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Al_2O_3/mullite/SiC powders synthesized by microwave-assisted carbothermal reduction of kaolin

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Abstract

Al_2O_3/mullite/SiC powders have been synthesized by microwave-assisted carbothermal reduction of kaolin. Kaolin, a low cost aluminosilicate, was mixed to carbon black to achieve the precursor blend which was dried, broken in mortar, sieved then reacted in a kitchen microwave oven for 45 min under reducing atmosphere. In order to compare the characteristics of the powders, conventional carbothermal reduction reaction was performed at 1450°C for 2 h. The as-reacted powders were characterized by X-ray diffraction and scanning electron microscopy to confirm the phase formation. Results obtained show Al_2O_3/mullite/SiC phase in XRD for both reaction routes, products which can be achieved only in temperature ranges of about 1450°C.

Keywords: A. Microwave processing; Synthesis; Carbothermal reduction

1. Introduction

Microwave heating is of interest for thermal processing of ceramics, as reviewed by Sutton [1]. Microwaves belong to electromagnetic spectra with wavelengths from 1 mm to 1 m. In opposition, visible waves, except lasers, are coherent and polarized. For microwave heating, the most commonly used frequency is 2.45 GHz, although 0.915 GHz is also found. The interaction of electromagnetic wave with molecular dipole results in rotation of the dipoles, and energy is dissipated as heat forms due to internal resistance to this rotation. Dielectric properties of the material are important to understand the microwaves/materials interaction. These properties include electronic polarization, atomic polarization, ionic polarization, ionic conduction, dipole (orientation) polarization, and Maxwell–Wagner polarization mechanisms. At microwaves useful frequencies, dipole polarization is thought to be the most important mechanism responsible by energy transfer at the molecular level [2,3].

The role of carbon in the microwave reaction is as a reduction agent and heating agent because it couples quickly with electromagnetic radiation, creating heating owing to the Joule effect. According to the literature [4,5], carbon black powders have superior microwave-absorbing ability compared to graphitic carbon of similar particle size. It was found that amorphous carbon powder (carbon black) is heated up to a relatively higher temperature (1270°C) within 2 min of microwave exposure compared to graphitic carbon (1077°C). This may be the difference in the modes of absorption of amorphous and graphitic forms of carbon and the high dielectric loss of amorphous carbon, due to the presence of a variety of defects [5]. This behavior is very important to obtain the carbothermal reduction reaction in a shorter time.

The microwave-assisted carbothermal reduction reaction (MWCR) is a novel technique employed by several researchers around the world in order to produce ceramic materials like silicon carbide (SiC) [6–9], titanium and tantalum carbide (TiC, TaC) [10], titanium, gallium and vanadium nitrides (TiN, GaN, VN) [5] and aluminium nitride (AlN) [11]. In most cases where microwave heating is involved, the carbothermal reduction reactions of the materials are very fast and simple. Microwave irradiation not only accelerates the reactions but

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also yields products of good crystalline and structural uniformity.

Carbothermal reduction of the SiO_2 in the clay, forming a volatile SiO gaseous species, is one potential process by which Al_2O_3 and SiO_2 can be separated. However, a favorable temperature range must be found, where the carbothermal reduction of SiO_2 to form SiO will proceed without reduction of the Al_2O_3 to form a volatile species. According to the thermodynamics observations of the carbothermal reduction of Al_2O_3, Wright [12] showed that at 1300–1500°C the only major oxide in the kaolin clay to be reduced by carbon will be SiO_2. The carbothermal reaction of clay and carbon to form and separate Al_2O_3 and SiO_2 was studied by Bechtold et al. [4]. These authors showed that the reaction (1) or its reactions (2) and (3) enough carbon was mixed with clay to reduce all the SiO_2 to SiO and additional carbon surrounding this mixture was used to satisfy reaction (4). To obtain high-purity Al_2O_3 that is free from SiO_2 and silicates, it is desirable to add a slight excess of carbon to the clay. This addition may result in Al_2O_3 with a small amount of SiC, rather than mullite, as a residual phase.

