Study of the oxidation and sintering behaviours of Al-Al₂O₃ powder mixture by using a home-style microwave oven

JEONG HYUN PARK, ZOU SAM AHN
Department of Ceramic Engineering, Yonsei University, Seodaemoon Gu, Seoul, Korea

By using a home-style microwave oven, Al–Al₂O₃ powder mixture could be heated and Al powder oxidized to convert the Al–Al₂O₃ powder mixture into an Al₂O₃ body and, subsequently, this Al₂O₃ body was sintered. The differences of powder characteristics which resulted from differently processed raw materials affected the oxidation behaviours, and these effects were more serious when a microwave oven was used than when a conventional furnace was used. Heating and oxidation mechanisms are discussed. Also the simultaneous oxidation and sintering of an Al–Al₂O₃ powder mixture were performed within 1 h by using microwave hybrid heating (MHH), which greatly reduced processing time and energy.

1. Introduction

Recently many studies have used microwaves in the area of material processing. In one instance a microwave oven was used to make a metal–ceramic composite [1, 2]. Metal is known to reflect microwaves, but since metal has finite conductivity, σ, microwaves can penetrate a metal to a depth known as the skin depth, δ, where the electric field falls to $1/e$ of its value at the surface. The skin depth is

$$\delta = [\rho/(\pi \mu f)]^{1/2} \qquad (1)$$

where

$$\mu = \mu_r \times \mu_o$$

where ρ is the resistivity of metal in $\Omega \, m^{-1}$, f is the frequency, μ is the permeability, μ_r is the relative permeability, and μ_o is the permeability of the vacuum. When metal is used, the surface area of metal powder is much larger than that of metal plate, where microwaves can penetrate. So these metal powders, mixed with ceramic powders, can be heated by microwaves.

Conventional ceramic sintering usually results in large shrinkage (15–20%), and this large shrinkage causes problems, e.g. fracture, the difficulty of predicting the final product size and the difficulty of forming a complicated shape. One of the processes to reduce this large shrinkage is the production of reaction bonded aluminium oxide (RBAO) [3, 4]. In this process it is possible to produce low shrinkage RBAO due to the fact that volume expansion of Al powder during oxidation in an Al–Al₂O₃ powder mixture, which has a good response to microwave heating, was oxidized in the home-style microwave oven and subsequently sintered to produce low shrinkage RBAO.

During the sintering procedure and the simultaneous oxidation and sintering procedure, a microwave hybrid heating (MHH) system was used [5]. MHH makes use of radiant–conduction heating to rapidly heat the sample through low temperature regions to a critical temperature, above which the microwave couples readily with the material. Here, SiC and zirconia were used to heat the specimen by radiation–conduction, and the SiC susceptor which was used in this experiment was plate instead of a bar [4] Fig. 1b. Since SiC has high thermal conductivity, an SiC plate can keep a uniform temperature inside the microwave cavity and greatly reduces the chance of thermal runaway of the zirconia susceptor.

In this work, the heating and oxidation mechanism, the effect of mass on specimen heating, the effect of differently processed starting powders on the oxidation and sintering behaviours, and simultaneous oxidation and sintering using MHH were studied.

