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Effect of La_2O_3 additives on the strength and microstructure of mullite ceramics obtained from coal gangue and γ-Al_2O_3

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Abstract

Self-strengthened mullite ceramics with interlocking columnar grains formed through enhanced anisotropic growth by adding La_2O_3 were prepared from coal gangue and γ-Al_2O_3 within the temperature range 1400–1550 °C and holding time of 4 h. The effects of La_2O_3 on the bending strength, microstructural evolution, and phase composition were studied. The results showed that the bending strength of the as-prepared ceramics was significantly improved by the addition of La_2O_3. For samples sintered at 1550 °C, the bending strength increased from 64 MPa to 218 MPa as the La_2O_3 content increased from 0 mol% to 10 mol%. X-ray diffraction analysis suggested that the formation temperature of secondary mullite was lowered by about 50 °C by adding La_2O_3. Scanning electron micrographs revealed that the La_2O_3-added mullite mostly existed in long, columnar form, with aspect ratios of 3–6, forming an interlocking network structure. The interlocking mullite columns, together with the enhanced densification behaviour, contributed to the improved bending strength.

Keywords: B. Microstructure; C. Strength; D. Clays; D. Mullite

1. Introduction

Coal gangue is a by-product of the mining, washing, and selection of coal [1]. Generally, coal gangue is a mixture of minerals containing carbonaceous shale, sandstone, shale, and conglomerate, with SiO_2 and Al_2O_3 as major chemical constituents [1]. Specifically, the so called carbonaceous kaolin, produced in North China, consists of kaolinite as its only mineral phase. It has been reported that, in China, the accumulative reserve of coal gangue has reached 3.8 billion tonnes and a further 200 million tonnes is produced annually [2,3]. The amount in reserve represents a pressing environmental problem rendering it necessary to investigate different methods of using coal gangue.

One important approach potentially able to use coal gangue is to prepare mullite ceramics by firing a coal gangue based mixture, to which Al_2O_3 is added to consume the amorphous SiO_2 generated at elevated temperatures and increase the amount of mullite in the final fired products [4–6]. This sintering process thus involves a sequenced two step mullite formation [5–8]. The formation of secondary mullite, however, requires a relatively high temperature and reactively sintered mullite, with its high porosity, has poor mechanical properties [4,9], which limits the application of mullite ceramics prepared in this way.

Previous studies [7,10] suggest that self-strengthening is an effective method of reinforcing the bulk mullite ceramic, in which columnar mullite grains are obtained during sintering. To date, several approaches such as adding AlF_3 [10–12], V_2O_5 [13,14], WO_3 [15], and NaH_2PO_4 [16] to related mixtures, as well as tape casting of kaolin [17–19], have been adopted to obtain self-strengthened mullite ceramics with in situ synthesised acicular or columnar

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mullite. Further studies [20,21] compared the effects of Y_2O_3, La_2O_3, and CeO_2 on the densification of mullite from mixtures of SiO_2 and Al_2O_3, indicating that samples with La_2O_3 had the best densification behaviour among the three doping cases. These aforementioned studies provide inspiring methods of preparing dense, and self-strengthened, mullite ceramics, while efforts are still being made with the aim of lowering the sintering temperature and improving the strength of the resulting mullite ceramics.

In this research, coal gangue was used to prepare mullite ceramics, which saw the incorporation of γ-Al_2O_3 powder and the addition of La_2O_3. The effects of adding La_2O_3 on the mullite's formation, bending strength, and microstructural evolution were investigated. The resulting mullite ceramics, sintered at relatively low temperatures with an excessive vitreous phase, were believed to be potential candidates for engineering ceramic applications such as wear plates, pump turbine blades, electro-technical porcelains.

