

Heat-resistant ceramics based on LAS-system non-metallic mineral and its thermal shock resistance

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$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) system-based ceramics have been prepared with petalite and kaolin and their thermal shock resistances investigated. Feed slurries in five combinations of petalite and kaolin composition between 40% and 60% were first prepared with 5, 15 and 35 μm fractions of petalite and slip casted into moulds. Then the casts were subjected to 2-stage sintering: in the first stage, at 850°C for 2 h and in the second stage, at 1200, 1250 and 1300°C for 2 h. Heating rate was 3°C per minute. The characteristics of sintering, microstructure, X-ray diffraction pattern and water absorption rate of the LAS ceramics produced were studied. Their thermal shock resistances were also measured by a directly flame contact method. Petalite was transformed into β -eucryptite and β -spodumene at temperatures higher than 1200°C. The LAS ceramics were found to have the highest thermal shock resistance at 1250°C. Even at the reduced addition of 45% petalite, the more the particle size of petalite increase, the better is thermal shock resistance of the LAS system ceramics.

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1. Introduction

Ceramic materials are excellent materials with infinite potentials due to more stabilized high-temperature properties than metallic or high-molecular materials. One of the most common applications related to high-temperature properties is for thermal shock cycling between high temperature and low temperature. Under the condition of this kind of rotation, thermal shock resistance of ceramics becomes an important factor. Especially silicate minerals containing lithium has good thermal stability, so they are widely used in fabricating a variety of ceramic materials. Petalite, in particular, has a chemical formula of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-8\text{SiO}_2$, and because of its superior thermal shock resistance, it is used an important raw material for heat-resistant ceramic products.

Hummel reported that natural petalite and spodumene have extremely low thermal expansion at 1250°C, and subsequent studies have revealed that the properties of low thermal expansion are resulted from (–) thermal expansion by β -eucryptite ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$) and (+) thermal expansion by β -spodumene ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$).^{1)–5)} Also, the research by Lee et al. shows that as SiO_2 is added to LAS ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$)-system materials, β -eucryptite is changed to β -spodumene, and high (–) thermal expansion of β -eucryptite is changed to a large amount of β -spodumene with low (+) thermal expansion so as to make thermal expansion rate close to zero.^{1)–6)}

This is attributed to thermo-chemical behavior properties of petalite, and that is when it is heated at 1093°C or higher, irreversible crystallographic inversion to β -spodumene ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$) and amorphous silica occurs within solid solution, and this crystalline phase is characterized of (+) thermal expansion.⁷⁾ However, petalite has little viscosity, so it is very difficult to apply a common slip casting. In this study, petalite, a LAS-system material with strong heat resistance, was fabricated to

have a variety of particle sizes and after adding a certain amount of kaolin with excellent viscosity and which makes slip casting easy, thermal shock resistance by particle sizes of petalite and the amount of added kaolin was examined and compared.⁸⁾

2. Experimental procedure

The result of chemical composition of samples by X-ray fluorescence spectrometer (XRF-1700, Shimadzu Co.) in Table 1, and Fig. 1 shows particle size distribution of petalite and kaolin as starting materials.

Table 1. Chemical Composition of Samples by XRF (mass%)

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Li_2O	Na ₂ O	K ₂ O	L.O.I.
Petalite	76.16	17.24	0.18	0.21	0.24	4.49	0.16	0.39	0.80
Kaolin	43.73	38.05	1.01	0.01	0.27	–	0.22	0.58	16.03

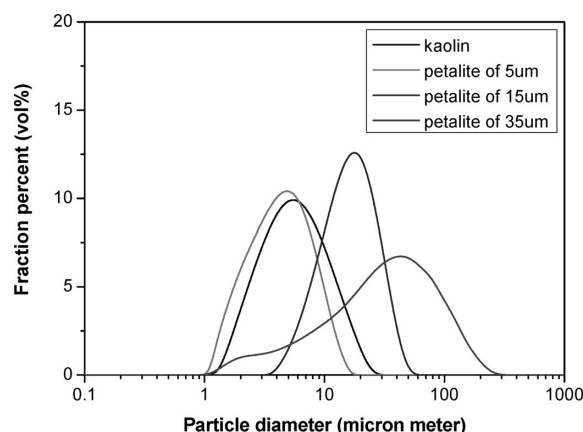


Fig. 1. Particle size distribution of kaolin and petalite powders.

