Effect of Micro SiC Addition on the Microstructure and Thermal Shock Resistance of 3D Printed Mullite Contained Ceramics

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Abstract. Currently, mullite contained ceramics printed by DIW 3D printing cannot be used in a high temperature environment for multicycle. In the fields of environmental protection and filtration of high-temperature flue gas, 3D printed mullite contained ceramics is in widely demanded owing to the variety of structures. Thus, application of these products have been limited due to their low thermal shock resistance. In order to improve the thermal shock resistance of 3D printed mullite contained ceramics for high-temperature flue gas filter, in this work, the effect of SiC micron particles addition on the thermal shock resistance was investigated. The thermal shock behavior of 3D printed mullite ceramics was explored using a conventional water quenching technique. Furthermore, XRD and SEM were used for determining phase composition and microstructure evaluation, respectively.

1. Introduction

It is well known that traditional ceramic forming techniques give rise to limitations in terms of long processing times, high cost and difficult of machining. Conversely, 3D printing is a unique manufacturing philosophy that enables the flexible preparation of highly complex and precise structures that are difficult to realize using traditional fabrication methods such as casting and machining. The emergence of three-dimensional (3D) printing technologies, also referred to as additive manufacturing (AM), is regarded as a manufacturing revolution [1,2]. So far, various 3D printing technologies have been employed to prepare highly complex structures with ceramic. For example, Zak C. Eckel et al[3] fabricated microlattice and honeycomb structures with polymer-derived ceramics using SLA 3D printing technology. Aditi Potdar et al[4] manufactured milli-scale reactors with porous structure by 3D inkjet-printing technology which can be extended. Smay J E et al[5] prepared 3D periodic structure with varying rod spacing of 250-750μm with concentrated silica gels by DIW 3D printing technology. It is the advantage of 3D printing that makes it a compatible method for manufacturing high temperature flue gas filters.

Mullite ceramics have attracted a lot of interest due to their high refractoriness, low thermal conductivity, low thermal expansion coefficient, lightweight, desirable dielectric properties and good
chemical inertness[6,7]. Researches on properties of mullite ceramics have been reported, currently. Wang W et al[8] developed silica/mullite fiber composite membranes with double-layer structure by a simple vacuum procedure for the removal of sub-micrometer dust. A kind of active powder made from Al-sol, Si-sol and AlF3 was introduced to create secondary structures for the network. And the network can be concluded that creating secondary structures for the mullite fibers was an effective method to improve the filtration efficiency of a fibrous filter[9]. W.E. Lee et al. reviewed the mullite formation from clays and clay-based vitreous ceramics, especially, Kaolin clay is the most common clay used[10]. A combined foam-gelcasting and microwave heating method developed for low temperature rapid preparation of high quality porous mullite ceramics. And the prepared porous products contained high levels of porosity [11]. However, there is a issue that need to be solved or further clarified. Due to the disadvantage of low thermal shock resistance of mullite ceramic, the mullite filter can not service in a high temperature environment for multicycle. Table 1 [12] gives some examples of temperature environment and applications for hot gas cleaning and their operating requirements.

Silicon carbide is widely used as a reinforcement phase in ceramic matrix composites (CMCs) owing to its ultrahigh strength, excellent refractoriness, and good oxidation resistance[13,14]. The SiC-fibre-reinforced SiC matrix composites (SiCf/SiCs) have various advantages in terms of their performance for use as special structural materials owing to their excellent properties such as a low density, high specific strength/modulus, stability in extreme environments, and oxidation resistance[15-18]. A composite material comprising mullite and SiC granules, prepared at lower temperatures, yielded a material having a heat expansion coefficient similar to SiC and the excellent chemical compatibility observed enhanced the high-temperature strength and resistance to thermal attack[19].

**Table 1. Applications for hot gas cleaning and their operational requirements[12]**

| Application                        | Temperature(K) | Gas environment                  | Filter device requirement                                      |
|-----------------------------------|----------------|----------------------------------|-----------------------------------------------------------------|
| Power generation                  |                |                                  |                                                                 |
| PFBC                              | 1073           | Oxidizing with alkali            | Turbine protection; meet environmental standards                |
| Integrated gasification combined cycle | 873-1073       | Reducing with alkali+ H2S        | Turbine protection; meet environmental standards, protect sulfur capture beds |
| Conventional                      | < 973          | Oxidizing                        | Meet environmental standards; low Δp                            |
| Chemical process                  |                |                                  | Enhanced product recovery; reduced environmental emissions; resource recovery; energy recovery |
| metal refining                    | 573-1023       | Varied, can be severe            |                                                                 |
| calcination/drying                |                |                                  | Reduc environmental emissions; protect downstream equipment      |
| catalytic cracking                |                |                                  |                                                                 |
| precious metal recovery           |                |                                  |                                                                 |
| Incineration                      | Up to 1273     | Oxidizing, containing reactive chemical species |                                                                 |
In order to raise the thermal shock resistance of 3D printed mullite contained ceramics, in the present work, the high-temperature flue gas filter was produced with slurry composed of kaolin clay and 0, 5, 10, 15, and 20 wt% SiC micron particles, which showed a good flowability and formability suitable for DIW. The effects of SiC addition on the sintering behavior and thermal shock resistance of the sintered 3D printed mullite contained ceramics were studied. Then, the properties (thermal decomposition behavior, bulk density, porosity and cold crushing strength) of 3D printed mullite ceramics high-temperature flue gas filter were characterized in detail. Moreover, the mechanism of the thermal shock resistance of 3D printed mullite contained ceramics was discussed from the perspective of SiC Addition.

