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Microstructural composite mullite derived from oxides via a high-energy ball milling process

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Abstract

High-energy ball milling had a great influence on phase formation and morphology development of mullite derived from oxide precursors. Mullite phase was formed at 1300 °C in an oxide mixture of Al_2O_3 and quartz without high-energy ball milling and the mullitization was not complete up to 1500 °C. After milling for 5 h, the mullitization temperature was reduced by about 200 °C. At the same time, mullite whiskers were obtained. Based on these results, microstructural composite mullite ceramics were proposed to be made from the mixtures of the oxide precursors with and without the high-energy ball milling. The unmilled precursor was sintered to equiaxed grains while the milled one resulted in anisotropic grains. The relative proportion of the equiaxed and anisotropic grains could be readily adjusted by the precursor mixtures. Moreover, the mullite crystallites coming from the milled precursor powder at low temperature acted as seeds to enhance the mullite phase formation of the composites. It is believed that the mullite whiskers produced in this way can also be used as reinforcing components to design structural composites of others materials.

Keywords: B. Composite; D. Mullite; High-energy ball milling; Anisotropic grain growth

1. Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) is promising oxide ceramic material for high temperature and structural applications due to its good mechanical strength, excellent thermal shock, high creep resistance, low thermal conductivity, and high-temperature stability [1]. However, mullite ceramics with equiaxed grains have relatively low fracture toughness. It is, therefore, necessary to use reinforced mullite ceramics for practical applications [2].

Reinforced mullite ceramics have been produced by introducing mullite whiskers/fibers [3] into equiaxe-grained mullite matrix. Mullite whiskers can be derived from aluminum fluoride via the solid–vapor reaction process [4] or xerogels and silica gels via thermally induced crystallization [5]. The introduction of mullite whiskers makes the processing relatively complicated and great care is required to prevent the whiskers from breaking. It is also difficult to produce mullite ceramics with large production in this way. Alternatively, fabrication of reinforced mullite ceramics, via an in situ anisotropic grain growth, is more feasible in comparison to whisker-addition-reinforcement [6]. In situ anisotropic grain growth was realized by thermal treatment, where an extremely high temperature (>1600 °C) is required to induce the anisotropic grain growth from mullite matrix of equiaxed grains [7]. However, such mullite ceramics did not demonstrate enhanced fracture toughness as desired, although interlock structures were achieved. This has been mainly attributed to the abnormal grain growth of mullite at the extremely high temperature. In this respect, it is desired to find out alternative strategies that allow for anisotropic grain growth of mullite at low temperature, in order to avoid abnormal grain growth.

Our earlier study indicated that mullite whiskers or anisotropic grains could be grown from oxide precursors that were activated by high-energy ball milling process [8]. We came up with the idea to produce mullite ceramics with in situ anisotropic structures consisting of normally-grained mullite and mullite whiskers or anisotropic grains by simply mixing oxide precursors with and without being subjected to the high-energy ball milling. This paper will present

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our preliminary experimental results on the microstructural mullite composites that have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

Commercially available quartz (SiO_2, 99.9% purity, Aldrich Chemical Company Inc., USA) and Al_2O_3 (>99% purity, Aldrich Chemical Company Inc., USA) powders were used as the starting materials with a nominal composition of $3Al_2O_3{\cdot}2SiO_2$. The mixture of the two oxides was thoroughly mixed via the conventional ball milling process, using ZrO_2 vials and balls as milling media. The mixture was divided into two groups, one of which was subjected to a high-energy ball milling. The high-energy ball milling operation was carried out using a Retsch PM400 type planetary ball milling system in air at room temperature for 5 h. A 250 ml tungsten carbide vial and 100 tungsten carbide balls with diameter of 10 mm were used as a milling medium. The milling speed was set to be 200 rpm. The ball-to-powder weight ratio was about 40:1. The two groups of powders (with and without the high-energy ball milling) were then mixture in a weight (molar) ratio of 75:25 (A), 50:50 (B), and 25:75 (C). The three groups, together with the unmilled and the milled powders, were compacted into pellets of 10 mm diameter, at a pressure of 50 MPa. The green pellets were sintered in a Carbolite RHF 1600 type furnace in air atmosphere, at temperatures from 1100 to 1400 °C for 4 h.

