.

In the past decades, rutile capacitors with complex shapes and large sizes were mainly made by extrusion forming and subsequent machining.[13] However, the whole procedure is too long (about 2 and a half months), and the machining of dried green bodies will result in a great deal of pollution and waste of raw materials. It is difficult to produce rutile capacitors with a large size, complex shape or containing numerous additives in the raw materials by using the traditional process. To overcome these disadvantages, the present authors developed a new route based on gelcasting,[14] by

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which the production cycle can be decreased to three weeks, and the dust caused by machining can be eliminated. Therefore, both production costs and the pollution can be reduced greatly, while the functional property can be improved greatly, especially the breakdown strength.

2. Experimental

2.1. Materials

The composition of the rutile mixture applied to extrusion forming is shown in Table 1. The commercial rutile powder and additives (Coke-oven Plant of Shanghai, China) are of industrial purity. The particle sizes of additives are about micrometer grade. The reagents that are used in this paper are as follows.

Solvent: deionized water with conductivity of 1.02 μS cm^{-1}.

Monomer: acrylamide (AM) produced by Mitsui Toatsu Chemical Inc., Japan.

Crosslinker: methylenebisacrylamide (MBAM) produced by Hongxing Biological and Chemical Factory of Beijing, China.

Initiator: $(NH_4)_2S_2O_8$ produced by Beijing Third Reagent Works, China.

Catalyst: *N*,*N*,*N*′,*N*′-tetraethylmethylenediamine (TEMED) produced by Xingfu Fine Chemical Institute.

Dispersants: a poly (methacrylic acid)-ammonium ($PMAA\text{-}NH_4$) solution produced by Chemical and Engineering University of Nanjing, China.

2.2. Procedure

The rutile mixture according to Table 1 was calcined for 2 h at 1170 °C and then ballmilled for 50 h, obtaining the calcined rutile mixture with d_{50} of 2 micrometer. The gelcasting process of the rutile mixture is described in Fig. 1. First, the calcined rutile mixture was dispersed into a premix solution, which has been prepared by dissolving AM and MBAM in deionized water. With the aid of a dispersant, the concentrated slurry with low viscosity was gained after balling for 24 h. The slurry was then degassed in the vacuum for 7 min after the initiator and catalyst were added. All the above steps were operated at room temperature. Afterwards, the slurry was cast into a steel mold which has been heated in an oven at 70 °C. After Coagulation, the demolded green bodies were dried, debindered and sintered.

Table 1
Composition of the rutile mixture (wt.%)

Main starting materials	Additives				
TiO_2	CaF_2	H_2WO_4	$BaCO_3$	ZnO	Bentonite
100	2	2	1	1	5

2.3. Testing methods

The partile size distributions were measured by BI-XDC particle size analyzer (Brookhaven Instrument Corp., USA). Zeta potentials were measured by Zeta-Plus (Brookhaven Instrument Corp., USA). With 0.5% solid volume loading the tested powder was dispersed into the deionized water respectively, and the adjustment of pH was achieved by addition of HCl or NaOH. Apparent viscosity of suspension was measured by a viscometer (MCR-300 mode, Physica Corporation, Germany). During the measurement the concentric cylinder (gap size is 1.13 mm) was used, and the shear rate increased from 0.1 to 100 1/s at 25 °C. The calcined rutile mixtures were examined by an X-rays diffraction instrument (D/MAX IIIB mode, Rigaku Corporation, Japan). The green body and sintered body were observed by S-450 scanning electric microscope (SEM) from Hitachi of Japan. Disk-shape green bodies of Φ30 mm×2 mm were prepared for electrical properties measurements. Silver slurry was pasted on the two main sides of the sintered compacts to form electrodes. The dielectric properties of these samples were measured at 1 MHz under room temperature, and the breakdown strength was measuring in silicon oil by applying a DC field between the two opposite electrodes.

