Synthesis of Al$_2$O$_3$/SiC Powders Using Microwave-Induced Combustion Reaction*

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Nanocomposites Al$_2$O$_3$/SiC powders have been synthesized by a microwave-induced combustion process using aluminium nitrate, β-SiC (powders) and urea. The effect of preheating the solution before the combustion reaction and the effect of the characteristic of the SiC powders, in the crystallization of the alumina, by combustion reaction were evaluated. The preheating of the liquid solution at about 150°C before heating in the microwave oven guaranteed the homogeneity of the solution and modified the characteristics of the products. The mechanism of heating in the microwave oven was favorable to the uniform emission of gases and fast dissipation of heat, promoting formation of different foam and nanocomposites Al$_2$O$_3$/SiC powders with characteristics that were different from those produced conventionally. The direct conversion of liquid solution to the final solid product was assured, and the segregation commonly found in conventional mixing of powders (alumina-SiC) was avoided. The different characteristics of the SiC powders have strong influence in the flame time of the combustion reaction and consequently in the crystallization of the alumina and characteristics of the Al$_2$O$_3$/SiC nanocomposites powders. The SiC particles were not oxidized during the reaction and partial reaction with alumina did not occur; SiC particles remained as a distinct and separate phase.

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1. Introduction

Worldwide interest in a new class of materials known as nanocomposites began in 1988 when Niihara & co-workers reported that the addition of 5 vol% of 0.3 μm SiC particles to an Al$_2$O$_3$ matrix resulted in significant strengthening and toughening.1–3 While the reinforcing particles are not strictly nanometer-sized, these materials have nonetheless become known as nanocomposites. This material could be obtained by conventional powder processing routes, but dispersion problems are often encountered. However, many impressive results have been obtained using sol-gel processing,4 polimeric precursors,5 CDV$^6$ and combustion synthesis$^6$ are being developed to know how to make a uniform dispersion of these particles of SiC within the fine grain ceramic matrix. Even so there are still many problems remaining to be solved, e.g. how to make a uniform dispersion of nanoparticles within the fine grain ceramic matrix. By combustion synthesis the added substances (SiC) can be homogeneously dispersed within the solution of aluminium nitrate preventing formation of the segregation.$^6$ The method exploits an exothermic, usually rapid and self-sustaining, chemical reaction between the desired metal salt, and a suitable organic fuel. The preheating of the aqueous solution of urea and the metal nitrate precursor to a sufficient temperature begin the decomposition of urea allowing homogeneous nucleation. This will release ammonium and hydroxide ions according to the reaction: CO(NH$_2$)$_2$ + 3H$_2$O → CO$_2$ + 2NH$_3$ + 2OH$^–$. The introduction of hydroxide ions increases the pH of the solution, which then causes hydrolysis of the metal cations to species with lower solubility.$^7$ The product, complexes of metal hydroxide (CMH), may then exceed its solubility by an amount large enough to allow homogeneous nucleation. The existing nuclei will continue to grow until the concentration of CMH drops below the solubility limit.

The mechanisms of the combustion synthesis reaction then involve dehydration, decomposition, swelling and burn.$^8$ It then foams, due to the gaseous decomposition products of the intermediates, causing enormous swelling of the reaction product. The foam itself most likely consists of polymers such as cyanuric acid (HNCO)$_3$ and polymeric nitrates, which are also combustible. Finally, the accumulation of the combustible mixture of gases causes the foam to burst into flame and burn to incandescence, with further swelling, producing an oxide powder.$^9$