2. Experimental procedure

Microwave processing experiments were carried out in air using a home-style microwave oven (Daewoo KOR111, 2.45 GHz, 650 W). Al₂O₃ powder used in this work was reagent grade (99.6 wt % purity, A-12, IKEI Co., Japan) and its average particle size was 16 μm and consisted of small Al₂O₃ grains (≈ 1 μm). Al powder was reagent grade (99.9 wt % purity, Junsei Chemical Co. Ltd, Japan) and had an average particle size of 23 μm and had flake shape. The volume percents of Al in Al–Al₂O₃ powder mixtures were 20, 35, 45, 50, 60 and 65, respectively. Fig. 2 shows scanning electron micrographs (SEM) of the starting powders. After weighing, three different Al–Al₂O₃ powder mixtures were prepared.
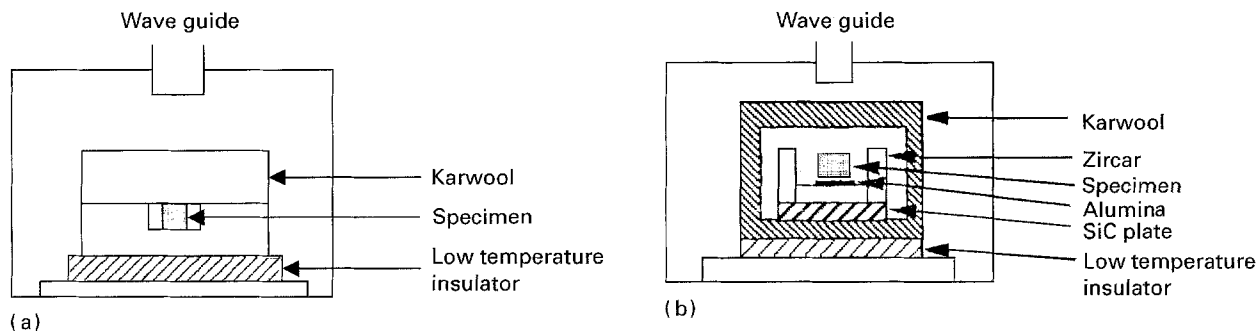
Figure 1 Schematic diagram of insulation box; (a) for oxidation experiment, and (b) for sintering experiment inside a home-style microwave oven.
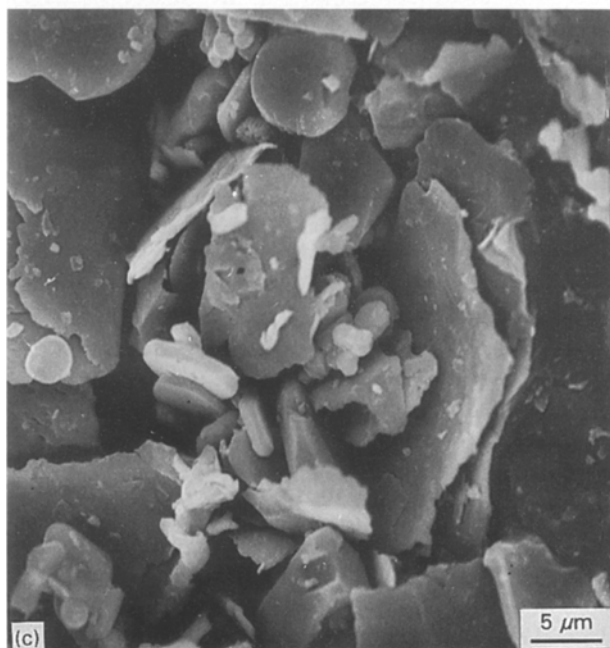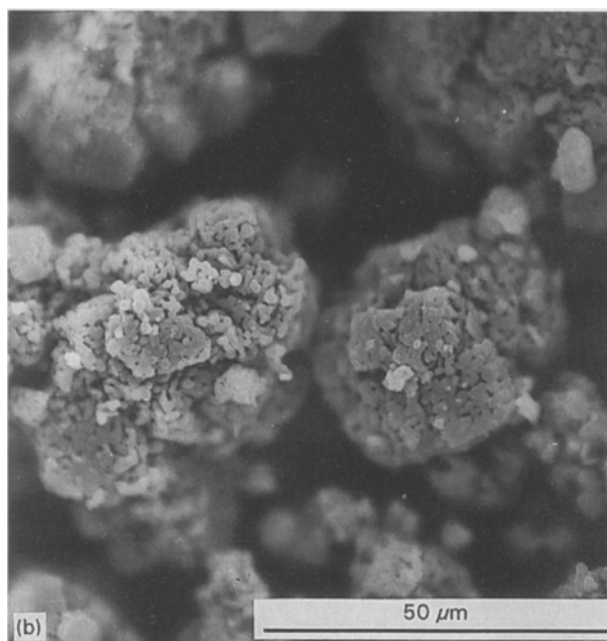

Figure 2 SEM photographs of starting materials: (a) Al powder, (b) A-12 Al_2O_3 powder, and (c) mixed and milled $Al-Al_2O_3$ powder mixture of 35 v/o Al content.

1. the first mixture was stirred with a magnetic bar for 3 h, and then mixed with a mortar and pestle for $1\frac{1}{2}$ h,

2. a second mixture was ball milled with an alumina ball media for 8 h and,

3. a third mixture was vibratory – milled for 1 h.

