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# Synthesizing $Al_2O_3$/SiC in a microwave oven: A study of process parameters

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**Abstract**

The effect of precursor milling, reaction time, microwave power level and gas flow on the microwave synthesis of $Al_2O_3$/SiC composite powder was investigated. Reactions were carried out in a semi-industrial microwave oven (Cober Inc., USA) allowing for the insertion of inert gas. Two reaction configurations were designed to perform the synthesis: a cylindrical thermally-insulated reactor and a pipe fluidized bed reactor (PFR). The precursor employed for the reaction in the two reactors was utilized in the form of pellets. A direct relation exists between saturation of the reaction atmosphere and the kinetics of carbothermal reduction. In addition to high levels of microwave radiation power (>1.5 kW), this favors the rapid formation of $Al_2O_3$/SiC.



*Keywords:* D. $Al_2O_3$/SiC; Synthesis; Carbothermal; Microwave

## 1. Introduction

Carbothermal reduction of clays is a known route to obtain ceramic powders [1]. This method consists of blending natural raw materials and a carbon-rich source, followed by heating in a reducing atmosphere.

The process is widely applied due to the use of less expensive raw materials compared to other synthesis methods. Reactions are usually conducted in electrical furnaces and about 3 h of soaking time at 1600 °C are required to produce the $Al_2O_3$/SiC composite. Efforts have been made to obtain $Al_2O_3$/SiC powders by microwave-assisted carbothermal reduction of natural raw materials blended with a carbon source [2,3]. Encouraging results have been achieved in terms of the resulting products and the economic aspects of the process. In the search for better results, studies have focused on improving raw materials by milling, revealing the important role of the precursor powder's average particle size [3]. The crystallinity of raw materials exerts a particular influence on the development of high temperature reactions [4].

Considering the unsusceptibility of aluminosilicates in general to microwave radiation, the carbon source employed in the process takes on a particularly important role in reaction heating, besides its role of reducing agent. Chianghong's [5] findings indicated that (amorphous) carbon black produces better results as a heating agent in microwave ovens than does graphite carbon of a similar particle size.

A number of studies have focused on the use of microwave-assisted carbothermal reduction reaction to synthesize ceramic materials such as SiC [5], β-SiAlON [6], TiC [7], TaC [7], $MgAl_2O_4$ [8]. These studies have shown that microwave energy allows the desired species to be synthesized at lower temperatures than do conventional routes. Considering the reaction to obtain β-SiAlON starting from natural raw materials, microwave heating triggered a different phase formation mechanism involving a single rapid stage [6]. This apparent improvement in chemical reactions is a common factor in microwave radiation used as an alternative energy source for processing materials, requiring lower activation energy and producing higher diffusion rates.

The chemical reaction to obtain SiC by the carbothermal reduction of silica can be written as follows:

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \quad (A)$$

However, the reduction reaction involves not only a single solid–solid type but also a solid–gas type reaction, in which species such as SiO are present [9].

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Decomposition of kaolinite occurs initially when aluminosilicate is used as a raw material for carbothermal reduction. Shown below are stoichiometric reactions that form $Al_2O_3$/SiC composites from kaolin [10].

$$3\underbrace{(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)}_{\text{Kaolinite}} \overset{500-1200\circ C}{\longrightarrow} \underbrace{Al_6Si_2O_{13}}_{\text{mullite}} + 4SiO_2 + 6H_2O \quad \text{(G)}$$

$$Al_6Si_2O_{13} + 4SiO_2 + 12C_{(s)} \overset{>1300\,^\circ C}{\longrightarrow} Al_6Si_2O_{13} + 4SiC_{(s)} + 8CO_{(g)} \quad \text{(H)}$$

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

The Gibbs free energy for overall carbothermal reaction of kaolinite is:

$$\Delta G = 0.599 - 0.33T\,(\text{kJ/mol}) \quad \text{(J)}$$

Earlier studies have confirmed that, in the presence of carbon and an argon atmosphere, the reducing conditions contribute toward the formation of mullite. The primary action of the inert atmosphere is to maintain the carbon in its elemental form during heating. Thermodynamic calculations for 1200 °C predict that the reaction (A) is thermodynamically favorable [11].

