Effects of Composite Sintering Additives: $\text{Al}(\text{OH})_3 + \text{Y}_2\text{O}_3 + \text{CaF}_2$ on the Performance of Porous Mullite Oxide-Bonded SiC Ceramics

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Dear Editor:

We are submitting the enclosed manuscript entitled '*Effects of composite sintering additives: $Al(OH)_3+Y_2O_3+CaF_2$ on the performance of porous mullite oxide-bonded SiC ceramics*' for your consideration as a research article in the *Journal of Advanced Ceramics*. The work described has not been published before and is not under consideration for publication anywhere. This work has been approved by all co-authors and the responsible authorities at the institutes where the work has been carried out.

In this work, a composite sintering additive system was proposed to modify the performances of mullite oxide-bonded SiC porous ceramics. Small variations of sintering additives significantly affected the phase composition, pore size/shape, density and flexural strength of porous SiC ceramics. Samples exhibited both good mullite densification and no detectable cristobalite phase, which has been difficult to realize at the same time. Thus fabricated mullite oxide-bonded SiC porous ceramics exhibited a flexural strength of 108 MPa at an apparent porosity of 40.28 vol%, 1.64 times the highest (66 MPa) reported mullite oxide-bonded SiC porous ceramics with comparable porosity, and comparable to that fabricated by SPS. Besides, additives act also as pore formers. The size and shape of pores change with additive composition, and additional pore formers are not necessary. Related models were established. This work provided a simple but effective way to enhance the performance of mullite oxide-bonded SiC porous ceramics. We believe it will inspire the whole society of porous ceramics that a small amount of additive can make big changes.

We consider that Prof. Yongsheng Liu (Northwestern Polytechnical University, yongshengliu@nwpu.edu.cn), Prof. Nahum Travitzky (University of Erlangen-Nuernberg, nahum.travitzky@fau.de) and Prof. Hailong Wang (Zhengzhou University, 119whl@zzu.edu.cn) are able to be potential referees of the manuscript in that they are proficient in the content that we have written.

We deeply appreciate your consideration of our work, and we're looking forward to

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Thanks a lot for your attention to our work.

Sincerely yours,

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**Effects of composite sintering additives: $\text{Al}(\text{OH})_3 + \text{Y}_2\text{O}_3 + \text{CaF}_2$ on the performance
of porous mullite oxide-bonded SiC ceramics**

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Abstract

A composite sintering additive system: $\text{Al}(\text{OH})_3 + \text{Y}_2\text{O}_3 + \text{CaF}_2$ was proposed for porous mullite oxide-bonded SiC ceramics. Small variations of sintering additives have significant influences on the phase composition, pore shape/size, density and flexural strength. Samples sintered at 1550 °C for 4 h in the air atmosphere realized both good mullite densification and no detectable cristobalite phase, which was difficult to be achieved at the same time. Besides, the composite sintering additive system also promoted the formation of columnar shape mullite, which acts as a reinforcement. Flexural strength as high as 108 MPa was achieved at an apparent porosity of 40.3 vol%, which is higher than that sintered by SPS technique. Moreover, those additives also act as pore formers determining the shape and size of pores. Around 8.9 μm strip-like, 11.8

μm continuous channel-like and $4.1\ \mu\text{m}$ irregular pores were obtained for $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_3\text{-Y}_2\text{O}_3$ and $\text{Al}(\text{OH})_3\text{-Y}_2\text{O}_3\text{-CaF}_2$ added samples, respectively. Corresponding phase evolution, sintering mechanisms and pore formation models were established. This work provides a simple way to modify the phase, pore size/shape, and strength of mullite oxide-bonded porous SiC ceramics by properly selecting sintering additives without any additional pore formers.

Keywords

Oxide-bonded SiC ceramics; porous ceramics; sintering additives; mullite; mechanical properties.

1. Introduction

Porous silicon carbide (SiC) ceramics are promising materials in fields of filters for diesel particulate and molten metals, membrane and catalyst supports, heat exchangers, gas purifiers, high-temperature insulators and wave absorption materials [1-10] due to their low density, high corrosion resistance, good chemical stability, high thermal shock resistance, low coefficient of thermal expansion and high specific strength at both room and elevated temperatures [11-15]. However, the highly covalent character of Si-C bond makes it very difficult to be sintered. Even though researchers have developed various methods to reduce the sintering temperature including additive assisted solid or liquid sintering [16-17] and spark plasma sintering (SPS) [18, 19], a temperature as high as $1700\text{-}2100\ ^\circ\text{C}$ is normally necessary. This increases the fabrication cost of porous SiC ceramics and inhibits their wider applications.

