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# Study of the synthesis of sialon phases from silica–aluminium powder mixture using microwave energy

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Using a domestic microwave oven, pellets of a silica–aluminium powder were ignited and a self-propagating high-temperature synthesis (SHS) reaction occurred to produce $Si + AlN + Al_2O_3$ as the resultant phases. Silicon AlN and $Al_2O_3$ were subsequently nitrated to synthesize sialon phases under a nitrogen atmosphere without cooling. Thus both the SHS process and the nitration were finished within one-step process, which could save processing time and energy. © *1998 Kluwer Academic Publishers*

## 1. Introduction

Sialon is a very attractive high-performance ceramic, and one of the methods to synthesize sialon phases is by using natural silica and aluminium powder as raw materials [1].

Microwave energy can interact with material in several ways. Metal tends to reflect microwaves, but since metals have finite electrical conductivity, microwaves can penetrate into the metal to a depth known as the skin depth, $\delta$, where the electrical field falls to $1/e$ of its value at the surface. Thus, fine metal powder can have such large microwave absorption volume that this powder could be readily heated [2]. Microwave processing was also reported to increase the diffusion coefficients [3], so that a higher reaction rate could be obtained.

For a silica–aluminium powder mixture, a carbothermal reaction was reported to occur [4]. A combustion synthesis reaction has been reported to be initiated by several methods [5]. In this experiment, microwave energy was used to ignite the combustion synthesis reactions, and the $Si + AlN + Al_2O_3$ products were subsequently nitrated under a nitrogen atmosphere without cooling, so that both the combustion synthesis and nitration could be finished within a one-step procedure. How the microwaves interacted with the $SiO_2$–Al powder mixture, and how they affected the self-propagating high-temperature synthesis (SHS) reaction was studied. A comparison of the results of nitration by using microwave energy with those using a conventional furnace, was made.

## 2. Experimental procedure

Microwave processing experiments were carried out in a nitrogen atmosphere using a domestic microwave oven (Gold Star, MR-400 M, 2.45 GHz, 220 V, 1000 W). Aluminium powder was reagent grade (99.9 wt% purity, Junsei Chemical Co. Ltd, Japan) and had an average particle size of 23 μm and was flake-shaped. Natural $SiO_2$ had 98% purity (Kyongil Chemical Co. Korea) and an average particle size of 20 μm, as shown in Fig. 1. $Si_3N_4$ powder was reagent grade (Ube E-10). The weight per cent of aluminium in the Al–$SiO_2$ powder mixtures was 40, 50 and 60, respectively. After weighing, Al–$SiO_2$ powder mixtures were ball milled with alumina balls for 24 h. In order to prevent hydration and oxidation, ethanol was used as a mixing solvent. After drying, the powder was uniaxially pressed into 2.5 g cylindrical pellets under $100\,kg\,cm^{-2}$ pressure in a cylindrical die with 18 mm diameter. For each run, four pellets were stacked in an insulation cavity, which amounted to 10 g.

To create an insulation cavity, a low-temperature insulation brick was placed on the bottom of microwave cavity, above which a high-temperature insulation brick was placed. Pellets were put in this high-temperature insulation brick, and were covered by another high-temperature insulation brick (Fig. 2). The temperature was measured using an Optical Pyrometer (Minolta Camera Co., TR-630A) through the 8 mm diameter hole in the middle of the front brick, and its size was small enough to allow black body radiation conditions to occur. Voltage controller was used to control temperature.

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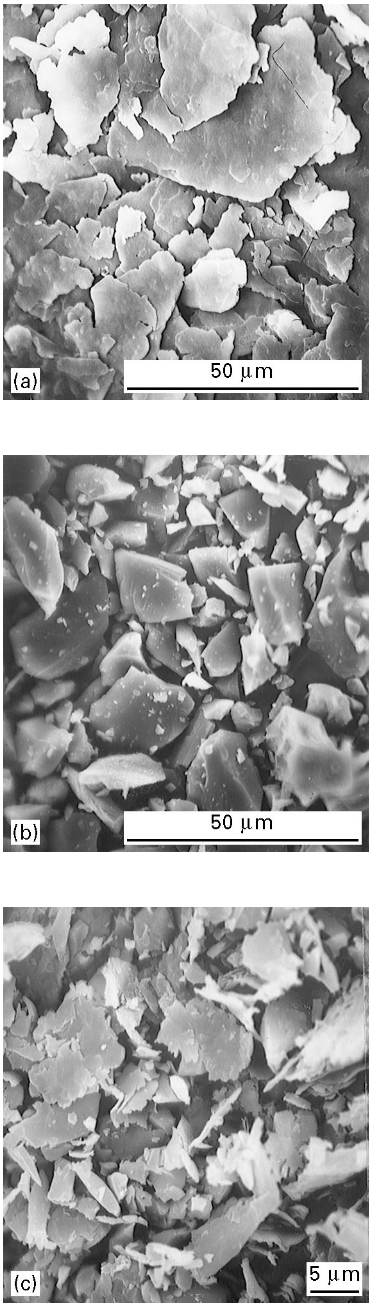

