Microstructural control of porous Al$_2$TiO$_5$ by using various starches as pore-forming agents

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Porous Al$_2$TiO$_5$ ceramics with various starches as pore-forming agents have been prepared by the reactive sintering method using fine-grained starting materials. Commercially available corn, potato and rice starches were used as the pore forming agents. TG–DTA and XRD studies revealed that the rice starch most promoted the formation of Al$_2$TiO$_5$ among the three starches, presumably due to its strong heat flow during the combustion. Al$_2$TiO$_5$ samples sintered with each starch contained a bimodal pore-size distribution, viz., slit-like pores with the size of $<\sim$20 µm, and continuous open-pores with the size of several µm. The thermal expansion behavior of the sample with 30 wt.% rice starch was similar to those without starch.

1. Introduction

Al$_2$TiO$_5$ has an orthorhombic pseudobrookite-type structure, where aluminum and titanium ions are in the center of MO$_6$ ochtahedra.[1] This pseudobrookite-type structure generally has a strong uniaxial anisotropy of thermal expansion, which generates significant microcracks in polycrystalline ceramics. The microcracks help to moderate the thermal expansion at high temperatures.[2),3)] Thanks to this behavior, Al$_2$TiO$_5$ exhibits prominent low thermal expansion and good thermal shock resistance. On the other hand, microcracks are known to deteriorate mechanical properties.[4),5)] Currently, Al$_2$TiO$_5$ is used as a coating material, an oxidation resistant material and an insulating material at high temperatures, due to its low thermal expansion, thermal shock resistance and corrosion resistance.

To date, porous Al$_2$TiO$_5$ is applied for third-generation diesel particulate filters (DPF).[6)–8)] To control the pore-size distribution in porous materials, pore-forming agents are often added to starting powders. Starches are often selected as the pore-forming agent with low environmental impact.[9),10)] They burn out at temperatures much lower (at around 300–500°C) than the sintering temperatures of most ceramics.

Hongzhi et al.[11)] reported the synthesis of porous Al$_2$TiO$_5$ ceramics by reactive sintering at 1400–1500°C using Al$_2$O$_3$ (10–30 µm) and TiO$_2$ (2–10 µm) powders with corn starch (5–20 µm) as a pore-forming agent. They reported that the sintered products had a bimodal-pore structure with the diameter of 50–200 and 2–6 µm, however, the detail of pore-structure characterization was not given in detail.

Recently, we have reported reactively-sintered porous Al$_2$TiO$_5$ ceramics by using potato starch as a pore-forming agent.[12)] In our previous report, α-Al$_2$O$_3$ and TiO$_2$ (rutile) mixed powders were prepared at first, and then, potato starch (ca. 5–80 µm) was blended to the mixed powder by using in an agate mortar. Although the porosity was partially controlled by the starch

addition, the final pore-size was too large (ca. 5–80 µm) as a structural material.

In this study, we prepared porous Al$_2$TiO$_5$ ceramics with corn, potato and rice starch as a pore-forming agent by the reactive sintering using fine-grained starting materials. The effect of starch addition was systematically investigated. It was possible to obtain finer and more homogeneous porous structure by modifying the experimental procedure.

2. Experimental procedure

2.1 Sample processing

As pore-forming agents, commercially available corn starch (Wako Pure Chemical Industries Ltd., Osaka, Japan), potato starch (Wako Pure Chemical Industries Ltd.) and rice starch (Sigma-Aldrich Japan LLC, Tokyo) powders were used.

As starting materials, α-Al$_2$O$_3$ powder (0.1 µm, 99.99% purity, TM-D, Taimei Chemical Co. Ltd., Nagano, Japan) and TiO$_2$ rutile powder (2 µm, 99.9% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) were used. The TiO$_2$ rutile phase is favored due to its less volumetric shrinkage after reactive sintering, although the TiO$_2$ anatase phase has higher reactivity with Al$_2$O$_3$.

