Journal of Alloys and Compounds 506 (2010) 777–783

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Tailoring the microstructure of mechanoactivated Al_2O_3 and SiO_2 mixtures with TiO_2 addition

T.S. Zhang[a,*], L.B. Kong[b], Z.H. Du[c], J. Ma[c], S. Li[a]

[a] School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[b] Temasek Laboratories, National University of Singapore, 21 Lower Kent Ridge Road, Singapore 119077, Singapore
[c] School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Article history:
Received 26 May 2010
Received in revised form 5 July 2010
Accepted 7 July 2010
Available online 15 July 2010

Keywords:
Mullite
Mechanoactivation
Whisker
Titanium dioxide
Sintering

ABSTRACT

This paper reports on the effect of TiO_2 on mullitization, anisotropic grain growth and densification of Al_2O_3 and SiO_2 mixtures, which are activated by a high-energy ball milling process using tungsten as milling media. High-energy activation significantly promotes mullitization in the mixture of Al_2O_3 and SiO_2 powders, and is a pre-requisite for the occurrence of anisotropic grain growth of mullite. There is a subtle interplay and competition between anisotropic grain growth and densification, depending on the amount of TiO_2. Small amount of TiO_2 has a positive effect on the phase formation and anisotropic grain growth of mullite, while high concentration of TiO_2 suppresses anisotropic grain growth, and thus is beneficial to densification. As a result, the microstructure and densification of the mullite ceramics can be manipulated by the doping levels of TiO_2.

1. Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) has a special crystal structure, where strong-bounded chains lie along the crystallographic *c*-axis, which allows its grains grow anisotropically in an unconstraint environment. This is why whiskers or needlelike mullite can be easily formed via vapor–solid synthesis [1–3] or molten salt flux [4]. Mullite with elongated grains has been widely used to fabricate reinforced ceramic materials. However, the techniques for synthesis of these elongated mullite grains have several disadvantages. For example, the vapor–solid synthesis requires facilities with high airtight. Reaction involving gaseous phases makes the processing complicated. The products produced by this way are therefore not cost-effective. An alternative way to produce interlocking microstructured mullite ceramics is via *in situ* processing technique. For a conventional solid-state reaction process, *in situ* anisotropic grain growth usually takes place at very high temperatures (>1600 °C) [5–8]. This is because mullite ceramics prepared in this way experienced densification before mullite phase formation. This suppressed anisotropic growth of mullite grains. In this case, ultra high temperature is essential for the formation of a eutectic liquid to maintain the anisotropic grain growth of mullite in a fully densified sample [5–8].

Kong et al. [9] recently developed an alternative technique to produce mullite whiskers at relatively low temperatures. They demonstrated that mullite whiskers can be readily fabricated in the Al_2O_3 and SiO_2 mixtures activated by a high-energy ball milling process (as referred to mechanical alloy or mechanoactivation). It is worth mentioning that although mechanical alloy has long been applied to the fabrication of mullite ceramics [10–14], mullite whiskers were first synthesized by Kong et al. [9]. Such an achievement may be mainly attributed to the two reasons. High density milling media (e.g., tungsten carbide) are essential to the development of high-quality mullite whiskers [9], while other researchers used lighter media, such as porcelain [10], silicon nitride [11,12] and alumina [13,14]. As a result, they have not observed obvious anisotropic growth. It seems that there could exist an energy threshold created by the milling process for the formation of mullite whiskers. On the other hand, it is important to use oxides (e.g., Al_2O_3 and SiO_2) as starting materials because hydroxides or hydrous materials could mitigate the energy created by high-energy balling milling [11].