Recently, oxide bonding sintering attracts more and more attention because it enables porous SiC ceramics to be sintered at a temperature lower than $1600\ ^\circ\text{C}$, which dramatically reduces the fabrication cost. The first oxide bonding phase studied is silica (SiO_2) in the cristobalite phase and/or amorphous form at room temperature [7, 20, 21]. When sintered in the air, SiC is oxidized into SiO_2 , which covers around SiC particles and bonds them together like sintering due to the viscous flow of the oxidation-derived

SiO₂ [22]. However, cristobalite undergoes a phase transition during cooling accompanied with around 6.4 vol% volume change, which tends to introduce cracks and lower the strength of SiC ceramics. Besides, the low mechanical property of silica limits the overall performance of oxide-bonded porous SiC. Therefore, SiO₂ content higher than 20 wt% in oxide-bonded SiC ceramics shows reduced flexural strength [7, 23].

Since mullite (3Al₂O₃·2SiO₂) exhibits a similar thermal expansion coefficient to SiC [24], better mechanical properties, good oxidation/corrosion resistance and thermal stability [25, 26], aluminium sources are introduced to react with the oxidation-derived SiO₂ and form mullite phase. Aluminium source includes alumina [27-29], Kaolin [30], aluminium hydroxide [31, 32], bauxite [33], fly ash [22, 34] and aluminium isopropoxide [35]. However, without any sintering additives, the mullitization temperature is high [36]. Increasing the sintering temperature for higher mullitization degree is also accompanied by severe oxidation of SiC and higher content of SiO₂ in cristobalite and amorphous silica. Decreasing the sintering temperature would be beneficial to remove the SiO₂ phase but at a cost of lower mullitization degree and density.

To solve this thorny problem, sintering additives are carefully selected to reduce the mullitization point, meanwhile, avoid severe oxidation. The addition of low melting point V₂O₅ effectively reduces the mullitization temperature from 1500 °C to 1100 °C [32]. Addition of MoO₃ could further reduce the mullitization point to around 900 °C. By carefully controlling the sintering condition, mullite rod or whiskers were observed with MoO₃-contained additives [27, 31, 34] benefiting the enhancement of flexural strength of SiC ceramics.

With these additives, the mullitization temperature is decreased and the oxidation of SiC is inhibited. However, at this low temperature, the mullite phase cannot be densified. Besides, pore former is generally used to generate pores in porous SiC ceramics. Here in this work, a composite additive system was developed to solve these issues at the same time, i.e. densification of mullite and no detectable cristobalite phase. More interestingly,

the additive could also act as a pore former. Its effect on the phase composition, pore size and shape, porosity, density and flexural strength were thoroughly investigated.

2. Materials and method

2.1 Sample preparation

Commercially available α -SiC ceramic powders (~ 800 nm, 99.9%, Hebei Yigui Welding Materials Co., Ltd., China) were chosen as the raw material, while $\text{Al}(\text{OH})_3$ (~ 10 μm , 99.99%, Aladdin Chemistry Co. Ltd., China), Y_2O_3 (~ 1 μm , 99.9%, Hebei Yigui Welding Materials Co., Ltd., China) and CaF_2 (~ 1 μm , 99.9%, Aladdin Chemistry Co., Ltd., China) powders were added as sintering additives. Compositions of specimens studied in this study were listed in Table 1. Poly (vinyl alcohol) (PVA, AR, Aladdin Chemistry Co. Ltd., China) and tetramethylammonium hydroxide (TMAH, AR, Aladdin Chemistry Co. Ltd., China) were used as binders and dispersant agents with the additional amount of 0.5 wt% and 1.5 wt% of the total weight of powders, respectively.

Table 1 Compositions of the green body and sintering condition used in this study

Samples	SiC:Al(OH) ₃ :Y ₂ O ₃ :CaF ₂ (weight ratio)	Sintering process
S1	100 : 0 : 0 : 0	
S2	100 : 55 : 0 : 0	
S3	100 : 55 : 2.5 : 0	1450 °C / 2 h in air
S4	100 : 55 : 2.5 : 1.5	
S4*	100 : 55 : 2.5 : 15	
S5	100 : 55 : 2.5 : 1.5	1550 °C / 4 h in air

The suspension with an initial solid loading of 40 wt% was prepared by mixing SiC, $\text{Al}(\text{OH})_3$, Y_2O_3 and CaF_2 powders with dispersant agents in deionized water. Then, it was planetary ball-milled (QM-3SP2, Nanjing University Instrument, China) for 3 h at a rotational speed of 300 rpm. After adding a PVA aqueous solution (7.5 wt%), the

suspension was ball-milled for an additional 2 h. The ratio of PVA aqueous solution to solid powders was 5 wt%. The obtained suspension was frozen dried, sieved through a 100-mesh sieve and uniaxially pressed under 80 MPa using a steel die. The obtained sample was dried at 90 °C for more than 24 h and then sintered in a chamber furnace (KSL-1400X-A3, Kejing Material Technology Co. LTD, Hefei, China) under different conditions as shown in Table 1.