Many factors influence the characteristics of the resulting powders, e.g., the morphology and reactivity of the starting powders, the amount of melting elements in the raw materials, the partial pressure ratio of gas species such as SiO, CO, $CO_2$ and Si formed during the reaction, and the reaction soaking temperature. This study investigated the effect of various processing parameters on the characteristics of $Al_2O_3$/SiC powders obtained by microwave-assisted carbothermal reduction (MWCR) of kaolin, since such a parameters played an important role on achieving the expected results.

## 2. Experimental

Kaolin (Minasolo, Brazil) was used as $Al_2O_3$ and $SiO_2$ source material. Earlier studies have confirmed the good performance of kaolin in conventional carbothermal reductions to produce composite powders of the $Al_2O_3$/SiC system [2].

Table 1
Chemical and mineralogical composition of the kaolin horii

| | |
|---|---|
| $SiO_2$ (%) | 43.20 |
| $Al_2O_3$ (%) | 39.10 |
| $TiO_2$ (%) | 0.09 |
| $Fe_2O_3$ (%) | 1.20 |
| CaO (%) | 0.58 |
| MgO (%) | 0.05 |
| $Na_2O$ (%) | 0.07 |
| $K_2O$ (%) | 0.80 |
| Loss by ignition (%) | 14.50 |
| Specific surface area | 10.68 |
| Minor phases (kaolinite) (%) | >95 |
| Major phases (quartz) (%) | <5 |

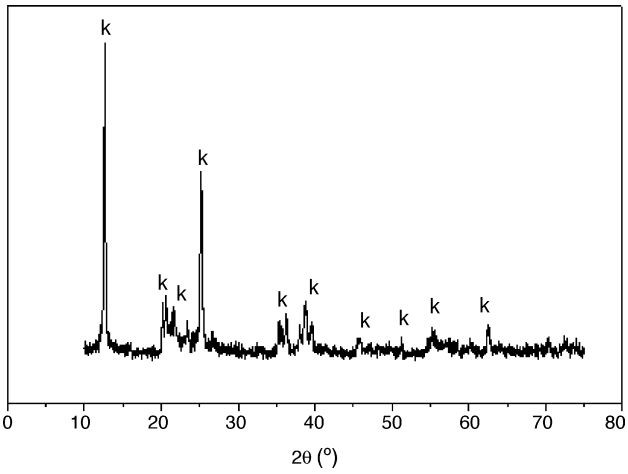


Fig. 1. XRD pattern of kaolin horii (k—kaolinite).

Furthermore, this material is a low cost aluminosilicate with a relatively pure composition (about 2.79% of contaminants) and good crystallinity. Table 1 gives a chemical analysis and the mineralogical composition of kaolin, while Fig. 1 shows its X-ray pattern. The carbon source utilized was carbon black with a specific surface area of 114.89 $m^2/g$ and an average particle size of about 70 nm.

To evaluate the effect of kaolin reactivity in MWCR, the kaolin was subjected to wet attrition milling (Union Process, Std-01). Milling was performed using water as the dispersant, ammonium polyacrilate as the deflocculant and a mullite grinding medium. Table 2 lists the nomenclature of the processed samples and their respective milling times.

The milled kaolin was freeze-dried in a lyophilizer (Micro Modulyo, Edwards), sieved, wet blended with carbon black in a 3/1 (carbon/kaolin) molar ratio and then extruded in the form of pellets.

The reactions were conducted in a semi-industrial microwave oven (Cober Eletronics, Inc.). Two reaction systems were designed to protect the oven and control the atmosphere (Systems 1 and 2), as depicted in Fig. 2. System 1 consisted of a cylindrical ceramic reactor completely insulated by low heat loss ceramic fibers. Argon was injected into the reactor through ceramic pipes. A certain argon pressure had to be maintained inside this chamber to prevent the presence of $O_2$, which can oxidize both carbon black and newly-formed SiC. A crucible containing the reaction precursor was placed inside the chamber (Fig. 2(a)). System 2 consisted of a pipe fluidized bed reactor (PFR) equipped with a low porosity ceramic tube coated with refractory fiber to avoid heat loss. An argon inlet was connected to the tube at one end and a gas collector at the