The Al$_2$O$_3$ and the TiO$_2$ rutile powders (Al:Ti = 2:1 in mole fraction) were wet-ball milled with 0–35 wt.% of each starch in ethanol for 2 h in a planetary ball-mill (acceleration: 4 g). Y-doped ZrO$_2$ balls were used as grinding media. In our previous study,[12)] the starches were blended after the ball-milling of Al$_2$O$_3$ and TiO$_2$ powders, however, in this study, the starches were added to the wet-ball milling from the beginning. The mixed slurry was dried, and then dry-ball milled for 2 h in a poly-ethylene bottle with Y-doped ZrO$_2$ balls. The obtained mixed powders were sieved through a 100-mesh screen ($<$150 µm). To obtain bulk porous Al$_2$TiO$_5$, the mixed powder was uniaxially mold-pressed at 11.3 MPa. Starch-added pellet samples ($\sim$1 g, $\sim$15 mm in diameter and $\sim$3 mm in thickness) were sintered at 1300–1400°C for 2 h in air. Samples without starch were also sintered at 1300–1500°C for 2 h. The heating ramp rate was 300°C/h. It is worth noting that no additives such as Fe$_2$O$_3$ or SiO$_2$ were added as a dopant, in order to obtain purer Al$_2$TiO$_5$.

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For the thermomechanical analysis (TMA) and the bending test, rectangular bar samples were also prepared by the same method except the shape and dimension. A metallic mold with the rectangular hole size of 6×60 mm was used. The sintered samples were machined to the dimensions of approximately $3 \times 4 \times 15$ mm (TMA) and $3 \times 4 \times 40$ mm (bending test).

2.2 Evaluation

The thermal decomposition behavior of starches was analyzed by thermogravimetry-differential thermal analysis (TG–DTA, DTG-50H, Shimadzu Co., Kyoto, Japan). The constituent phases of the bulk materials were analyzed by X-ray diffractometry (XRD, Multiflex, Cu-Kα, 40 kV and 40 mA, Rigaku, Tokyo, Japan). Bulk density of sintered pellets was measured from dimension and mass. The microstructure of porous Al₂TiO₅ was characterized using scanning electron microscopy (SEM; JSM-6500F, JEOL, Japan). Fractured surface of the pellet samples (parallel to the uniaxial mold-pressing direction) was observed. Bulk thermal expansion was evaluated by thermomechanical analysis (TMA, Thermo plus EVO II, Rigaku). The direction of TMA measurement was perpendicular to the uniaxial mold-pressing direction.

Flexural strength was measured by the three-point bending test (AG-I 20 kNT, Shimadzu Co.), using a span length of 30 mm and crosshead speed of 0.5 mm/min (JIS-R1601).

3. Results and discussion

3.1 Microstructure and TG–DTA analyses of starches

Figure 1 shows scanning electron microscope images of the different starch morphologies. Grain size of corn, potato and rice starches were approximately 2–20, 5–80 and 2–50 μm, respectively. The corn starch consisted of relatively uniform grains, while the potato starch had a broad grain-size distribution, and the rice starch had an intermediate grain-size distribution.

Figure 2 shows TG–DTA curves of (a) corn, (b) potato and (c) rice starches at the heating rate of 5°C/min. The TG–DTA results

clearly showed that the decomposition of each starch completed at ∼500°C. The heat flow of rice starch had a very strong exothermic peak around 500°C, which increased the local temperature and resulted in the loop curves of TG–DTA [Fig. 2(c)]. Even at reduced heating rate (2.5°C/min), the TG curve still showed a loop at ∼300°C [Fig. 2(d)]. These results suggest the peculiarity in calorific value for the rice starch among the three.