2.2 Characterization

X-ray diffraction (XRD) patterns were acquired using an X-ray diffractometer (Rigaku D/max 2500 PC, Japan, Cu K α , λ = 0.1548 nm) from the powder obtained by crushing and grinding sintered samples. The weight percentage of SiC, cristobalite and mullite in crystalline phases, was obtained by the Rietveld refinement method. The delta Gibbs energy was calculated by the reaction equations calculation software HSC Chemistry (version 9.3.0.9, Outotec). Scanning electron microscopy (SEM, JEOL JSM-7800, Japan) equipped with an energy dispersive spectrometer (EDS) and scanning electron microscopy (SEM, Phenom Pro, Netherlands) were used to investigate the microstructure of prepared porous mullite oxide-bonded SiC ceramics. Nanoscale and micrometre-scale pore-size measurements were separately conducted using porosimetry (AutoPore IV 9500 V1.09, Micromeritics Co. LTD, Shanghai, China) and ImageJ software on three different SEM images including at least 100 pores in each image, same method as reported by Minas et al [37]. The apparent porosity was measured by Archimedes' method using deionized water. The flexural strength was measured at room temperature by three-point bending tests (3PBT) in an Instron 4505 using at least 5 samples per condition. The velocity of the mobile crosshead was 0.2 mm/min with a span of 20 mm. The dimension of samples was approximately 3×4×25 mm.

3. Results and discussion

3.1 Phase analysis

Phases of sintered samples were shown in Fig. 1 and their weight percentage was given in Table 2. Without any additive in sample S1, SiC and cristobalite phases were detected

due to the oxidation of SiC sintered in the air as shown in the following reactions:

With the addition of $\text{Al}(\text{OH})_3$ in sample S2, the diffraction peak of the cristobalite phase became sharper as shown in Fig. 1(B), indicating higher crystallinity of cristobalite phase with introduction of $\text{Al}(\text{OH})_3$. Besides, mullite phase appeared as presented in Fig. 1(A, C). This is due to the reaction of $\text{Al}(\text{OH})_3$ with the oxidation-derived SiO_2 :

Although mullite phase was successfully formed, the weight percentage of cristobalite in crystalline phases increased from 4.5 wt% to 6.1 wt%. This might due to that the additive as an impurity enhances the oxidation of SiC. A similar phenomenon was found with the impurity addition of Al_2O_3 , Fe_2O_3 and TiO_2 [35]. As for S3 with the combined $\text{Al}(\text{OH})_3$ - Y_2O_3 additive, SiC, cristobalite and mullite phases still appeared, but with a much lower cristobalite content (2.7 wt%) in crystalline phases. It is reported that Y_2O_3 and Al_2O_3 form Y-Al-Si-O liquid phase at temperatures below 1400 °C [38], which could promote mass transport and mullitization process.

CaF_2 was further introduced to form a new additive system marked as S4. The diffraction peak of cristobalite phase disappeared (Fig. 1(B)). Only SiC and mullite phases were observed (Fig. 1(A, C)). Interestingly, the percentage of SiC increased from 61.9 wt% for S3 to 67.6 wt% for S4. We correlate this to the enhanced mullitization promoting the transformation from silica on the surface of SiC particle into mullite. Since the diffusion coefficient of oxygen in mullite is much lower than that in silica ($\sim 10^{-20} \text{ cm}^2/\text{s}$ versus $\sim 10^{-13} \text{ cm}^2/\text{s}$ at 1500 K [39]), the mullite on the surface of SiC particle can work as an oxygen diffusion barrier to slow down the oxidation SiC resulting in a higher content of SiC.

To further study the reaction mechanism, the amount of CaF_2 was further increased 10 times higher and marked as S4. Anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phase was observed in XRD pattern as shown in Fig. 1(D). This reaction at 1450 °C was shown in Eq. (5),

forming anorthite and releasing HF at the same time.

To clarify whether this reaction is possible or not, the delta Gibbs energy (ΔG) of Eq. (5) was calculated and given in Fig. 1(E). The value of ΔG of Eq. (5) becomes negative when the temperature is higher than 1010 °C. Therefore, Eq. (5) is thermodynamically favourite, in which the anorthite was formed and HF was released. The released HF then reacts with Al_2O_3 to form a gaseous AIOF intermediate product via Eq. (6), which is reported during the fabrication of Al_2O_3 whiskers through HF [40]. The product HF might also react with SiO_2 to form SiF_4 as listed in Eq. (7) [41].

Finally, gaseous AIOF and SiF_4 react to form mullite (Eq. (8)). This reaction was also previously confirmed during the fabrication of mullite nanowires through NaF, Al_2O_3 and mica [42]. The newly formed product of HF will be again acting as a reactant for Eq. (6, 7).

Besides, it is also reported that the addition of CaF_2 did reduce the viscosity of Y_2O_3 - Al_2O_3 - SiO_2 glass melt [43], which further promotes mass transport thus the mullitization process.

