ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Microstructural evolution and densification behavior of porous kaolin-based mullite ceramic added with MoO_3

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ARTICLE INFO

Keywords:
Mullite
Sintering
Grain growth
Densification

ABSTRACT

Microstructural evolution and densification behavior of porous kaolin-based mullite ceramic added with MoO_3 were investigated. The results indicated that MoO_3 addition not only lowered the secondary mullitization temperature to below 950 °C, but also facilitated effectively the anisotropic growth of mullite grains. Fine mullite whiskers grew and interlocked with one another in the pre-existing pore regions, in-situ forming a stiff 3D skeleton structure of mullite whiskers, which arrested further densification of the sample. On the other hand, due to the great capillary attraction of small pores, the liquid phase tended to spread over small grains, which favored the growth from small mullite grains into whiskers at the expense of the liquid phase. Consequently, competitive mechanisms of sintering and crystal growth of mullite functioned, which further limited the sample densification. As a result, the total linear shrinkage of the sample added with MoO_3 after firing at 1400 °C was only -2.75%, and its porosity was retained at as high as 67%.

1. Introduction

Porous mullite ceramics are used extensively in many important industrial sectors/areas, including catalyst support, gas/liquid filtration, purification separation and thermal insulation, because of their many desirable properties, such as good high-temperature strength, excellent chemical and thermal durability, low expansion coefficient and high thermal shock resistance [1]. They can be specifically produced from relatively inexpensive clay minerals, such as kaolin [2–6], kyanite [7,8], and fly ash [9,10], so their overall production cost and sintering temperature are lower than in the case of pure alumina.

The main routes to production of macro-porous ceramics include (i) partial sintering, (ii) sacrificial agents, (iii) replica templates, and (iv) direct foaming [11]. The partial sintering, as a simple and cost-effective technique, has been used successfully to prepare porous ceramics with homogeneous pore structures and narrow pore size distributions [12]. Nevertheless, to achieve an optimal combination of physical and chemical properties, porosity and pore size/morphology need to be carefully controlled. With partial sintering, the microstructure (size, morphology, and orientation of grains and pores, etc.) is usually tailored by controlling morphology and size of raw materials and sintering parameters. Mullite crystals exhibit several morphologies: granular, short columnar and acicular [13]. Among them, the acicular crystal is regarded as the most desirable morphology, owing to its high aspect ratio and strength [14–16] which make it very effective in ceramics toughening and porosity and filtration efficiency enhancement, via preventing microcrack propagation and forming an inter-locked network structure, respectively.

The quantity and morphology of mullite crystals during sintering depend not only on firing temperature but also on the quantity of liquid formed at the temperature, since the mullite formation reaction between quartz and alumina is controlled by a dissolution-precipitation mechanism [17]. Various types/amounts of sintering aids such as P_2O_5 [18], CaO [19,20], B_2O_3 [18], MgO [20–22], TiO_2 [18], Y_2O_3 [22,23], V_2O_5 [24] and WO_3 [25–27] have been examined to lower the formation temperature of SiO_2-rich liquid, so as to promote the anisotropic growth of mullite grain. Unfortunately, the formation of transient viscous liquid phase also facilitates particle rearrangement and species diffusion/mass transport [28], accelerating the densification, i.e., decreasing the porosity. Thus, for many products prepared with sintering additives, it is difficult to retain a relatively high porosity level via partial sintering.

Despite this, our recent work has found that porous Kaolin-based mullite ceramics with open porosity as high as 67% can be successfully prepared by using MoO_3 as a sintering additive [29]. Some other researchers also demonstrated that MoO_3 addition can lower the mullitization temperature and accelerate the anisotropic growth of mullite whiskers [25,26]. Nevertheless, the relationship between mullitization

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https://doi.org/10.1016/j.ceramint.2018.06.266
Received 24 May 2018; Accepted 29 June 2018
0272-8842/

Please cite this article as: Hou, Z., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.06.266

and densification of kaolin-based mullite still remains unclear. To address this issue, microstructural evolution and densification behavior of porous Kaolin-based mullite added with MoO_3 have been investigated in detail in this work.

2. Experimental

Kaolin clay (Xinzhou, Shanxi Province, China) and Al_2O_3 (Guangcheng Chemical Reagent Ltd., Tianjin, China) were used as the main starting materials. The former was calcined and then ball-milled to about 15 μm in average. MoO_3 (99.5% pure, Kermel Chemical Reagent Ltd., Tianjin, China) was used as a sintering aid.

Kaolin, Al_2O_3 and MoO_3 in the ratios corresponding to the nominal chemical compositions of $(3Al_2O_3{\cdot}2SiO_2)_{0.9}$ $(MoO_3)_{0.1}$ were weighted and ball-milled in ethanol for 12 h using a polyethylene bottle with alumina balls. After oven drying, the mixed powders were uniaxially pressed at 70 MPa, forming pellet samples of 40 mm in diameter and 6.5–8 mm in thickness. These green samples were placed in alumina crucibles and fired for 2 h in air in a muffle furnace at a given temperature between 950 and 1400 °C.

Open porosities were measured in distilled water using the Archimedes' method. Total linear shrinkage ($(l - l_0) / l_0$, where l_0 is the initial length and l is the final length) associated with sintering was established from direct measurements of sample dimensions before and after firing. X-ray diffraction (XRD, Philips Co. Ltd, Holland) analysis was applied to identify crystalline phases in fired samples, and a field emission scanning electron microscope (FESEM, S-4800) was used to examine their overall microstructure and phase morphology.