2. Experimental

Coal gangue (from Junger Opencast Mine, Inner Mongolia, China) and industrial alumina (γ-$Al_2O_3 > 97\%$, from Zibo, Shandong, China) were used as the starting materials. The chemical components of the coal gangue are shown in Table 1: the total combined content of SiO_2 and Al_2O_3 was 98.2% (the loss on ignition was not calculated). The as-received gangue was firstly ground to pass a 200 mesh sieve and calcined at 800 °C for 2 h to remove any organic impurities. A series of amounts of La_2O_3 (purity > 99.9%) in molar ratios: 0 mol%, 5 mol%, 10 mol%, and 20 mol% of the final mullite yield was added into a mixture of 45.61% w/w of the heat-activated coal gangue and 54.39% w/w γ-Al_2O_3. The mixed powders were ball-milled for 6 h and dried at 100 °C for 12 h, and then pressed into bar compacts under an isostatic pressure of 200 MPa. The green bodies were sintered in a high temperature furnace (at 1400–1550 °C), with a holding time therein of 4 h and subsequently allowed to cool naturally.

The bulk density and apparent porosity of the sintered samples were measured based on Archimedes' principle. The bending strength was measured under static, monotonic, three-point bending conditions at room temperature on a Reger Universal Testing Machine (Shenzhen, China), with a lower span of 20 mm and a displacement rate of 0.5 mm/min. X-ray diffraction (XRD; XD-3, Purkinje General Instrument Co., Ltd.) using Cu Kα_1 radiation ($\lambda = 1.5406$ Å) with a scanning rate of 8° min^{-1} and scanning electron microscopy (SEM; JEM-6460 LV microscope, Japan) were used for phase analysis and microstructural evolution studies, respectively.

3. Results and discussion

3.1. *Effect of adding La_2O_3 on the mullitization of coal gangue and γ-Al_2O_3*

The XRD patterns of the initial coal gangue (a: kaolinite; b: metakaolinite) are shown in Fig. 1, suggesting that kaolinite, the only mineral phase present, transformed to metakaolinite after pre-calcination at 800 °C. Fig. 2 illustrates the XRD patterns of samples with different amounts of La_2O_3 sintered at 1400–1550 °C for 4 h. The crystalline phases of the sintered products were: mullite, corundum, and cristobalite. When sintered at 1500 °C, samples with 5 mol% La_2O_3 addition already achieved near-complete mullitization; all the XRD peaks were indexed to the orthorhombic structure.

The XRD patterns of the 1400 °C-sintered sample with 5 mol% La_2O_3 addition and samples sintered at 1400, 1450, and 1500 °C with 0 mol% La_2O_3 were compared. In the 0 mol% La_2O_3 added sample, cristobalite was detected until 1450 °C, while when 5 mol% La_2O_3 was added, cristobalite was not detected in the 1400 °C-sintered samples, suggesting that the secondary mullite's formation temperature was lowered by about 50 °C due to the addition of La_2O_3.

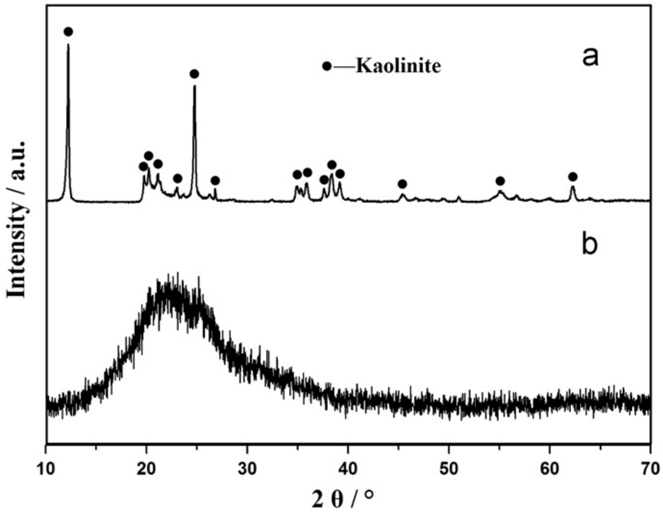

Fig. 1. XRD patterns of the coal gangue: (a) as-received coal gangue (kaolinite) and (b) coal gangue after being calcined at 800 °C for 2 h (metakaolinite).

