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A low-temperature fabrication route for enhancing mechanical properties and corrosion resistance of porous mullite ceramics through homogeneously mullite sol-coating method

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Porous ceramics were fabricated by mullite sol-coated mullite powder (homogeneously sol-coated) through sol-gel method using expanded polystyrene (EPS) as pore former. In this work, mullite formed in the coating layer was characterized by XRD. The effect of mullite sol coating content and sintering temperature on the microstructure and mechanical properties of porous mullite ceramics was investigated. Homogeneously sol-coated sample sintered at 1450 ºC with 30 wt.% mullite sol coating exhibited a remarkable flexural strength of 24 MPa at 53% apparent porosity. It showed that the interlocking structure formed from homogeneously sol-coated sample was helpful to enhance the mechanical strength and thermal alkali corrosion resistance of the porous mullite ceramics.

Key word: Porous ceramics, Corrosion resistance, Homogeneously, Mullite.

Introduction

Porous ceramics has attracted increasing attention for its successful applications in many industries such as catalyst carriers, lightweight structural materials, filters for molten metal and hot exhaust gases.[1-3] Porous ceramics fabricated by conventional methods usually use feldspar, quart and clay as the sintering aids. In general, there is a high volume fraction of glassy phase due to the existence of amorphous silica or impurities.[4] Such conventional porous ceramics often get collapse and jam pores issues, and this will cause lower porosity, mechanical properties and thermal corrosion resistance.[5] Especially for porous ceramics used as hot gases filters which were often used under thermal shocks and corrosion condition.[6] The weak mechanical strength and thermal corrosion resistance of glassy phase need to be improved urgently.

Many efforts have accordingly been devoted to reinforce the porous ceramics, such as whisker, short-fiber and sol-gel coating. Li *et al*.[7] fabricated porous mullite ceramics, which were reinforced by in situ synthesized mullite whiskers. Lang *et al*.[8] produced porous mullite ceramics reinforced by mullite fiber, and investigated the effect of sintering temperature, mullite fiber content and sintering aid on porosity and strength of porous mullite ceramics. Among these methods, sol-gel coating reinforcement is an effective approach to improve the properties of materials.[9,10] Producing coatings by this way presents a lot of advantages such as low sintering temperature, cost effectiveness and the possibility of coating on different substrates even with complex geometries.[11-13]

Mullite is one of the most important candidate materials for porous ceramics, due to its high strength, low thermal expansion, good stability at high temperature and excellent creep resistance.[14,15] Usually mullite formation temperature is above 1500 ºC when alumina and silica mixtures are used as starting components. Many attempts were reported for reducing the formation temperature of mullite.[16] Homogeneously sol-coated process can help to fabricate a uniformly crystalline phase and thermal expansion coefficient of the sintered sample at low temperature, the homogeneously properties in physics and chemistry can be expected. However, there are few reports on the research of porous mullite ceramics fabricated from homogeneously sol-coated method.

Here we report a homogeneously coating on mullite particles where the mullitization occurs completely as low as 1250 ºC. Homogeneously coated sol transforms to liquid binder during sintering to form an interlocking structure, which leads to a remarkable improvement in mechanical properties and thermal alkali corrosion resistance. Producing porous ceramics by this method brings a lot of advantages including pure phase product and simple technique. Moreover, it can be widely used in industrial exhaust filter area.

Experimental Procedures

Mullite powder (~ 100 μm, 99% purity, Meilin Mullite

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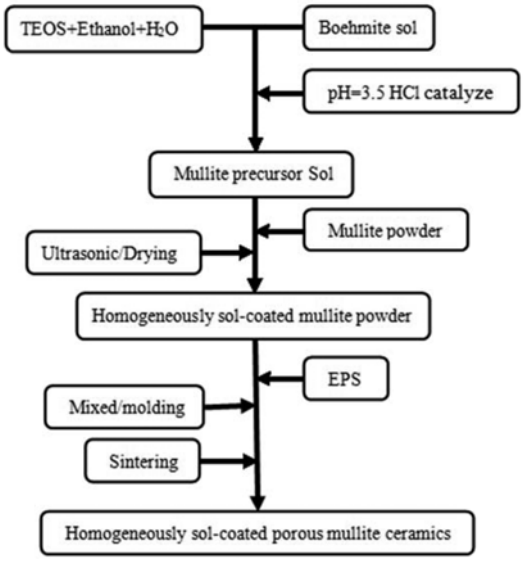

Fig. 1. Flow chart for the synthesis of homogeneously sol-coated sample.