**Table 2.** Chemical composition of raw materials( wt%)

| Raw materials | SiO₂ | CaO  | Fe₂O₃ | Al₂O₃   | MgO  | Na₂O |
|---------------|------|------|-------|---------|------|------|
| Kaolin        | 66.61| 0.20 | 1.68  | 18.78   | 0.85 | 6.62 |

2. Experimental

1.1. Raw material and green body preparation

The experimental raw materials used in this research is kaolin clay. Its chemical composition was shown in Table 2. Compositions with 0, 5, 10, 15 and 20 wt% SiC micron particles, kaolin and 20 wt% water were mixed together by a vacuum pug mill to make a slurry that can be used directly for 3D printing. Then four types of samples were printed by a DIW 3D printer(SYNOp-SOURCE).

All structured high-temperature flue gas filters are made of mixed slurry with an internal diameter of 1 mm and were designed using the CAD software SolidWorks 2014. The base structure of such a high-temperature flue gas filter is shown in Figure 1. The samples were prepared using a DIW 3D printer and extrusion system to build the structures layer by layer with programming controlled movements in the x, y and z- axis. Dimension of a sample was set as 40 mm in X-axis, 20 mm in Y-axis and 10 mm in Z-axis. Then the parameters of 3D printer were set by Simplify 3D Software: the diameter of the needle is 1mm, the height of the layer is 0.7mm, and the printing speed is 6000mm/min, without supporting or heating. The printed green bodies were shown in Figure 2.

![Figure 1. The base structure of a high-temperature flue gas filter.](image)

The green body was printed by DIW 3D printing technology, so residual water in green body need be dislodged. In this study, a dryer(JC101) was adopted to remove residual water. The temperature of the dryer was set to 383K × 8h.
Green bodies were sintered by a muffle furnace(SX18-4-5YM, China) at 1473K × 3h, 1523K × 3h, 1573K × 3h, 1623K × 3h.

The experimental Flowchart of filter by DIW technique was shown in Figure 3.

1.2. Characterization

The phase composition of sintered samples with different structures were characterized by XRD(Philips X’ pert-MPD, Holland). And the microstructure was examined on a field emission scanning electron microscope (ZeissIGMAHD, Germany). The bulk density and porosity were determined by the Archimedes drainage method. The cold crushing strength of samples perpendicular to layer were tested by testing apparatus(DPK-500N, China). The water quench test was performed by recording the number of quenching to evaluate the thermal shock resistance, and the process was
repeated until the sample was broken (the sample was heated to 1073K for 30min, and then rapidly immersed in water).

3. Results and discussion

Figure 4 shows the variation of the apparent porosities and bulk density as a function of SiC addition and sintering temperature, respectively. As shown in figure 5, apparent porosity of prepared samples increased with increasing the SiC addition from 5wt% to 20wt%. Furthermore, it is worth noting that the apparent porosity of the samples without SiC addition decreased (from 31.15% to 25.73%) with increasing the sintering temperature from 1473K to 1623K.

As for the bulk density, as illustrated in Figure 4b, it increased with increasing the sintering temperature from 1473K to 1623K when the samples composed with kaolin clay only. And the bulk density of prepared samples increased with increasing the SiC content from 5wt% to 20wt%, sintered from 1473K to 1623K, could be attributed to the following reasons: 1) In theory, SiC cannot participate in sintering reaction of ceramic matrix at the temperature in this experiment, which results in the change of bulk density of samples under various conditions; 2) As the theoretical density of SiC is larger than that of mullite, the volume density of samples will also increase with the increasing of SiC content and temperature.

![Figure 4](image1.png)

**Figure 4.** The bulk density and apparent porosity of the mullite contained ceramic printed by DIW technique sintered at different temperatures with different SiC additions.