Table 1
Chemical composition of the raw coal gangue used in this study.

Component (w/w %)												
SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	H_2O^-	P_2O_5	MnO	LOI[a]
45.55	37.56	0.10	0.13	0.44	0.43	0.16	0.21	0.37	0.55	0.03	0.01	15.30

[a] Loss on ignition.

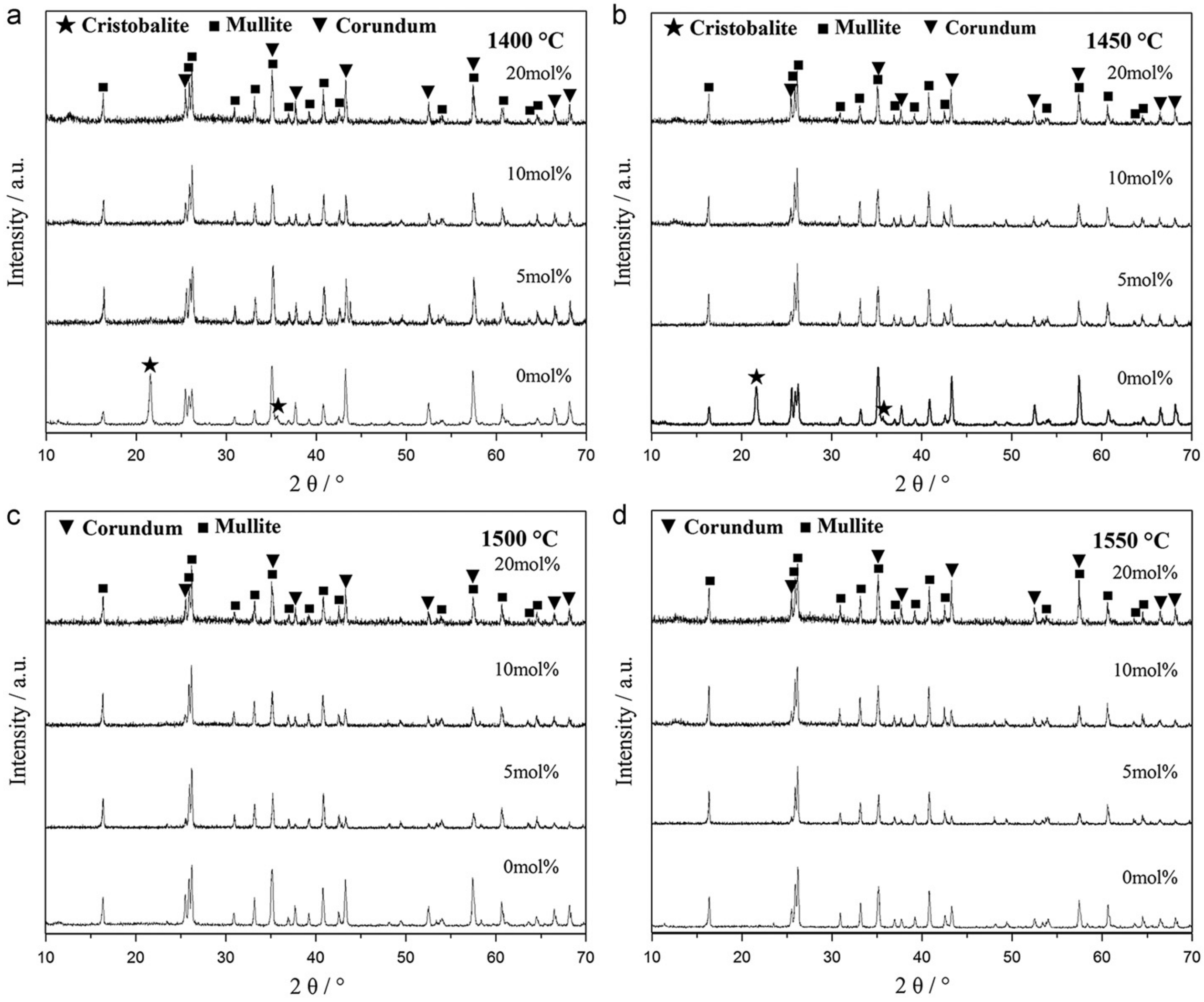

Fig. 2. XRD patterns of the samples with different La_2O_3 adding amount sintered at different temperatures: (a) 1400 °C, (b) 1450 °C, (c) 1500 °C, and (d) 1550 °C.

As reported elsewhere [22,23], the mullitization of this kaolinite–alumina mixture follows Reactions (1)–(4):

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad (450\text{–}550\ ^\circ C) \tag{1}$$

$$2(Al_2O_3 \cdot 2SiO_2) \rightarrow 2Al_2O_3 \cdot 3SiO_2 + SiO_2\ (\text{amorphous})\ (950\text{–}1050\ ^\circ C) \tag{2}$$

$$3(2Al_2O_3 \cdot 3SiO_2) \rightarrow 2(3Al_2O_3 \cdot 2SiO_2) + 5SiO_2\ (\text{amorphous})\ (>1050\ ^\circ C) \tag{3}$$

$$2SiO_2\ (\text{amorphous}) + 3Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 \tag{4}$$

At temperatures above 1050 °C, primary mullite was derived from the decomposition of Al–Si spinel (Reaction (3)), and excess amorphous SiO_2, together with trace impurities, formed vitreous phase. This vitreous phase was believed to be consumed by Al_2O_3 and $(La,Al,Si)_xO_y$ liquid (*LAS* liquid), forming secondary mullite (Reaction (4)) and a grain boundary phase (*GB* phase), respectively.

