Fabrication of Fiber Reinforced Porous Ceramic Composite Setter Produced by Organic Flocculating Method and Its Thermal Shock Behavior

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有機沈殿法による繊維強化多孔質セラミック複合セッターの作製とその熱衝撃挙動

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Fiber reinforced ceramic composite setter was produced by Organic Flocculating Method. Its mechanical and thermal properties were studied. Air-quenching method, combined with theoretical analysis of thermal shock behavior, was employed to determine the bending strength drop of the composite setter and the critical temperature of composite setter with different fiber contents after thermal shock. Results from air-quenching method show that the drop of bending strength after suffered thermal shock becomes severe with increasing fiber content in the composite setter. Phase transformation to cristobalite within 200–300°C temperature range was accompanied by abnormal thermal expansion and it is considered to contribute to the low thermal shock resistance of composite setters with high fiber content.

[Received July 19, 2002; Accepted November 6, 2002]

Key-words: Fiber reinforced ceramic composite, Porous, Air-quenching, Thermal shock, Thermal expansion, Fiber damage

1. Introduction

Glass ceramic substrates have attracted more and more attention recently, not only because they can be made much smoother and flatter and but also because they can be sintered at lower temperature than traditional alumina substrate. To sinter these glass ceramic substrates it is extremely important for the organic binder, which is contained in the greensheet and will be burnt into gaseous substances with temperature getting higher, to be released efficiently in a very short time during sintering process, otherwise it will cause surface bending or color change of glass ceramic substrates and thus degrade their qualities.^{1)–3)} This requires the load-bearing subplate upon which the glass substrates are sintered having relatively favorable gas-permeability, which is often represented by high porosity or low apparent density. The stacking pattern of glass substrate during sintering process is illustrated in Fig. 1. In addition, the composite setter with high temperature thermal shock resis-

tance is also desirable to ensure the quality of the glass substrate since the setter is subjected to abruptly cooling and heating thermal conditions during the sintering process. Therefore, it requires that the setter has both high porosity and high thermal shock resistance.

Compared to the monolithic ceramics, fiber reinforced (FR) ceramic composite has been reported to have the potential for improved thermal shock resistance because of its superior properties, including high fracture toughness and associated high strain of failure.^{4),5)} In the traditional FR ceramic composite fabrication process, fiber and powder are usually mixed by ball milling method to prepare the preform body and then sintered by the means of hot press. This traditional method is best for producing compacted ceramic composites but not suitable for preparing the composite with high gas-permeability. Recently sol-gel method has also been applied to fabricate the preform body. Although this method, also, has been proved being the best way so far, its application to porous composite is still under investigation. One problem, however, is that the cost of sol-gel method is very high and thus its practical application is greatly restricted. In this research, organic flocculating method (for short, OFM) was developed to produce porous ceramic composite consisting of ceramic fiber and powder.¹⁾ Its details will be given in the Experimental section. The apparent density of FR composite prepared by OFM can be controlled within $0.6 \sim 1.5 \times 10^3 \text{ kg/m}^3$. This method has successfully been employed to fabricate the composites with various levels of porosity. Because of the novel and distinctive fabricating process, the thermal shock behavior of FR porous ceramic composite setter produced from OFM will inevitably have features far different from the traditional FR compacted ceramic composite. The thermal shock behavior, particularly, the effect of fiber content on the thermal shock behavior is mainly investigated at the present stage. The theoretical evaluation based on the work of Hasselman⁶⁾ and

Fig. 1. Stacking pattern of glass ceramic substrate during sintering process.

experimental method, i.e. air-quenching method, are jointly employed to evaluate the thermal shock behavior of FR porous ceramic composite setter produced by OFM.