3.2 Constituent phases and density

Figure 3 shows the XRD patterns of Al₂TiO₅ samples with and without starch additions sintered at 1300°C. From Fig. 3(a), corn starch addition clearly promoted Al₂TiO₅ formation; the more corn starch added, the more Al₂TiO₅ phase formed. On the other hand, Fig. 3(b) shows that 10–20 wt.% potato starch addition suppressed Al₂TiO₅ formation. The addition of 30 wt.% potato starch promoted the Al₂TiO₅ formation, compared to 0 wt.% addition. These complicated results can be explained by the following assumption. With the 10–20 wt.% potato starch
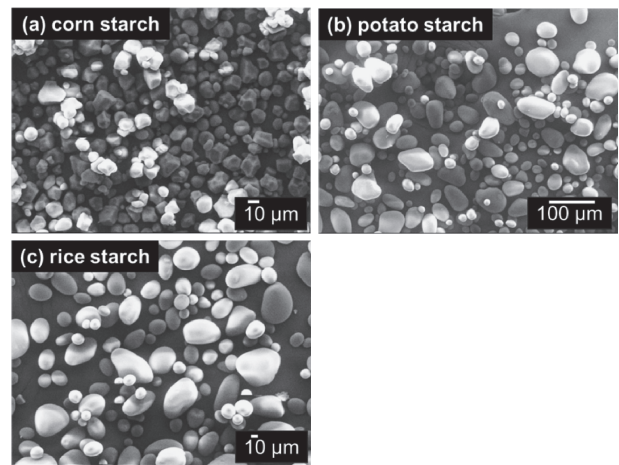

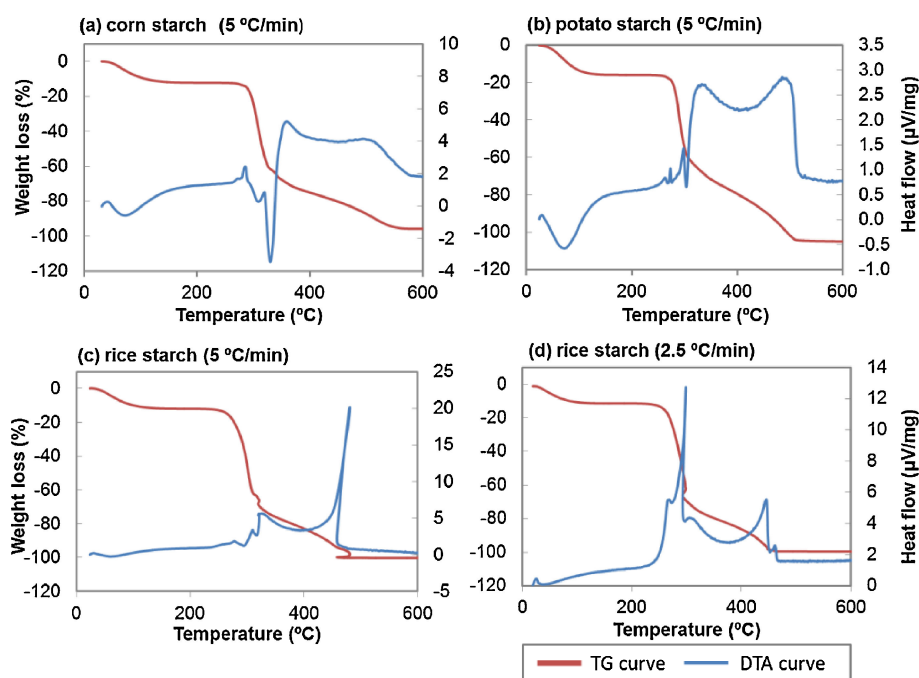Fig. 1. SEM images of (a) corn starch, (b) potato starch, and (c) rice starch.