Table 2
Samples and its milling time

| Sample | Milling time (h) |
|---|---|
| SM | 0 |
| C8h | 8 |
| C16h | 16 |
| C24h | 24 |

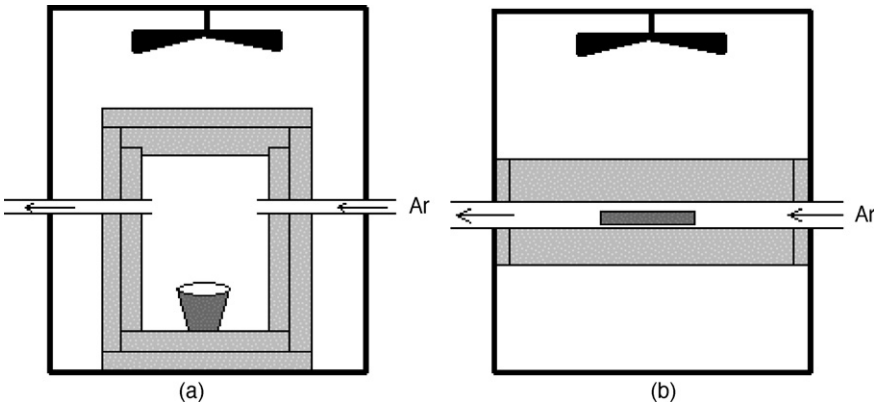


Fig. 2. (a and b) Reaction systems.

other. A rectangular crucible containing the precursor was inserted into the tube at the center of the oven cavity.

In System 1, the samples were exposed to 2.5 kW for 30 min. To compare the performance of the two systems, sample C16h was reacted separately in both systems. For the comparative reactions, 1.0 kW was applied for 20 min. After the reaction, all the powders obtained were calcined at 500 °C for 3 h to remove residual carbon. The reaction yield was evaluated by means of mass reduction of precursor, which was around 46%, according to results reported elsewhere [2,3].

The powders were characterized by X-ray diffractometry (XRD) (Siemens D500), scanning electronic microscopy (SEM) (Phillips XL30 FEG), identifying their particle size distribution (Micromeritics Sedigraph 5100) and specific surface area (SSA) (BET, Micromeritics Gemini 2370).

## 3. Results and discussions

Fig. 3 shows the particle size distribution and specific surface area (SSA) of the kaolin after the milling process. After 24 h, the SSA showed an increase from 21.3 to 36.0 $m^2/g$, confirming the effectiveness of the attrition milling process. This result was corroborated by the SEM analysis.

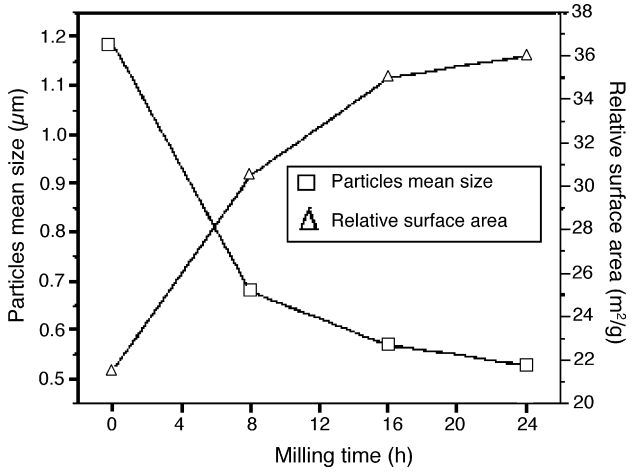


Fig. 3. Particles average size (□) and relative superficial area (△) vs. milling time.

SEM investigations of the kaolin after milling proved that the particle size was effectively decreased, as one can be seen in Fig. 4(a and b). This result certifies the efficiency of attrition milling for particles size reducing, that was from 3 to 1 μm.

Fig. 5 shows the X-ray pattern of the samples reacted in System 1 under the same heating conditions (30 min, 2.5 kW).