For most experiments the powder mixed with a mortar and pestle was used. In order to prevent hydration and oxidation, ethanol was used as a mixing solvent. After drying, powders were pressed into 2 or 4 g cylindrical pellets under $150\ kg\,cm^{-2}$ of pressure in a cylindrical die with 18 mm diameter.

For oxidation experiments, a low temperature insulation brick was placed on the bottom of the microwave cavity, above which a high temperature insulation brick was placed. A small hole which was a little larger than the size of specimen was drilled in the middle of the top surface of the insulation brick, and the sample was placed in this hole, Fig. 1a. One more insulation brick was placed as a cover. For the sintering experiment and the simultaneous·oxidation and sintering experiment, an SiC plate was placed as a heater on the high temperature insulation brick, and then zirconia fibre bricks (Zircar Products Inc., ZYZ-3) were placed as susceptors inside which the sample was placed. Both the zirconia brick and the SiC plate were covered by a high temperature insulation brick, Fig. 1b. The temperature was measured using an optical pyrometer (Minolta Camera Co., TR-630A)

through an 8 mm diameter hole in the middle of the front brick, whose size was sufficiently small to allow for a black body condition. The bulk density was measured using Archimedes' principle.

3. Results and discussion
3.1. Heating and oxidation behaviours, and the effect of mass

Since the solid state oxidation of Al is extremely slow under 200 °C, up to this temperature the specimen was heated only by surface ohmic currents on Al powder. Above this temperature, initially the contribution of the heat of Al oxidation to the temperature increment of the specimen was small. As the temperature of the specimen increased, the oxidation of Al increased and this heat of Al oxidation accelerated the temperature increment of the specimen. The surface ohmic current and the heat of Al oxidation heated the specimen to the critical temperature of Al_2O_3, so that eventually A-12 Al_2O_3 and the oxidized Al_2O_3 could absorb microwaves for heating to higher temperature. In this work control of the supplying voltage was needed to control the fast heating rate of the specimens. After oxidation procedure, more than 75 wt % of absolute oxidation of Al occurred within 40 min for the 50 vol % Al content specimen. This happened because microwaves heated only the Al powder selectively in the $Al-Al_2O_3$ powder mixture due to the surface ohmic current. Also, the fast heating rate of this system ($> 50\,°C\,min^{-1}$) increased the oxidation of Al. Therefore, the use of microwave energy could be an effective method for oxidizing metal powder in metal–ceramic composites.

Fig. 3 shows the regions of specimens with different Al contents and forming pressures which can be heated over 700 °C within 15 min by using a 650 W home-style microwave oven when sample masses were 2 and 4 g. The other specimens were not heated at all following 15 min microwave running. But, when the mass of the specimen was increased, for example for a 20 vol % Al content specimen with 10 g mass, the specimen was heated easily. Since the resistivity of the metal increases as temperature increases, and the specimen with higher mass for the same shape can store heat more effectively inside the specimen than the specimen with lower mass, the resistivity of metal powder increased more rapidly for higher mass specimen. This increment of resistivity deepened the skin depth so that a greater volume of metal powder could absorb microwaves according to Equation 1. Theoretically for one order difference of resistivity, the average size Al powder in this experiment has 80% more volume which can absorb microwaves.

When 50 vol % Al content specimen with 1 g mass was used as a substrate which heats up very rapidly and 20 vol % Al content specimen with 2 g mass which does not heat up at all was put over 1 g 50 vol % Al content specimen in a microwave oven, a 20 vol % Al content specimen heated up slowly from the bottom part to the top part of specimen. At this time since the temperature of the bottom part of the 20 vol % Al content specimen was below 800 °C, and below this temperature Al_2O_3 does not absorb
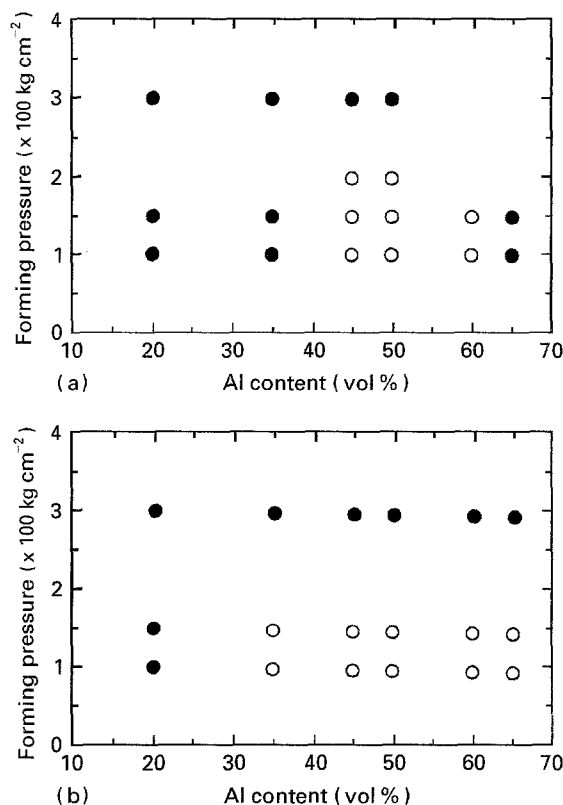