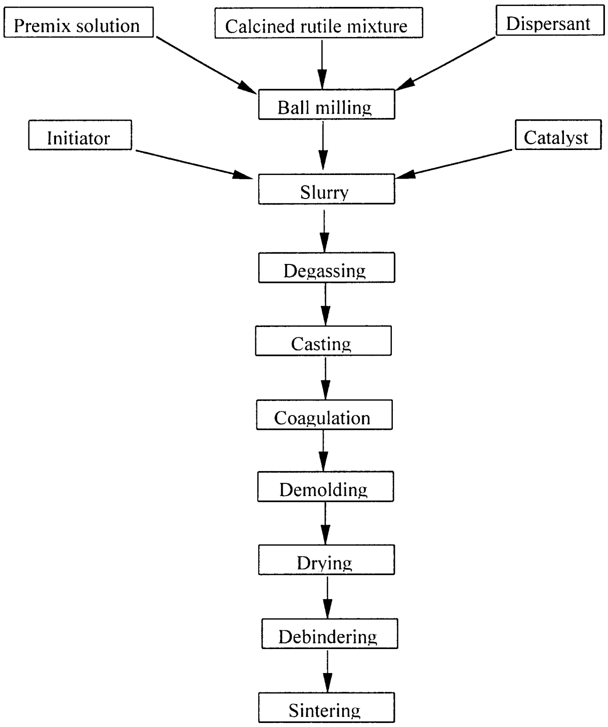

Fig. 1. The flow chart of gelcasting of calcined rutile mixture.

3. Results and discussion

3.1. The influence of sintering additives on the flow behavior

Generally, many kinds of additives are added to the rutile powder, such as $BaCO_3$, ZnO, CaF_2, H_2WO_4, and bentonite, to improve the sintering behaviors and the electro-properties. Bentonite, usually an extrusion aid, can also lower the sintering temperature, so it was considered as a sintering aid in our experiment. At relatively lower temperature, fusible phase resulted from $BaCO_3$, ZnO and CaF_2 maybe come into being, causing the decrease of sintering temperature. H_2WO_4 can lead to fine crystal grain of rutile, hence it will play a roll of increasing the dielectric properties of rutile.

Since zeta potential of all these components are greatly different, it is difficult to disperse all these powders suitable for gelcasting. Rutile powder containing each kind of aid (5 wt.% of rutile) in Table 1 was dispersed into deionized water respectively. To Keep definite solid volume loading, the added quantity of the deionize water was decided by means of content of different sintered aid and its density. H_2WO_4 particle is difficult to disperse into basic medium due to its acidity, while the concentrated rutile suspension expects to be prepared in basic condition. According to Fig. 2, $BaCO_3$, ZnO and CaF_2 have a slight influence on the viscosity of the rutile suspension, while bentonite has a relatively large influence. From the viscosity measurement, concentrated suspension of pure rutile shows a pronounced shear-thinning behaviour,[15,16] which is similar to pure alumina gelcasting slip. However, according to Fig. 3, the rheological characteristics of rutile mixture slip prove to be shear thickening due to the existence of bentonite, and the more bentonite is contained, the more obviously the viscosity changes. When absorbing water, bentonite particles dilate up to thirty times,[17] changing the volume fraction greatly, which results in the increment of slurry viscosity and the shear thickening phenomenon. Since the viscosity of the slurry with 5 wt.% of bentonite is too large (about 6 Pa s), the slurry is not suitable for gelcasting.

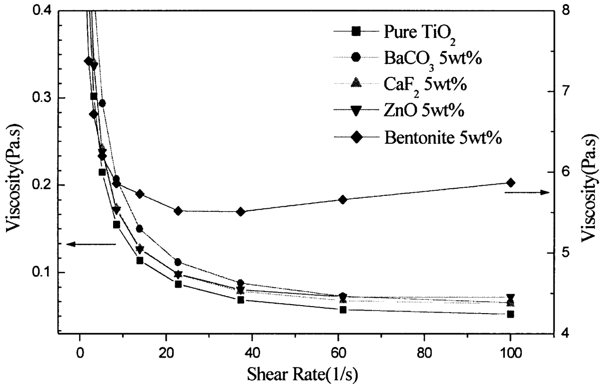

Fig. 2. Influence of the sintering additives on rutile flow behaviour.