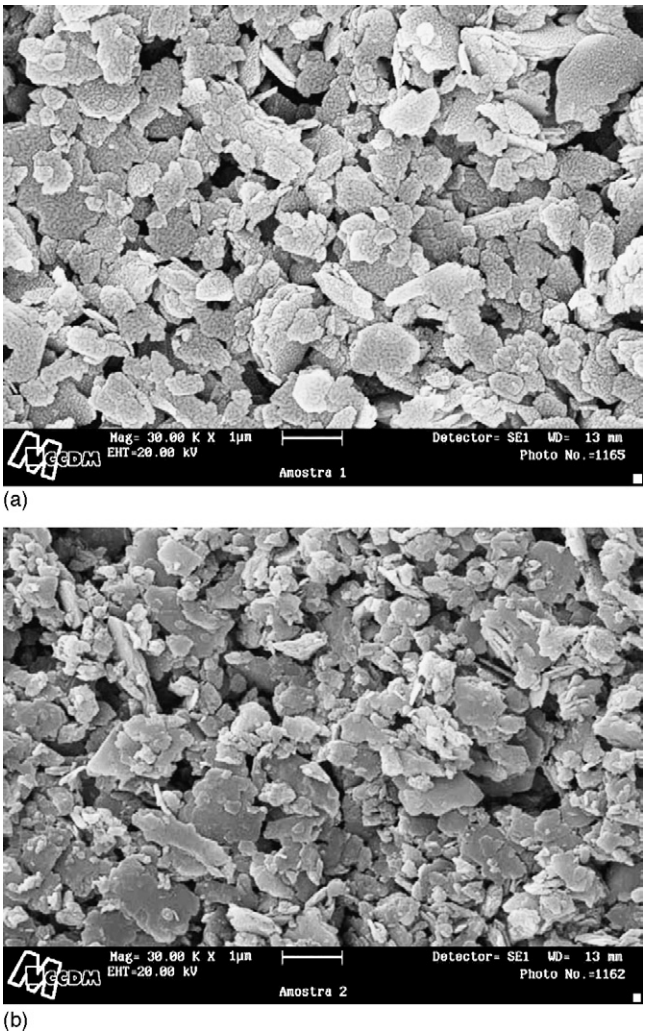


Fig. 4. Kaolinite particles: (a) sample as received and (b) sample C16h.

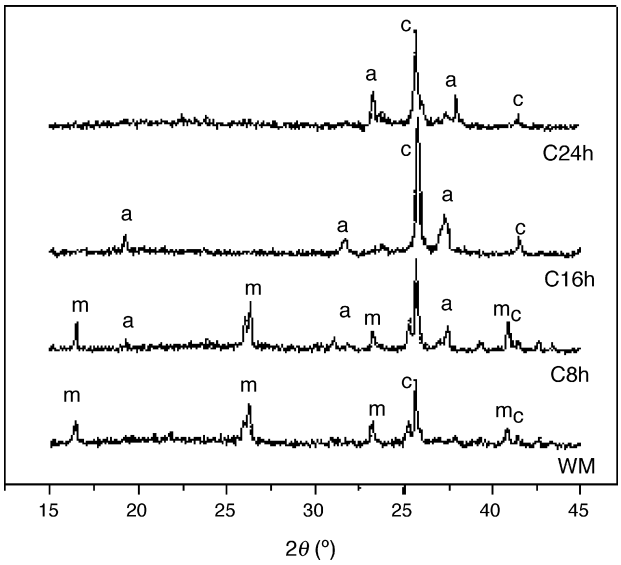


Fig. 5. XRD pattern of reaction products (system 1); m = mullite, c = SiC and a = $Al_2O_3$.

A direct correlation was observed between the phases formed during the reactions and the SSA of the raw material.

The reaction conditions were appropriate to allow for total reduction of the free silica in all the samples, but total transformation of mullite into $Al_2O_3$ and $SiO_2$ occurred only in samples with a lower specific surface area (C16h and C24h). The reaction kinetics in these samples was superior. The XRD results also showed mullite in the reaction products WM and C8h. Therefore, the reduction of the precursor's average particle size was a key factor in the total reduction of free energy in the system, favoring the rapid formation of $Al_2O_3$/SiC at a lower temperature. Samples C16h and C24h showed similar results in terms of phases formed, since their SSA were similar.