As for S5 with a higher sintering temperature and longer dwelling time, SiC and mullite phases were still main phases without any detectable cristobalite phase, even under such a relatively harsh condition (1550 °C, 4h). Normally the oxidation of SiC becomes more severe at higher temperature in the air atmosphere, thus less amount of SiC left. However, the weight percentage of SiC in the crystalline phase of S5 sintered at 1550°C was higher than that of S4 sintered at 1450°C, i.e. 69.5 wt% v.s. 67.6 wt% as listed in Table 2. This might due to that the higher sintering temperature promoted the transformation of silica to mullite and the lower oxygen diffusion coefficient in mullite as mentioned afore. Besides, the releasing of Al^{3+} and Si^{4+} in the forms of gaseous AIOF and SiF_4 also affects the weight percentage of SiC.

Figure 1 XRD patterns of SiC ceramics sintered with different additives/sintering conditions (S1: none/1450 °C-2h, S2: $\text{Al}(\text{OH})_3$ /1450 °C-2h, S3: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3$ /1450 °C-2h, S4: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3+\text{CaF}_2$ /1450 °C-2h, S5: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3+\text{CaF}_2$ /1550 °C-4h): (A) The overall pattern; The local magnification of the main diffraction peak of (B) cristobalite and (C) mullite phases; (D) XRD pattern of the sample (S4*) sintered at 1450 °C for 2 h with the same additive as S4 but ten times higher content of CaF_2 (weight ratio of $\text{SiC} : \text{Al}(\text{OH})_3 : \text{Y}_2\text{O}_3 : \text{CaF}_2 = 100 : 55 : 2.5 : 15$); (E) The calculated delta Gibbs energy-temperature curve of Eq. (5).

Table 2 Weight percentage of different crystalline phases.

Sample	SiC (wt%)	Cristobalite (wt%)	Mullite (wt%)
S1	95.5	4.5	-
S2	61.3	6.1	32.5
S3	61.9	2.7	35.4
S4	67.6	-	32.4
S5	69.5	-	30.5

3.2 Microstructure evolution

In Fig. 2(A), a smooth surface without obvious pores was observed for the cross-section

of S1 at low magnification. Some local areas with irregular shapes were observed brighter than other areas. Some cracks were seen along the outline of the brightened area as shown in higher magnification (Fig. 2(F)), which might result from the incompatible volume change of the cristobalite during cooling. Although no pore former was used in this study, a larger number of nanoscale pores appeared as seen from the insert image in Fig. 2(F). These pores should be caused by the packing arrangements of nano-sized SiC powders and we will come to this point later in the section 3.5.

Figure 2 SEM at different magnification (A-E: $\times 500$, F-J: $\times 5000$) of SiC ceramics with different additives/sintering conditions (A, F: none/ $1450\text{ }^{\circ}\text{C}$ -2h B, G: $\text{Al}(\text{OH})_3$ / $1450\text{ }^{\circ}\text{C}$ -2h, C, H: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3$ / $1450\text{ }^{\circ}\text{C}$ -2h, D, I: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3+\text{CaF}_2$ / $1450\text{ }^{\circ}\text{C}$ -2h, E, J: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3+\text{CaF}_2$ / $1550\text{ }^{\circ}\text{C}$ -4h).

On the contrary, plenty of micrometre-scale strip-shape pores randomly distributed at the cross-section of S2 with 55 wt% $\text{Al}(\text{OH})_3$ as additive shown in Fig. 2(B, G). When 1.6 wt% Y_2O_3 was further added in sample S3, a coral-like porous structure was formed (Fig. 2(C)), which exhibited a continuous-channel observed at higher magnification (Fig. 2(H)). With further addition of 1 wt% CaF_2 for S4, irregular shape and non-continuous smaller size pores were illustrated in Fig. 2(D). Many condensed columnar bars/grains were randomly distributed among small SiC particles (Fig. 2(I)). With the same additives but increased sintering temperature and dwelling time for S5, no apparent changes were observed in the cross-section morphology as compared to S4 (Fig. 2(E) and (J)).

As can be seen, with a little change of additives, the morphology of sintered SiC ceramics varied a lot. To figure out the mechanism behind it, more detailed studies were conducted. The distribution of $\text{Al}(\text{OH})_3$ additive in the green body was investigated along with element distributions and presented in Fig. 3(A). Some larger size particles randomly distributed in the green body as marked by the white dotted line in the left image in Fig. 3(A). The particle size of $\text{Al}(\text{OH})_3$ used in this study was around 10 μm . Combined with the element distribution, these larger size particles should be $\text{Al}(\text{OH})_3$ additive decorated among SiC particles. While after sintering, strip-like pores were observed as shown in Fig. 3(B), which is similar in size to the $\text{Al}(\text{OH})_3$ additive particles. Many small particles, as well as some big irregular particles, were observed in the cross-section shown in Fig. 3(B). Based on EDS measurement, the small particles are SiC as they were mainly composed of Si and C. The large particle was mainly composed of Al, O and a small amount of Si. Since Al only existed in the form of mullite as shown from XRD results in Fig. 1(A), it can be inferred that these large particles contain the mullite phase. At higher magnification (Fig. 3(C)), it can be observed that there were many crystals on the wall of the pore exhibiting unique morphology like a tabular multilayer structure. According to EDS measurement, the crystal mainly contained Al, O and Si and probably be mullite phase. The addition of Y_2O_3 into this system didn't change the morphology of the mullite crystal in S3. Therefore, it was not showing here.