X-ray diffraction analysis of the powders was performed using a Rigaku (Tokyo, Japan) ultima+ type diffractometer (XRD) with Cu Kα radiation. The average particle size and size distribution of the mixtures with and without the high-energy ball milling process were estimated on the basis of the Brunauer–Emmett–Teller (BET) specific surface area (Model ASAP 2000) using nitrogen as the absorption gas. The density of the mullite ceramics was measured by a Mirage MD-200S (ALFA Mirage Co. Ltd., Japan) type electronic densimeter using water as the liquid medium. The microstructure and grain morphology of the sintered samples were examined using a JEOL (Tokyo, Japan) JSM-6340F type field emission scanning electronic microscope (FESEM).

3. Results and discussion

Figs. 1 and 2 show the XRD patterns of the sintered mixture of Al_2O_3 and quartz before and after the high-energy ball milling. For the unmilled system, 1100 °C sample consists mainly of the precursor oxides with a small fraction of crystobalite, indicating the occurrence of the phase transformation from quartz to crystobalite at this temperature. After sintering at 1200 °C, more crytobalite can be detected, while no mullite phase is observed. Although mullite phase

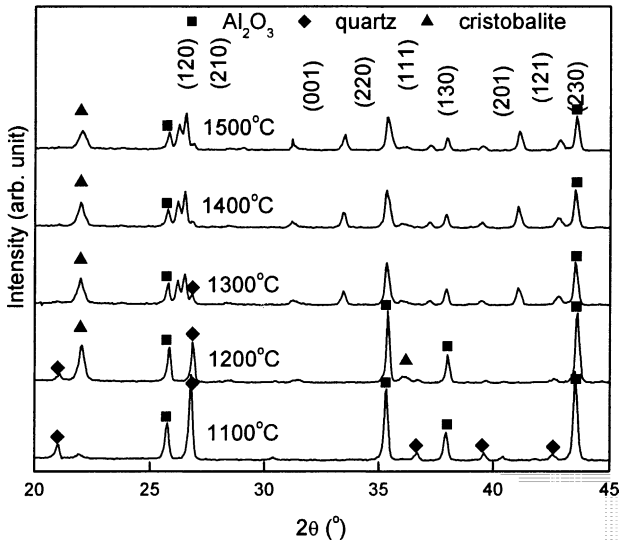

Fig. 1. XRD patterns of the unmilled mixture of Al_2O_3 and quartz sintered at different temperatures.

is formed at 1300 °C, the mullitization is not complete and quartz is still observable. Moreover, the mullitization is not complete up to 1500 °C since Al_2O_3 and crystobalite still appear in the XRD pattern. In contrast, for the milled group, mullite phase formation occurs at 1100 °C, which is 200 °C lower than that required by its unmilled counterpart. Also, the mullitization is almost complete at 1200 °C. The reduced mullitization temperature of the milled mixture can be readily attributed to its refined grains/particles as a result of the high-energy ball milling. This explanation has been confirmed by XRD, SEM, and BET analysis [9].

The high-energy ball milling not only reduced the mullite phase formation temperature of the Al_2O_3 and quartz mixture, but also resulted in great difference in morphol-

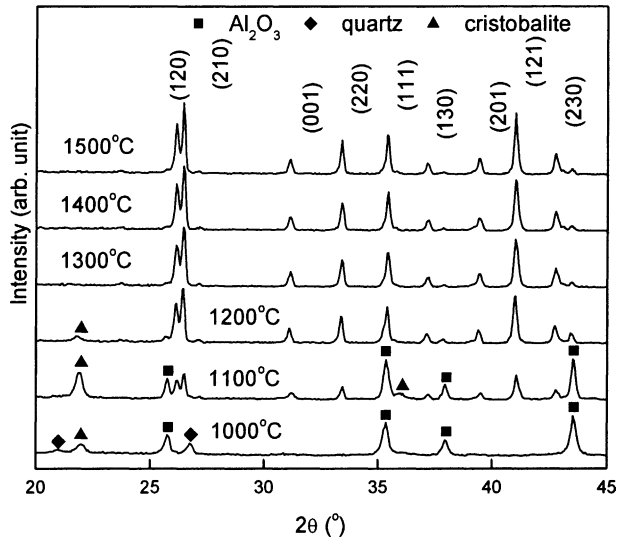

Fig. 2. XRD patterns of the milled mixture of Al_2O_3 and quartz sintered at different temperatures.

