Morphological Characteristics of Al_2O_3/Mullite/SiC Powders from Microwave Carbothermal Reduction Reaction

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Abstract

The microwave process offers several advantages over conventional processes, including energy savings, shorter processing time, improved product uniformity and yields, and improved properties. In the present work, Al_2O_3/mullite/SiC powders were synthesized through the carbothermal reduction reaction of aluminosilicates in the presence of carbon black as a reducing agent. Precursor powders were compacted in pellet form and then reacted in a microwave oven operating at 2,45 GHz with a maximum power level of 980 W. In order to maintain a uniformly reactive atmosphere inside the microwave cavity, a Pyrex glass reaction chamber was introduced. The resulting powders, analyzed by SEM, presented features similar to those of products obtained by conventional carbothermal reduction in the same temperature range, including whiskers, fibrous clusters and spheres of SiC, Al_2O_3 and mullite particles.

Introduction

The use of microwave heating to synthesize ceramic materials is justified by several factors. The main advantage of this novel technique over conventional heating processes is the reduction it offers in manufacturing costs resulting from energy savings and shorter process times. Moreover, the use of different atmospheres and vacuum, and the possibility of heating transparent materials by using susceptive materials, are additional positive points. The main mechanisms responsible for heating in microwave coupling or absorbing are dipolar rotation within the material, electrical conduction and ionic migration (1, 2).

Microwave-assisted carbothermal reduction reaction (MWCR) has been used to synthesize ceramic materials such as sialons (2), SiC (3-6), TiC and TaC (7), TiN, GaN and VN (8), and AlN (9). Microwave heating makes carbothermal reduction a very fast and simple process due to its differential heating mechanism when compared to conventional heating processes. Carbon plays a dual role in microwave carbothermal reduction, acting as a reducing agent to form SiC from SiO_2 and as the heat generator due to the Joule effect caused by dipolar rotation. With regard to heating capability, amorphous carbon has a greater microwave-absorbing ability than crystalline carbon with a similar particle size. The reported results of ref. (8) indicate that carbon black reaches a temperature of 1533 K in only 2 min. of microwave exposure while graphite reaches 1350 K in the same 2 min. In the present study, microwave-assisted carbothermal reduction (MWCR) of kaolin was performed to obtain Al_2O_3/mullite/SiC powders and to compare these products with those obtained by a conventional process (CCR). A SEM investigation was made to determine what differences were noticeable in samples prepared by these two synthesis routes.

Materials and Methods

Al_2O_3/mullite/SiC powders were synthesized by the CCR and MWCR methods, starting from a precursor blend composed of a low-cost aluminosilicate (Kaolin Horii) and amorphous carbon (carbon black). The precursor was pelletized to enhance the contact area between the components and was then reacted for 45 min. in a domestic microwave oven (BRASTEMP) operating at 2.45 GHz, with a maximum power level of 980W. Reactions were performed in a mullite crucible. A uniform reaction atmosphere inside the microwave oven was essential to achieve an optimal reaction condition and to prevent oxidation of the products. To this end, a Pyrex glass reaction chamber was introduced to maintain a certain argon pressure within the cavity. Another way to minimize oxidation of the reaction products was to use an excess of carbon black in the mixture (3:1) with kaolin. This excess carbon favors heating of the precursor. The resulting powders were characterized by X-ray diffraction (Kristaloflex D500) to verify the phase formation, and by scanning electron microscopy (Carl Zeiss 940A) to characterize the powders morphologically.

Results and Discussion

Figure 1 shows the general morphological aspect of the powder reacted by MWCR, evidencing SiC-rich spheres and whiskers. Large amounts of these morphological components were present throughout the samples.

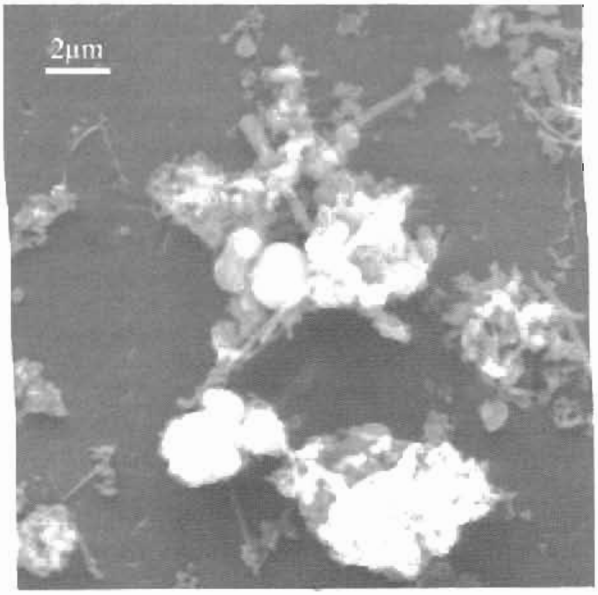

Figure 1. General morphological aspect of the powders reacted by MWCR

Based on the XRD results, which confirmed the phase formation, the following reactions can be proposed:

$3(Al_2O_3.\ 2SiO_2.\ 2H_2O) \rightarrow Al_6Si_2O_{13} + 4SiO_2 + 6H_2O$ (A)

$Al_6Si_2O_{13} + 4SiO_2 + 12C_{(s)} \rightarrow Al_6Si_2O_{13} + 4SiC + 8CO$ (B)

$Al_6Si_2O_{13} + 4SiO_2 + 18C_{(s)} \rightarrow 3Al_2O_{3(s)} + 6SiC_{(s)} + 12CO_{(g)}$ (C)

Mullite decomposition into Al_2O_3 occurs up to 1350°C, when SiO_2 is reduced to form SiC. The temperature could not be measured during the MWCR procedure owing to the impossibility of inserting metallic thermocouples into the cavity while the oven was on. However, based on reactions A to C, one can deduce that the temperature reached at least 1400°C in certain regions of the sample, as illustrated by the presence of Al_2O_3. Figure 2 shows some morphologies found in powders resulting from the MWCR of a kaolin/carbon blend.

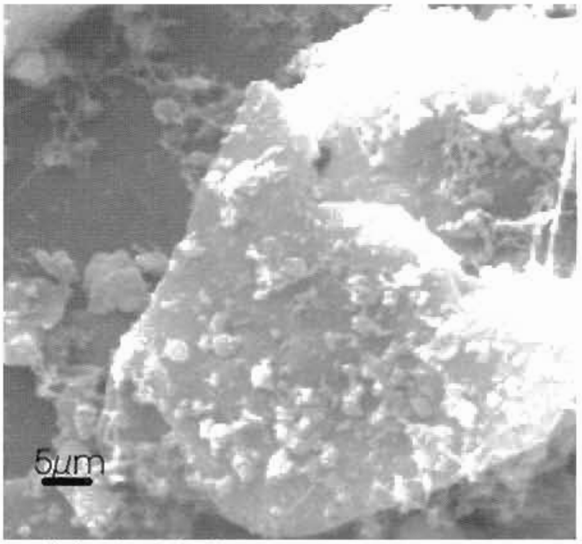

Figure 2. Mullite particle covered with SiC whiskers and spheres

Figure 3 shows some details of whiskers, while Figure 4 reveals the wooly structures of SiC growth during the MWCR.

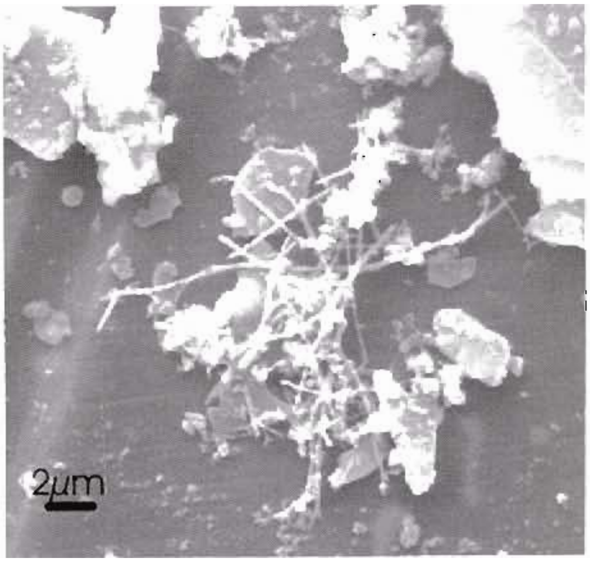

Figure 3. SiC whiskers grown by the VLS process

The nature of the carbothermal reduction reaction is predominantly that of a vapor phase reaction, which favors the growth of SiC in whisker form by the VLS (Vapor-Liquid-Solid) mechanism (Figure 3). The presence of SiC-rich spheres at the tip of whiskers resulted from the deposition of Si and C atoms on the catalyst sites present in the precursor, such as K, Fe and Ti (10, 11).