The mullitization temperature of SiO_2 and Al_2O_3 could be lowered by adding La_2O_3, as reported previously [24]. In the present coal gangue–alumina system, it was confirmed to have been lowered by about 50 °C as revealed by the XRD analysis. The lowered mullitization temperature can be readily explained by the formation mechanism for the secondary mullite, known as a dissolution–precipitation process, which was promoted by *LAS* liquid assisted diffusion [23]. Thus, the formation of the secondary mullite in the presence of La_2O_3 at high temperatures could be expressed as Reactions (5) and (6):

$$La_2O_3 + Al_2O_3 + SiO_2 \rightarrow LAS\ \text{eutectic melt} \tag{5}$$

$$Al_2O_3 + SiO_2 + LAS\ \text{eutectic melt} \rightarrow 3Al_2O_3 \cdot 2SiO_2 + GB\ \text{phase} \tag{6}$$

Although the eutectic temperature of the La_2O_3–Al_2O_3–SiO_2 ternary system has been reported to have different values (Kolitsch et al. [25]: *c.* 1200 °C; Murakami and Yamamoto [26]: *c.* 1380 °C), the *LAS* melt would be formed at temperatures (1400–1550 °C) used in this research. In spite of that, $La_2Si_2O_7$ [27], $La_{14}Si_9O_{39}$ [27], and $LaAl_{11}O_{18}$ [28] have been reported to be stable compounds in the La_2O_3–Al_2O_3–SiO_2 system: no La_2O_3 or La_2O_3 related compounds were found in the XRD measurements regardless of the added levels of La_2O_3 (Fig. 2), a similar result to those reported in the literature pertaining to related studies [20,24]. Considering the volumetric shrinkage of the La_2O_3 added samples after sintering, it was assumed that La_2O_3 was mostly transformed to *LAS* liquid and existed as a *GB* phase.