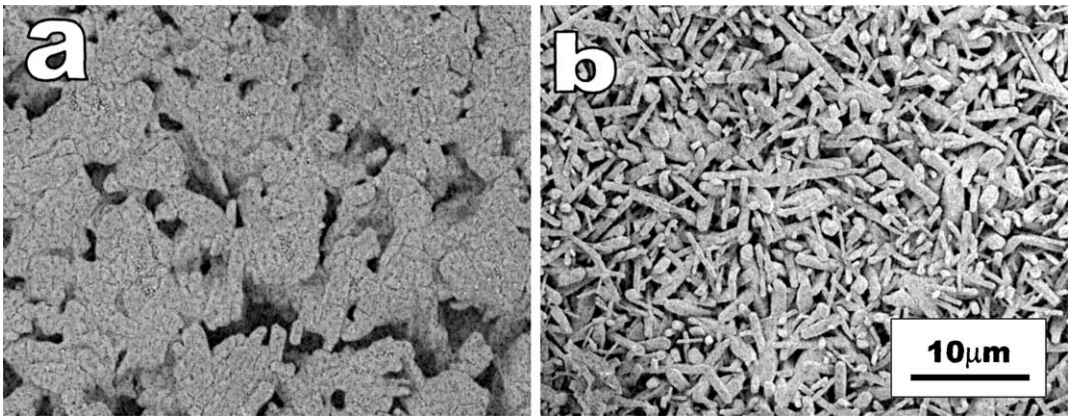

Fig. 3. SEM images of the mixture of Al_2O_3 and quartz sintered at 1400 °C for 4 h: (a) unmilled and (b) milled.

ogy of the mullite grains. Representative SEM images of the 1400 °C-sintered samples of the unmilled and milled powders are shown in Fig. 3. The unmilled samples are sintered to ceramics with equiaxed grains, while mullite whiskers are grown from the milled powders. The formation of the mullite whiskers in the milled powders is closely related to the lowered mullitization temperature. It is recognized that, due to its special structure, mullite grains have a strong tendency to grow anisotropically if the growth takes place in an unconstrained environment [10]. The milled mixture mullitized at low temperature, at which densification was not significant (dilatometer result not shown) [11]. Therefore, anisotropic grain growth is allowed. The temperature at which the anisotropic grain growth occurs in this way is much lower than that required by the high-temperature treatment [7]. With these results, we came up with the idea to prepare microstructural composite mullite ceramics by mixing the powders with and without the high-energy ball milling. The unmilled powders served as the sources of equiaxed while the milled resulted in anisotropic mullite grains.

Fig. 4 shows the XRD patterns of the mixtures with different composition of unmilled and milled precursor powders, sintered at different temperatures. For sample C sintered at 1100 °C, three phases are observed. They are Al_2O_3, quartz, and crystobalite. It means that mullite formation did not occur at this temperature for the C group and only a fraction of quartz transforms into crystobalite. After sintering at 1200 °C, mullite crystallite appears as a minor phase, which can be considered to be from the milled precursors. At the same time, transformation of quartz into crystobalite is almost complete, which is similar to that shown in Fig. 1. However, an almost complete mullitization is observed at 1300 °C, which is better than in the unmilled powders (Fig. 1). The enhanced mullitization behavior can be explained by seeding mechanism [12]. The mullite crystallites formed from the milled powders at low temperature served as seeds, which in turn reduced the mullitization temperature of the unmilled powder. As the proportion of the milled powder increases, both the transformation quartz into crystobalite and mullitization occurred at lower temperature, which is understandable through Figs. 1 and 2.

The SEM images of the three groups sintered at different temperatures are shown in Figs. 5 and 6. Fig. 5 shows