*Figure 1* Scanning electron micrographs of the starting powders: (a) Al, (b) $SiO_2$ and (c) mixed powder.

In order to control the atmosphere, a large Pyrex beaker was used, as shown in Fig. 2, and a vacuum seal was pasted on the bottom part of beaker. Three nitrogen-gas inlet pipes were installed around the bottom part of the beaker, and inside the beaker the insulation box was designed to rotate, to avoid any directional effects on the pellets during nitration. The nitrogen flow rate was $3\,cm^3 s^{-1}$.

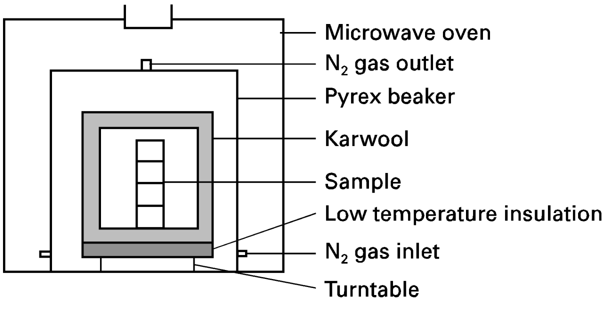

*Figure 2* Schematic diagram of the insulation box and microwave cavity.

## 3. Results and discussion

Initially, the $SiO_2 + Al$ powder mixture was heated due to the surface ohmic current on the aluminium powder. As discussed previously [6, 7], depending on the characteristics of the powder and the forming pressure, the heating behaviour of the pellets varied. In this 50 wt% Al + 50 wt% $SiO_2$ system, the powder mixed with a mortar and pestle for 2 h did not ignite, even after 15 min microwave running. However, the powder which was ball milled for 6 h took 5 min to ignite, and the powder subjected to 24 h ball milling took $1\frac{1}{2}$ min. Fig. 3 shows scanning electron micrographs of these powders. It is seen that fine powder absorbs more microwave energy so that the pellet made with fine powder can reach the ignition temperature faster. In a previous work [6] the characteristics of the powder were very important factors, as they are here, in this microwave-assisted SHS reaction. Four pellets were stacked in this experiment, and ignition always started among the pellets; this is a different phenomenon from that in previous work [5] which reported that ignition started from the core of the pellet. This phenomenon is probably caused by the fact that aluminium powder has a flaky shape, so that it can line up to form large aluminium plates on the top and bottom of the pressed pellet, which seemed to cause arc ignition among the pellets. After ignition, the combustion wave propagated radially from the top and bottom of the pellet to the centre. When this pellet was ignited by an electric arc at room temperature, without using a microwave oven, a non-steady state spin mode combustion wave propagated, but it soon stopped in the middle of pellet. Thus reaction was incomplete.

It is known that $\tan\delta$ increases almost exponentially with temperature and the temperature of the front part of the wave became very high due to the thermal conduction. Thus, this part absorbed microwave energy very efficiently and enabled the SHS reaction to be completed. This is an advantage of microwave-assisted SHS reaction over the chemical reaction, because microwave processing does not need expensive chemicals and the chemicals replacement for every SHS reaction. Chun [4] and Umebayashi and Kobayshi [1] used a furnace to finish the carbothermal reaction, and reported that unreacted aluminium was left after the reaction. However, in this work, no aluminium peak was observed in X-ray powder diffraction (XRD) analysis, which means that microwave-assisted SHS is a better method. This microwave-assisted SHS reaction gave better results than in previous works [1, 4].

