



# Porous acicular mullite obtained by controlled oxidation of waste molybdenum disilicide



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## ABSTRACT

Porous acicular mullite was fabricated by using waste MoSi<sub>2</sub> heating element and Al<sub>2</sub>O<sub>3</sub>. Careful calcination of the pulverized heating element led to the formation of a mixture of MoO<sub>3</sub> and amorphous SiO<sub>2</sub>. This mixture was employed as both SiO<sub>2</sub> precursor and pore former. The oxidation of MoSi<sub>2</sub> and mullite formation were studied. The effect of fabrication temperature on phase composition, porosity, grain morphology, and compressive strength of sintered mullite was examined. Pure mullite with porosity of more than 60% and compressive strength of ~20 MPa was obtained at temperature as low as 1300 °C. The microstructure consisted of elongated, rectangular, prism-like grains which are known to be effective in filtration of diesel engine exhaust. The increase in sintering temperature caused the change of grain morphology and reduction in compressive strength.

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## 1. Introduction

Mullite ceramics (3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>) has been extensively studied over the past two decades because of good combination of properties such as high melting point, low thermal-expansion coefficient, good thermal shock resistance, and excellent chemical stability at elevated temperature [1,2]. These properties are especially important for porous mullite which is widely used as catalyst, catalyst support, and filter material for filtration of molten metal as well as hot gasses [3,4]. Although the catalyst and filter materials are normally not subjected to a considerable mechanical load, they need a certain level of strength which allows easy handling and, very often, canning process [5,6]. Besides high porosity (50–80%), the additional design requirements for ceramic filters are specific and narrow pore size distribution, low pressure drop across the filter, and good erosion resistance since the material is exposed to impact of high velocity particles in the gas stream. These requirements are particularly important for the filters used for removal of fine particles from hot gasses. These particles may considerably reduce the efficiency of operation after some time by forming a cake at the surface of inlet side of the filter or by clogging the pores [7,8]. Therefore, it is quite desired to have the possibility of periodical cleaning, i.e., regeneration of the filter

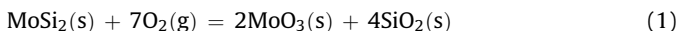
which is normally done by either backfilling with compressed air or burning of the trapped particles at high temperature [9]. This is an additional reason which makes high temperature ceramics such as mullite a material of choice for filter application.

It is well known that the porosity of ceramics can be effectively controlled by varying sintering conditions such as sintering temperature and time [10]. However, the fairly high porosity of about 50–80%, which is required for the filter application, is normally achieved with the help of pore-forming agent. The pore-forming agent is usually graphite powder [11] or some organic compound that burns out or decomposes at temperatures below 700 °C [12–14], which is considerably lower than the temperature of mullite fabrication (1000–1500 °C). The porosity and pore size are strongly affected by the properties and the amount of agent added to the raw material. Although the mullite ceramics can be easily fabricated by sintering of stoichiometric mixture of SiO<sub>2</sub> (silica) and Al<sub>2</sub>O<sub>3</sub> (alumina) [11], there is a constant effort to develop methods which would use the relatively cheap and abundant silica and alumina precursors such as kaolinite [15]. The exploitation of natural raw material enables the reduction of production cost and thus the fabrication of mullite in an economical way. This is especially important for large-scale production such as production of mullite filters. The production cost can be additionally reduced by utilizing by-products and waste material as a source of silica and alumina. A several studies have shown that fly ash, which mainly consists of silica and alumina, can be effectively used in mullite fabrication [16].

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Furthermore, other waste materials, such as molybdenum disilicide ( $\text{MoSi}_2$ ), could be also converted, under certain conditions, into one of mullite constituents.