Figure 3 The regions of specimens with different Al contents and forming pressures which can be heated over 700 °C when the sample mass was (a) 2 g, and (b) 4 g: (O) can be heated, (●) cannot be heated.

microwaves, the only material which absorbed microwaves was the Al powder. Thus, the increased resistivity of Al powder due to conducted heat from the bottom layer and some contribution of the heat of solid state oxidation of Al raised the temperature of 20 vol % Al content specimen. This experiment shows that the resistivity of Al powder is the main absorption mechanism of microwaves in this system.

For specimens which contained more than 35 vol % Al content and were uniaxially pressed over more than $250\,kg\,cm^{-2}$, these were not heated, probably because the large flaky shaped Al powder particles may connect with one another to become large Al plates due to the forming pressure. But for specimens with lower Al content and high forming pressure, why these specimens were not heated cannot be explained.

3.2. The effect of particle size distribution, average particle size and shape on oxidation behaviour

Fig. 4a shows the microstructure of the vibratory milled powder. This SEM photograph shows that the particle size distribution is quite narrow. When 2 g of this vibratory milled powder was uniaxially pressed with $150\,kg\,cm^{-2}$ and this pellet was heated in a microwave cavity, oxidation occurred so violently that this pellet lost its original form. Also, when this pellet was heated conventionally at the heating rate of $4\,°C\,min^{-1}$ and was held for 30 min at 1400 °C, the surface of the specimen was so rough and the density was so low that the specimen was easily broken.
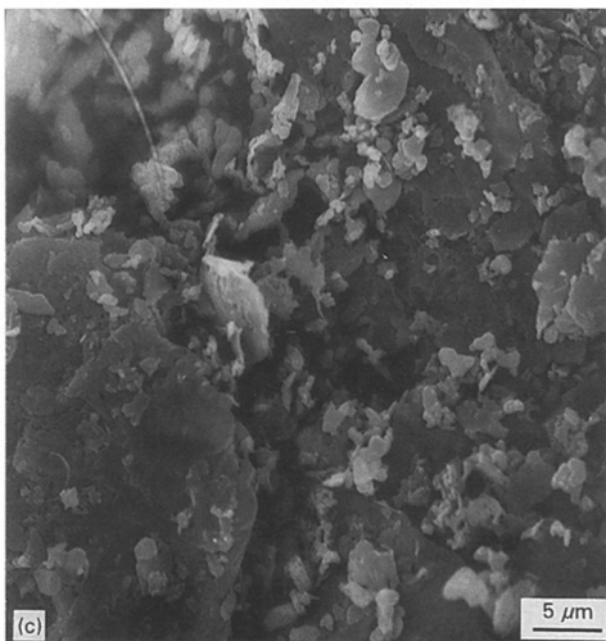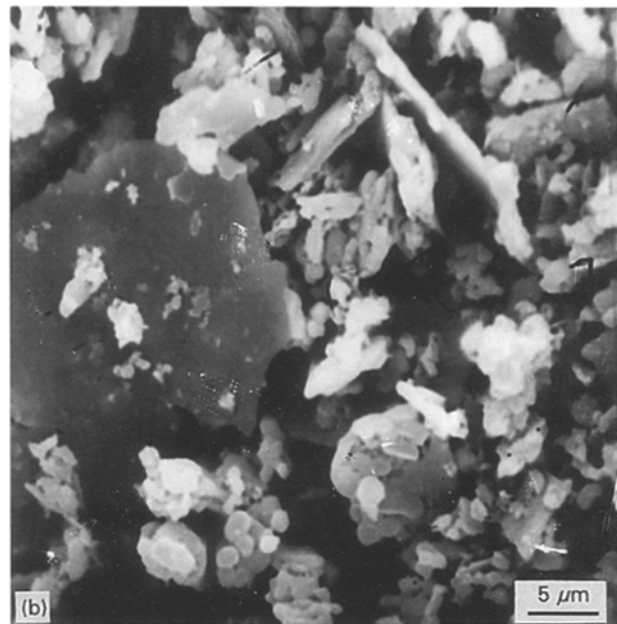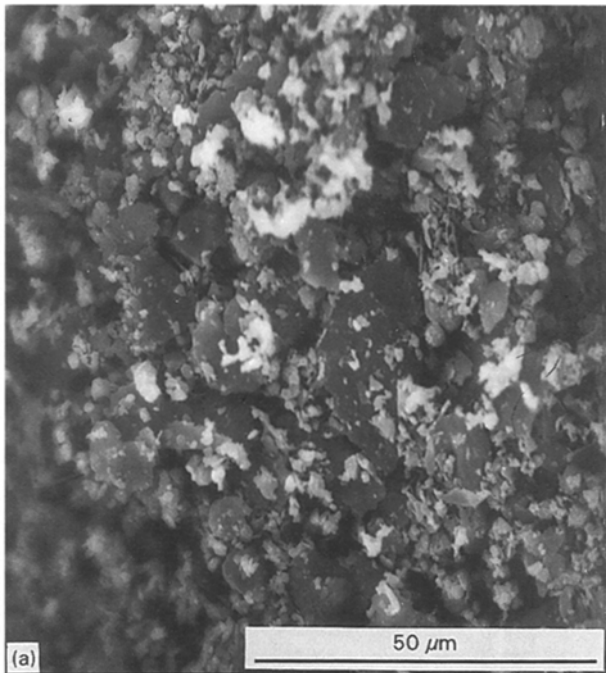
Figure 4 SEM photographs of (a) vibratory milled powder, (b) mixed powder with mortar and pestle, and (c) ball milled powder.