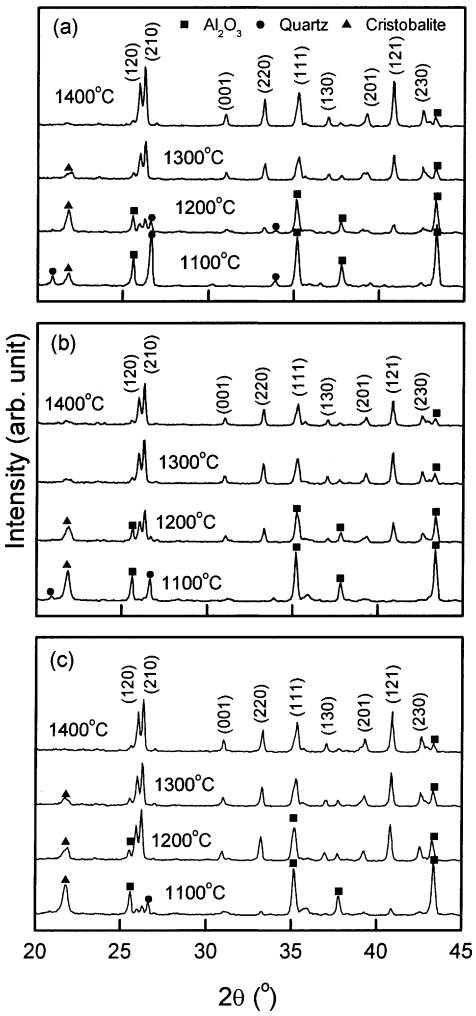

Fig. 4. XRD patterns of the mixtures sintered at 1100–1400 °C for 4 h: (a) 25/75 (C), (b) 50:50 (B), and (c) 75:25 (A).

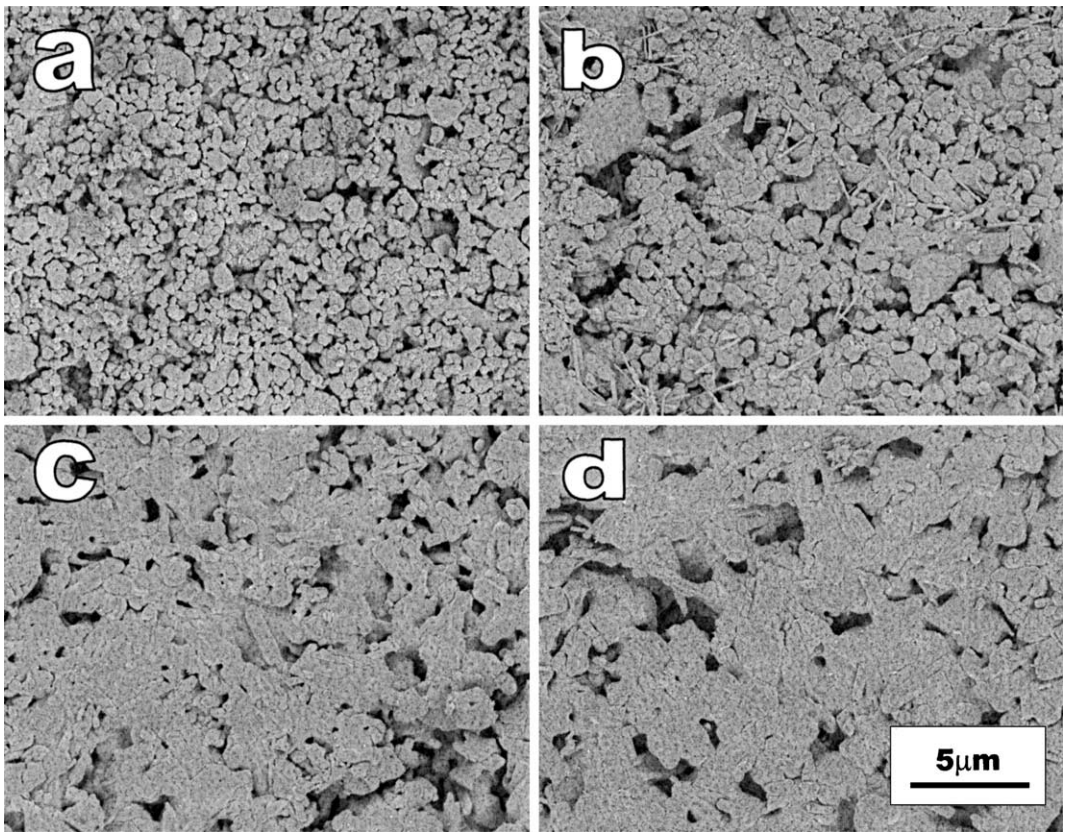

Fig. 5. SEM images of sample 25:75 (C) for 4 h at: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, and (d) 1400 °C.