Because in a domestic microwave oven it is hard to control input power, a 6 kW microwave generator (Model S6F, Cober Electronics Co., USA), which can control input power, was used to determine the influence of microwave power on the SHS reaction. Two

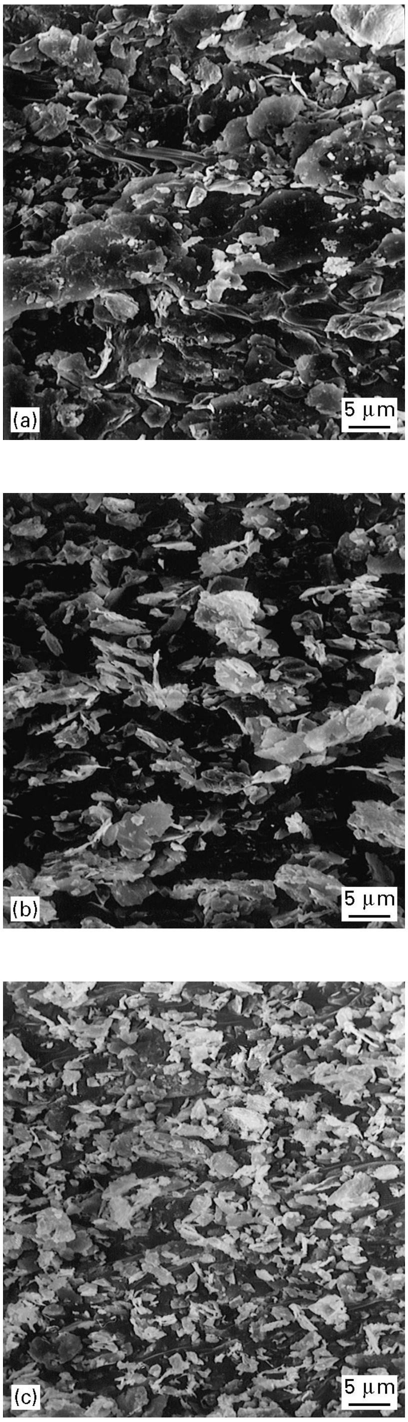

*Figure 3* Scanning electron micrographs of Al–$SiO_2$: (a) powder milled with mortar and pestle for 2 h, (b) powder ball-milled for 6 h, and (c) powder ball-milled for 24 h.

pellets, weighing 8 g and containing 50 wt% Al, were placed in a nitrogen atmosphere in the microwave cavity. When the input power was 800 W, the combustion wave stopped in the middle of the bottom pellet. Owing to the incomplete reaction, the unreacted aluminium and $SiO_2$ were left, as determined by XRD analysis. When the input power was 2000 W, combustion waves propagated into the whole pellets, at a velocity faster than that at the 800 W input power. In addition, the combustion temperature appeared to be higher than that in the 800 W case, and reaction was completed, so that only Si, AlN and $Al_2O_3$ reactants were left, as determined by XRD analysis. As the microwave power increased, the wave and the front part of the wave could absorb more microwave energy, which resulted in the increment of wave velocity and the completed combustion synthesis reaction. The above experiment shows how much the microwaves assisted the SHS reaction, and that it might be possible to control the SHS reaction by using microwave energy.

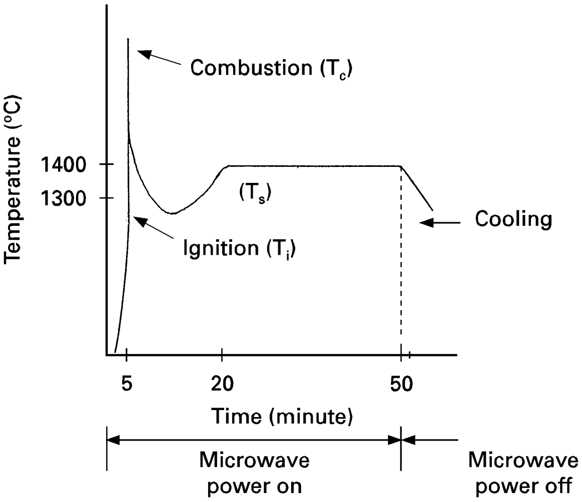

*Figure 4* Temperature versus time relationship.