3.2. Effect of adding La_2O_3 on the bending strength and densification behaviour of mullite ceramics

The effects of La_2O_3 dose on the bending strength of the prepared mullite ceramics sintered at 1400–1550 °C were revealed in Fig. 3. A significant improvement was found in samples sintered at higher temperatures with the same level of La_2O_3. Moreover, the bending strength of the samples sintered at 1550 °C increased from 64 MPa to 218 MPa when the La_2O_3 content was increased from 0 mol% to 10 mol%. The highest bending strength (218 MPa) was achieved at 10 mol% La_2O_3 dose and a temperature of 1550 °C. It was worth noting that, at 1550 °C, the ceramic with 20 mol% La_2O_3 had a slightly lower bending strength (202 MPa) than that of the ceramic with 10 mol% La_2O_3 (218 MPa). This decreased bending strength was most likely to have been due to excessive amounts of *GB* phase being generated, indicating that the La_2O_3 dose should be controlled.

Table 2 summarised the physical parameters of the as-prepared ceramics with different amounts of La_2O_3 at various temperatures. Of the 10 mol% La_2O_3 added samples, the bulk density increased from 2.11 g cm^{-3} (1400 °C) to 2.97 g cm^{-3} (1550 °C) (runs (5)–(8)). Elevated temperature also bestowed a beneficial effect on the densification of the 0 mol% La_2O_3 added specimens (runs (1)–(4)). Thus, temperature significantly affected the densification of the final specimens. Moreover, the apparent porosity decreased with increasing La_2O_3 addition at 1500 °C and 1550 °C, suggesting that La_2O_3 had strong glass-forming tendencies with SiO_2 and Al_2O_3. Note that the bulk density of 1550 °C-sintered samples with 20 mol% La_2O_3 reached 3.20 g cm^{-3} (run (10)), which was slightly higher than the theoretical density of mullite (3.16 g cm^{-3}) [23]. A similar result had been reported by Kong [20] where a La_2O_3-doped mullite ceramic reached a density of 3.32 g cm^{-3}.

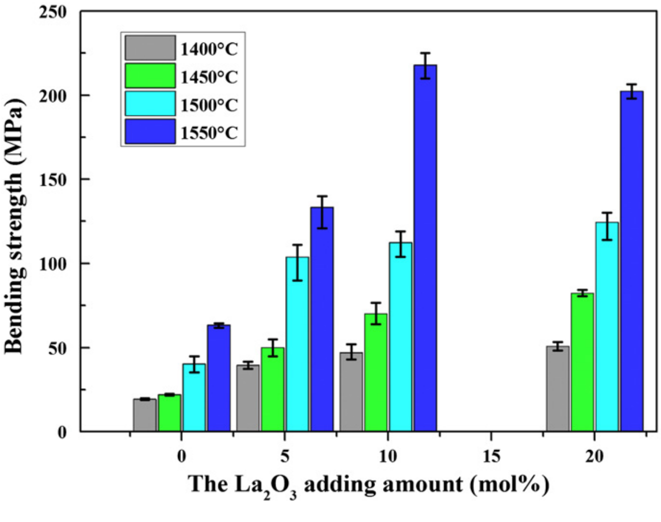

Fig. 3. Bending strength versus La_2O_3 content at different sintering temperatures.

Table 2
Influence of temperature and La_2O_3 content on the bulk density and apparent porosity of the as-prepared ceramics.

Run	Temperature (°C)	La_2O_3 (mol%)	Bulk density (g cm^{-3})	Apparent porosity (%)
1	1400	0	1.89	41.84
2	1450	0	1.93	40.51
3	1500	0	1.99	38.17
4	1550	0	2.16	33.30
5	1400	10	2.11	37.11
6	1450	10	2.19	33.74
7	1500	10	2.63	17.84
8	1550	10	2.97	3.05
9	1550	5	2.71	10.93
10	1550	20	3.20	0.03