3.2. Calcining of the rutile mixture

In general, calcining can remove volatile impurities, chemicals bonded water, physical-absorbed water and improves the purity of the raw materials.[18] Furthermore, it can also help to form stable crystal phases and densify particles, which results in improved properties of the ceramic part.

In our experiment, the rutile mixture was calcined at high temperature and subsequently ball-milled for fifty hours. Through the XRD pattern (as shown in Fig. 4), there are some other peaks besides rutile peaks for the mixture calcined at 900 °C.[1] Compared to the XRD pattern for the un-milled mixture, more complex peaks, which do not represent rutile, are found in that for

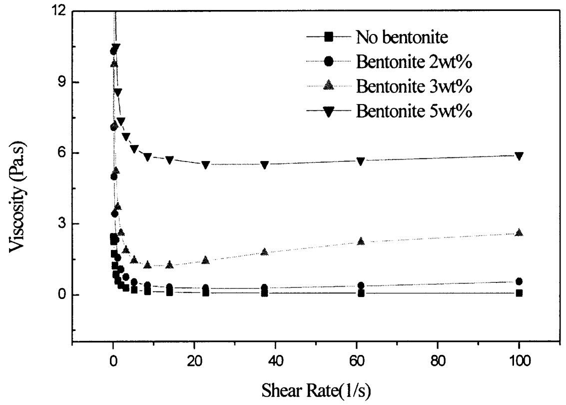

Fig. 3. Influence of the addition of bentonite on rutile flow behaviour.

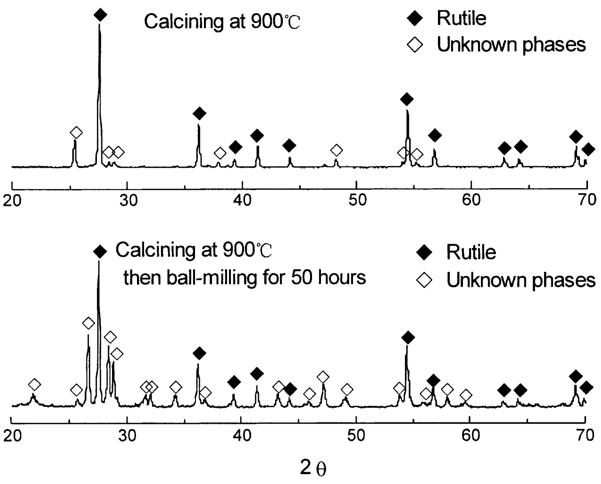

Fig. 4. XRD pattern of the rutile mixture calcined at 900 °C.

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[1] To observe the diffraction peak obviously, the ratio of rutile to sum of additives is changed to 1:1.

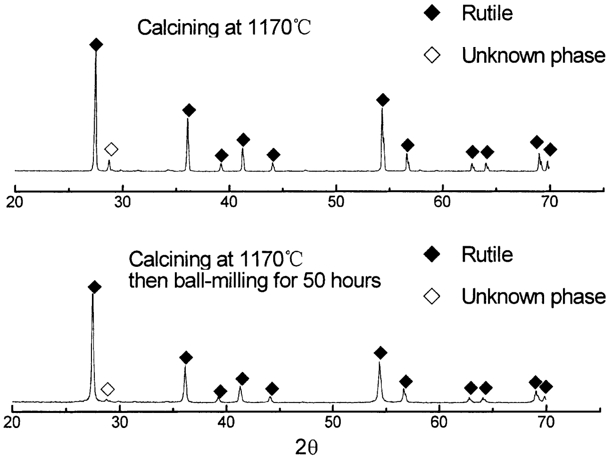

Fig. 5. XRD pattern of the rutile mixture calcined at 1170 °C.

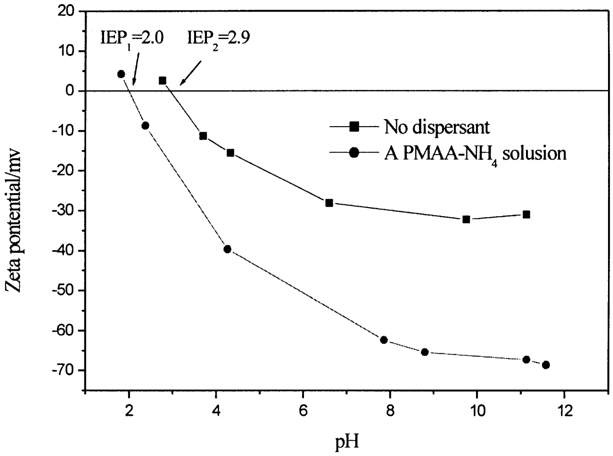

Fig. 6. Relationship between zeta potential and pH value.