Fig. 2. TG–DTA curves of (a) corn starch, (b) potato starch, (c) rice starch (5°C/min) and (d) rice starch (2.5°C/min).
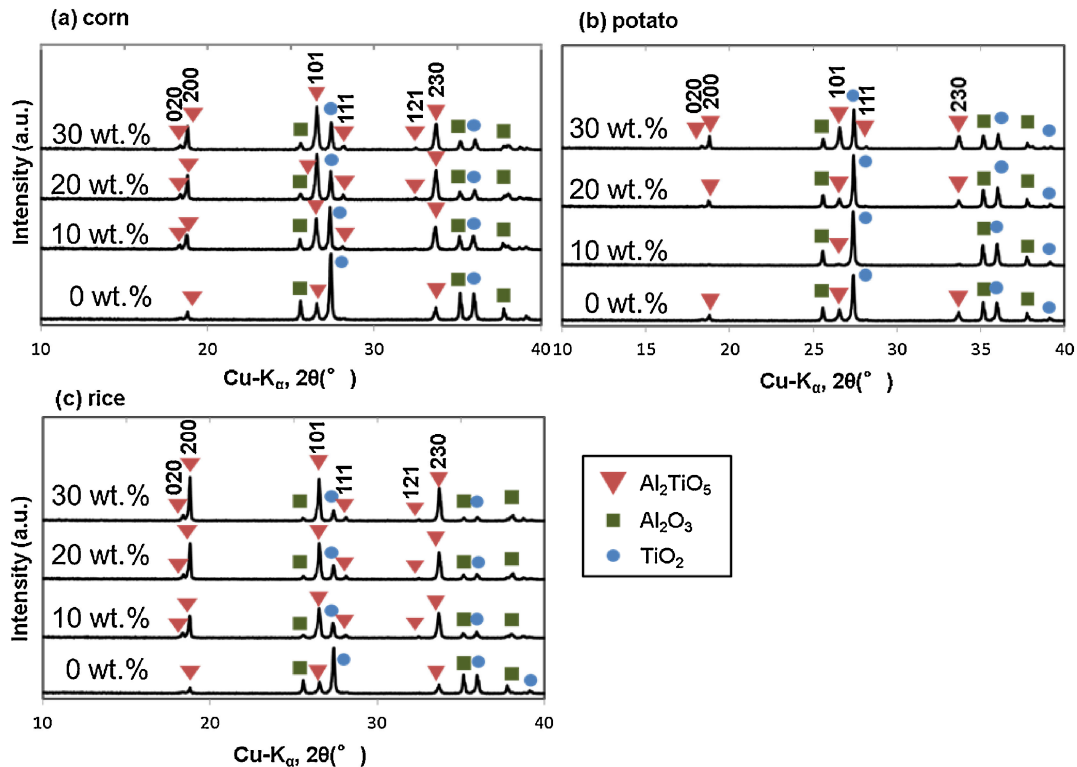
Fig. 3. XRD patterns of Al_2TiO_5 samples sintered at 1300°C with (a) corn starch, (b) potato starch, and (c) rice starch.

addition, the large grain size of potato starch inhibited the contact of Al_2O_3 and TiO_2 grains. On the other hand, with the 30 wt.% potato starch addition, the heat from the combustion might assist the solid state reaction between Al_2O_3 and TiO_2. Among the three pore-forming agent, rice starch had the most prominent effect on promoting the Al_2TiO_5 formation [Fig. 3(c)]. Although the combustion temperatures of starches are far less from the sintering temperature, the strong heat flow of rice starch [as shown in Fig. 2(c)] should promote the Al_2TiO_5 formation. In our previous paper,[12] starch mixing was mildly done after the ball-milling of Al_2O_3 and TiO_2. For that case, Al_2TiO_5 phase formation was observed for the sample with 10 wt.% potato starch sintered at 1300°C, which is different from the current study. The difference between previous and current studies indirectly suggests the change of dispersion state of starch particles.

Figure 4 shows bulk density of porous Al_2TiO_5 samples sintered at 1300 and 1400°C with different amount of starch addition. The bulk density decreased with increasing the starch content. The samples sintered with >30 wt.% potato starch, ≥35 wt.% corn starch, and ≥35 wt.% rice starch easily pulverized, probably due to the insufficient neck growth. The difference in the sample-shape instability for each starch (i.e., ~30 or ~35 wt.%) can be explained by the different particle-size distribution as shown in Fig. 1. The bulk densities of samples sintered at 1300°C were generally higher than those at 1400°C, as reported in previous works.[12]–[14] This is due to samples sintered at 1300°C containing more un-reacted Al_2O_3 and TiO_2 than those sintered at 1400°C (in particular with 10 wt.% starches). The theoretical density of Al_2TiO_5 ($d = 3.69\,g/cm^3$) was less than those of α-Al_2O_3 ($d = 3.99\,g/cm^3$) and TiO_2 rutile ($d = 4.25\,g/cm^3$).