Micro-powder Co. Ltd., Jiangsu, China), TEOS (AR, Guibao chemical Co. Ltd., Zhejiang, China), $Al(NO_3)_3 \cdot 9H_2O$ (99% purity, Sinopharm Chemical Reagent Co. Ltd., Tianjin, China) were used as raw materials, and EPS micro beads (~ 100 μm, Zhanwang Chemical Co. Ltd., Jiangsu, China) was employed as the pore-forming agent.

Mullite sol was prepared by the reaction between boehmite sol and silica sol. Boehmite sol could be obtained from $Al(NO_3)_3 \cdot 9H_2O$ by controlling precipitation followed by peptisation with ethanol as reported earlier.[17] Tetraethyl orthosilicate (TEOS) was hydrolyzed with distilled water (TEOS/H_2O/Ethanol: 1/4/2) and the silica sol was obtained. To catalyze hydrolysis and condensation reactions, pH was adjusted to 3.5 by adding hydrochloric acid (HCl, 1 M). Four batches of homogeneouslyly sol-coated powder were prepared by mixing different mass ratio mullite powders into the mullite sol through ultrasonic dispersion to obtain a stable suspension. The suspension had been stirred for 10 h in order to achieve the slurry. After drying in an oven, homogeneously sol-coated mullite powder and EPS micro beads (fixed to 50 vol.%) were mixed and pressed into rectangular bars of 3.0 mm × 4.0 mm × 36.0 mm. The specimens were sintered at various temperatures. Detailed flow chart is provided in Fig. 1. In order to compare the thermal alkali corrosion resistance, uncoated sample was prepared by mixing the mullite powder, sintering additives (feldspar, kaolin clay etc.) and EPS (50 vol.%).

X-ray patterns of the samples were tested by X-ray diffractometer (Phillips, PW1700) with Cu Kα radiation (λ = 0.15406 nm). Open porosity was determined by the Archimedes displacement method with distilled water as a liquid medium. Specimens were made to a dimension of 3.0 mm × 4.0 mm × 36.0 mm to evaluate their flexural strength via three-point bending test (Shimadzu, Autograph AG-I) with a support distance of 30.0 mm and a cross-head speed of 0.5 mm/min. Four specimens were tested to obtain the average flexural strength. The microstructures of fractured sintered specimens were observed with scanning electron microscopy (Hitachi, S-4700). The specimens were placed in NaOH (10 wt.%) aqueous solutions on an electrical plate and boiled at 105 ºC for 8 h afterwards.

Results and Discussion

XRD analysis

Fig. 2 shows XRD patterns of the mullite precursor gels sintered at different temperatures. XRD results of the sample calcined at 1000 ºC indicate the synthesis of a quasi crystal Al-Si spinel. However, the mullite phase could not be detected. It can be found that the coexistence of sharp Al-Si spinel diffraction peak and large amounts of mullite phase occurs when the samples were calcined at 1150 ºC. It indicates that the mullite formation starts in the temperature range of 1000 ºC to 1150 ºC. When it reaches to 1250 ºC, extensive mullitization phenomenon occurs, and Al-Si spinel peaks almost completely disappear. The formation of mullite at low temperature is attributed to the homogeneously mixing of nano sized boehmite and silica through the sol-gel process.[18] The crystallisation development in this material followed the mechanisms proposed by Chakraborty and Wang. Chakraborty *et al*.[19] suggested that if boehmite is precipitated during gelification process, the resultant gel would be diphasic in character and it would transform to Al-Si spinel as an intermediary phase. Wang *et al*.[20] showed that The as-prepared precipitation powders are composed of AACH and amorphous silica, which convert to mullite via the Al-Si spinel phase and it is almost complete