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO + CO \tag{1}$$

$$SiO_{2(s)} + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)} \tag{2}$$

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \tag{3}$$

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)} \tag{4}$$

These results showed that the mullite phase depends on the stoichiometric quantities of carbon and ideal temperature range. Specifically, the reduction of kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) by carbon under argon atmosphere has been studied by several authors [13,14] at temperatures ranging from 1000 to 1600°C using stoichiometric, sub-stoichiometric and over-stoichiometric quantities of carbon and graphite. Theoretical stoichiometric reactions to achieve Al_2O_3/SiC composites from kaolin/carbon blend by conventional heating are shown below:

$$3(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O) \times \overset{500\text{–}1200^{\circ}C}{\rightarrow} \underset{\text{Mullite}}{Al_6Si_2O_{13}} + 4SiO_2 + 6H_2O \tag{A}$$

$$\underset{\text{Mullite}}{Al_6Si_2O_{13}} + \underset{\text{Cristobalite}}{4SiO_2} + 12C_{(s)} \overset{>1350^{\circ}C}{\rightarrow} Al_6Si_2O_{13} + 4SiC_{(s)} + 8CO_{(g)} \tag{B}$$

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

The proportions of Al_2O_3, SiO_2 and carbon will vary depending upon the extent of the SiC phase desired in the final composites. The Al_2O_3/mullite/SiC composite can be obtained considering the intermediate step between 1350 and 1500°C (reaction B or C) by conventional heating. Then, the aim of this work was to study the microwave-assisted carbothermal reduction reaction (MWCR) of kaolin along with carbon black in order to produce Al_2O_3/mullite/SiC powders in shorter time duration and compare these results with those obtained through conventional carbothermal reduction reaction (CCR).

2. Materials and methods

In order to produce Al_2O_3/mullite/SiC powders through MWCR and CCR, starting from natural aluminosilicate it was essential to prepare a precursor constituted by a blend of the aluminosilicate with carbon black. Kaolin (Horii) was chosen owing to its relative purity (total contaminants less then 2.79%), average particle size of 1 μm, low cost and it had been used in other work to produce ceramic powders [13]. Commercial carbon black was the source of carbon. Stoichiometric composition was mixed in distilled water for 1 h, dried, broken in a mortar and sieved. A commercial surfactant was added to help the dispersion of the powders. The dried powder was pelletized and then reacted in a kitchen microwave oven (Brastemp), operating at 2.45 GHz. In order to avoid alumina crucible thermal shock, the oven power was selected according to the setup established in Table 1. Maximum power level (100%) represents 980 W.

The uniformity in reaction atmosphere inside the microwave cavity was important to reach an optimal reaction condition and avoid oxidation of the products. In this context, a Pyrex glass reaction chamber was introduced to maintain a certain argon pressure within it. The kitchen microwave oven and the glass reaction chamber used to create the necessary atmosphere inside the microwave cavity are shown in Fig. 1. The CCR was made in a furnace with graphite resistance under argon atmosphere, at 1450°C for 2 h. The precursor employed for CCR was the same for MWCR. Resulting powders were characterized by X-ray diffraction (Kristaloflex D500) to verify the phase formation, by scanning elec-

Table
Oven power setup

Time (min)	Power (%)
2	30
3	60
40	100

Fig. 1. Microwave oven and glass atmosphere chamber used to create the necessary atmosphere.

tron microscopy (Carl Zeiss 940A) to verify morphological characterization of the powders and BET to assess the specific surface area.