For 1300°C samples, when comparing the density decreasing behavior with increasing the starch content, density decrease was steeper in the order of potato > corn ~ rice. This order is in good agreement with the XRD analysis in Fig. 3 (i.e., existence of
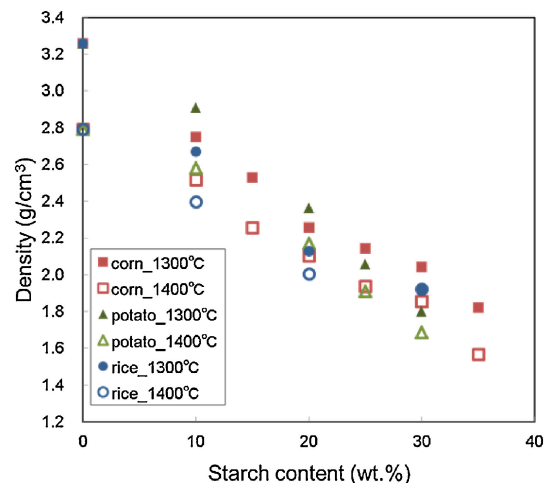

Fig. 4. Bulk density of porous Al_2TiO_5 samples sintered at 1300 and 1400°C with different amount of starch addition.

un-reacted Al_2O_3 and TiO_2). For 1400°C samples (with sufficient Al_2TiO_5 formation), density decreasing behavior was almost parallel for three samples, except the 25–30 wt.% potato starch addition. This exception can be attributable to the large initial particle size of the potato starch, resulting in the larger pores as described in the next section.

3.3 Microstructure

Microstructure of Al_2TiO_5 samples sintered without the addition of starch is shown in **Fig. 5**. Samples sintered at 1300 and 1400°C had a fine and homogeneous microstructure with some microcracks. Sample sintered at 1300°C contained finer three dimensional continuous pores with the size of <1 μm, whereas
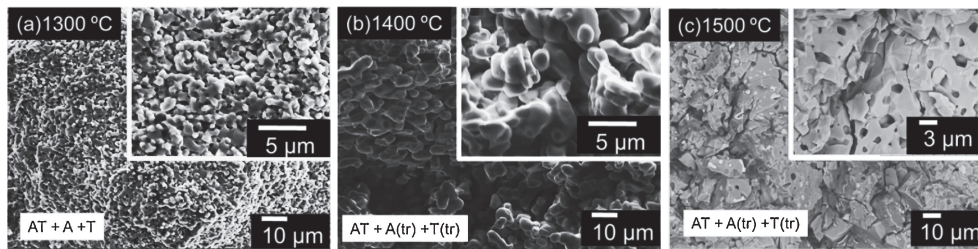
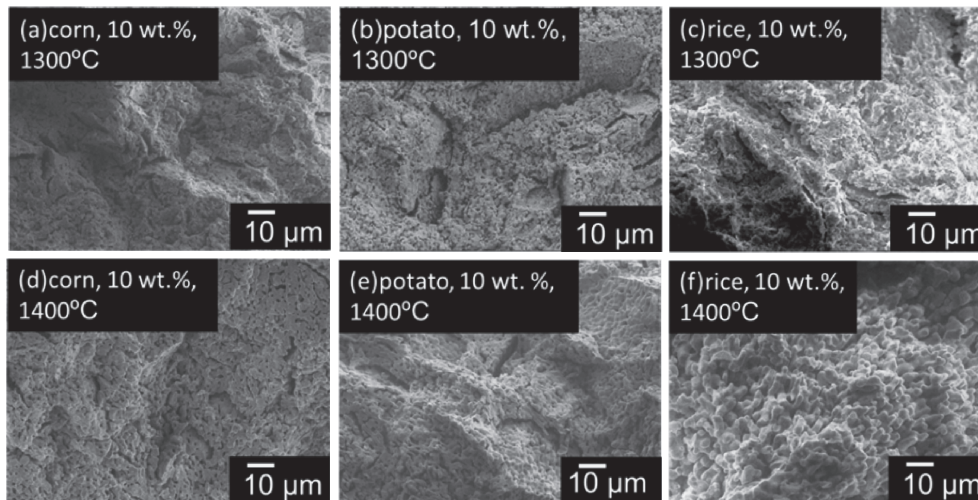Fig. 5.   Microstructure of Al$_2$TiO$_5$ samples sintered without starches.