After ignition, the exothermic heat of the SHS reaction kept the reacted part of pellet at a comparatively high temperature (Fig. 4). Thus, the temperature of pellet could be increased to more than 1300 °C due to the increased tan δ of the reacted part, which led to the synthesis of sialon phases, as shown in Tables I and II. The microwave processing can make both the SHS reaction and nitration into a one-step process. This work shows the possibility that after SHS reaction, a specimen could be continuously nitrated, oxidized or sintered, without cooling, by using microwave energy.

During the SHS reaction, an optical pyrometer cannot read the correct temperature. Thus, in this work, the combustion temperatures were very roughly compared by observing the colour and the intensity of the exothermic reaction. Even though the experimental conditions were same, the combustion temperature appeared to be different for each experiment in the microwave oven. In order to determine what caused this phenomenon, the input power and the conditions of arc-ignition were varied. First, a constant input voltage was used, but the combustion temperature still appeared to be different for each reaction. Aluminium powder was added between the pellets to ascertain the cause. The combustion temperature seemed to be higher with the addition of aluminium powder than without it. A greater amount of aluminium powder between the pellets resulted in a higher combustion temperature. When sufficient aluminium powder was added to form an aluminium layer between the pellets, the combustion temperature appeared to be very high, and power was cut off 5 min after the SHS reaction started. In this experiment, XRD analysis showed that sialon phases were formed,

TABLE I Comparison of XRD results for 50 wt% Al + 50 wt% $SiO_2$ specimen

| | Temperature/time | Reaction products |
|---|---|---|
| Umebayashi [1] | 1400 °C, 5 h | β-sialon > $Al_2O_3$ > AlN > 15R-sialon > > Si |
| Present work | 1400 °C, $1\frac{1}{2}$ h | $Al_2O_3 \simeq$ β-sialon > 15R-sialon > Si $\simeq$ AlN |

TABLE II Comparison of XRD results for when a microwave was used and for when a conventional furnace was used for 50 wt% Al + 50 wt% $SiO_2$ + 10 wt% $Si_3N_4$ specimen

| | Temperature/time | Reaction products |
|---|---|---|
| Conventional furnace | 1450 °C, 4 h | $Al_2O_3 \simeq$ β-sialon |
| Microwave | 1450 °C, 1 h | β-sialon > 15R-sialon > $Al_2O_3$ |

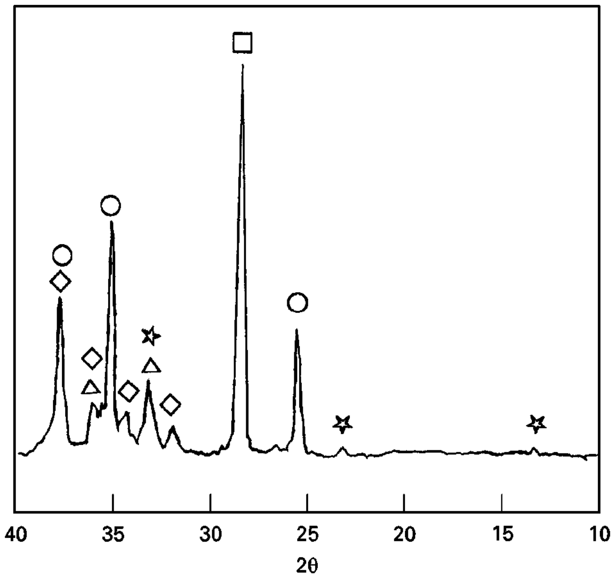

*Figure 5* XRD analysis of 50 wt% Al + 50 wt% $SiO_2$ content specimen which shows the formation of sialon phases. (☆) β-sialon, (○) α-$Al_2O_3$, (◇) 15R-sialon, (□) Si, (△) AlN.