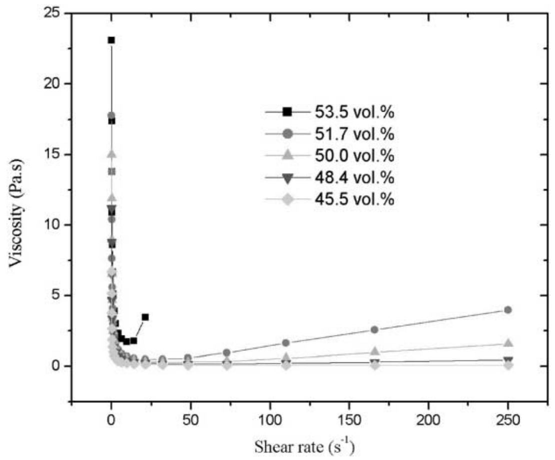

Fig. 7. Rheological behavior of rutile suspension at different solids loading.

ball-milled. This case means that new phases come into being during the ball-milling procedure. However, almost no other peaks besides rutile are found in the XRD pattern for the rutile mixture calcined at 1170 °C (as shown in Fig. 5); even after ball-milling, other peaks do not appear. Therefore, a conclusion can be drawn that when calcined at 1170 °C, phases in the mixture will be unified even after ball-milling. In summery, when calcined at 1170 °C, the additives can form fusible phase unobservable by X-rays; hence the harm influence of H_2WO_4 and bentonite mentioned above can be removed, the interaction between the rutile mixture and water can also be avoided. Therefore, the suitable suspension for gelcasting can be obtained easily.

3.3. The rheological behaviour of the calcined rutile mixture

Fig. 6 shows relationship between Zeta potential and pH value of rutile mixture calcined at 1170 °C. When a dispersant (a PMAA-NH4 solution) is added, Zeta potential of rutile mixture is greatly improved. The dispersant results in the change of the particle surface charge as well as electrochemical double layer at the solid/liquid face because of its adsorption at the particle interface. The negative groups on the polymer chain make the zeta potential more negative, imparting stability to the particles against flocculation. The adsorption obviously decreases the elecrtrophoretic mobility, shifts IEP (isoelectric point) of system to low pH values and improves the absolute value of Zeta potential.[19,20]

Fig. 7 includes curves for rheological behavior of the rutile mixture calcined at 1170 °C at different solid loading. The figure indicates that the viscosity of the slurry increases gently with increase in solid loading, and the slurries are of shear-thinning and subsequently shear-thickening. When its solid loading is more than 52%, the slurry changes from shear-thinning to shear-thickening very fast, and its lowest viscosity is higher than 1 Pa s, hence the slurry does not fit gelcasting. While the solid loading is less than 52%, it is applicable for gelcasting for the relatively low viscosity (shear rate <80 S^{-1}).

3.4. Gelcasting of the calcined rutile mixture

Fig. 8 is a micrography of the green bodies cast from the slurry of the rutile mixture calcined at 1170 °C with 51.7 vol.% solid loading. It can be seen that the monomer has been polymerized efficiently, and the homogeneous microstructure can be achieved. Fig. 9 indicates that all close pores in the rutile parts are removed, which result in good microstructure after sintering. The functional properties were measured respectively, which is listed in Table 2. Among these parameters, the breakdown strength is increased largely from original 12.6 kV/mm to more than 23.6 kV/mm.