With the combined $\text{Al}(\text{OH})_3 + \text{Y}_2\text{O}_3 + \text{CaF}_2$ additive, some columnar grains with a size of several micrometres were observed (Fig. 4(A)). According to EDS measurement and XRD results, these should be mullite crystals. Similar large columnar mullite grains were also observed for samples sintered at 1550 $^{\circ}\text{C}$ as shown in Fig. 4(B), indicating this phenomenon is mainly due to the additive system rather than the sintering condition used in this study. This result indicates that such a composite sintering additive system could promote the mullite phase to preferentially grow along a specific axis, which might be in the same way as the formation of the rod-like mullite [27, 28] and the mullite whisker [33, 34] reported in other work. Combined with the element distribution in Fig. 4(B), it can be inferred that small particles were SiC and larger ones were mullite phase. It is worth

noting that most of the small particle was not isolated from each other like the case in samples S1~S4, but bonded together with sharing boundaries.

Figure 3 The micromorphology and the element distribution of S2: $\text{Al}(\text{OH})_3$ as the additive/ sintered at 1450 °C for 2 h (A) before and (B) after sintering. The morphology and the element composition of the crystal inside the pore in S2 (C).

Figure 4 The morphology of the bar and the nearby element distribution in S4: $\text{Al}(\text{OH})_3+\text{Y}_2\text{O}_3+\text{CaF}_2$ as additives sintered at 1450 °C for 2 h (A) and S5: with the same additive sintered at 1550 °C for 4 h (B).

Therefore, the additive has an important effect on the microstructure of porous mullite oxide-bonded SiC ceramics. No micrometre-scale but only nano-scale pores were

observed without any additive. Strip-like large-sized pores were found for $\text{Al}(\text{OH})_3$ added samples. With further addition of a small amount of Y_2O_3 , pores were found to be locally connected. Irregularly shaped pores and columnar mullite bars were found as the feature for samples with $\text{Al}(\text{OH})_3$ - Y_2O_3 - CaF_2 combined additives.

3.3 Pore size distribution

The pore-size measurement of the micrometre-scale pores (strip-shape ones in S2, continuous channel-shape in S3 and irregular ones in S4 and S5) and their pore-size distributions were shown in Fig. 5 (A). Since there were no micrometre-scale pores in S1, its pore size distribution was not measured through this method. As shown in Fig. 5 (A), all these samples exhibited a mono-peak pore-size distribution with average pore diameters (d_{ave}) $\sim 8.9 \mu\text{m}$, $11.8 \mu\text{m}$, $5.0 \mu\text{m}$ and $4.1 \mu\text{m}$ for S2, S3, S4 and S5, respectively. With addition of Y_2O_3 in S3, a significant increase of $2.9 \mu\text{m}$ absolute value in average pore size was observed as compared to S2 with only $\text{Al}(\text{OH})_3$ as additive. This coincides with the microstructure observation that strip-shape pores were locally connected forming larger ones in S3. By adding CaF_2 inside additives in S4, a sharp decrease of $6.8 \mu\text{m}$ in average pore size was found as compared to S3. Besides, the pore-size distribution became much narrower. Further rising the sintering temperature/time in S5, the average pore size was further slightly decreased with the narrowest distribution.

As observed in the insert image in Fig. 2(F), there exhibited many nanoscale pores in S1. Therefore, porosimetry was used to conduct the nanoscale pore-size measurement for all samples and the result is shown in Fig. 5(B). The sample S1 exhibited a mono-peak pore-size distribution with an average pore size of around 100 nm. With additives, the pore-size distribution changed to bi-modal types. Positions of both two peaks moved to a larger size from S2 to S5 continuously. The average pore size increased from 100 nm for S1, to 118 nm, 166 nm, 197 nm and 328 nm for S2~S5, respectively. Since pore size is closely related to the packing arrangements of powders, the pore size is strongly dependent on the size of starting powders [26]. The relatively large addition amount ($\sim 35 \text{ wt\%}$ for S2-S5) of $\text{Al}(\text{OH})_3$ powders with a size of $\sim 10 \mu\text{m}$, much larger than SiC powders used in

this work, should be the reason for this increment of sub-microscale size pores.