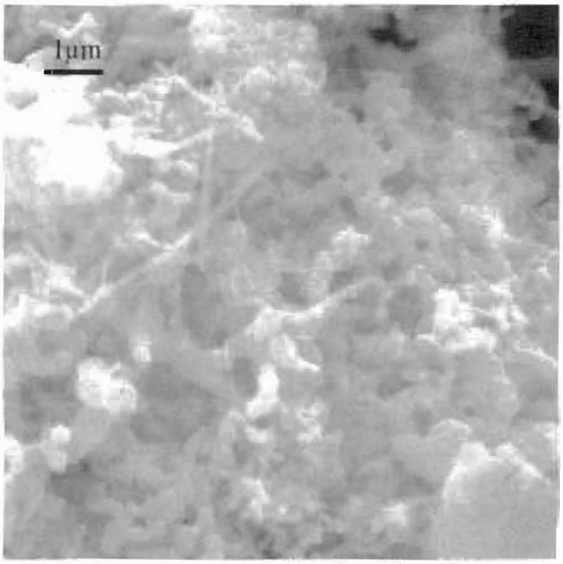

Figure 4. Wooly structures resulting from the side-branching growth caused by SiO and CO saturation

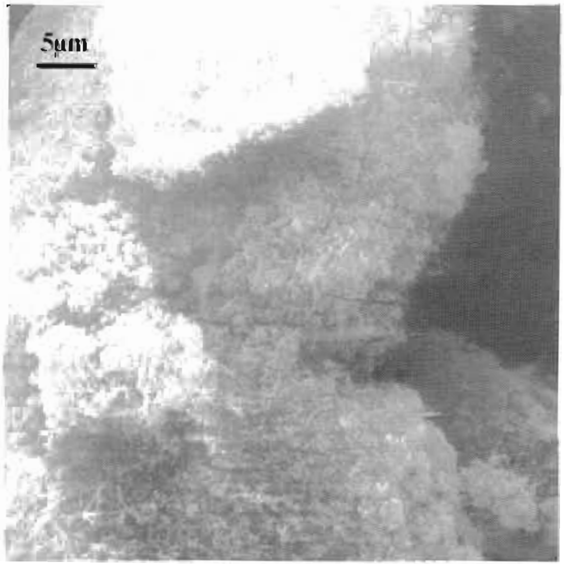

Figure 5. Wooly SiC structures covering alumina particles

An EDS analysis revealed the presence of potassium and iron in Si-rich areas corresponding to SiC. When the catalyst sites become saturated, side-branched type growth occurs and wooly structures are created. As reported previously for conventional carbothermal reduction reaction (11), the amount of impurities in the precursor (Fe = 0.49%, K = 1.38%) was crucial to the growth of these SiC structures in the samples from the MWCR.

Moreover, wooly SiC structures result from a supersaturated micro-atmosphere of SiO and CO gases inside the reaction chamber, due to the close interaction between aluminosilicate and carbon particles in the pellet. Figure 5 shows wooly structures covering Al_2O_3 particles.

Therefore, if one aims to obtain only particles, instead of whiskers, as the final reaction product, an impurity-free precursor is required. Figure 6 depicts all the morphological components detected in the samples: Al_2O_3 and mullite particles, SiC whiskers and wooly structures.

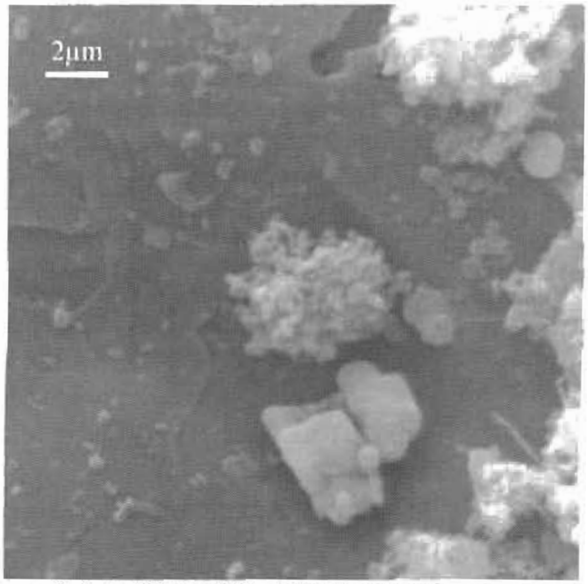

Figure 6. A mullite particle covered with SiC whiskers, wooly structures, spheres, and Al_2O_3 particles

The morphological characteristics of Al_2O_3/mullite/SiC powders synthesized by MWCR in only 45 min therefore indicate that impurities present in the precursor (kaolin), namely potassium and iron, acted as a catalyst for the growth of SiC whiskers and wooly structures by the VLS mechanism. According to the theoretical reaction formation, microwave heating of the kaolin/carbon blend reached a temperature of up to 1400°C.

Acknowledgments

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