3. Results

Figs. 2 and 3 show the XRD patterns of the mixed powders obtained through MWCR and CCR of kaolin. It was possible to observe that the crystalline phases resulting from MWCR are similar to those obtained by CCR. This last reaction proceeded in 2 h at 1450°C, thus it denoted that the MWCR reached a temperature up to 1400°C, required for the decomposition of mullite to Al_2O_3 and SiO_2 (reactions B and C), and reduction of SiO_2 by the carbon to form SiC (reaction C). The results showed that the heating in the microwave oven was distinctly different from the heating in the normal furnace. In the microwave oven, the heating with microwave start in the central region of the pellets, resulted in two distinct zones: a lighter central region completely surrounded by a darker zone. It was established by XRD that the outer zone was primarily mullite with a small percentage of Al_2O_3 and much more SiC than in the central zone with primarily Al_2O_3 and small percentages of mullite and SiC. Both CO and SiO gas must diffuse out of the pellets. However, in the furnace, the carbothermal reaction began at the outer edge of the pellets and then progressed into the central region. The aspects of the pellets showed two distinct zones: a darker central region completely surrounded by a lighter zone. It was established by XRD that the outer zone was primarily Al_2O_3 with small percentages of mullite and SiC, whereas the inner region was primarily mullite with a small percentage of Al_2O_3 and much more SiC than in the outer zone. These results from the heating in the normal furnace were in close agreement with those observed by Bechtold [12]. Fig. 4 shows a schematic illustration of the process steps and effect of the heating mechanism in the carbothermal reduction reaction.

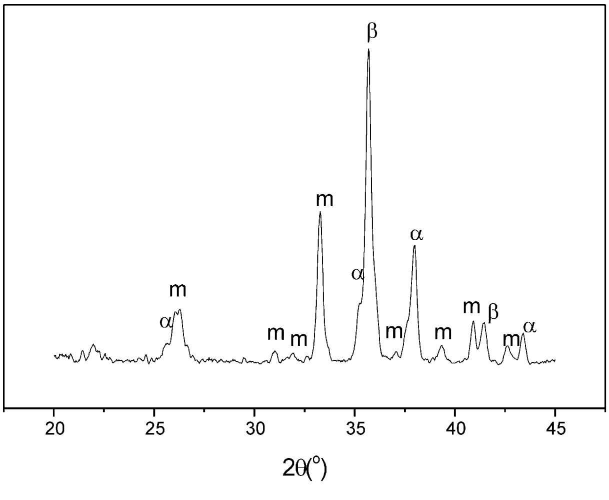

Fig. 2. XRD pattern of Al_2O_3/mullite/SiC powders obtained starting from kaolin, through MWCR; α = α–Al_2O_3, β = β-SiC, m = mullite.

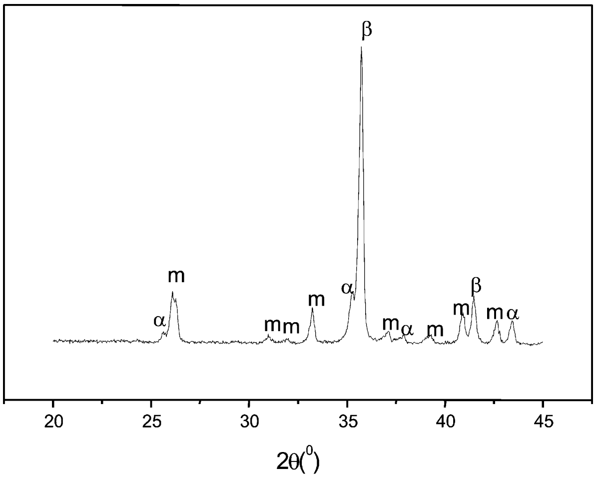

Fig. 3. XRD pattern of Al_2O_3/mullite/SiC powders obtained starting from kaolin, through CCR; α = α–Al_2O_3, β = β-SiC, m = mullite.