![Figure 5](image2.png)

**Figure 5.** The linear shrinkage of the mullite contained ceramic printed by DIW technique sintered at different temperatures with different SiC additions.
Figure 5 shows the linear shrinkage of printed samples with different SiC sintered at different temperatures. Illustrated by graphs, after firing, the volume of the sample shrinks from 7.01% to 12.15%. The linear shrinkage decreased with the increase of SiC content at the same sintering temperature. When SiC content ranged from 0 wt% to 5 wt%, with the sintered temperature increased, the linear shrinkage of samples increased. While SiC content exceeded 10wt%, the linear shrinkage of samples decreased with the sintered temperature increasing.

SiC reacts with high-temperature oxygen according to the following (Eq. (1)):

$$\text{SiC(s)} + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + \text{CO(}\text{g})$$  

As SiC is oxidized, it will be covered by silica (SiO$_2$), and the schematic of silicon carbide oxide layer was shown in figure 6. When the thickness of the oxide layer is insufficient, the carbon monoxide gas can escape quickly, and the flowable silicon dioxide can fill the pore generated by the gas escape. As the oxidation process progresses, the thickness of the oxide layer increased. In this case, it is difficult for the carbon monoxide gas to escape from the oxide layer, resulting in the formation of pore in the oxide layer with residual carbon monoxide. In addition, the amorphous silica can promote the sintering of the composites to a certain extent. With the increase of temperature, the amorphous silica can be transformed into quartz, accompanied by a certain volume expansion, which is also the reason for the change of linear shrinkage rate after sintering. Combining the results of Figure 4 and Figure 5, it can be inferred that the changes of apparent porosity and bulk density of samples are related to the oxidation reaction of SiC and O$_2$.

The influence of sintering temperatures and SiC additions on the phase evolution of the porous 3D printed ceramics is displayed in Figure 7. XRD results show the mainly phases are mullite, cristobalite, quartz and SiC. With increasing SiC content from 0wt% to 20wt%, the peak intensity of mullite was remain unchanged sintered at 1523K. And the peak intensity of cristobalite was observed to increase due to the increasing of SiC content from 0wt% to 20wt%. Further increasing the sintering temperature to 1573K, the peak intensity of the SiC phase increased significantly.

![Figure 6. Schematic of silicon carbide oxide layer.](image)

![Figure 7. XRD patterns of the mullite contained ceramic printed by DIW technique sintered at different temperatures with different SiC additions (a) Sintered at 1523K; (b) Sintered at 1573K.](image)
Figure 8 shows the compressive strength of 3D printed ceramic with SiC content from 0wt% to 20wt% sintered at different temperatures. With the increase of SiC content from 0wt% to 20wt%, all samples sintered at different temperatures, the compressive strength decreased. In addition, samples with the content of SiC 0wt%, 5wt%, 10wt%, 15wt% and 20wt%, the compressive strength of 3D printed samples increased with the temperatures increasing from 1473K to 1623K.

![Figure 8. Compression strength of the mullite contained ceramic printed by DIW technique sintered at different temperatures with different SiC additions.](image)

As shown in Figure 9, when the sample was under loading, load is mainly distributed in base structure and shell. And the compressive strength of samples can be divided into three different stages: (1) the strength of each sintered slurry line that extracted from the nozzle of 3D printer play a role when the sample was under loading; (2) the strength of junctions in the base structure between lines in X axis and lines in Y axis woven by the 3D printer; (3) the strength of junctions between parallel lines in the shell. The strength of junctions greatly affects the overall compressive strength of the specimen.

![Figure 9. Schematic of mullite contained ceramic printed by DIW technique under loading.](image)

The thermal shock times of 3D printed samples with different SiC contents sintered at 1473K, 1523K, 1573K and 1623K were displayed in Figure 10. At 1473K, 1523K, 1573K and 1623K, samples without SiC exhibited the worst thermal shock resistance, samples with SiC content 20wt%
exhibited the best thermal shock resistance. When SiC content is constant, with the sintering temperature increased, the thermal shock resistance of the sample decreased. This is because SiC is more prone to oxidation reaction at higher temperature, resulting in thicker oxide layer, and this amorphous silicon dioxide thermal conductivity is very low. The sample with 20 SiC exhibits the maximum thermal shock resistance (reached 22 times) after sintering at 1473K.

![Graph showing thermal shock resistance vs. SiC addition](image)

**Figure 10.** Thermal shock resistance of the mullite contained ceramic printed by DIW technique sintered at different temperatures with different SiC additions.

To investigate the microstructure and sintering of junctions between slurry lines, a loose morphology of 3D printed ceramics with different SiC contents, sintered at 1523K, were revealed in Figure 11. It can be seen from the figure that the structure of high-temperature flue gas filter designed by software has been realized. The microstructures of specimens with different SiC contents show relatively uniform bonding degree on the X-axis, Y-axis and Z-axis. With the increase of the SiC addition, the bonding degree of lap joints in all directions increased gradually. When the content of SiC was up to 20wt%, the bonding degree of lap joints in all directions was the highest. It shows that the active silica formed by SiC oxidation plays a role in promoting sintering.