The use of a porous homogeneous precursor in the form of pellets was very interesting owing to the need to remove excess CO in the reaction atmosphere. Reaction (A) was extremely endothermic, and if the excess CO had not been removed, a very high temperature would have been required to achieve the reaction rate. The excess carbon in the precursor (3/1 molar ratio) also plays an important role in the process. Reported results indicate that an over-stoichiometric molar ratio favors the reaction kinetics [12], the total removal of intermediate solid phases [4], and the yield of the final products, in addition to preventing the possible oxidation of those products.

The morphologies of the powder samples WM, C8h, C16h and C24h obtained with System 1 are illustrated in Fig. 6(a–d). These results indicate the presence of large amounts of SiC whiskers in many of the morphologies, and the presence of spheres at the tips of several whiskers. This finding can be attributed to the presence of some metallic impurities such as iron and potassium in the raw material (kaolin), which act as catalysts in the growth process of VLS whiskers and allow SiC to form at lower temperatures. However, fibrous clusters of SiC whiskers were created, indicating that the level of SiO and CO in the reaction atmosphere led to supersaturation of these gas species. Such clusters usually grow around a catalytic site. Mullite and corundum particles were also observed.

The reactions were carried out in System 1 for 30 min, using 2.5 kW of power to produce the desired product (samples C16h and C24h). In comparison with the conventional route (3 h of soaking time at 1600 °C), the use of this system in the

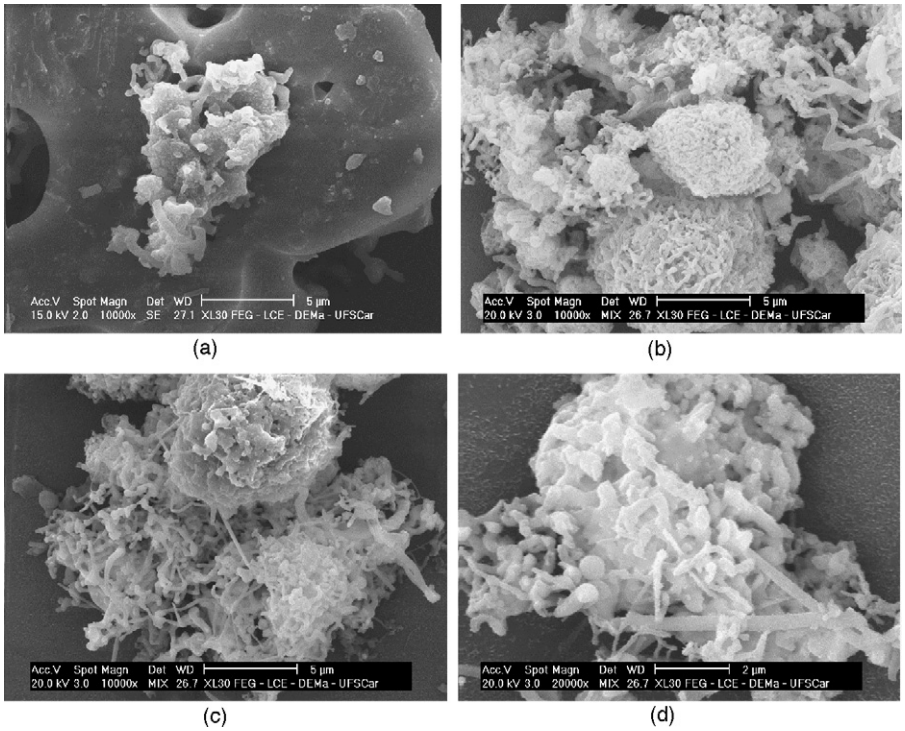


Fig. 6. (a) SiC whiskers and mullite particle (sample WM); (b) SiC fibrous clusters (sample C16h); (c) SiC fibrous clusters and SiC acicular whiskers (sample C24h); and (d) presence of spheres on the tip of SiC whiskers (sample C24h).