The nature of carbothermal reduction reaction is predominantly a vapor phase reaction that results in the formation of SiC in whisker form, when catalyst sites are present in the precursor. In both cases studied in this

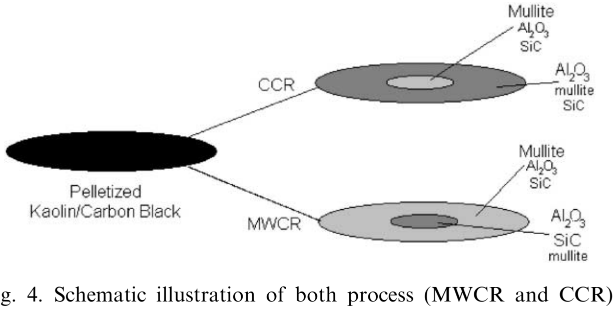

Fig. 4. Schematic illustration of both process (MWCR and CCR), and effect of the heating mechanism in the carbothermal reduction reaction.

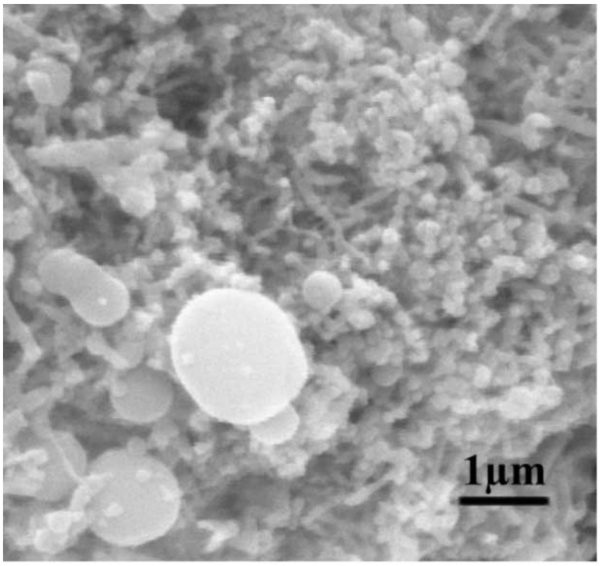

Fig. 5. SEM micrograph of SiC spheres formed by VLS process.

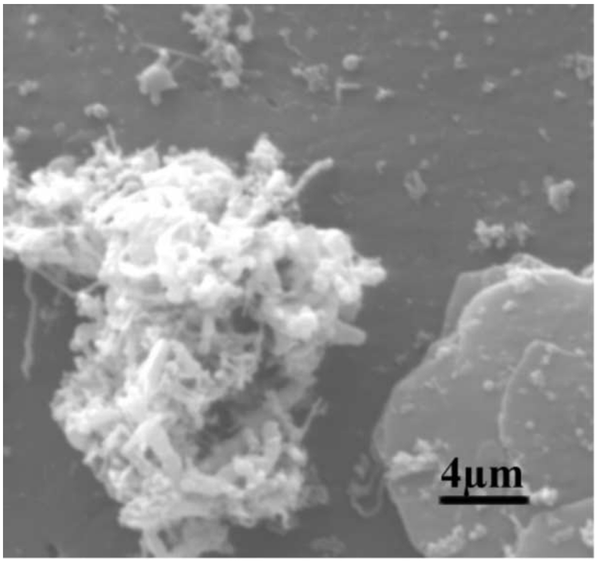

Fig. 6. SiC fibrous cluster and mullite plate formed during MWCR.

work (MWCR and CCR) EDS analysis carried out showed the presence of iron and potassium in silicon rich areas, corresponding to SiC. This is due to elements, which are present in raw material (Fe = 0.49%, K = 1.38%) and act as catalyst to the whisker growth of SiC probably through VLS process, as one can be assumed by the presence of SiC spheres at the tip of whiskers. Fig. 5 shows some of these SiC spheres formed in the tips of whiskers in a sample obtained through MWCR of kaolin.