TiO_2 is a common impurity present in mullite. As a result, studies on TiO_2 doping effects have been carried out by many researchers [15–19]. It is reported that solubility limits of TiO_2 are in the range of 3.8–4.2 and 4.1–4.4 wt% TiO_2 for 3:2 and 2:1 mullites [19], respectively. Anisotropic growth takes place at >1500 °C in gel-derived millite ceramics with the addition of TiO_2 exceeding the solubility limit [17,18]. There is no reports regarding TiO_2 doping on mechanoactivated mixtures of Al_2O_3 and SiO_2 (with tungsten car-

* Corresponding author.
E-mail address: T.Zhang@unsw.edu.au (T.S. Zhang).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.07.069

bide media), although a range of other additives, such as Fe_2O_3 [20], CoO [20], NiO [20], B_2O_3 [21], and W_2O_3 [9], have been explored. These dopants have been identified to play a single role in affecting mullitization, densification, or anisotropic growth of the milled mixtures of Al_2O_3 and SiO_2. Interestingly, as will be presented in this study, TiO_2 can play multiple roles in affecting mullitization, densification and anisotropic growth. Also, some observations regarding TiO_2 doping found in the present work are significantly different from those observed when using gel-derived mullite precursors [16,17,19].

2. Experimental

Al_2O_3 (AKP-30, Japan), SiO_2 (Alfa Aesar-Johson Matthey Copmoany, USA) and TiO_2 (99.5+% purity, Aldrich Chemical Company Inc., USA) were used as starting materials. Mixtures of Al_2O_3 and SiO_2 with a composition of mullite ($3Al_2O_3{\cdot}2SiO_2$), doped with TiO_2 of 1–10 wt%, were first thoroughly mixed for 5 h with a conventional milling. After that, each composition was divided into two parts, one of which was subjected to a high-energy ball milling. About 20 g powders were milled for 5 h, using a Retsch PM400 type planetary ball milling system. A 250 ml tungsten carbide vial, together with 100 tungsten carbide balls of 10 mm, was used as milling media. The weight ratio of ball-to-powder was about 40:1 and milling speed was 200 rpm. The milled and unmilled mixture powders were then pressed uniaxially into pellets of 10 mm diameter, at a pressure of 50 MPa. Green pellets were then sintered in a Carbolite RHF 1600 type furnace in air for 5 h at temperatures ranging from 1100 to 1500 °C at heating and cooling rate of 10 °C/min. Selected samples were polished using a 0.5 μm diamond paste and annealed for 0.5 h at temperatures of 50 °C lower than the corresponding sintering temperatures.

X-ray diffraction analysis on the as-milled powders and the sintered samples was performed at room temperature. All samples were scanned over 20–45° at a scanning speed of 1 °/min, using a Rigaku ultima+ type diffractometer (XRD) with Cu Kα radiation at 50 kV and 30 mA. Densification behaviors of the samples were monitored in air using a Setaram Setsys 16/18 type dilatometer at a heating rate of 10 °C/min. Microstructures of the sintered samples were examined using a JEOL JSM-6340F type field emission scanning electronic microscope (FESEM). For the samples doped with 0–10 wt% TiO_2 and sintered at 1500 °C for 5 h, the well polished and thermally etched ones were used for microstructural observation, while the rest of SEM micrographs are obtained from the natural surfaces of the sintered mullites. Densities of the sintered samples were estimated from their mass and physical dimension.

3. Results

3.1. Mullitization

In the mixture of Al_2O_3 and SiO_2, without high-energy ball milling and TiO_2 addition, the formation of mullite is very difficult. Only a trace of mullite is detectable by XRD in the sample sintered at 1400 °C, while full mullitization cannot be achieved after sintering at 1500 °C for 5 h [9]. The presence of TiO_2 exhibits a positive effect on the phase formation of mullite from the mixture of Al_2O_3 and SiO_2. It is demonstrated that mullite is detectable in the mixture with 5 wt% TiO_2 after sintering at 1300 °C, which is 100 °C lower than that of the undoped samples. At 1500 °C, almost full mullitization can be achieved (Fig. 1). However, the enhancement in mullite formation is not simply increasing with increasing concentration of TiO_2. Further increase in TiO_2 content (>5 wt%) leads to a poor mullitization behavior. Interestingly, as will be shown later, for the milled samples, 1 wt% TiO_2 is the best concentration for mullitization.