After the reaction begins, the above described method is self-sustaining, reaching high temperatures that ensure crystallization and the formation of oxides in a short period of time and releasing large amounts of gases, which prevent less agglomeration of the particles that are formed. This method is therefore considered simple; involving few steps and producing powders with the desired composition and crystalline structure. Temperature and reaction time are the two most important factors to control phase transformation during the process of combustion synthesis. Optimal temperature/time conditions vary from one material to another and the intrinsic phase transformation is fixed and characteristic of each system. General theoretical studies of the self-sustaining reaction system demonstrate that increasing the density of the medium and the reaction heat and reducing the mediums heat loss by convection and radiation can facilitate the combustion synthesis reaction. The reaction conditions may be adjusted by adjusting the fuel content and the surrounding temperature.$^{10}$ Thus, the properties of combustion-prepared powders depend on the fuel and on the combustion flame employed. Combustion synthesis has been used to produce of any kind of single phase, multiphase or composite on a nanophase-scale.$^{11–14}$

Microwave-induced combustion reaction has a potential to make the very fine second phase homogeneously dispersed in the matrix by tailoring a wide range of processing param-

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The synthesis of fine Al_{2}O_{3}/SiC by combustion synthesis has already been reported. Furthermore, some literature exists on the enhancement of chemical reactions in a microwave. The intent of this contribution is to combine these two procedures in a new process for the synthesis of nanocomposites Al_{2}O_{3}/SiC powders. The effect of two different β-SiC (0.3 μm and 0.6 μm) in the combustion reaction and on the characteristics of the resulting powders is also reported.

2. Experimental Procedure

In this study, the synthesis process involves the combustion of redox mixtures containing the desired metal ions, oxidizing reactant (O) and a fuel (F) as a reducing agent. The materials for this mixture were aluminum nitrate—Al(NO_{3})_{3}·9H_{2}O (Alfa Aesar) and urea—CO(NH_{2})_{2} (Fisher Chemicals) as the oxidizing reactant and fuel, respectively. The two different silicon carbide particles were obtained from Ibelon Co. (mean particle size < 0.3 μm) and from Performance Ceramics Company, (ASC-26, mean particle size < 0.6 μm). Table 1 shows the complete characterization of both SiC. The prepared solutions were mixed in a cylindrical Pyrex container. Three different synthesis routes were studied: (i) preheated on a hot plate and then heated in the microwave oven, (MICRP); (ii) directly heated in the microwave oven, (MICRD); (iii) preheated on a hot plate and then heated in a normal furnace, (CCR). For the MICRP and CCRP routes, the stoichiometric composition was initially heated up to 110°C on a hot plate for the purpose of achieving a good dissolution of the aluminum nitrate and urea in a small amount of water. As the temperature increased, dissolution occurred and a homogeneous solution was produced. Before boiling, it was transferred directly into the microwave oven (MICRP) or into a muffle furnace preheated at 500°C (CCR). For the MICRD, the stoichiometric composition was transferred directly into the microwave oven after the components were mixed at room temperature (no preheating of the mixtures). The microwave oven used was a conventional kitchen model microwave (Goldstar, 900 W, and 2.45 GHz).

The as-prepared reaction products were characterized by X-ray diffraction (Philips diffractometer model APD 3720 using CuKα radiation) and scanning electron microscopy (Leica Cambridge Stereo Scan model 440, at 20 kV after Au coating, and Jeol model JSM-6400). The surface area was determined using the BET method (Quantasorb Quanta-
Table 2  The combustion reaction duration by conventional and microwave techniques.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>MICRP6</th>
<th>CCRP6</th>
<th>MICRD6</th>
<th>MICRP3</th>
<th>CCRP3</th>
<th>MICRD3</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 2</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Time (s)</td>
<td>28</td>
<td>90</td>
<td>37</td>
<td>11</td>
<td>28</td>
<td>15</td>
</tr>
</tbody>
</table>

Time*-time of the total combustion reaction
MICRP6, CCRP6 and MICRD6-routes with β-SiC 0.6 μm particle size.
MICRP3, CCRP3 and MICRD3-routes with β-SiC 0.3 μm particle size.

Fig. 1  X-ray powders diffraction patterns of Al₂O₃/SiC as prepared by MICRP with 0.6 μm SiC powder (n = ammonium nitrate, α = alumina and s = silicon carbide).