3. Results and discussion

Fig. 1 shows XRD patterns of MoO_3 added samples after 2 h firing at 950–1400 °C. At 950 °C, both cristobalite (SiO_2, tetragonal) and mullite were detected. Upon increasing temperature to 1100 °C, the former decreased whereas the latter increased. Upon further increasing temperature to 1200 °C, cristobalite disappeared, and essentially single phase mullite was formed. Further increasing temperature to 1400 °C did not result in any phase changes, although the mullite peaks became higher due to enhanced crystallization. It is worthwhile to note the splitting of (120) and (210) peaks at around 26° (2θ) at 950 °C (Fig. 2), as reported previously [26]. The above results suggested that *Secondary* mullite ($3Al_2O_3{\cdot}2SiO_2$, orthorhombic) had been formed at 950 °C in the samples added with MoO_3 [30].

As experimentally verified, the reaction mechanism of kaolin-Al_2O_3 transformation to mullite can be described as follows [31]. At 980 °C, an intermediate aluminosilicate phase is formed from Kaolin, which is followed by mullite nucleation and subsequent crystallization of this aluminosilicate phase. Mullite is formed initially in the tetragonal structure and the excess SiO_2 is exsolved. Upon increasing temperature to 1150–1250 °C, the tetragonal mullite gradually transforms to orthorhombic mullite. Meanwhile, the excess SiO_2 reacts with Al_2O_3 forming a binary aluminosilicate glassy phase, and nucleation of orthorhombic mullite takes place.

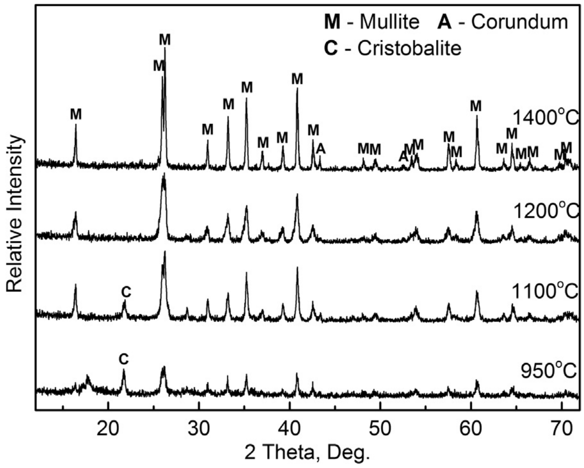

Fig. 1. XRD patterns of MoO_3 added samples after 2 h firing at 950–1400 °C.

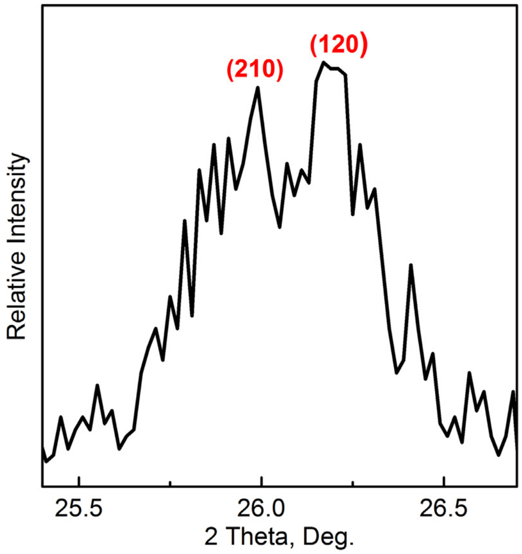

Fig. 2. (120) and (210) reflections of MoO_3 added sample after 2 h firing at 950 °C.

Throughout the entire reaction process of kaolin, the aluminosilicate glassy phase plays an essential role in the mullite formation. External addition of a fluxing oxide facilitates the formation of a low melting aluminosilicate glassy phase, accelerating the mullite nucleation. The effects of different fluxing oxides on the mullite formation have been investigated [26,29]. Among the sintering aids, only MoO_3 was found to be able to lower the secondary mullite formation temperature to below 980 °C. When MoO_3 is present, no intermediate tetragonal mullite is formed, so Kaolin reacts with Al_2O_3, transforming directly into orthorhombic mullite.

Fig. 3 illustrates microstructural evolution of the MoO_3 added samples fired at different temperature for 2 h. Pre-existing pores were evidently seen in the sample fired at 1100 °C (Fig. 3A). Significant amounts of high aspect ratio whiskers grew around the pre-existing pores and extended to the middle regions (Fig. 3A1). Upon increasing the firing temperature to 1200 °C, mullite grains around the pre-existing pores grew rapidly in preferential directions, forming mullite whiskers which subsequently divided the pre-existing pores into many more smaller pores (Fig. 3B1). Nevertheless, the grains in pseudo clusters grew much more sluggishly (Fig. 3B2). Upon further increasing the firing temperature to 1300 °C, the mullite grains in the pseudo clusters grew in both length and width directions and the clusters disintegrated evidently (Fig. 3C2). Meanwhile, the mullite grains near the pore regions continued to grow (Fig. 3C1). However, upon finally increasing the firing temperature to 1400 °C, the morphologies of mullite grains near the pore regions remained unchanged (Fig. 3D1) whereas rod-like mullite in the pseudo clusters grew thicker and longer, and interlocked with one another (Fig. 3D2). As a result, a uniform porous microstructure comprising essentially mullite whiskers was formed (Fig. 3D).

The morphological evolution of mullite phases in different regions shown in Fig. 3 can be explained in term of the liquid phase formation and distribution. Due to the low melting point (795 °C) and strong fluxing ability of MoO_3, its addition lowered the formation temperature of aluminosilicate liquid phase to below 950 °C and at the same time decreased effectively the viscosity of the liquid phase, which was