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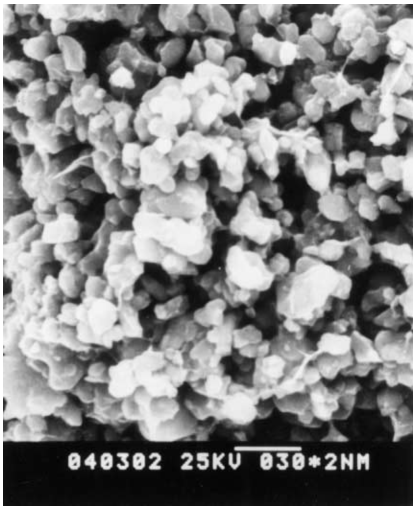

Fig. 8. Micrography of the green bodies gelcasted from the slurry of rutile mixture.

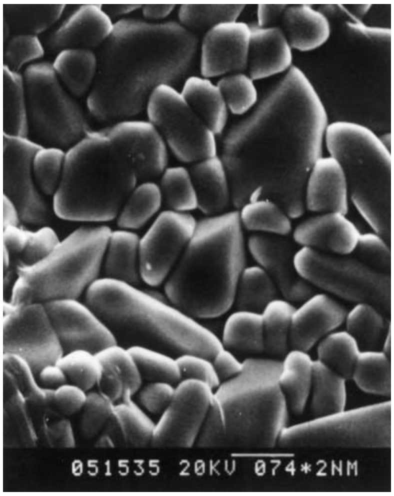

Fig. 9. The microstructure of the parts produced by gelcasting.

Table 2
Properties of the rutile sintered body by gelcasting

Tested sample	ε_1	$tg\delta_1$			EnP (kV/mm)	EnP (kV/mm)[a]
		20±2 °C	85±2 °C	H_2O		
1	81.9	0.5	0.3	0.3	25.0	13.2
2	80.9	0.4	0.2	0.2	22.0	12.7
3	81.1	0.4	0.2	0.2	22.5	13.2
4	80.3	0.3	0.1	0.3	22.6	12.9
5	80.2	0.4	0.2	0.4	22.7	11.3
6	80.9	0.6	0.4	0.5	25.0	12.2
7	81.0	0.4	0.2	0.5	24.6	14.1
8	80.8	0.4	0.2	0.4	23.6	11.7
9	81.7	0.4	0.2	0.5	22.7	12.3
10	80.6	0.5	0.3	0.5	25.2	12.2
Average value	80.9	0.4	0.2	0.4	23.6	12.6

[a] The breakdown strength of the rutile sintered body by extrusion forming.

colloidal processing.[21,22] During the gelcasting processing, aggregates of powders could be removed in a well dispersed suspension and homogeneous green bodies can be obtained from the suspension by enough degassing,[23] hence the microstructure of gelcast parts after sintering is homogeneous. It is well known that the dielectric breakdown phenomenon of dielectrics is structure-sensitive, and breakdown strength values vary widely according to the characteristics of the microstructure of dielectric materials.[24] By gelcasting, since the microstructure of the sintered bodies of ruitle mixture can be improved, the breakdown can be improved greatly.

4. Conclusions

The high power rutile capacitor can be prepared by extrusion forming, mixing many sorts of sintering aids and processing aid. Among these aids, $BaCO_3$, ZnO and CaF_2 have a slight influence on the viscosity of the rutile suspension, while beonnite and H_2WO_4 have notable influence. Particularly, the more bentonite, the more increment of viscosity is shown in the mixture. The rutile mixture applied to extrusion forming is calcined at 1170 °C, the fusible phase could come into being, so the harm influence of beonnite and H_2WO_4 mentioned above can be removed; the interaction between the rutile mixture and water can also be avoid. Hence, the suitable suspension for gelcasting can be botained easily. With the aid of the dispersant, a PMAAN solution, a concentrated rutile suspension of 51.7 vol.% with low viscosity (about 0.40 Pa s) is successfully prepared. By the measure of calcining, the complex rutile mixture applied to extrusion forming is suitable for gelcasting; the good microstructure and the properties can be achieved. For example, breakdown strength is improved from original 12.6 kV/mm to more than 23.6 kV/mm.

Acknowledgements

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References

1. Omatete, O. O., Janney, M. A. and Sterklow, R. A., Gelcasting—a new ceramic forming process. *Ceram. Bull.*, 1991, **70**(10), 1641–1649.
2. Young, A. C., Omatete, O. O., Janney, M. A. and Strehlow, A., Gelcasting of alumina. *J. Am. Ceram. Soc.*, 1991, **74**(31), 612–618.