This paper describes a successful attempt to fabricate highly porous mullite by utilizing waste  $\text{MoSi}_2$  heating elements. Although the annual production of  $\text{MoSi}_2$  heating elements is considerable, about 80,000 tones, there is no report on the use of waste  $\text{MoSi}_2$  in mullite fabrication. It will be shown that the careful calcination of  $\text{MoSi}_2$  (Eq. (1)) [17] yields a mixture of  $\text{MoO}_3$  and amorphous  $\text{SiO}_2$ , which can be effectively employed not only as a source of silica but also as a pore former.



Namely,  $\text{MoO}_3$  evaporates at temperature considerable lower than the sintering temperature introducing an additional porosity into powder compacts. It is also important to indicate that the obtained mullite consisted of elongated needle-like grains. This type of grain morphology has been reported to be essential for developing highly porous filter material with strong mechanical integrity [6]. The effect of sintering temperature on properties of fabricated mullite was studied.

## 2. Material and methods

### 2.1. Sample preparation

The used  $\text{MoSi}_2$  heating element (Super Kanthal 1700 °C, made by Bulten–Kanthal AB, Sweden) was crushed and pulverized in vibratory mill for 1 h. The obtained powder (denoted as PHE, Pulverized Heating Element) was calcined at temperature ranging from 500 to 1200 °C for different calcination time. The powder obtained after 24 h long calcination at 500 °C (denoted as PHE500) consisted of  $\text{MoO}_3$ , residual  $\text{MoSi}_2$ , and amorphous  $\text{SiO}_2$ , and was therefore used as a source of  $\text{SiO}_2$  for the mullite fabrication. X-ray diffraction (XRD) analysis showed that the crystalline fraction of PHE500 powder consisted of 13 wt.% of residual  $\text{MoSi}_2$  and 87 wt.% of  $\text{MoO}_3$ . Bearing in mind that the amorphous  $\text{SiO}_2$  present in PHE500 cannot be detected by XRD it can be concluded that the fractions of  $\text{MoO}_3$  and residual  $\text{MoSi}_2$  in PHE500 are lower than those determined by XRD. Assuming that the oxidation of  $\text{MoSi}_2$  follows Eq. (1) it was calculated that PHE500 powder should approximately contain 7.5 wt.% of the residual  $\text{MoSi}_2$ , 50.4 wt.% of  $\text{MoO}_3$ , and 42.1 wt.% of amorphous  $\text{SiO}_2$ . The residual  $\text{MoSi}_2$  is expected to completely oxidize during sintering (>1000 °C) and yield an additional amount of  $\text{SiO}_2$  prior to the mullite formation. Simple calculation based on Eq. (1) shows that 100 g of PHE500 will yield ~48 g of  $\text{SiO}_2$ . Knowing that  $\text{Al}_2\text{O}_3/\text{SiO}_2$  weight ratio in mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is 72/28 it was estimated that  $\text{Al}_2\text{O}_3/\text{PHE500}$  weight ratio in starting mixture must be 55/45 in order to fabricate mullite. The calculated amounts of PHE500 and  $\text{Al}_2\text{O}_3$  powder (Alcoa A-16 SG, Bauxite, USA) were homogenized by ball milling in a plastic jar using  $\text{Al}_2\text{O}_3$  balls as milling media and methanol as a liquid vehicle. After milling for 12 h, the mix was dried at 90 °C followed by sieving. The thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of the obtained mixture were performed in air (flow rate:  $200 \text{ cm}^3 \text{ min}^{-1}$ ; heating rate:  $20 \text{ °C min}^{-1}$ ) from room temperature up to 1400 °C on a SDT Q600 instrument (TA Instruments). After sieving, the mixture was pressed into cylindrical compacts ( $\varnothing = 8 \text{ mm}$ , height ~ 10 mm) under a pressure of 60 MPa. The samples were sintered at temperature ranging from 1200 to 1500 °C for 4 h in air with a heating rate of  $5 \text{ °C/min}$ . Four-hour long hold at 750 °C was employed to ensure a complete evaporation of  $\text{MoO}_3$ . The sintered samples were machined in order to make upper and lower planes perfectly parallel.