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Petalite and kaolin were used as main materials of heat-resistant ceramic foundation and after dividing the mean particle sizes of petalite into 5 μm , 15 μm , and 35 μm by an air classification, foundations for slip casting were fabricated with different mixing ratios with kaolin, which are shown in **Table 2**. One of clay minerals with excellent viscosity, kaolin, was used to increase the moldability of the foundation and it was used as a source to supply SiO_2 needed to change petalite to β -eucryptite or β -spodumene at high temperature.

Figure 2 shows a flow chart of procedures to fabricate a heat-resistant ceramic foundation and samples by a slip casting method for a thermal shock experiment. For an additive, sodium silicate which is frequently used in slip casting was used as a dispersing agent. The samples molded with different compositions and different particle sizes by using slip casting were heated to 850°C at the rate of 3°C/min and after being maintained for 2 h,

Table 2. Composition of Samples with Different Mean Sizes of Petalite Powder

Samples	Mean size of petalite (μm)	Composition (mass%)	
		Content of petalite	Content of kaolin
S-1	5	40	60
S-2		45	55
S-3		50	50
S-4		55	45
S-5		60	40
M-1	15	40	60
M-2		45	55
M-3		50	50
M-4		55	45
M-5		60	40
L-1	35	40	60
L-2		45	55
L-3		50	50
L-4		55	45
L-5		60	40

it was naturally cooled down in a furnace. The natural cooling rate was approximately 1°C/min. Like this, the samples from the first round were heated again at the rate of 3°C/min up to 1200°C, 1250°C, and 1300°C and then naturally cooled down to the room temperature to fabricate the second round of samples.

So far, the uniform heating test and the heat resistance test with water-quenching have been applied to evaluate heat resistance such as Japanese Industrial Standard (JIS) R1618, JIS R1676 and S2400. However, these methods cannot realize a heat resistance test with simulation of an actual temperature gradient, because the inner temperature distribution of the sample is automatically determined by their shape, material, and test environment only.^{9)–12)}

Thermal shock experiment for heat-resistant ceramics specified in Korean Industrial Standard (KS) L1003 instructs that in the case of direct-heating (high heat-resistance) ceramics, after leaving in thermal chamber pre-heated to have temperature difference (difference between heating temperature and water temperature) up to 350°C for one hour, the samples were inserted into the water at $24 \pm 3^\circ\text{C}$ to cool them to the water temperature and then they were taken out to examine for existence of defects (cracks) in the foundation or glaze.¹³⁾ However, when a sample is inserted in the pre-heated thermal chamber, the temperature on the whole surface of a sample steadily increases, making thermal expansion (or contraction) of the whole surface consistent. Thus, it was decided that this was not appropriate to examine thermal shock resistance that occurs locally on the surface while the temperature was increasing; and in this research, as shown in **Fig. 3**, a direct heating method to heat up the surface of a sample with flame. This method does not heat up the surface of a sample uniformly with large temperature deviation depending on where flame has contact, so thermal expansion (or contraction) of the whole surface becomes very uneven. Therefore, it makes it easy to examine thermal shock resistance that could occur locally on the surface when temperature goes up. After repeating a process of heating up three points of a sample to the average temperature of 390°C and inserting it to the water with room temperature right away for five times, thermal shock resistance was examined.