Fig. 6.   Microstructure of Al$_2$TiO$_5$ samples sintered with (a) corn starch at 1300°C, (b) potato starch at 1300°C, (c) rice starch at 1300°C, (d) corn starch at 1400°C, (e) potato starch at 1400°C, and (f) rice starch at 1400°C.

the sample sintered at 1400°C also contained continuous pores with the size of several μm. The sample at 1500°C contained closed pores of <3 μm in size as well as significant microcracks.

Figure 6 shows the microstructure of Al$_2$TiO$_5$ samples with different starch additions sintered at 1300 and 1400°C. Samples sintered with corn starch [Figs. 6(a) and 6(d)] contained large slit-like pores about <20 μm as well as 3-D continuous open pores. It is thought that crushed finer starches might be agglomerated during mixing and form slit-like pores. Samples sintered with potato starch [Figs. 6(b) and 6(e)] also had slit-like pores and 3-D continuous open pores. However, a larger number of slit-like pores were observed in the potato-starch added samples when compared to the corn-starch added samples.

In both corn- and potato-starch added samples, the number of slit-like pores increased with increasing the starch content (not shown). Samples sintered with rice starch [Figs. 6(c) and 6(f)] also contained some slit-like pores with 3-D continuous open pores. However, the number of slit-like pores was fewer in the rice starch samples than those with corn and potato starches. As can be seen in Figs. 6(c) and 6(f), the rice starch addition formed the largest Al$_2$TiO$_5$ grains, which is explained by the large heat flow observed in Fig. 2(c).

Figure 7 shows an enlargement image of the slit-like pores in the potato-starch added sample. The origin of the slit-like pores might be the compressed agglomerates of starch particles. However, correlation between uniaxial-molding direction and slit direction did not clearly exist, probably due to the relatively low uniaxial pressure during the molding.
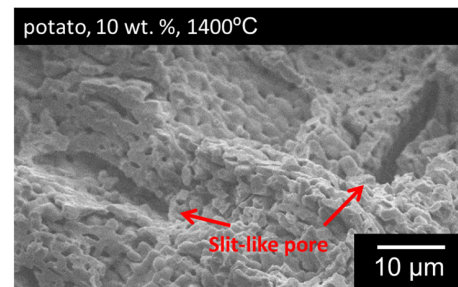

Fig. 7.   Enlarged image of slit-like pores.