These routes, controlled combustion reactions in both the microwave and conventional furnace to obtain Al₂O₃/SiC powders was possible with 0.6 μm size SiC particles by MICRD, MICRP and CCRP. Figure 1 shows the X-ray diffraction patterns of Al₂O₃/SiC powders produced by MICRP6. The possibility of using additions of ammonium nitrate (as extra oxidant in the proportion of 1:3 molar urea and ammonium nitrate) to increase the flame temperature and its duration in the reaction was investigated for the 0.3 μm size β-SiC. The high temperature was sustained longer, but not long enough to promote crystallization of the alumina via all routes. Figure 2 shows these X-ray diffraction patterns of the powders produced by MICRD and CCRP with 0.3 μm and 0.6 μm β-SiC.

Moreover, the influence of the oxidizer/fuel ratio in the re-duct reaction for the 0.3 μm size β-SiC was investigated where the samples were prepared with one-and-one half and twice the amount of the stoichiometric urea content. Namely, it was to find out if the urea contents below stoichiometric were enough to trigger the explosive combustion of the fuel and the subsequent decomposition of the salts, and how that ratio affected the characteristics of the powders produced. Both the observed behavior and the X-ray diffraction patterns were affected by the oxidizer/fuel ratio. The mixture prepared with twice the amount a stoichiometric urea ignited easily. The high temperature was sustained longer, but not long enough to promote complete crystallization of the desired phase (Fig. 3).

With these results, we can conclude that the combustion reaction was strongly affected by the characters of the SiC for particles < 0.3 μm. We have an indication that the heating rate of the Al(OH)(NO₃)₃/SiC gel depends on dielectric behavior of the SiC, that depends of its size particles.

Fig. 2  X-ray powders diffraction patterns of Al₂O₃/SiC as prepared by CCRP and by MICRP with 0.3 and 0.6 μm SiC powder (n = ammonium nitrate, α = alumina and s = silicon carbide).

Fig. 3  X-ray powders diffraction patterns of Al₂O₃/SiC as prepared by CCRP and by MICRP with one- and one half (a) and twice (b) the amount of stoichiometric urea content. (n = ammonium nitrate, α = alumina and s = silicon carbide).

Table 3  Characteristics of the as-prepared Al₂O₃/SiC powders.

<table>
<thead>
<tr>
<th>Routes</th>
<th>Powder density [g/cm³]</th>
<th>Specific surface area (BET) [m²/g]</th>
<th>Particle size [μm]</th>
<th>50% average agglomerate size [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MICRP6</td>
<td>3.26</td>
<td>73.98</td>
<td>0.02</td>
<td>1.30</td>
</tr>
<tr>
<td>CCRP6</td>
<td>3.48</td>
<td>36.39</td>
<td>0.05</td>
<td>1.50</td>
</tr>
<tr>
<td>MICRD6</td>
<td>3.76</td>
<td>37.50</td>
<td>0.04</td>
<td>1.45</td>
</tr>
</tbody>
</table>

*From surface area.

Table 3 shows the characteristics of the Al₂O₃/SiC (0.6 μm). Pycnometry analysis showed that the densities for the powders were in the range of 3.26 to 3.76 g/cm³. The specific surface areas (BET) and the particle sizes (Couler Counter) are in the range of 36.39 to 73.98 m²/g and 0.02 to 0.05 μm, respectively. The results also confirmed that the reaction kinetics changed with the route used. The exothermicity of the reaction changed and, consequently, the characteristics of the foam and powders were altered. Less dense Al₂O₃/SiC powders was obtained by the microwave process with preheating (MICRP6). The degree of porosity was a direct consequence of how the gases escaped during
the combustion reaction. Figure 4 shows the morphological aspect of the foam obtained by MICRP6. Due to the increased uniformity of the solution by the pre-heating and escaping gas when heated in the microwave oven, the dissipation of the heat was fast and yielded the fluffiest foam. If heat dissipation is slow and flame time extend, the polymeric intermediates caused pre-sintering of the powders, like the CCRP6. Figure 5 shows this aspect morphological of the more dense foam CCRP6 and MICRD6. Consequently, less dense Al₂O₃/SiC powders were produced using the microwave process (MICRP6) as compared to the conventional processes (CCRP6) and (MICRD6). Figure 6 shows details of CCRP6 calcined at 600°C/2 h. The micrograph inhibites aggregated particles. Figure 7 shows nanoparticles of SiC on the surface of the Al₂O₃ particle of CCRP6 calcined at 600°C/2 h. The SiC was estimated by silicon ion detected by EDS analyses.