Absorption rate was calculated in the following process depending on measurements of absorption rate, bulk specific gravity, apparent specific gravity and apparent porosity of KS L4008 ceramics: after a sample is dried in an oven at $110 \pm 5^\circ\text{C}$

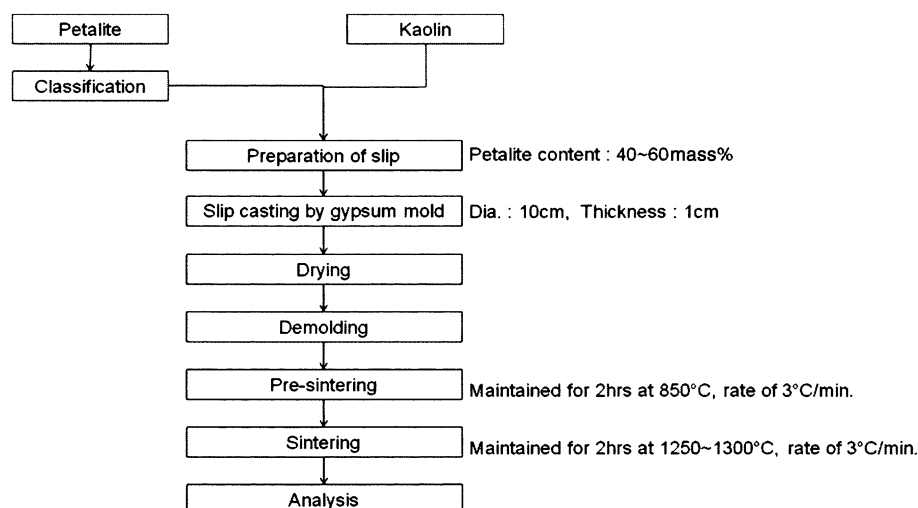


Fig. 2. Flow chart of experimental procedure.

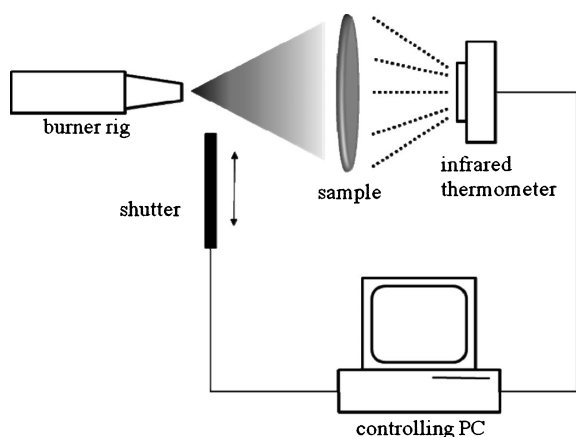


Fig. 3. Schematic diagram of the burner apparatus for thermal shock resistance.

Table 3. Results of Thermal Shock Resistance Test (○: strong, ×: weak)

Temp. (°C)	Samples														
	S (5 μm petalite)					M (15 μm petalite)					L (35 μm petalite)				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
1200	×	×	×	×	○	×	×	×	×	○	×	×	×	○	○
1250	×	×	×	×	○	×	×	○	○	○	×	○	○	○	○
1300	×	×	×	×	○	×	×	×	×	○	×	×	×	×	○

until it is constant, it is cooled down in desiccator and its mass is measured (D). Then, the sample is placed in a container with distilled water and boiled for 5 h and after impregnating it for 24 h, the mass of the sample is measured (M). Moisture absorption rate (A) is calculated with a formula $A = [(M - D)/D] \times 100$.¹⁴⁾

Thermal expansion coefficient of samples was measured by dilatometer (DIL-402C, Netzsch Co., Ltd., Germany).

3. Results and discussion

3.1 Changes in compositions for slip casting

When a foundation for slip casting is fabricated so that the mixing ratio of petalite and kaolin exceeds the range of 40–60 mass% that is shown in Table 2, it is difficult to demold it after slip is poured into a plaster mold and dried because as the content of petalite increases, contraction rate and viscosity drastically decrease; so, the maximum content of petalite was set at less than 60%. Also, since petalite which is performed for LAS material for heat-resistant shock is one of the high-priced minerals, this study aims to examine composition ratios with superior heat resistance and thermal shock resistance while minimizing the use of petalite.

3.2 Thermal shock resistance

When petalite is heated up more than 1000°C, irreversible crystallo-graphic inversion occurs to make it β -spodumene solid solution. Since it has extremely small thermal expansion coefficient, by adding petalite to ceramic products with a problem in thermal shock resistance, it can be improved.