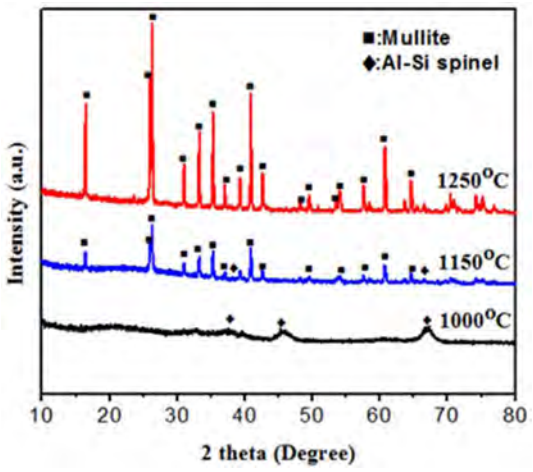

Fig. 2. XRD patterns of mullite precursor gels calcined at various temperatures.

at 1250 °C. Moreover, it exhibits a stoichiometric composition pure phase mullite structure in the specimen sintered at 1250 °C (JCPDS-15-0776). Since the porous mullite ceramics have been fabricated by the homogeneously sol-coated process, the properties of porous mullite ceramics can be improved in many ways.

Coating content and sintering temperature

Coating content

The effect of coating content on the microstructure of the homogeneously sol-coated samples is shown in Fig. 3. For the sample with 10 wt.% coating contents, it can be seen in Fig. 3(a) that mullite particles are loose contacted by sintering necks. It suggests that original mullite powders could not be completely coated with low coating content, which resulted in lamellar connection mullite particles. The forming process of the lamellar mullite connection can be described by Guo's report. Guo *et al*.[21] suggested that in the sintering process, TEOS transformed into the silica and the remaining mullite with a special lamellar connection structure constructed the main body of the porous ceramics. With increasing coating content, homogeneously coating layer becomes more strongly connected to the matrix particles (Fig. 3b). When coating content increases to 30 wt.% (Fig. 3c), it can be obviously seen that the homogeneously sol-coated mullite particles are steadily interconnected by sintering necks. Fig. 3(d) shows the microstructure of the sintered sample with 40 wt.% coating contents. It indicates that the flexural strength would be increased at high temperature, but excess low viscous liquid agglomerant will flow into some small pores from stacking mullite particles and fill them up so that only larger pores are left and that could lead to the decreasing of porosity.[22]

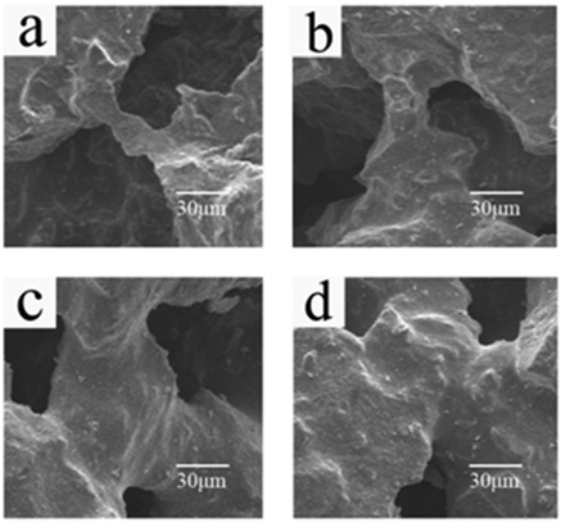

Fig. 3. SEM micrographs of homogeneously sol-coated samples with different coating content (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.% and (d) 40 wt.%, respectively.

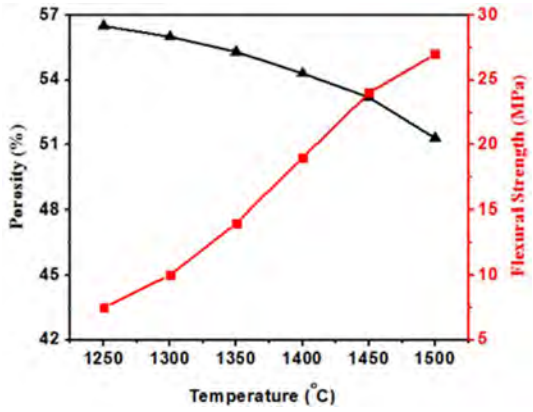

Fig. 4. Porosity and flexural strength of homogeneously sol-coated samples sintered at different temperatures.