Ball milled powder has a wider particle size distribution than powder mixed with a mortar and pestle, Fig. 4c. Powder mixed with a mortar and pestle has a little larger particle size than ball milled powder, Fig. 4b. When this mortar and pestle mixed powder was uniaxially pressed, the pellet did not show cracks at all on the side wall of the specimen with a 30 mm height. But for the ball milled powder, the specimen showed several cracks on the side wall of the specimen only 3 mm high. When this pellet was oxidized in a conventional furnace, fewer cracks showed on the side wall of the specimen than when a microwave oven was used. Also, Fig. 5 shows differential thermal analysis (DTA) and thermogravimetric (TGA) results for three different powders which show different behaviours.

As was seen from the above examples, powder preparation processing is very critical for producing

RBAO using microwave energy. So, the particle size distribution and the average particle size of the starting powder play important roles in the oxidation and sintering behaviour of this RBAO system. These had more serious effects on oxidation behaviour in the microwave cavity than in the conventional furnace; since, depending on the particle size distribution and the average particle size of the starting powder, there are different microwave absorption volumes in the Al powder, and these different volumes, in turn, resulted in different heating rates, and the Al powder itself is a heating element in the microwave cavity.

The reason why the vibratory milled specimen showed violent oxidation can be explained as follows. For powder having a wide particle size distribution, small Al grains absorbed microwaves easily and oxidized to become Al_2O_3. Since these small oxidized Al_2O_3 grains had good sinterability, these made bonds with other grains. But for vibratory milled powders, which have the narrowest particle size distribution and the largest particle size among three differently processed powders, not many such small grains existed. Instead a lot of medium sized Al particles existed. At a certain temperature, which depends upon the heating rate, the Al_2O_3 scale of the Al surface was ruptured by volume expansion resulting from Al oxidation, the volume expansion of melted Al, Al vapour pressure inside surface Al_2O_3 scale, and the thermal expansion mismatch