2. Experimental

2.1 Preparation of the composite body by OFM

Organic flocculating method (OFM) involves dispersing a mixture of ceramic fiber and oxide powders in a media of water, adding a polymer reagent to improve the flocculation and obtain a stable suspension, draining and filtering this suspension by vacuum into a preform, and then desiccating and sintering it to get the final product. Its procedure diagram is illustrated in Fig. 2. In this research, five composite setters (S-1, 2, 3, 4, 5) with different fiber content (15%, 20%, 25%, 30%, 50%) were fabricated by using OFM and used as test materials for thermal shock examination. The detailed process is as follows; α - Al_2O_3 powder (particle size less than $7\ \mu\text{m}$) and ceramic fiber (average diameter $3\ \mu\text{m}$) were dispersed and coagulated in the water. This fiber is made by air-blowing process²⁾ and consists of 47 mass% Al_2O_3 and 53 mass% SiO_2 . The fiber is amorphous originally and is crystallized into mullite around 1000°C . Silica sol (ST-40) with 40 mass% SiO_2 was added to promote agglomeration between powder and fiber after firing. A kind of starch³⁾ acting as a polymer flocculation binder is also added into the slurry. The composition ratio and the amount of individual constituents are listed in Table 1. This mixture was drained and filtered by vacuum absorbing pipe, as illustrated in Fig. 2. The final forming process was implemented by an oil pressure apparatus and a plate precursor with dimensions of $148 \times 148 \times 21\ \text{mm}$. This precursor after desiccated at 100°C for 12 h was then sintered at 1350°C for 3 h. The specimens of composite setter used for the thermal shock test were cut from the sintered as-products into the dimension $40 \times 130 \times 5.5\ \text{mm}$. The crystal phases of the composite setter with different fiber content after sintered at 1350°C were identified by X-ray diffraction (XRD) (Rigaku, RINT2000) using $\text{Cu K}\alpha$ radiation.

Fig. 2. Schematic diagram OFM procedure.

Table 1. Composition Ratio

	Fiber(g)	Alumina (g)	
S-1 (15% fiber)	67.5	360	Silica sol: 56.3(g) Silica content: 22.5g
S-2 (20% fiber)	90	337.5	
S-3 (35% fiber)	112.5	315	Polymer flocculation binder: 787.5g
S-4 (40% fiber)	135	292.5	
S-5 (50% fiber)	225	202.5	

2.2 Properties of ceramic composite setter

The room temperature three-point bending strength σ was measured under the condition that loading span was 100 mm with a crosshead speed of 1.5 mm/min. The Young's modulus E was calculated from the experiential function

$$E = (P/\delta) \times (l/t)^3/4w$$

P/δ : The slope of the stress-strain recording curve.

w, l, t : The width, loading span and thickness of the specimen, respectively.

The thermal expansion coefficient α of the sample with the dimensions of $14.62 \times \phi 5\ \text{mm}$ was measured at the heating rate of $5.0^\circ\text{C}/\text{min}$ (temperature range from 25°C to 1400°C). The hot-wire method was used to measure the thermal conductivity κ of the porous composite. To meet the height requirement from the hot-wire method in this study, we produced samples with dimensions of $148 \times 148 \times 50\ \text{mm}$ while keeping the apparent density same with the one with dimensions of $148 \times 148 \times 21\ \text{mm}$.

2.3 Theoretical evaluation and experimental test of thermal shock behavior

In this research, the following Hasselman's thermal shock resistance equations were employed to evaluate thermal shock behavior of composite setter theoretically.