By using slips fabricated with compositions in Table 2, the samples were molded at 1200, 1250 and 1300°C and Table 3 shows the results of thermal shock resistance measured by using the direct heating method. The thermal shock resistance of each

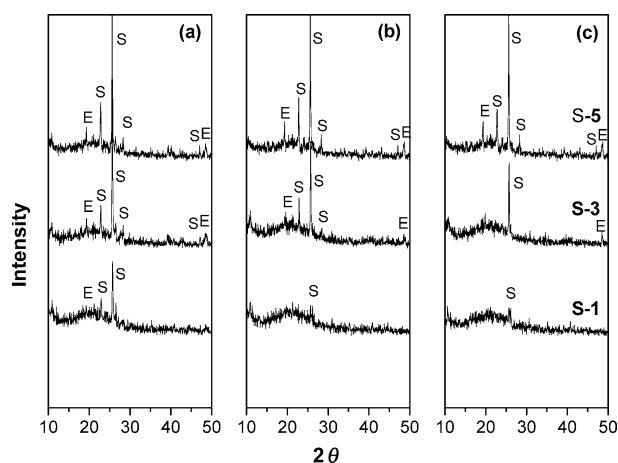


Fig. 4. XRD patterns of S series sample at various sintering temperature; (a) 1200°C, (b) 1250°C, (c) 1300°C.

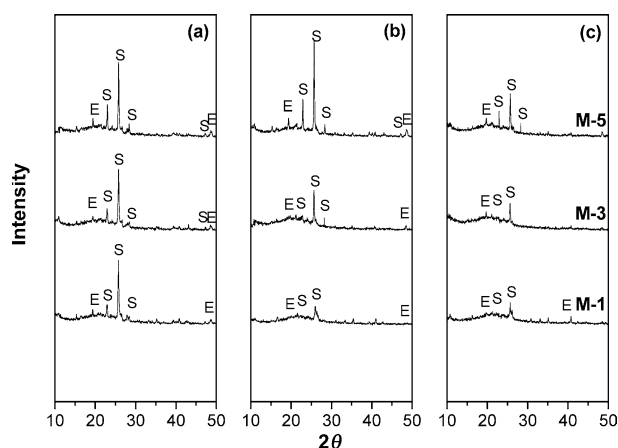


Fig. 5. XRD patterns of M series sample at different sintering temperatures; (a) 1200°C, (b) 1250°C, (c) 1300°C.

sample was repeatedly measured more than 10 times, and the circle means strong thermal shock resistance, which has not any cracks in the sample to be observed by the naked eye. On the contrary, the cross means weak thermal shock resistance, which has more than one crack.

At the sintering temperature of 1200°C, as the particle size of petalite was larger, thermal shock resistance was excellent even with a small amount of petalite. When the sintering temperature was 1250°C, thermal shock resistance was the best when the contents of petalite were 60% in the S sample with the small size of petalite particles; 50% in the M sample with the medium size; and 45% in the L sample with the large size. However, when the sintering temperature was 1300°C and over, the effect of thermal shock temperature was almost non except for the case when the content of petalite was 60%. Therefore, in order to fabricate materials with strong thermal shock resistance, the sintering temperature should be lower than 1300°C.

3.3 X-Ray diffraction patterns

Figure 4, 5 and 6 are the results of sintering the samples – S, M, and L – in Table 2 at 1200, 1250, and 1300°C and crushing them to particle size less than 200 mesh and then analyzing them with XRD (Model D5005 Diffractometer, Bruker, Germany) showing the phase shifts of β -spodumene and β -eucryptite.

However, because main peaks of β -spodumene, β -eucryptite and lithium aluminum silicate group are similar angles, when two minerals are loaded together, it is very difficult to clearly understand a quantitative relationship between the two. However, the peaks that appear around 19°, 23° or 28° can be differentiated to a certain extent, so the peaks at these three angles were focused to analyze XRD patterns.

Figure 4 illustrates the changes of XRD patterns in the S sample with the smallest size of petalite particles by petalite contents and sintering temperatures. As shown in Table 3, the samples of S-1 and S-3 all had cracks, indicating low thermal shock resistance. It was found that compared to β -eucryptite peak around 19°, peak intensity of β -spodumene at 23° was lower than the S-5 sample with great thermal shock resistance, and then peak intensity of β -spodumene at around 28° tends to be relatively higher.