3.3. Effect of adding La_2O_3 on the microstructural evolution of the mullite ceramics

Previous studies [6,9] of mullite formation mechanisms in kaolinite–alumina mixtures have pointed out that the primary mullite forms from the decomposition of metakaolinite, while secondary mullite forms from a major solution–precipitation process via a transitory liquid phase as well as a minor solid state inter-diffusion [6], correspondingly forming two kinds of morphology (*i.e.*, mullite with elongated and equiaxial grains) and a bimodal crystallite size distribution [7]. This type of microstructure with two different morphologies of mullite was confirmed in the present study, while an interlocking network structure with elongated mullite was observed in cases with added La_2O_3. Fig. 4 shows the microstructure of the fracture surface of the mullite ceramics. In the 1500 °C-sintered sample with 0 mol% La_2O_3 (Fig. 4a), mullite with elongated grains and equiaxial grains were observed. However, when 5 or 10 mol% La_2O_3 was added, the equiaxial grains were elongated to become columnar (Fig. 4b and c). Fig. 4d showed an interlocking network structure of elongated mullite with aspect ratios of 3–6, which demonstrated a higher growth rate of mullite grains along the longitudinal direction. Thus, adding La_2O_3 enhanced the yield of columnar mullite in its ceramic body.

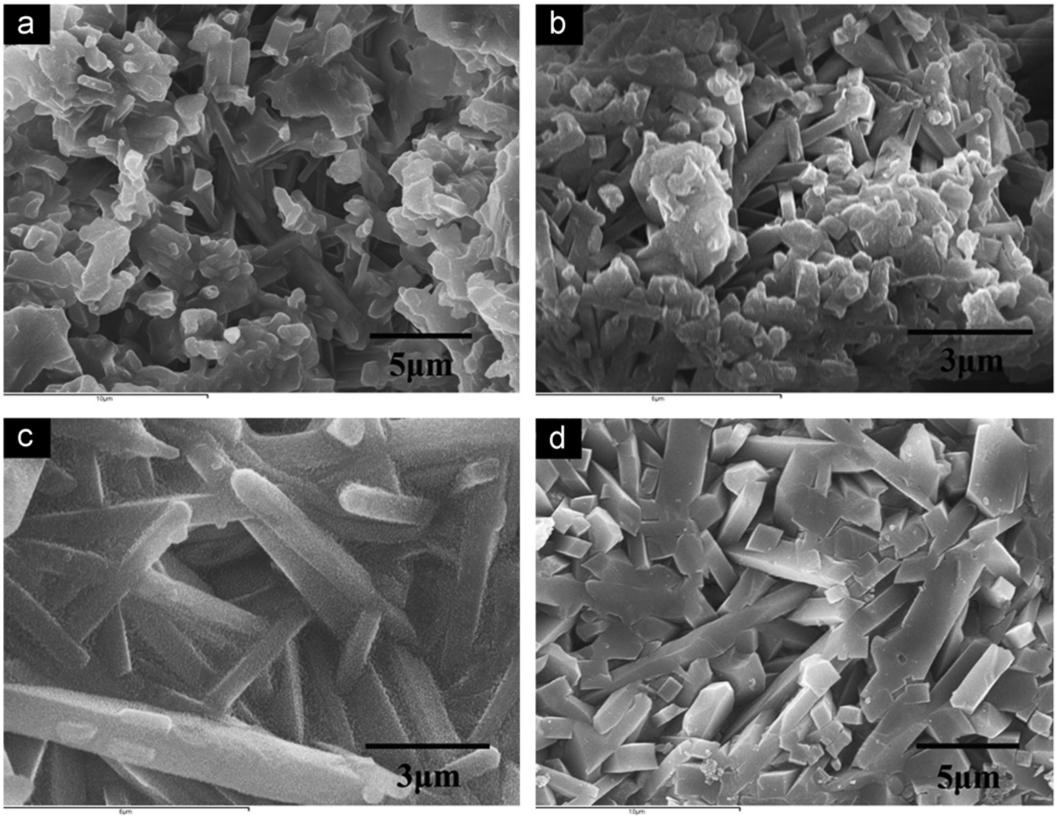

Fig. 4. The effect of La_2O_3 content on the formation of interlocking mullite grains sintered at 1500 °C revealed in SEM images: (a) 0 mol% La_2O_3, (b) 5 mol%, (c) 10 mol%, and (d) 20 mol%. The fracture surface of the samples was etched with 20 wt% hydrofluoric acid solution at 25 °C for 90 s before characterisation.