Figure 5 Pore-size distribution of micrometre-scale pores (A) (strip-shape ones in S2, continuous channel-like ones in S3 and irregular ones in S4 and S5) and nanoscale pores (B) for sintered porous mullite oxide-bonded SiC ceramics.

3.4 Physical and mechanical properties

As shown in Fig. 6(A), the density value continuously decreased from 2.98 to 2.93, 2.90 and 2.82 for S2, S3 and S4, respectively. While for S5 with increased sintering temperature to 1550 $^{\circ}\text{C}$ and prolonged sintering time to 4 h, there was a dramatic increase of the density to 3.2 g/cm^3 . With the introduction of Al^{3+} , some of the SiO_2 was transformed into mullite phase. However, mullite densification is generally poor at 1450 $^{\circ}\text{C}$. Besides, the mullite phase exhibits a relatively lower density (2.01~2.45 g/cm^3 [44]) compared to cristobalite and aluminosilicate glass (2.32~2.38 and 2.62~2.67 g/cm^3 , respectively). Therefore, the more amount of mullite phase contains, the smaller the density is. The higher density of S5 is due to the better sintering behaviour of the mullite phase as it is difficult for SiC to be densified under such a sintering condition. This result indicates that such a composite sintering additive system could help to densify the mullite phase at 1550 $^{\circ}\text{C}/4\text{h}$ without any detectable cristobalite phase in porous mullite oxide-bonded SiC ceramics, which is difficult to achieve at the same time.

As shown in Fig. 6 (B), the apparent porosity of samples S1~S4 exhibited a similar value of around 35% without any dependence on additive systems. Considering that no pore

formers were used, the same sintering condition except a tiny amount difference in additives, this is understandable. Interestingly, there was an increase of 5.01 vol% absolute porosity value for S5, although it exhibited the highest density. We correlate this to the sintering shrinkage and the mass loss, which will be illustrated in details later in the section 3.5.

The flexural strength of porous oxide-bonded SiC without any sintering additive, i.e., S1, was 21 MPa as shown in Fig. 6 (C) at an apparent porosity 34.93 vol%. With additive of $\text{Al}(\text{OH})_3$ in S2, the strength dropped to 11 MPa, only half of that of control. Since there were plenty of large strip-like pores observed in sample S2 as shown in Fig. 2 (B, G), they act as defects inducing stress concentration and poor mechanical performance. Poorly densified mullite might be another reason for this low strength. With the combined additive of $\text{Al}(\text{OH})_3\text{-Y}_2\text{O}_3$, the flexural strength of S3 increased to 39 MPa. The increased amount of mullite and the decreased amount of cristobalite should be the main reasons for this improvement. The remarkable growth of flexural strength for S4 to 71 MPa was achieved, which is two times of the control, 7.6% higher than the highest (66 MPa) reported currently for porous mullite oxide-bonded SiC ceramics at a comparable porosity, even close to that sintered at 1950 °C in Ar atmosphere (42 vol% porosity, 76 MPa) [45]. The formation of columnar mullite bars, as well as the compressed formation of cristobalite, comprehensively induces this high strength, although S4 had the lowest density. The low content of the cristobalite phase avoids crack formation caused by the incompatible volume change during cooling. These columnar mullite grains distributed randomly among SiC particles functions as reinforcement. The flexural strength for S5 further enhanced to 108 MPa at an even highest apparent porosity 40.29 vol% by adding CaF_2 inside additives. This value is 1.64 times of the highest (66 MPa) reported mullite oxide-bonded SiC porous ceramics with comparable porosity [29], and higher than those sintered by SPS technique at 1800°C in vacuum or sintering at 1900°C in helium atmosphere [18] as listed in Table 3. The flexural strength of porous ceramics generally decreases with increasing porosity. However, the opposite result was observed in S5. A 0.38 g/cm^3 absolute increment of density for S5 was confirmed as compared to S4 (Fig.

6(A). It is well known that pure SiC is difficult to be densified under such a sintering condition. The increase in density should be attributed to the better densification behaviour of the mullite phase. Densified mullite phase could bond SiC particles stronger together. Besides, the columnar shape of the mullite phase acts as reinforcement to further enhance the strength of SiC ceramics. This result indicates that enhanced densification and columnar shape of the mullite phase play significant roles in the mechanical property of porous mullite oxide-bonded SiC ceramics.

Figure 6 Physical and mechanical properties (apparent porosity (A), density (B), flexural strength (C)) of porous SiC ceramics with different additives/sintering conditions (S1: none/1450 °C-2h, S2: Al(OH)₃/1450 °C-2h, S3: Al(OH)₃+Y₂O₃/1450 °C-2h, S4: Al(OH)₃+Y₂O₃+CaF₂/1450 °C-2h, S5: Al(OH)₃+Y₂O₃+CaF₂/1550 °C-4h).