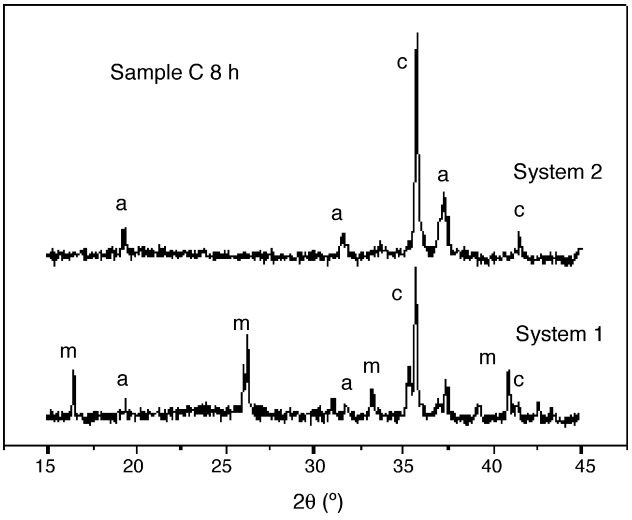


Fig. 7. XRD pattern of comparative reaction products between systems 1 and 2 (sample C8h); m = mullite, c = SiC and a = $Al_2O_3$.

microwave oven resulted in a significant saving of energy (reduced processing time).

The performance of Systems 1 and 2 was compared based on the reaction of sample C8h under the same conditions (20 min and 1.0 kW of power) in the two systems. This comparison is depicted in the X-ray pattern of Fig. 7, showing how the reaction system affects the final products. The reaction conducted in System 2 was complete, i.e., the precursor was fully converted to $Al_2O_3$/SiC, leaving behind no residual mullite phase. This performance confirmed the system's superior energy absorption in the microwave carbothermal reduction reaction, since it probably favored the precursor's absorption of microwave energy. Therefore, only a small amount of refractory materials were required to thermally insulate the oven. Furthermore, the pipe geometry allowed the excess CO to be removed outside the system, speeding up the reaction kinetics. The resulting particles morphology from both system reactions are expected to be similar, with the difference on the presence of mullite particles at the reaction product of system 1.

Another key aspect is the partial pressure of argon inside the system. Observations have indicated that a high argon flow through the inlet pipe favors the reaction kinetics. This fact is related with the removal of excess CO outside the system, displacing the reaction for the formation of products and decreasing the Gibbs free energy ($\Delta G$) [13–15]. However, the gas pressure must be carefully controlled to prevent argon ionization (plasma), which may yield energy absorption that decreases the reaction kinetics. The appearance of plasma can also cause damage by thermal shock in the reaction system.

Table 3 lists the specific surface area data of the powders synthesized by System 1. These results are in agreement with the high content of fibrous clusters of SiC whiskers created, shown in Fig. 6(a–d).

Table 3
Specific surface area of the processed powder (system 1) obtained by BET

| Sample | Specific surface area ($m^2$/g) |
|---|---|
| WM | 4.81 |
| C8h | 4.88 |
| C16h | 4.46 |
| C24h | 5.09 |

## 4. Conclusions

$Al_2O_3$/SiC composite was successfully synthesized by the rapid microwave-assisted carbothermal reduction of kaolin and carbon black (20 and 30 min). The reaction system applied in the synthesis exerted a major influence on the time and radiation power required to produce the composite devoid of residual phase. Moreover, phenomena such as gas ionization (plasma), thermal runaway and thermal shock must be controlled to avoid not only energy dispersion but also damage to and loss of equipment. Thanks to its pipe geometry, which provided effective energy distribution, System 2 successfully produced $Al_2O_3$/SiC composite in less time (20 min) using lower power (1.0 kW) than System 1, which took 30 min and 2.5 kW to produce the same product. An adequate argon flow was essential to improve the reaction kinetics, for it acted to remove the excess CO, thus decreasing the system's $\Delta G$. The presence of impurities (kaolin) such as iron and potassium in the raw material influenced the morphology of the powder after the reactions, yielding SiC whiskers grown by the VLS process.

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