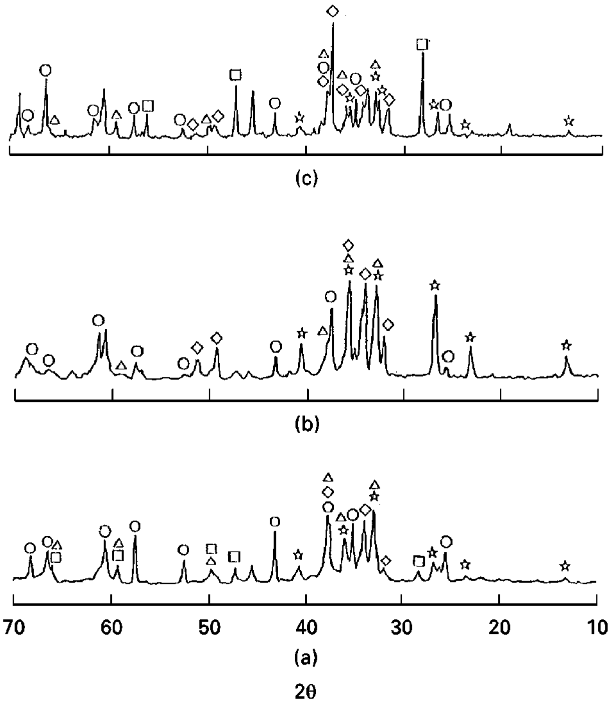

*Figure 6* XRD patterns of (a) 50 wt% Al + 50 wt% $SiO_2$ content specimen which was nitrated at 1400 °C for 1 h, (b) 50 wt% Al + 50 wt% $SiO_2$ + 10 wt% $Si_3N_4$ content specimen which was nitrated at 1450 °C for 1 h and (c) 60 wt% Al + 40 wt% $SiO_2$ content specimen which was nitrated at 1450 °C for 30 min. (☆) β-sialon, (○) α-$Al_2O_3$, (◇) 15R-sialon, (□) Si, (△) AlN.

as shown in Fig. 5. Thus one of the reasons for the difference in the combustion temperature for each SHS reaction might be due to the different amounts of aluminium content, especially in the top and bottom layer of the pellet.

Table I shows a comparison between this work and other work [8] for 50 wt% Al + 50 wt% $SiO_2$ content pellet. The data show that the synthesis rate of sialon phases by microwave processing is higher than that of conventional processing. XRD data are shown in Fig. 6a. Because it was difficult for a domestic microwave oven to be used for more than 1 h, pure sialon phases were not obtained. However, if a laboratory-scale microwave generator (e.g. Cober, Model S6F, USA) was used, it was possible to obtain almost pure sialon phases.

Other workers [8] claimed that the $Al_2O_3$ oxidation layer on the aluminium powder lowered the diffusion rate of diffusing species, so that the conventional synthesis of the sialon phase took longer time. However, in the microwave-assisted SHS process, this does not cause a problem, because the SHS reaction occurred rapidly enough to rupture the surface $Al_2O_3$ layer. A surface $SiO_2$ layer on the silicon grain probably existed, but due to the ohmic current [6] which flowed on the surface layer of the silicon grains and heated this layer rapidly enough to rupture it, the $SiO_2$ layer could not hinder the nitration process.

When 10 wt% $Si_3N_4$ powder was added to a 50 wt% Al + 50 wt% $SiO_2$ pellet, the formation of β-sialon was easier, because the added $Si_3N_4$ acted as nucleation seeds [8], as shown in Fig. 6b and Table II. The same pellet was conventionally heated at 1450 °C for 4 h in a nitrogen atmosphere and this synthesis result was compared with the microwave processed one. Again, Table II shows that microwave processing took less time to synthesize the sialon phases.

The 5 g pellet containing 40 wt% Al + 60 wt% $SiO_2$, could not be ignited, even after 30 min microwave running. The specimen with 10 g mass did ignite but the temperature could not be raised above 1200 °C after ignition. Thus, this pellet did not form sialon phases due to this low temperature. Compared with the previous work [6] in which 40 wt% Al + 60 wt% $Al_2O_3$ content pellet was easily heated, the reason why this 40 wt% Al + 60 wt% $SiO_2$ content pellet could not be heated is probably due to the differences in powder characteristics (especially powder size and surface area) and the differences in thermal conductivities among $SiO_2$, aluminium and $Al_2O_3$.

The 60 wt% Al + 40 wt% $SiO_2$ content pellet was ignited easily, and was nitrated at 1450 °C for 30 min. The compositions of the resultant phases were 15R-sialon > Si > β-sialon = $Al_2O_3$ > AlN as shown in Fig. 6c. This composition probably exceeded the solid solubility limit of β-sialon, so the resultant phases contained more aluminium rich phases.

## 4. Conclusions

1. Sialon phases were synthesized from natural silica–aluminium powder mixture within short processing time.

2. The Al–$SiO_2$ powder mixture was combustion synthesized, without cooling, and the products were subsequently synthesized into sialon phases under a nitrogen atmosphere in a domestic microwave oven, which a chemical furnace cannot provide.

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