$$R' = \frac{\sigma_f(1-\nu)}{E\alpha} \quad (1)$$

$$R'' = \frac{E}{\sigma_f^2(1-\nu)} \quad (2)$$

σ_f : The failure stress, E : Young's modulus,

ν : Poisson's ratio, α : Coefficient of thermal expansion

R' in Eq. (1) is equal to the critical temperature difference for initiation of crack propagation that ceramics can sustain after suffered thermal shock. R'' here represents the minimum elastic energy at fracture available for crack propagation, in other words, the resistance against strength reduction due to crack propagation after thermal stress exceeds the failure stress of ceramics. The R' and R'' values of setters were both calculated here. In addition, an air-quenching technique was jointly employed to evaluate the thermal shock behavior of samples. The reason that air-quenching method is selected rather than water-quenching lies in the high porosity in the composite setter. As for the experimental procedure, the heated specimens were quenched to room temperature in the air just after they were kept in a furnace at different temperatures (300°C , 450°C , 550°C , 700°C , respectively) for 30 min. To ensure the cooling conditions, compulsory air convection was introduced by fan. This heating-cooling operation was repeated by 3, 7, 10 times for each sample at each temperature point. Because it was difficult to observe the crack propagation on the surface of composite at high temperature, the thermal shock damage of composite was evaluated by the residual three-point bending strength measured after the sample suffered thermal shock. All the fracture surfaces of samples were analyzed by SEM (JEOL, JSM-T300) observation.

3. Results and discussion

3.1 X-ray diffraction

The X-ray diffraction patterns of composite setters with different fiber content in Fig. 3 shows that the diffraction peaks of mullite become stronger with the increase of the fiber content while the corundum peak shows an opposite tendency. It also can be seen here that the diffraction peak of cristobalite shows an increasing trend with the increase of fiber content. This change suggests that the cristobalite is

Fig. 3. XRD patterns of composite setter with five different fiber contents.

primarily crystallized from the glass phase contained in the ceramic fiber instead of being crystallized from the silica sol, otherwise no change in diffraction peak would be detected as the silica sol was added by the same amount in all five samples.

3.2 Mechanical and thermal properties of composite setters

3.2.1 Mechanical property

Table 2 shows the mechanical properties of five samples with different fiber content. It is seen here the bending strength σ and Young's modulus E are increased with the increase of fiber content. These results demonstrate that the fiber should play a role in enhancing bending strength of composite setter produced by OFM.

As traditional setters based on Al_2O_3 , ZrO_2 or mullite are mainly produced from the powder sintering process, thus they are highly compacted and have relatively high apparent density¹⁾ ($2\sim 5 \times 10^3 \text{ kg/m}^3$). However, the apparent densities of setter with different fiber content produced by OFM are approximately $1.00 \times 10^3 \text{ kg/m}^3$, much lower than those of traditional ones, as showed in Table 2.

3.2.2 Thermal conductivity

As a multiphase material, the resulting thermal conductivity of ceramic porous composite setter is supposed to be influenced by the presences of both dispersed phase i.e. ceramic fiber here and pore phase.⁷⁾⁻⁹⁾ A linearly proportional relationship was reported to exist between the bulk density and porosity for the composite setter.^{1),3)} Thus we assumed that there is no apparent difference in porosity among these samples because the bulk densities of five composite setters listed in Table 2 are approximately equal. The comparisons of resultant conductivity of composite setter were mainly focused on the variation of fiber content. Figure 4 shows that the thermal conductivity decreases with an increase in fiber content, reaching its lowest value with a fiber content of 50%. These results are in good agreement with the result estimated by the following Maxwell-Eucken equation,⁷⁾ in which the resultant conductivity decreases with the increase of volume percent of disperse phase v_d

$$k_m \cong k_c [(1 - v_d)] / [(1 + v_d)] = \frac{-2k_c v_d}{1 + \omega_d} + k_c \quad (3)$$

where k_c and k_d represent the conductivity of continuous phase and dispersed phase, respectively.

3.2.3 Thermal expansion

The linear thermal expansion curves of composite with different fiber contents are illustrated in Fig. 5. The distin-

Table 2. Mechanical Properties of Composite Setters

Sample (Fiber) content)	σ /MPa	E /GPa	ρ /g/cm ³
S-1 (15%)	7.44	8.88	1.04
S-2 (20%)	7.69	8.89	0.96
S-3 (25%)	7.93	8.93	0.96
S-4 (30%)	8.93	9.64	0.96
S-5 (50%)	12.15	11.77	1.00

Fig. 4. Thermal conductivity of composite setters as a function of fiber content.