between melted Al and surface Al_2O_3 scale. The problem is that too many medium size Al powder particles simultaneously ruptured the surface Al_2O_3 scales, and a lot of melted Al spilled out from the ruptured surface Al_2O_3 scale, which increased the oxidation rate and produced large heat of Al oxidation. This large heat of Al oxidation, in turn, raised the temperature of the specimen so rapidly that
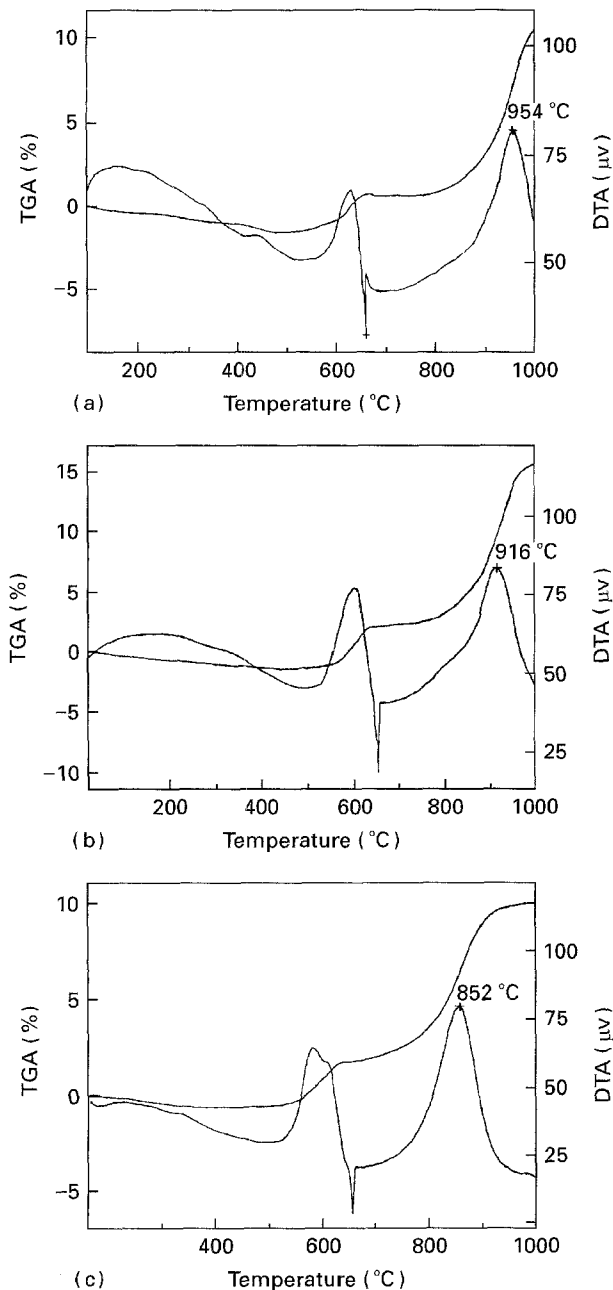
Figure 5 DTA and TGA curves for differently processed starting powders.

were found in the broken specimen. So, large size Al powders with spherical particles are not suitable for producing reaction bonded aluminium oxide in a microwave cavity.

3.3. Sintering using microwave hybrid heating

Fig. 6a shows the fractured surface of the oxidized specimen. Small Al_2O_3 grains which oxidized from Al powder are shown together with large A-12 Al_2O_3 grains. These small oxidized grains had such high reactivity that these grains started to grow at a lower sintering temperature compared with the original A-12 Al_2O_3 grains. Fig. 6b shows the fractured surface of a 4 g 35 vol % Al content specimen which was sintered at 1640 °C for 20 min; column structure was not observed [7]. This is because, during mixing with a mortar and pestle, the size of very large Al powder was so reduced by A-12 Al_2O_3 that such large Al powder which was the cause of column structure did not exist. This SEM photograph shows that these small oxidized grains grew to large grains and some of them bonded to A-12 Al_2O_3 grains and also A-12 Al_2O_3 grains grew into one another or with small Al_2O_3 grains. Since A-12 alumina is an agglomerate consisting of small size alumina and it was difficult to mix $Al-Al_2O_3$ powder mixture homogeneously, giving a peculiar particle size distribution and microstructure; many large open pores did not disappear after the sintering process. Also A-12 alumina was not made for densification purposes, so the density was not good. In order to produce a high density specimen, other submicrometre size alumina with a size reducing agent should be used. Porous alumina was 72% bulk density and 9% thickness change was made. The sintering procedure took 1 h, and the total processing time was less than 2 h.

the oxidation rate eventually accelerated, which resulted in violent oxidation in the microwave cavity.