Fig. 2 shows the XRD patterns of the samples, derived from the milled mixture of Al_2O_3 and SiO_2 without TiO_2, sintered at different temperatures for 5 h. After sintering at 1100 °C, no mullite phase can be detected by XRD (Fig. 2a). The diffraction peaks can be ascribed to quartz and α-Al_2O_3. A trace of cristobalite is found in the XRD pattern (Fig. 2a), due to partial and total phase transformation of quartz and alumina during sintering at this temperature. Compared to the unmilled samples, 5-h-milled mixture became much more reactive. Almost entire mullitization (IDD No. 15-776) is observed in the sample sintered at 1200 °C (Fig. 2b). This temperature is nearly 200–300 °C lower than that required by the unmilled mixture, which is even comparable to gel-derived diphasic mullite precursors. The great enhancement in mullitization in the high-energy ball milled mixture can be readily attributed to the significant refinement in the particles/grains of Al_2O_3 and SiO_2 [9,20] as well as the formation of Al–O–Si bonds created during the milling process [11,12].

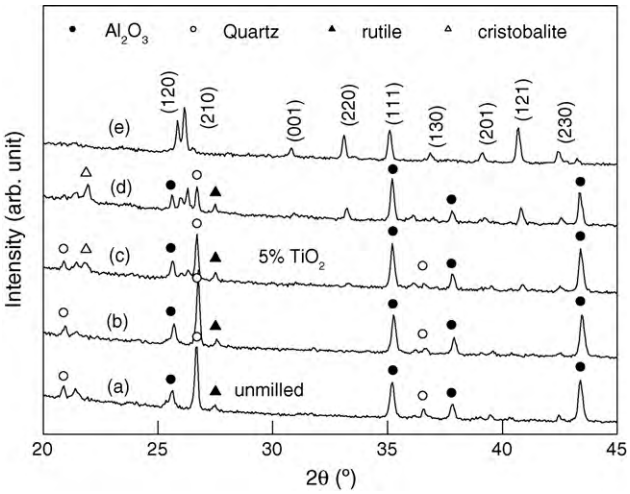

Fig. 1. XRD patterns of the unmilled mixtures with 5 wt% TiO_2 sintered at 1500 °C for 5 h at various temperatures: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C and (e) 1500 °C.

XRD patterns of the milled samples doped with 1 wt% TiO_2 sintered at various temperatures are shown in Fig. 3. Compared to the undoped samples (Fig. 2), 1 wt% TiO_2 demonstrates a positive effect on the mullite phase formation. As evidenced by Fig. 3a, mullite is main phase in the 1100 °C-sintered sample.

A careful inspection of the 1200 °C-sintered samples with different TiO_2 contents (Fig. 4) indicates that the mullitization of the samples with >3 wt% TiO_2 is poorer than the samples with TiO_2 levels of ≤1 wt%. It seems that adding more TiO_2 prevents the combination of Al_2O_3 and SiO_2 from forming mullite as the XRD peak intensities of unreacted Al_2O_3 increase with increasing the level of TiO_2. The optimal concentration of TiO_2 (1 wt%) for the milled mixtures is significantly lower than that (5 wt%) for the unmilled samples, which is probably attributed to the fact that the effectiveness of TiO_2 is increased as a result of the high-energy ball milling which leads to the refinement of TiO_2 particles. In addition,

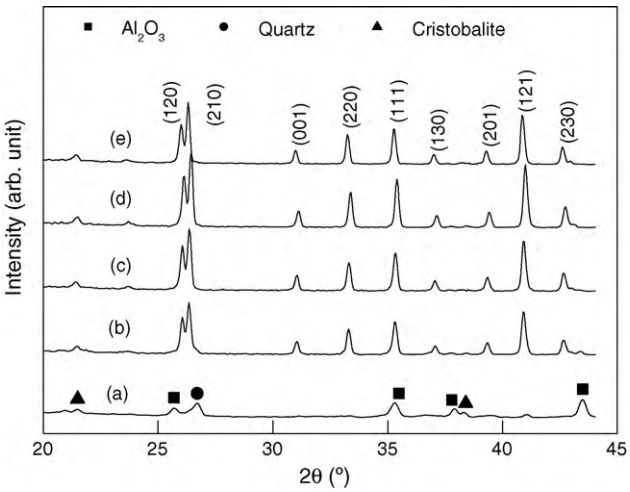

Fig. 2. XRD patterns of the milled mixture without TiO_2 sintered for 5 h at various temperatures: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C and (e) 1500 °C.