Fig. 5. Thermal expansion of composite setters with five different fiber contents as a function of temperature.

guishing features of these curves are the abnormal thermal expansion occurring in the temperature range from 200°C to 300°C, which corresponds well to the $\alpha \leftrightarrow \beta$ phase transformation of cristobalite. This abnormal expansion becomes greater with the increase of fiber content, as shown in the enlarged figure top-left. High thermal expansion generally is not favorable for resistance to thermal shock. Because the cristobalite here is crystallized from the glass phase contained in the ceramic fiber, we would infer that the presence of glass phase in fiber is probably detrimental to the thermal shock behavior of composite setter.

3.3 Analysis of thermal shock behavior

3.3.1 Theoretical discussion of thermal shock behavior

The theoretical values of R' and R'' calculated by Hasselman's equations are shown in Fig. 6. The left side shows R' , which represents the ability to resist crack generation in the composite setter and is referred to the theoretical critical temperature difference (ΔT). It is seen from Fig. 6 that the value of R' decreases slightly with the increase of fiber content. The right side shows R'' , which represents the ability for composite setter to resist the drop of bending strength due to crack propagation. It shows that the ability to resist crack propagation falls quickly with the increase of fiber content and the composite setter with 50% fiber content has the lowest value. Thus a high fiber content composite setter theoretically tends to have inferior thermal shock resistance.

3.3.2 Experimental evaluation of thermal shock behavior

The dependences of residual bending strength of composite setters on air-quenching temperature after suffered thermal shock are shown in Fig. 7, and the dependences on fiber content at different thermal shock cycles in Fig. 8.

Figure 7 shows the drop of bending strength becomes much more distinct with the increase of fiber content. There exists a critical air-quenching temperature at which the residual bending strength shows a sudden drop as shown Fig. 7. The critical temperature in this experiment is approximately 550°C for four samples except the case of the composite setter with 50% fiber content. This sample was fractured after only the third thermal shock cycle at 550°C. Below this temperature the composite setter showed no ob-

vious strength change, even though they were subjected to up to 13 thermal shock cycles, as illustrated in Fig. 8.

Both experimental and theoretical results demonstrated that the composite setter with high fiber content had poor thermal shock behavior, though higher fiber content in composite setter led to higher bending strength, which has been discussed in Sec. 3.2.1

3.3.3 Fracture analysis of composite setter

To investigate the fracture mechanism of composite setter, the fracture surfaces of sample with 50% fiber content were observed by SEM. Figure 9(a) shows that the fracture surface of composite setter is naturally broken due to thermal stress after being air-quenched at 550°C, and that the

Fig. 7. Dependence of residual bending strength of composite setters on air-quenching temperature.

Fig. 6. Relationship between thermal shock resistance R' , R'' and fiber content of composite setter.

Fig. 8. Bending strength change of composite setter after being quenched from 300°C.

Fig. 9. SEM micrograph of a fracture surface of 50% fiber contained composite setter after being air-quenched from 550°C (a) and a fracture surface of the composite setter from the measurement of three-point bending strength at room temperature (b).

fracture surface mainly consists of cross sections of fibers. This indicates that the composite setter fractured in the form of fiber damage after thermal shock and that the fiber in the composite setter body is fragile to thermal stress. Figure 9(b) shows the fracture surface of the composite setter with 50% fiber content under mechanical stress in the three-point bending strength measurement at room temperature, without any thermal shock introduced. The damage caused by mechanical stress is also observed being fractured in the form of fiber damage. The data listed in Table 2 show that the composite setter with higher fiber content has much higher bending strength. This indicates that the ceramic fiber does have superior mechanical properties and actually plays a reinforcing role on strength before thermal shock introduced. Therefore it is significant to discuss what happened to the fiber before and after thermal shock.