### 2.2. Sample characterization

The phase composition of starting powders as well as the sintered samples was determined by X-ray diffraction (XRD) analysis on a Siemens D500 diffractometer using  $\text{Cu K}\alpha$  radiation with a Ni filter. Bulk density and open porosity were determined by the Archimedes' method using xylene. Compressive strength measurement was carried out on Instron M 1185 testing machine. Microstructures were examined by Scanning electron microscopy (SEM) using a JEOL-JSM-5800LV microscope. The composition of sintered samples was also analysed by Energy dispersive X-ray spectroscopy (EDS).

## 3. Results and discussion

### 3.1. Phase composition

XRD patterns of uncalcined PHE and PHE calcined at different temperatures are presented in Fig. 1. As can be seen, the uncalcined PHE mainly consists of  $\text{MoSi}_2$  and small amount of  $\text{Mo}_5\text{Si}_3$  (~5 wt.%). The presence of  $\text{Mo}_5\text{Si}_3$  is the result of oxidation of heating element and consequent formation of thin  $\text{SiO}_2$  surface layer during operation at high temperature [18]. Thus, it is quite expected that the certain amount of compound reach in Mo, such as  $\text{Mo}_5\text{Si}_3$ , can be formed beneath the silica surface layer due to Si concentration depletion. On the other hand, the calcined PHEs do not contain this phase, regardless of temperature. It is evident from Fig. 1 that the calcination temperature of 1000 °C is sufficiently high to cause the crystallization of  $\text{SiO}_2$  as proposed by Eq. (1). Beside cristobalite, which is the main polymorph of silica, small amount of quartz was also detected. Based on this, it can be concluded that the waste  $\text{MoSi}_2$  heating elements can be effectively used as a source of  $\text{SiO}_2$  for mullite fabrication. Although Eq. (1) predicts the formation of fairly large amount of  $\text{MoO}_3$ , the content of this compound was almost negligible in the samples calcined at 900 and 1000 °C. The sample calcined at 1200 °C does not contain any traces of  $\text{MoO}_3$ . This is all expected knowing that  $\text{MoO}_3$  evaporates at temperatures higher than 800 °C [19]. Unfortunately, for the porous mullite fabrication, it is important to avoid the evaporation of newly created  $\text{MoO}_3$  as well as to completely oxidize  $\text{MoSi}_2$ . As mentioned before,  $\text{MoO}_3$  should be a pore former and therefore its evaporation must occur during sintering of powder compacts. Several studies have reported that  $\text{MoO}_3$  can be retained by prolonged calcinations of

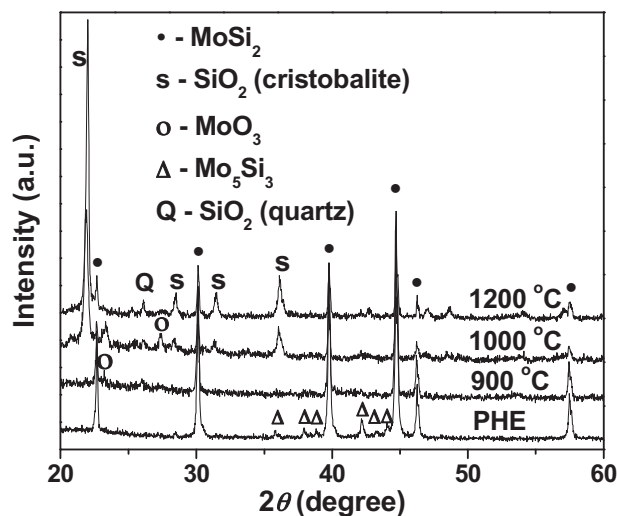


Fig. 1. XRD patterns of uncalcined pulverized heating element (PHE) and PHE calcined at 900, 1000, and 1200 °C for 30 min.

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