![Micrographs of ceramic microstructure](image)

**Figure 11.** Fracture surface of samples the mullite contained ceramic printed by DIW technique sintered at 1523K with different SiC additions.
To further study the microstructure and spatial distribution of the pores, Figure 12 shows higher magnification SEM micrographs of 3D printed ceramics with different SiC contents, prepared at 1523K, respectively. It can be seen from the fracture microstructure that with the increase of content of SiC, there are more obvious pores in the fracture surface, and the distribution of pores in the fracture surface is more uniform. It is speculated that the pore formation may be due to the excessive oxidation reaction of SiC and the excessive thickness of the oxide layer, which makes it difficult for the generated carbon monoxide gas to overcome the resistance to escape and stay in the interior[20].

Figure 12. Microstructure of samples the mullite contained ceramic printed by DIW technique sintered at 1523K with different SiC additions.

4. Results and discussion
The effects of 3D printed mullite contained ceramic with microsized SiC were determined in this study. The properties of mullite ceramics was influenced by a combination of a certain amount of raw materials and the addition of SiC.

(1) The addition of SiC powder can promote the sintering of 3D printed mullite contained ceramics due to the oxidation reaction of SiC to produce active silica. The larger the amount of SiC powder added, the more obvious the sintering promotion effect on the samples.

(2) With the increasing of the sintered temperature, the oxidation reaction of silicon carbide was stronger, and the influence on the properties of 3D printed mullite contained ceramics was greater.

(3) When SiC powder is added, the mineral composition of samples sintered at various temperatures is mainly mullite, quartz and cristobalite.

(4) The thermal shock resistance of 3D printed mullite contained ceramics can be significantly improved by introducing SiC micro-powder after firing at various temperatures.

(5) 3D printed mullite contained ceramic flue gas filters in high temperature environment for multi-cycle is expected to be realized.

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References
[1] Chen Z, Li Z, Li J, Liu C, Liu C, Li Y, Wang P, He Y, Lao C, Fu Y 2018 Journal of the European Ceramic Society 39 661
[2] Galeta T, Raos P, Stojšič J, Pakši I 2016 Procedia Engineering 149 100
[3] Eckel Z C, Zhou C, Martin J H, Jacobsen A J, Carter W B, Schaedler T A 2016 Science 351 58
[4] Aditi P, Leen C J, Simon K 2019 Chemical Engineering Journal 363 337
[5] Smay J E, Gratson G M, Shepherd R F, Cesarano J, Lewis J 2010 Advanced Materials 14 1279
[6] Schneider H, Fischer R X, Schreuer J. Mullite 2015 Journal of the American Ceramic Society 98 2948
[7] Hammel E C, Ighodaro L R, Okoli O I 2014 Ceramics International 40 15351
[8] Wang W, Hu X, Li L, Jing W, Guo A, Du H 2019 Ceramics International 45 6723
[9] Liu Q, Xue T, Yang L, Hu X, Du H 2016 Journal of the European Ceramic Society 36 1691
[10] Lee W E, Souza G P, Mcconville C J, Tarvornpanich T, Iqbal Y 2008 Journal of the European Ceramic Society 28 465
[11] Han L, Deng X, Li F, Huang L, Pei Y, Dong L, Li S, Jia Q, Zhang H, Zhang S 2018 Ceramics International 44 14728
[12] Seville J, Chuah T, Sibanda V, Knight P 2003 Advanced Powder Technol. 14 657
[13] Gou Y, Wang H, Jian K 2017 Journal of the European Ceramic Society 37 907
[14] Sun X, Yin X, Fan X, Ma X, Cao X, Cheng L, Zhang L 2018 Journal of the European Ceramic Society 38 479
[15] Z. Luo, H. Cao, H. Ren, X. Zhou 2016 Ceramics International 42 3250
[16] Wang H, Feng Q, Wang Z, Zhou H, Kan Y, Hu J, Dong S 2017 Corrosion Science 124 131
[17] Novitskaya E, Khalifa H E, Graeve O A 2018 Materials Letters 213 286
[18] Liu H, Cheng H, Wang J, Tang G 2010 Ceramics International 36 2033
[19] Wang W, Chen W, Liu H 2019 Ceramics International 45 9852
[20] Terrani K A, Pint B A, Parish C M, Silva C M, Snead L L, Katoh Y 2014 Journal of the American Ceramic Society 97 2331
[21] Kim W S and Lee J W 2017 J. Aip Advances. 7 095022.