Figure 5 shows the changes of XRD patterns in the M sample with the medium size of petalite particles by petalite contents and sintering temperatures. Similarly with Fig. 4, peak intensity of β -spodumene at 23° was higher than β -eucryptite peak at 19°. It is suggested that the samples, (a) M-5, (b) M-3, (b) M-5, and (c) M-5, with a clear peak of β -spodumene at 28° have strong thermal shock resistance, which agrees with the results in Table 3.

Figure 6 shows the changes of XRD patterns in the L sample with the largest size of petalite particles by petalite contents and sintering temperatures. Same as the results in Fig. 4 and Fig. 5, compared to β -eucryptite peak at around 18°, peak intensity of β -spodumene at 28° was higher; it is suggested that the samples (a) L-3, (a) L-5, (b) L-3, (b) L-5, and (c) L-5 with distinct β -spodumene peak at 23° had the strongest thermal shock resistance. This is same as the results in Table 3 from thermal shock

experiment with a direct heating method. While (a) L-1, (b) L-1 and (c) L-1 have shown distinct β -spodumene peak at 28°, peak intensity of β -eucryptite around 18° and of β -spodumene around 23° were barely observed. From the experimental results in Table 3, it was found that all three samples had weak thermal shock resistance. When all peaks were observed at β -eucryptite peak around 18°, β -spodumene peak around 23°, and β -spodumene peak around 28°, and when β -spodumene peak around 23° has stronger intensity than β -eucryptite peak at 18°, it could be suggested that thermal shock resistance is excellent.

3.4 X-Ray diffraction patterns and thermal shock resistance

When thermal expansions in crystal lattices of β -spodumene and β -eucryptite were compared, it was found that β -spodumene had (+) thermal expansion on the c spiral axis and (−) thermal expansion on a -axis that is at the right angle to c -axis. In the bulk, it eventually has (+) thermal expansion, but thermal expansion coefficient is close to 0. β -eucryptite has the exact opposite pattern to β -spodumene. It is known to have (−) thermal expansion in the end and the absolute value of thermal expansion coefficient is larger than that of β -spodumene.^{7),15)}

Therefore, in the quantitative relationship between β -spodumene and β -eucryptite, only when the amount of β -spodumene is markedly larger than that of β -eucryptite, the total thermal expansion coefficient reaches close to zero. This means that as shown from the analysis of XRD patterns in Fig. 4, 5, and 6, it has a correlation with intensity of the peaks that occur around 18°, 23° and 28°. That is, the analysis results of XRD patterns that peak intensity of β -spodumene is markedly higher than that of β -eucryptite quantitatively indicates that the content of β -spodumene is more than that of β -eucryptite. When β -spodumene peak around 28° is clearly observed, it means that the absolute value of thermal expansion coefficient between the two is close to zero.

3.5 Thermal shock resistance and water absorption rate

The samples were made with the compositions in Table 2 and then sintered at different temperatures and their water absorption rates were measured by using the KS L4008 method (Table 4).¹⁴⁾ The experimental results showed that absorption rate increases, as the content of petalite increases or particle size increases and that it tends to decrease, as the sintering temperature increases. When the sintering temperature is 1200°C, as the content of petalite increases, absorption rate rapidly increases also that when petalite content reaches 60 mass%, absorption rate is about 20 mass%. This suggests that at 1200°C, phase transfer of petalite does not occur sufficiently. Therefore, when absorption rate is considered, the sintering temperature should be higher than 1200°C.