Table 3 Characterization and processing parameters of porous SiC ceramics fabricated by mullite oxide-bonding and various sintering methods (at the porosity from 35 vol% to 45 vol%) [16-18, 22, 25-28, 30, 33, 43-46].

Apparent porosity (vol%)	Flexural strength (MPa)	Sintering method	Raw materials (besides SiC)	Sintering temperature/ atmosphere	Detected crystalline phase (besides SiC)	Anisotropic mullite morphology	Reference
36.8	23		ρ -Al ₂ O ₃ , MgCO ₃ , talc, kaolin, K ₂ O·Al ₂ O ₃ ·6SiO ₂	1400 °C / air	mul+cris	-	[46]
42	23		Al(NO ₃) ₃ , tetraethoxysilane (TEOS)	1300 °C / air	mul+cris	-	[47]
42	25		Al(NO ₃) ₃ , TEOS	1300 °C / air	mul+cris	rod-like	[48]
43.3	25		kaolin, α -Al ₂ O ₃ , MoO ₃	1450 °C / air	mul+cris+quar	whisker	[30]
38.4	36	mullite oxide-bonded	fly ash, MoO ₃	1000 °C / air	mul+cris	whisker	[22]
36.3	37		Al(OH) ₃ , V ₂ O ₅	1300 °C / air	mul+cris	whisker	[32]
33	40		Al ₂ O ₃ , Mg(NO ₃) ₂ ·6H ₂ O, Al(NO ₃) ₃ ·9H ₂ O, TEOS	1400 °C / air	mul+cris+alum+cor	whisker	[27]
38.7	41		α -Al ₂ O ₃ , aluminium isopropoxide (AIP)	1450 °C / air	mul+cris+alum	-	[35]
45.3	50		photovoltaic solid waste (PSW), Si, Al ₂ O ₃ , MoO ₃	1000 °C / air	mul+cris	rod-like	[28]
45.4	66		PSW, γ -Al ₂ O ₃ , MoO ₃	1000 °C / air	mul+cris	rod-like	[29]
40.3	108		Al(OH) ₃ , Y ₂ O ₃ , CaF ₂	1550 °C / air	mul	columnar	this work
42	76	recrystallization sintering	--	1950 °C / Ar	-	-	[45]
35	102	liquid sintering	-	1900 °C / He	-	-	[17]
35.7	103	spark plasma sintering	-	1800 °C / Vac	-	-	[18]
34.2	128	solid sintering	-	2150 °C / Ar	-	-	[16]

3.5 Pore formation models

Since no pore formers and the same/small amount of organic additives were used in this work, two questions logically raised: how does the pore form and why the porosity is similar for most samples. There might be a similar and dominant mechanism for all specimen. Let's first look at S1 without any sintering additives. The particle size of SiC powder used in this study was around 800 nm. The green body was pressed under 80 MPa and sintering was conducted at 1450 °C. Under this condition, there should be plenty of nanoscale pores formed by the packing arrangements of nano-sized SiC powders as schematically shown in Fig. 7(A)-i. During sintering, the surface of SiC particles is oxidized to silica which viscously flows at the sintering temperature (Fig. 7(A)-ii). However, mass transfer of SiC is difficult to occur at this sintering condition. Therefore, the SiC particle is not able to move but bonded together by the oxidized SiO₂, remaining/leaving small pores behind as illustrated in Fig. 7(A)-iii. Since the particle of SiC was in the nano-sized range, the volume of pores formed by this powder packing should be large, which is a dominant phenomenon. Therefore, the porosity of almost all samples (especially S1 to S4) showed similar porosity values as described afore. When Al-source is introduced, Al³⁺ and O²⁻ ions are supposed to transfer through the oxidation-derived SiO₂ glass and react with it to form mullite phase (Fig. 7(A)-iv). The bonding phase will be mullite instead of silica as shown in Fig. 7(A)-v. The pore formation mechanism is still the same. Therefore, all samples shared a similar porosity level.

However, as seen from microstructures shown in Fig.2, besides these nanoscale pores, there were many micrometre-scale pores observed including strip-like pores in S2, continuous channel-like pores in S3 and irregular-shaped ones in S4. These might be caused by other mechanisms. It was noticed that the strip-like pore in S2 was on the same scale as the Al(OH)₃ raw powder used in this work. The study of the formation mechanism of mullite phase [39] confirms that the diffusion of Al³⁺ and O²⁻ rather than that of Si⁴⁺ determines the formation of mullite because the diffusion coefficient of the latter is 2~7 orders of magnitude lower than the former. Based on this, we hypothesize that the large size pore might be formed due to the consumption of Al(OH)₃, which escapes/diffuses