As the metal melts at high temperatures, it attracts Si and C atoms from the vapor to the catalyst to form whiskers. When saturation of these atoms occurred in the liquid catalyst, the growth is side branched type, resulting in formation of fibrous structure [14], as shown in Fig. 6. These fibrous clusters and also whiskers are found in all samples surveyed. Fig. 7a shows the morphological aspects of the powder obtained by MWCR during 45 min. SiC whiskers and fibrous clusters are present, as well as mullite and Al_2O_3 plates. These results are in agreement with XRD patterns. Fig. 7b shows the morphological aspects of the powder obtained by CCR. Again, it was possible to observe SiC fibrous clusters.

A wide range view in the sample suggested that the powders synthesized from kaolin by CCR possess a greater amount of SiC fibrous clusters than those obtained by MWCR. BET results confirmed this affirmation, as can be seen in Table 2. The side branched type growth results in the greatest aggregation of CCR powders, presumably due to the longer reaction time in CCR (1450°/2 h) compared with MWCR (45 min).

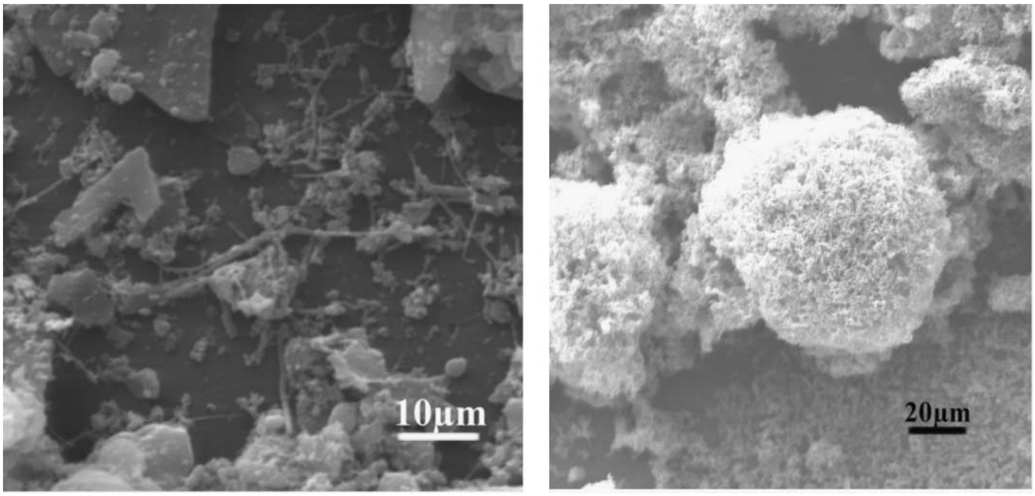

Fig. 7. SEM micrograph of powders from CCR: (a) SiC whiskers, mullite and Al_2O_3 plate; (b) SiC fibrous clusters.

Table 2
Specific surface area of powders obtained by MWCR and CCR

	Specific surface area (m^2/g)
MWCR	4.46
CCR	1.98

4. Conclusions

It was possible to synthesize Al_2O_3/mullite/SiC powders through the microwave-assisted carbothermal reduction in only 45 min. The heating in the microwave oven was distinctly different from the heating in the normal oven. In the microwave oven, the carbothermal reduction began in the inner region of the pellets and then progressed into the outer region, resulting in two distinct zones: a lighter central region completely surrounded by a darker zone. It was established by XRD that the outer zone was primarily mullite with a small percentage of Al_2O_3 and much more SiC than the central zone with primarily Al_2O_3 and small percentages of mullite and SiC.

XRD patterns indicated that powders from MWCR resembled in composition those obtained by CCR during 2 h at 1450°C. Morphological aspects of MWCR powders showed formation of SiC whiskers and fibrous clusters which were also found in powders from CCR, however CCR presented a larger amount of SiC fibrous clusters than in MWCR owing to reaction time of 2 h in CCR that favored the powder aggregation.

Acknowledgements

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