The result in Fig. 5 has showed that the abnormal thermal expansion due to $\alpha \leftrightarrow \beta$ phase transformation of cristobalite, which occurred in the temperature range 200–300°C becomes greater with increase of fiber content. High thermal expansion is generally considered to be unfavorable for improvement of thermal shock resistance. This abnormal thermal expansion may contribute to account for the poor thermal shock behavior of composite setter with high fiber content. The composite setter with higher fiber content will suffer more severe thermal shock in the heating-cooling process because the more thermal stress is supposed to be developed due to the greater amount of cristobalite crystallized in the temperature range 200–300°C. It should be very significant to conduct a further study to investigate the effect of presence of cristobalite on thermal shock behavior by refraining the glass phase contained in the ceramic fiber from crystallizing into cristobalite.

4. Summary

Fiber reinforced ceramic composite setter was produced by OFM. Its mechanical and thermal properties were studied. Air-quenching method, combined with theoretical analysis of thermal shock behavior of composite setter produced by OFM, was employed to determine the bending strength drop of the composite setter and the critical temperature of composite setter with different fiber contents after thermal shock.

(1) Ceramic fiber in composite body plays a great role in improving bending strength of composite setter.

(2) The change of thermal conductivity of composite setter as function of fiber content is in agreement with the

estimation from Maxwell-Eucken equation.

(3) Abnormal thermal expansion of composite setter occurred during 200–300°C temperature range. It corresponds to the $\alpha \leftrightarrow \beta$ cristobalite phase transition. This abnormal expansion is considered to have direct impact on the thermal shock behavior of composite setter after suffered thermal shock.

(4) The theoretical analysis based on Hasselman's equations show that composite setter with high fiber content tends to have inferior thermal shock property.

(5) The results from air-quenching method show that the critical air quenching temperature is approximately 550°C. The drop of bending strength after suffered thermal shock becomes much severe with the increase of fiber content.

(6) The composite setter with higher fiber content will suffer from more intensive thermal shock in the heating-cooling process because the more thermal stress is supposed to be developed due to the greater abnormal thermal expansion happening in the 200–300°C temperature range.

Acknowledgement The author would like to acknowledge Prof. Yasuhiro Tanabe at Center for Materials Design, Materials and Structures Laboratory, Tokyo Institute of Technology, Steven Shiffman at the University of Missouri-Rolla (USA) and Tadashi Ootsuka at the Research & Development Laboratory of Isolite Insulating Products Co., Ltd. for their fruitful advice and cooperation.

References

- 1) Fukino, Y. H., *Electroheat*, Vol. 101, pp. 1–9 (1998) [in Japanese].
- 2) Fukino, Y. H., Kokai-Tokkyo-Koho, 208318 (1997) [in Japanese].
- 3) Fukino, Y. H., Kokai-Tokkyo-Koho, 227246 (1997) [in Japanese].
- 4) Wang, H. Y. and Singh, R. N., *Ceram. Eng. Sci. Proc.*, Vol. 15, pp. 292–302 (1994).
- 5) Singh, R. N. and Wang, H. Y., *Ceram. Eng. Sci. Proc.*, Vol. 16, pp. 699–707 (1995).
- 6) Hasselman, D. P. H., *Am. Ceram. Soc. Bull.*, Vol. 49, pp. 1033–1037 (1970).
- 7) Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., "Introduction to Ceramics," John Wiley & Sons, New York (1975) pp. 634–637 (ISBN 0-471-47860-1).
- 8) Kagawa, Y. and Hatta, H., "Tailoring Ceramic Composite," AGNE Shofusha (1990) p. 18, (ISBN 4-900508-15-2) [in Japanese].
- 9) Am. Ceram. Soc., *Ceramic Source'86*, Annual Source Book, Vol. 1 (1996).