Sintering temperature

Fig. 4 shows the porosity and flexural strength of the homogeneously coated samples sintered at various temperatures. With increasing sintering temperature, the apparent porosity decreases, whereas flexural strength of specimens increases. The flexural strength is mainly affected by the bonding necks among particles, porosity and microcracks. The specimens possess a higher flexural strength due to its thicker necks, lower porosity and fewer microcracks.[23] The reinforcement of porous mullite ceramics is attributed to the thermally activated mechanisms, condensation reactions lead to the increase of the mullite gel network connectivity. The homogeneously gel becomes more and more reticulated and finally turns into sintering necks.[24,25] As homogeneously coating phase formed a reinforced interlocking network structure at sintering temperature, mullite particles are bonded by the thicker sintering necks. It can be illustrated that specimens will reach the best performance point at 1450 °C with a high porosity of 53% and remarkable flexural strength of 24 MPa.

Reinforcement mechanism

The microstructure schematic illustration of sintered homogeneously coated sample is shown in Fig. 5(a). It could be clearly seen that the homogeneously sol-coated layer are uniformly distributed on the surface of mullite particles. The formation of homogeneously sol-coated particles can be attributed to the electrical double-layer (EDL) theory based on Li's study.[26] It was suggested that the requirement of overall electro-neutrality in the interfacial region resulted in forming of a oppositely charged counterion diffuse layer adjacent to the particle surface, thus electrical double layers form. Colloid particles that carrying positive charge can binder the mullite particles that carry negative charge under appropriate pH condition, thus homogeneously sol could be attached uniformly to the surface of mullite particles. Fig. 5(b) shows the SEM micrograph of homogeneously sol-coated sample

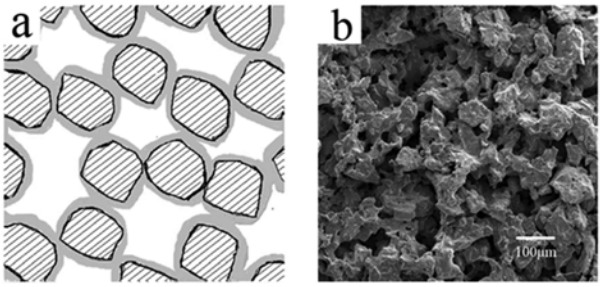

Fig. 5. (a) Microstructure schematic illustration of sintered homogeneously sol-coated sample and (b) typical SEM micrograph of homogeneously sol-coated sample sintering at 1450 °C, respectively.

sintered at 1450 °C with a mullite sol coating content of 30 wt.%. It illustrated that homogeneously precursor became liquid binder at 1450 °C and constructed an interlocking structure. This structure enhanced the flexural strength effectively. Formation of this structure could be attributed to the special crystal structure of mullite, where strong-bounded chains lie along the crystallographic c-axis, which allows sintering necks grow anisotropically in an unconstraint environment.[27] The pore sizes (about 80-100 μm diameter) are suitable for porous mullite ceramics in filtering impurities such as industrial hot exhaust gases.

Thermal alkali corrosion resistance

Fig. 6 shows the mass loss percent of the uncoated and homogeneously sol-coated samples after corrosion in the 10 wt.% NaOH solution, for various corrosion times. With increasing boiling time, the mass loss percent of homogeneously sol-coated sample increased slightly, but rapidly for uncoated sample. Even after boiled for 8 h, the mass of homogeneously sol-coated sample only reduced 1.25 wt.%. But for uncoated sample, the mass loss could be as high as 10.31 wt.%. Fig. 7 displays the flexural strength loss ratios of the uncoated and homogeneously sol-coated samples after boiled in the 10 wt.% NaOH solution. After corrosion for 8 h in strong alkali, the average flexural strength of homogeneously sol-coated samples is still 21.5 MPa and its loss in strength is only 10.4%, while the loss in strength of uncoated sample is 29.38% after same boiling time. These phenomena are further proved by the SEM micrographs.