It was assumed that a long-range diffusion process, favoured by adding La_2O_3, provided the necessary nutrients for the growth of these mullite seeds which grew as their crystallisation habit, *i.e.*, to be orthorhombic needles or columns. The presence of a considerable amount of $(La,Al,Si)_xO_y$ liquid also made it possible for the solution of tiny mullite grains and their later crystallisation on large grains. Hence, by adjusting the La_2O_3 dose and the process sintering parameters, mullite with different amounts of elongated grains with controlled aspect ratios could be obtained.

4. Conclusions

The self-strengthened mullite ceramics with interlocking columnar grains were prepared by sintering coal gangue and γ-Al_2O_3 mixtures assisted with La_2O_3 dosing within the temperature range 1400–1550 °C and holding time of 4 h. The effects of adding La_2O_3 on the bending strength and microstructure of the mullite ceramics were described. La_2O_3, as an additive, favoured the anisotropic growth of mullite grains, resulting in an interlocking network structure, which, together with enhanced densification behaviour, improved the bending strength of the resulting mullite ceramics. This study may provide an alternative method of consuming the abundance of coal gangue in North China to produce mullite-based engineering materials.

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References

[1] C. Li, J.H. Wan, H.H. Sun, L.T. Li, Investigation on the activation of coal gangue by a new compound method, Journal of Hazardous Materials 179 (2010) 515–520.

[2] M. Yang, Z.X. Guo, Y.S. Deng, X.L. Xing, K.H. Qiu, Preparation of CaO–Al_2O_3–SiO_2 glass ceramics from coal gangue, International Journal of Mineral Processing 102 (2012) 112–115.

[3] N. Zhang, H.H. Sun, X.M. Liu, J.X. Zhang, Earl-age characteristics of red mud-coal gangue cementitious material, Journal of Hazardous Materials 167 (2009) 927–932.

[4] C.Y. Chen, G.S. Lan, W.H. Tuan, Preparation of mullite by the reaction sinteringof kaolinite and alumina, Journal of the European Ceramic Society 20 (2000) 2519–2525.

[5] Y.F. Chen, M.C. Wang, M.H. Hon, Kinetics of secondary mullite formation in kaolin–Al_2O_3 ceramics, Scripta Materialia 51 (2004) 231–235.

[6] Y.F. Chen, M.C. Wang, M.H. Hon, Secondary mullite formation in kaolin–Al_2O_3 ceramics, Journal of Materials Research 19 (2004) 806–814.

[7] M.A. Sainz, F.J. Serrano, J.M. Amigo, J. Bastida, A. Caballero, XRD microstructural analysis of mullite obtained from kaolinite–alumina mixtures, Journal of the European Ceramic Society 20 (2000) 403–412.

[8] W. Yan, N. Li, B.Q. Han, A study of the development of crystal shape of mulliteprepared from $Al(OH)_3$ and kaolinite gangue, Journal of Ceramic Processing Research 11 (2010) 733–735.

[9] K.C. Liu, G. Thomas, A. Caballero, J.S. Moya, S. Deaza, Mullite formation in kaolinite–α-alumina, Acta Metallurgica et Materialia 42 (1994) 489–495.

[10] S.H. Li, H.Y. Du, A.R. Guo, H. Hu, D. Yang, Preparation of self-reinforcement of porous mullite ceramics through in situ synthesis of mullite whisker in flyash body, Ceramics International 38 (2012) 1027–1032.

[11] K. Okada, N. Otuska, Synthesis of mullite whiskers and their application in composites, Journal of the American Ceramic Society 74 (1991) 2414–2418.