and reacts with oxidized silica to form mullite, leaving a pore behind, as schematically illustrated in Fig. 7(B)-ii. Therefore, $\text{Al}(\text{OH})_3$ acts not only as an Al-source additive but also as a potential pore former. The size and shape of $\text{Al}(\text{OH})_3$ in the green body is inherited to be pores after sintering. With the addition of Y_2O_3 , the Y-Al-Si-O liquid phase forms at temperatures above 1400 °C [38]. The liquid phase flows into continuous and irregular shapes. When this liquid phase is consumed with the formation of mullite phase, locally connected channel-like pores are formed as observed in S3 and schematically illustrated in Fig. 7(B)-iii and iv. When CaF_2 is further added in S4, the liquid phase, as well as gas phases, are involved in the reaction as shown in the reaction mechanism. Columnar mullite grains are formed randomly near the pore, which divides the previous channel-like pores into many small independent and irregular shape pores (Fig. 7(B)-v). It can be concluded that $\text{Al}(\text{OH})_3$ not only provides Al_2O_3 for mullite formation but also works as the pore former. A small amount of Y_2O_3 and/or CaF_2 addition changes the reaction mechanism thus the pore shape and size.

According to Fig. 6(B), although the different shape of pores was observed with the introduction of additives, the apparent porosity of S2~S4 was very similar with only a small variation of 0.32~0.43 vol%. The consumption of Al^{3+} and O^{2-} induces not only various-shaped pores but also the formation of Al^{3+} compounds (including mullite and/or aluminosilicate glass). The stress relaxation resulted from dehydration of $\text{Al}(\text{OH})_3$ and pyrolysis of organic additives might also affect the porosity. Comprehensively considering all these effects, the volume changes with variation of the final density of Al^{3+} compounds (ρ_{Al}) was calculated and shown in Fig. 7(C). When ρ_{Al} is higher than 2.42 g/cm³, a negative volume change occurs, suggesting an increase of porosity value due to the shrinkage of volume. The average density of mullite and aluminosilicate glass (2.01~2.45 g/cm³ sintered at 1400~1500 °C [44] and 2.62~2.67 g/cm³) is right near the value of 2.42 g/cm³. Therefore, no big difference in porosity was observed from sample S1 to S4. While better sintering phenomenon occurred for sample S5 accompanied with a higher density of mullite (3.35~3.45 g/cm³ sintered at 1500~1600 °C [44]). This would result in a larger volume shrinkage at around 5 vol% according to Fig. 7(C) and increased

apparent porosity. As shown in Fig. 6(B), the actual increase of porosity was 5.01 vol%, which is highly consistent with the calculated result.

(A)

(B)

(C)

Figure 7 The schematic illustration of how the pore forms due to (A) the packing arrangements of powders and (B) the introduction of the $Al(OH)_3$ particle, (C) the volume change of Al^{3+} compounds after sintering.

Rooted in these discussions, we could therefore conclude that the small variation of additives not only changes the sintering behaviour but also the pore forming mechanism, thus the performance of ceramics. By simply design proper additives, it is possible to

solve problems of high mullite densification and no detectable cristobalite phase at the same time.

4. Conclusions

In this study, a composite sintering additive system was proposed. Sintering additives have significant influences on the phase composition, micromorphology, pore shape and size, density and flexural strength of porous mullite oxide-bonded SiC ceramics. Only addition of $\text{Al}(\text{OH})_3$ did react with silica and form mullite phase but with an increasing amount of cristobalite phase. Addition of Y_2O_3 promoted the formation of mullite phase and constrains the formation of cristobalite phase. Further addition of CaF_2 enhanced the formation and densification of mullite phase without any detectable cristobalite phase. Nanoscale pores formed by the packing of SiC particles are the dominant mechanism for porous oxide-bonded SiC ceramics. Therefore, most of the samples shared the same level of porosity. Additives also act as pore formers to affect the size and shape of microscale pores. Strip-like pores were obtained for $\text{Al}(\text{OH})_3$ added samples, continuous channel-like and smaller irregular ones for $\text{Al}(\text{OH})_3$ - Y_2O_3 and $\text{Al}(\text{OH})_3$ - Y_2O_3 - CaF_2 added ones, respectively. The addition of CaF_2 not only promoted the densification of mullite, but also the formation of columnar shape mullite acting as a reinforcement. Flexural strength reached 108 MPa at an apparent porosity of 40.3 vol% for SiC ceramics sintered at 1550 °C for 4 h in the air without any addition of pore formers.

It can be seen that small variations of additives affect the performance dramatically. The composite sintering additive system: $\text{Al}(\text{OH})_3 + \text{Y}_2\text{O}_3 + \text{CaF}_2$, is beneficial to realize both good mullite densification and no detectable cristobalite phase at the same time along with columnar shaped mullite grains for enhanced mechanical performance. Although the content of additives and the sintering conditions need further modification, we hope such a composite sintering additive system could promote the development of porous mullite oxide-bonded SiC ceramics and inspire the community with new design strategies.

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Figures

Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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(A)

(B)

(C)

Figure 7

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