SEM micrographs of uncoated and homogeneously sol-coated fracture surface are shown in Fig. 8, which were corroded in the 10 wt.% NaOH solution at 105 °C for 8 h. Plenty of white corrosion surface marking and cleavages crack could be detected on the surface of the uncoated sample after long time thermal alkali solution corrosion (Fig. 8a). During the experiment, feldspar and kaolin clay were added as sintering aids in the fabrication process of uncoated sample. Sintered kaolin clay was firstly corroded in the thermal alkali solution due to its impurities and abundant free silica.[28] The

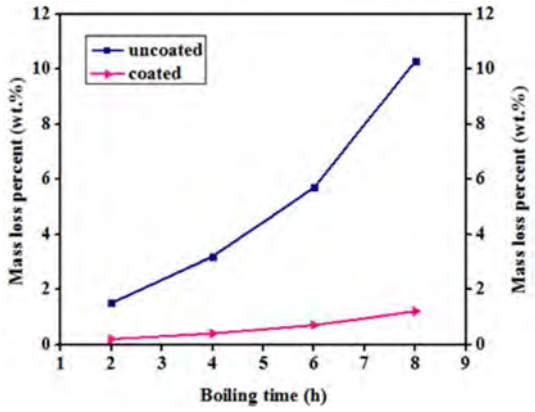

Fig. 6. The mass loss percent of uncoated and homogeneously sol-coated samples boiled in 10 wt.% NaOH solution after 8 h.

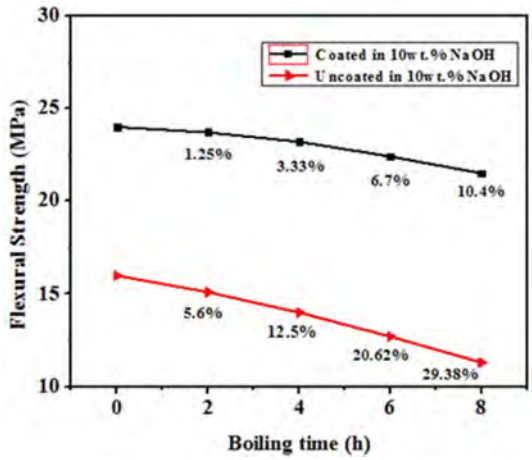

Fig. 7. The flexural strength loss ratios of uncoated and homogeneously sol-coated samples boiled in 10 wt.% NaOH solution after 8 h.

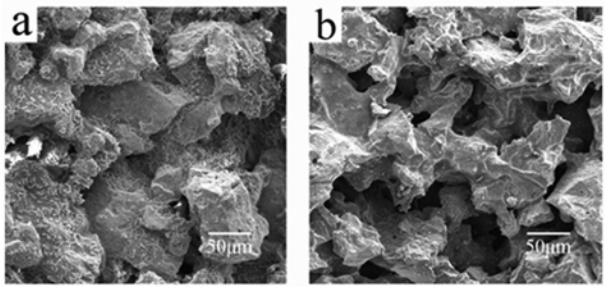

Fig. 8. SEM micrographs of the porous mullite ceramics (a) uncoated and (b) homogeneously sol-coated sample corroded in 10 wt.% NaOH for 8 h.

reaction between SiO_2, Al_2O_3 and OH^- can be indexed in Eq. (1) and (2) as follows:

$$SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O \quad (1)$$

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O \quad (2)$$

The produced meta-aluminate and silicate dissolved into water easily, therefore, the mass and fracture strength of uncoated sample would decrease quickly.

Compared with the uncoated sample, microstructure of the homogeneously sol-coated sample remained almost the same as before corrosion (Fig. 8b). In the present work, the amount and connecting area of interlocking structure effectively prevents from initial serious corrosion between sintering necks and OH^- from eroding the interior.[29] As a consequence, homogeneously sol-coated process promoted the thermal alkali corrosion resistance of porous mullite ceramics essentially.

Conclusions

Porous mullite ceramics were prepared by a low-temperature homogeneously sol-coated method. Complete formation of mullite occurred at 1250 °C as indicated by XRD analysis. The porous mullite ceramics with 30 wt.% mullite sol coating content sintered at 1450 °C showed an open porosity of 53% and flexural strength of about 24 MPa. Mullite precursor transformed into liquid binder and finally constructed an interlocking structure at 1450 °C which enhanced the mechanical property and thermal alkali resistance effectively.

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