3. Janney, M. A. and Omatete, O. O., Method for molding ceramic powders using a water-based gelcasting. US Patent 5028362, 1991-98.
4. Janney, M. A. and Omatete, O. O., Method for molding ceramic powders using a water-based gelcatsing. US Patent 5145908, 1992-97.
5. Janney, M. A., Method for forming ceramic powders into complex shapes. US Patent 4894194, 1990,1–16.
6. Bossel, C., Dutta, J., Houiet, R., Hilgorn, J. and Hofmann, H., Processing of nano-scaled silicon powders to prepare slip cast structural ceramics. *Mater. Sci. Eng.*, 1995, **A204**(1–2), 107–112.
7. Huang, Y., Ma, L. G., Tang, Q., Yang, J. L. and Xie, Z. P., Surface oxidation to improve water-based gelcasting of silicon nitride. *J. Mater. Sci.*, 2000, **35**(14), 3519–3524.
8. Nunn, S. D. and Kirby, G. H., Green machining of gelcast ceramic materials. *Ceram. Eng. Sci. Proc.*, 1996, **17**(3), 209–213.
9. Sun, L., Gao, L., Guo, J. K. and Yan, D. S., Gelcasting of nanosize Y-TZP. *Acta Mater.*, 1996, **9**(6), 489–492.
10. Waesche, B. and Steinborn, G., Influence of slip viscosity on the mechanical properties of high purity alumina made by gelcasting, *Key. Eng. Mater.*, 1997, **132**–**136**(1), 374–377.
11. Li, B. R., Wang, X. Z. and Zhang, X. L., *Inorganic Dielectric*. Science and Technology University of Huazhong Press, China, pp. 50–56.
12. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. John Wiley & Sons, USA, pp. 913–931.
13. Yang, J. L., Xie, Z. P., Ma, J. C., Huang, Y., Zhao, J. S. and Fan, Q. S., Study on gelcasting processing of high power rutile capacitor. *Key Eng. Mater.*, 1999, **161–163**, 517–520.
14. Ma, L. G., Huang, Y. and Yang, J. L. *et al.*, Improving the breadown strength of rutile capacitor by gelcasting. *J. Mater. Sci. Lett.*, 2001, **20**(14), 1285–1288.
15. Mikulášek, P., Wakeman, R. J. and Marchant, J. Q., Crossflow microfiltration of shear-thinning aqueous titanium dioxide dispersions. *Chem. Eng. J.*, 1998, **69**(1), 53–61.
16. Mikulášek, P., Wakeman, R. J. and Marchant, J. Q., The influence of pH and temperature on the rheology and stability of aqueous titanium dioxide dispersions. *Chem. Eng. J.*, 1997, **67**(2), 97–102.
17. Du, H. Q. and Tang, S. Q., *Ceramic Material and Recipe*. Light Industry Press, 1986.
18. Liu, K. S., *Principle of Ceramic Technology*. Science and Technology University of Huanan Press, 1990.
19. Strauss, H., Heegh, H. and Sreienitz, I., Effect of PAA adsorption on stability and rheology of TiO_2 dispersion. *Chem. Eng. Sci.*, 1993, **48**(2), 323–332.
20. Chen, X. B., Cheng, H. M. and Ma, J. M., A study on the stability and rheological behavior of concentrated TiO_2 dispersions. *Powder Technol.*, 1998, **99**(2), 171–176.
21. Lange, F. F., Powder processing science and technology for increased reliability. *J. Am. Ceram. Soc.*, 1989, **72**(1), 3–15.
22. Pugh, R. J. and Bergström, L. eds. *Surface and Colloid Chemistry in Advanced Ceramics Processing*. Marcel Dekker, New York, 1994.
23. Zhou, L. J., Huang, Y. and Xie, Z. P., Gelcasting of concentrated silicon carbide suspension. *J. Eur. Ceram. Soc.*, 2000, **20**, 85–90.
24. Yamashita, K., Koumoto, K., Takata, M. and Yanagida, H.,