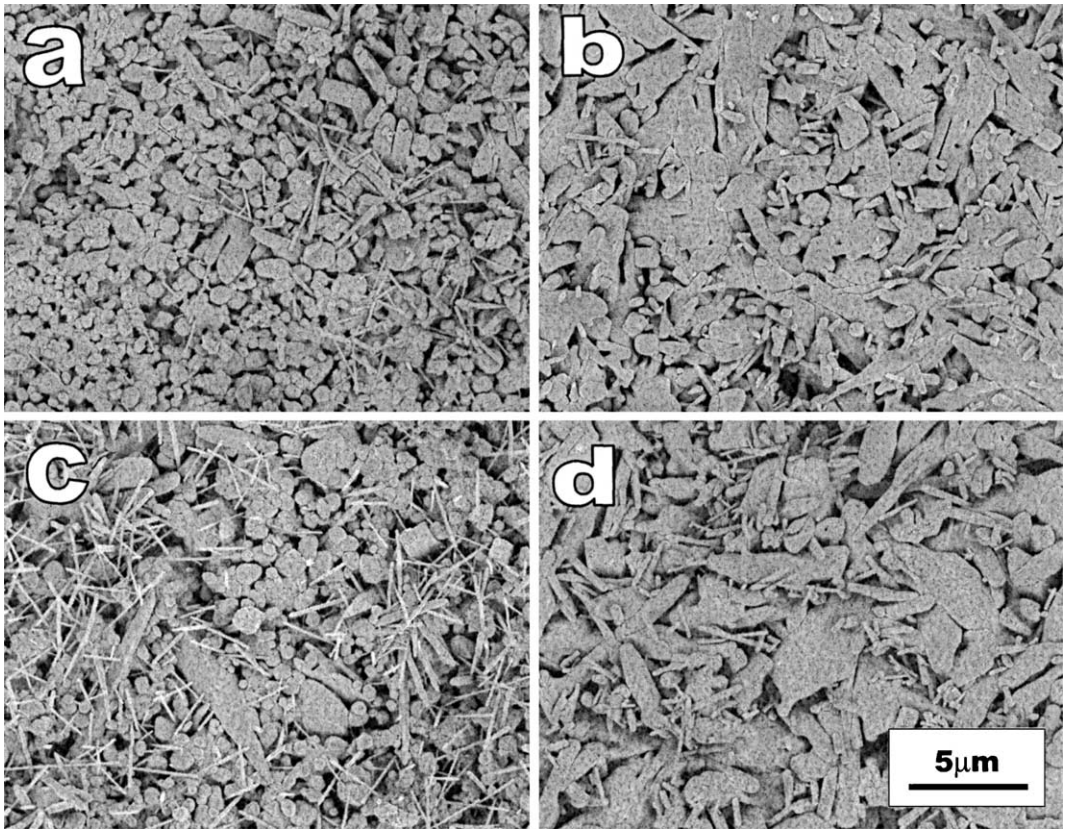

Fig. 6. SEM images of samples B (a/b) and A (c/d) sintered at 1100 °C (a/c) and 1400 °C (b/d).

that 1100 °C-sintered sample C consists only of equiaxed grains. At this temperature, mullite phase is not formed. As the sintering temperature increased to 1200 °C, one can find some thin whiskers distributed in the equiaxed grain matrix, where the whiskers are mullite while the equiaxed grains may still be the precursor oxides. This observation is consistent with the XRD result shown in Fig. 4a. After sintering at 1300 °C, the dimension of both the whiskers and the equiaxed grains increases, with relatively larger proportion of the mullite whiskers compared to the 1200 °C-sample. Further increase in sintering temperature leads only to a simultaneous growth of both the whiskers and the equiaxed grains, without significant change in their relative proportion. Selected SEM images of samples B and A are shown in Fig. 6. With increasing proportion of the milled powders, the amount of whiskers increases. Therefore, the microstructural composites of mullite ceramics can be designed by adjusting the proportion of the precursors with and without the high-energy ball milling.

With this approach, microstructural composites can be prepared at relatively low temperature, thus avoiding the occurrence of abnormal grain growth which is a general occurrence when high temperature treatment is used [7]. The microstructure of the mullite composites should be further modified if other techniques such as hot isostatic pressing (HIP) or spark plasma sintering (SPS) are used. It is believed that microstructural composites of other materials with mullite whiskers as reinforcing components can also be fabricated in a similar way.

4. Conclusions

High-energy ball milling reduced the mullitization temperature of oxide precursors (Al_2O_3 and quartz) and allowed for anisotropic grain growth to form mullite whiskers, both of which were attributed to the refined grains/particles of the oxides as a result of the high-energy ball milling. Microstructural composite mullite ceramics with both equiaxed and anisotropic grains were derived from the mixtures of Al_2O_3 and quartz with and without high-energy ball milling. One can use this technique to design reinforced mullite and other ceramic materials.

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