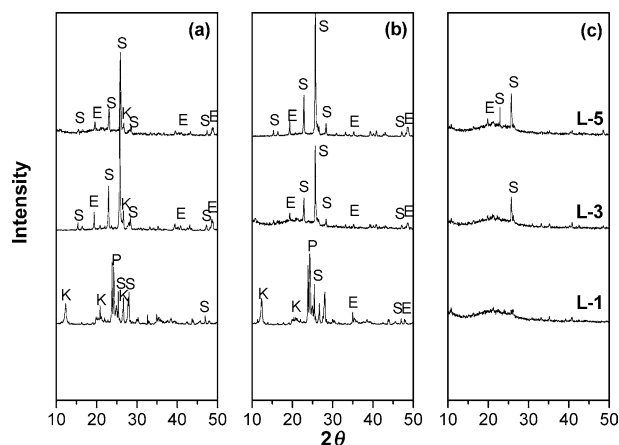


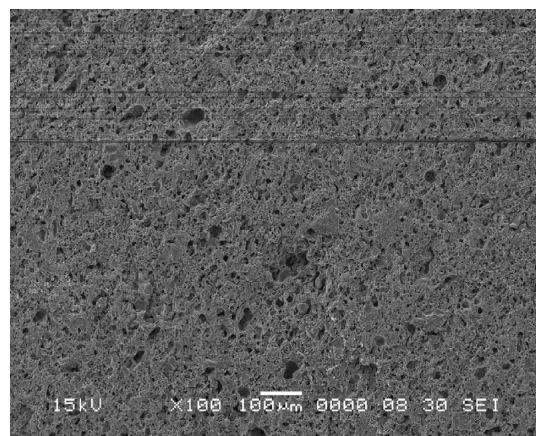
Fig. 6. XRD patterns of L series sample at various sintering temperature; (a) 1200°C, (b) 1250°C, (c) 1300°C.

Table 4. Water Absorption Rate of Samples by the KS L4008 Method (unit: mass%)

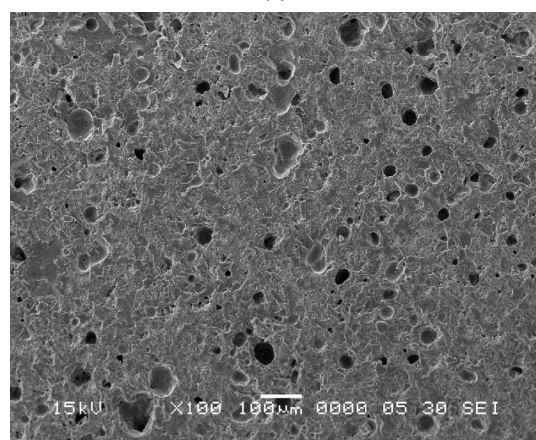
Temp. (°C)	Samples														
	S (5 μ m petalite)					M (15 μ m petalite)					L (35 μ m petalite)				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
1200	0.33	3.76	10.62	13.89	18.82	1.18	7.72	11.78	15.13	19.20	6.82	11.67	16.38	20.21	23.31
1250	0.03	0.04	0.20	1.73	2.02	0.02	0.06	1.12	2.22	2.69	0.02	0.15	1.54	2.32	2.86
1300	0.03	0.04	0.32	0.82	1.01	0.03	0.05	0.09	1.29	1.91	0.04	0.07	0.1	1.35	2.45

By comparing the results of thermal shock resistance experiment in Table 2 and the results of absorption rate experiment in Table 3, appropriate sintering temperatures were drawn. As a result, it was concluded that when thermal shock resistance is high, sintering temperature should be lower than 1300°C and higher than 1200°C, so the optimal sintering temperature should be around 1250°C.

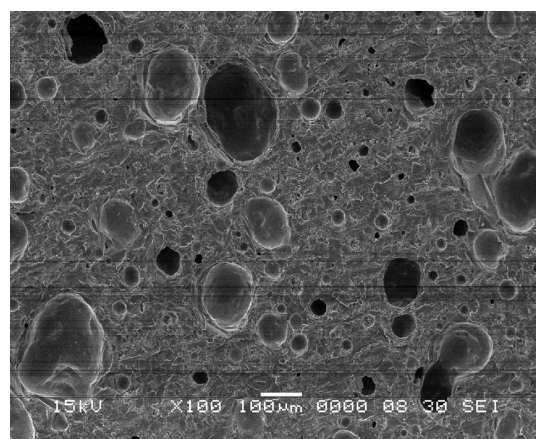
The samples were fabricated by sintering the sample with L-3 composition at 1200°C, 1250°C and 1300°C, and Fig. 7 show SEM (JSM-6390A, JEOL Ltd.) pictures for the honed side of the