[12] P. Peng, C. Sorrell, Preparation of mullite whiskers from topaz decomposition, Materials Letters 58 (2004) 1288–1291.

[13] J.H. Li, H.W. Ma, W.H. Huang, Effect of V_2O_5 on the properties of mullite ceramics synthesized from high-aluminum fly ash and bauxite, Journal of Hazardous Materials 166 (2009) 1535–1539.

[14] L.B. Kong, Y.B. Gan, J. Ma, T.S. Zhang, F. Boey, R.F. Zhang, Mullite phase formation and reaction sequences with the presence of pentoxides, Journal of Alloys and Compounds 351 (2003) 264–272.

[15] L.B. Kong, H. Huang, T.S. Zhang, J. Ma, F. Boey, R.F. Zhang, Z.H. Wang, Growth of mullite whiskers in mechanochemically activated oxides doped with WO_3, Journal of the European Ceramic Society 23 (2003) 2257–2264.

[16] Y.M. Park, T.Y. Yang, S.Y. Yoon, R. Stevens, H.C. Park, Mullite whiskers derived from coal fly ash, Materials Science and Engineering A 454 (2007) 518–522.

[17] L.B. Kong, T.S. Zhang, J. Ma, F. Boey, Anistropic grain growth in mullite powders as a result of high-energy ball milling, Journal of the American Ceramic Society 90 (2007) 4055–4058.

[18] K.H. Yang, J.H. Wu, C.H. Hsi, H.Y. Lu, Morphologically textured mullite in sintered tape-cast kaolin, Journal of the American Ceramic Society 94 (2011) 938–944.

[19] C.Y. Chen, W.H. Tuan, Evolution of mullite texture on firing tape-cast kaolin bodies, Journal of the American Ceramic Society 85 (2002) 1121–1126.

[20] L.B. Kong, T.S. Zhang, J. Ma, F. Boey, R.F. Zhang, Mullite phase formation in oxide mixtures in the presence of Y_2O_3, La_2O_3 and CeO_2, Journal of Alloys and Compounds 372 (2004) 290–299.

[21] J.H. She, P. Mechnich, M. Schmücker, H. Schneider, Low-temperature reaction-sintering of mullite ceramics with an Y_2O_3 addition, Ceramics International 27 (2001) 847–852.

[22] Y.F. Chen, M.C. Wang, M.H. Hon, Phase transformation and growth of mullite in kaolin ceramics, Journal of the European Ceramic Society 24 (2004) 2389–2397.

[23] H. Schneider, J. Schreuer, B. Hildmann, Structure and properties of mullite—a review, Journal of the European Ceramic Society 28 (2008) 329–344.

[24] I. Regiani, W.L.E. Magalhães, D.P.F. Souza, C.O.P. Santos, M.F. Souza, Nucleation and growth of mullite whisker from lanthanum-doped aluminosilicate melts, Journal of the American Ceramic Society 85 (2002) 232–238.

[25] U. Kolitsch, H.J. Seifert, F. Aldinger, Phase relationships in the systems Re_2O_3–Al_2O_3–SiO_2 (RE = rare earth element, Y, and Sc), Journal of Phase Equilibria 19 (1998) 426–433.

[26] Y. Murakami, H. Yamamoto, Phase equilibria and properties of glasses in the Al_2O_3–Yb_2O_3–SiO_2 system, Journal of the Ceramic Society of Japan 101 (1993) 1101–1106.

[27] D. Mazza, S. Ronchetti, Study on the Al_2O_3–SiO_2–La_2O_3 ternary system at 1300 °C, Materials Research Bulletin 34 (1999) 1375–1382.

[28] M. Yasuoka, K. Hirao, M.E. Brito, S. Kanzaki, High strength and high-fracture-toughness ceramics in the $Al_2O_3/LaAl_{11}O_{18}$ systems, Journal of the American Ceramic Society 78 (1995) 1853–1856.