The fine particles of Al₂O₃/SiC produced by the MICRP route were related to the beneficial action of both preheating and heating with microwaves. The preheating, contributing to the complete dissolution of aluminum nitrate and urea in water that resulted in a homogeneous solution, favored the formation of the Al₂O₃/SiC in a shorter flame time, and prevented particle growth. In the microwave oven, the volumetric heating by the microwaves caused multiple ignitions throughout the solution and resulted in a uniform product. In the furnace, ignition began at a single point on the bottom of the beaker and then progressed circularly into the surroundings. Figure 8 shows this aspect of the foam after the MICRP6 and CCRP6. In the furnace combustion, the foam formed was circular around the ignition point. However, the foam of the microwave-induced combustion reaction was uniformly formed throughout the reactant. These effects were in close agreement, with those observed by Park and Kiminami. It appears that the morphology of the microwave combustion product was due to uniform heating associated with the microwave process.

The different characteristics of the Al₂O₃/SiC foam reflected the different effects of the preheating and the combustion reaction. The foams obtained by MICRP process were fluffier than those prepared with the CCRP process. Additionally, the density of the powders was lower in the MICRP6 and CCRP6 than those synthesized in the microwave without preheating.

The average agglomerate size obtained was well below 1.5μm. These results agreed with those obtained by BET analysis and appeared to be correlated to the agglomerate characteristics of the as-synthesized powder. The formation of the α-Al₂O₃ phase indicated that the temperature was high enough to reach full crystallization (> 1100°C) of this
phase during combustion. The reaction was intense and the resulting dry foam (light gray) increased in volume, homogeneously. The absence of any form of SiO₂ and/or mullite phase suggest that SiC particles were not oxidized during the reaction and partial reaction with alumina did not occur; that is, the SiC particles remained unaltered. This result may be attributed to the short reaction time in all cases, even though a high temperature was reached during the combustion.

The preheating effect of the solution before heating in the microwave oven promoted homogeneous nucleation and lead to finer Al₂O₃/SiC powders. The reaction produces a powder with morphology similar to the foam-like structure present in the boiled viscous solution; the foam-like structure of Al₂O₃/SiC powders reflects the inherent nature of the reaction associated with the presence of large amount of gases, high temperature, and short reaction time. The SiC was uniformly distributed in the matrix of alumina.

4. Conclusions

The results obtained in this study show that the crystallization of alumina by the combustion reaction was strongly affected by the size particles of the β-SiC. With the presence of 0.6 μm size β-SiC the flame time of the combustion reaction was long enough to promote the formation of the Al₂O₃/SiC nanocomposites powders. Rapid internal heating with microwaves lead to a reduction in the synthesis time and promoted the formation of more fluffy foams and less dense powders than those produced conventionally. When 0.3 μm size β-SiC was used under same conditions, the flame time of the combustion reaction was not long enough to promote full crystallization of α-Al₂O₃. The addition of ammonium nitrate (as extra oxidant) and one-and-one half and twice the amount of urea were not sufficient promote complete crystallization of the desired phase. The preheating effect of the solution before heating in the microwave oven promoted homogeneous nucleation and lead to finer Al₂O₃/SiC powders. The SiC particles were not oxidized during the reaction and partial reaction with alumina did not occur; SiC particles remained as a distinct and separate phase.
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