(a)



(b)



(c)

Fig. 7. SEM photographs of specimens at different sintered temperatures of L-3 composition; (a) 1200°C, (b) 1250°C, (c) 1300°C.

samples. Figure 7(a) shows a typical eucryptite porous structure which has high porosity and low thoroughness because an excessive amount of liquid phase is formed rather than thorough crystallization due to low sintering temperature.^{16,17)} In Fig. 7(c), the surface appears almost amorphous, and this agrees with the results of XRD analysis on L-3 in Fig. 6(c). Figure 7(b) is the middle stage between Fig. 7(a) and (c), in which because of (+) thermal expansion caused by phase transfer from eucryptite porous structure to β -spodumene, porosity has remarkably decreased compared to Fig. 7(a). Also, when the porosity of sintered sample is high, numerous vacant spaces absorb shock from thermal expansion or contraction, strengthening thermal shock resistance.

3.6 Thermal expansion coefficient

Figure 8 shows the relationship between particle sizes of petalite and coefficients of thermal expansion, and these samples with content of petalite 50 mass% were sintered at 1250°C. Their coefficient of thermal expansion decreased, as the particle size of petalite increasing from 5 μm to 35 μm in Fig. 8. The coefficient was 0.1781×10^{-6} in case of the particle size 35 μm , and it was the lowest value.

4. Conclusions

In this study, starting from petalite and kaolin, LAS-system ceramics were fabricated by using slip casting method, and then the effects of the particle sizes and content ratios of petalite and sintering temperatures on thermal shock resistance was examined and the following conclusions were obtained.

(1) Main peaks on XRD patterns of β -spodumene, β -eucryptite and lithium aluminum silicate group have almost similar 2-theta values, but it was found that by comparing peak intensity of β -eucryptite at 18°, β -spodumene at 23° and β -spodumene at 28°, approximate quantification was possible.

(2) When the content of β -spodumene with the absolute number of (+) thermal expansion coefficient smaller than the absolute number of (−) thermal expansion coefficient of β -eucryptite is large, the total expansion coefficient is closer to zero, increasing thermal shock resistance.

(3) In XRD patterns, when peak intensity of β -spodumene at 23° is markedly higher than that of β -eucryptite at 18°, and β -spodumene peak at 28° is distinctly observed, it means that the content of β -spodumene is larger than β -eucryptite and that the

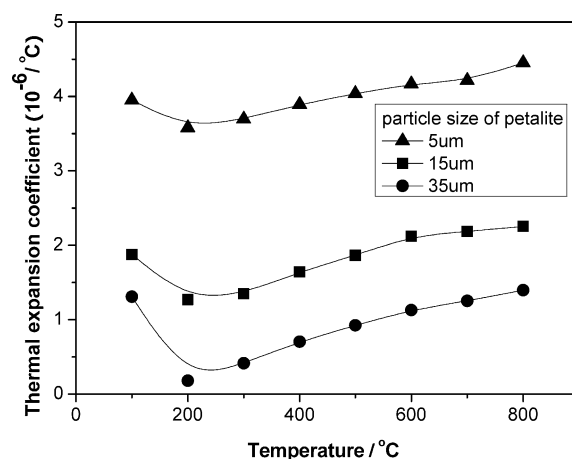


Fig. 8. Change of thermal expansion coefficient at various temperature; petalite content of 50 mass% and sintering temperature of 1250°C.

absolute value of thermal expansion coefficient between the two is close to zero.

(4) Water absorption rate tends to increase as the content of petalite increases or the particle size becomes larger; and, as the sintering temperature increases, water absorption rate tends to decrease.

(5) In order to fabricate LAS-system ceramics with large thermal shock resistance, the most appropriate sintering temperature is 1250°C. Here if the particle size of petalite increases from 5 μm to 35 μm , even though the content of petalite is reduced to 45 mass%, it has good thermal shock resistance. This could be attributed to that in the case of large particles, porosity inside the sintered sample increases and numerous vacant spaces absorb and dissolve shock from thermal expansion and contraction.

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