3.4   Thermal expansion behavior

Figure 8 shows the thermal expansion of Al$_2$TiO$_5$ samples sintered at 1400°C with each starch addition (a–c) and without starch (d). Figure 8(d) also includes the thermal expansion data for Al$_2$TiO$_5$ sintered at 1300°C without starch. For the sample with corn starch additions [Fig. 8(a)], the thermal expansion increased with increasing the starch content. However, the sample with corn starch additions showed relatively low thermal expansion. For the sample with potato starch [Fig. 8(b)], the thermal expansion behavior was comparable to that of samples with corn starch additions. The lower thermal expansion for the potato starch can be explained by the formation of slit-like pores as shown in Fig. 6(b), which may act like microcracks for pure Al$_2$TiO$_5$. For the rice-starch added samples [Fig. 8(c)], increasing the starch content did not make a noticeable difference in the
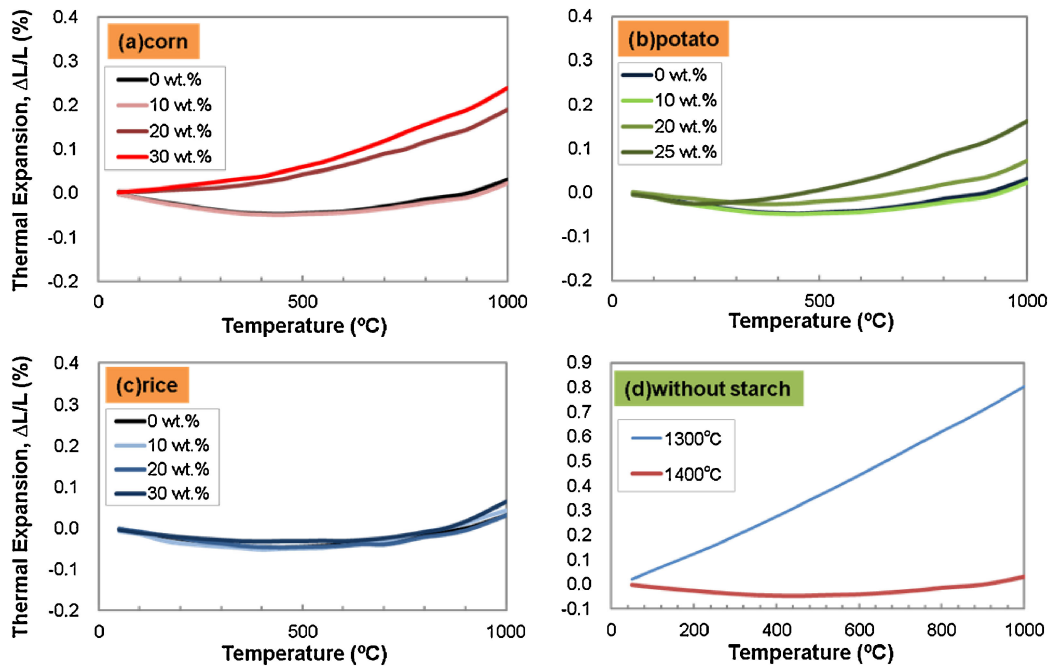
Fig. 8. Thermal expansion of Al_2TiO_5 samples sintered at 1400°C (a) with corn starch (b) with potato starch, (c) with rice starch, and (d) without starch. For (d), the data for 1300°C was also given.

Table 1. The 3-point bending strength of porous Al_2TiO_5 with each starch

Bending Strength (MPa)	Startch content (wt.%)			
	0	10	20	30
Corn	10	9	4	3
Potato	10	8	4	2 (25 wt.%)
Rice	10	7	4	3

thermal expansion. The thermal expansion values of the sample with starch are comparable to that of the sample without starch. This unique behavior for the rice starch can be also attributed to the large heat flow [Fig. 2(c)], resulting in the grain growth of Al_2TiO_5 and microcrack formation [Fig. 6(c)]. In the case of samples without starch additions [Fig. 8(d)], samples sintered at 1300°C had much higher thermal expansion than 1400°C. This phenomenon can be explained by the existence of un-reacted Al_2O_3 and TiO_2 in the samples sintered at 1300°C (Fig. 3), which suggests that 1300°C is not sufficient for the reactive sintering of Al_2O_3 and TiO_2. As shown in **Table 1**, Al_2TiO_5 samples with 10 wt.% starch had comparable strength as that without starch. Further study on mechanical properties is on-going.

4. Conclusions

In this study, we have prepared porous Al_2TiO_5 ceramics with corn, potato and rice starch as a pore-forming agent, by reactive sintering method using fine-grained starting materials. Among these three starches, rice starch promoted the formation of Al_2TiO_5 phase by its high heat flow via the combustion. Samples sintered with starches had large (<20 μm) slit-like pores as well as a 3-D continuous open pore structure. Sample with rice starch additions showed no increase in thermal expansion, even with increasing starch content.

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