It was not clear why only powder which was mixed with a mortar and pestle for $1\frac{1}{2}$ h could produce low shrinkage RBAO. But compared with ball milled powder which showed cracks on the side wall of the specimen and had a wider particle size distribution, the absence of very small size Al and/or large size Al might be the answer to this question.

The Al powder of spherical shape with an average particle size of 40 μm (Aldrich Co.) was also used in the $Al-Al_2O_3$ powder mixture. This mixture was heated up initially to emit red light, but 5 min later this mixture did not heated at all. Since, for the same particle size, the spherical shaped Al powder contains more Al content than the flake shape Al powder, this spherical Al powder spilled more melted Al, which eventually connected with one another to become a large Al piece. After the experiment, large Al sheets

3.4. Simultaneous oxidation and sintering using microwave hybrid heating

In order to reduce the thickness change, 35 v/o Al content powder was isopressed under 20 000 p.s.i. into 4 g cylindrical pellets. This specimen cannot be heated by itself at room temperature in a microwave cavity as was discussed in Fig. 3. But in the MHH system the specimen can be oxidized initially by SiC and zirconia susceptors and later can be sintered at a high temperature by absorbing microwaves. In order to see effect of microwaves on the oxidation behaviour, conventional fast heating experiment was performed under a similar heating schedule. Fig. 7 shows a comparison of the relative oxidation amount of 35 v/o Al specimen treated by MHH with that of the same composition specimen treated by conventional fast heating. From this figure, it can be seen that there is a microwave effect due to the surface ohmic current of Al powder. In the MHH system, the surface temperature of 35 v/o Al content specimen increased at the same heating rate as in the conventional fast heating. But in the MHH system, the temperature increment of Al powder brought about the increment
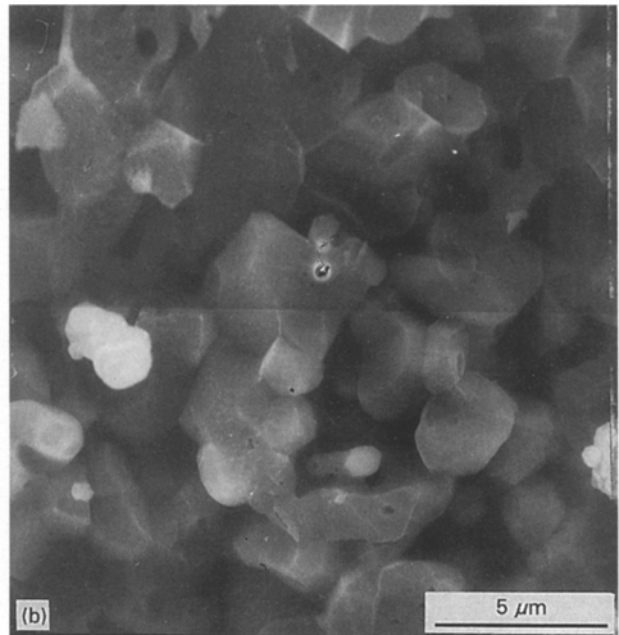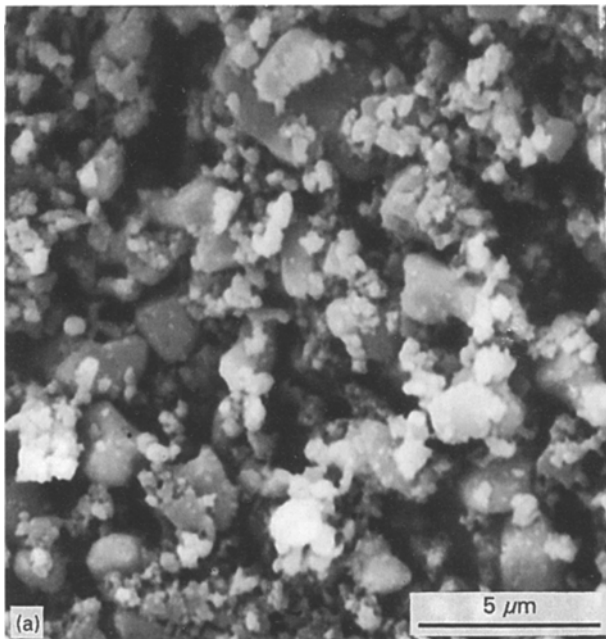
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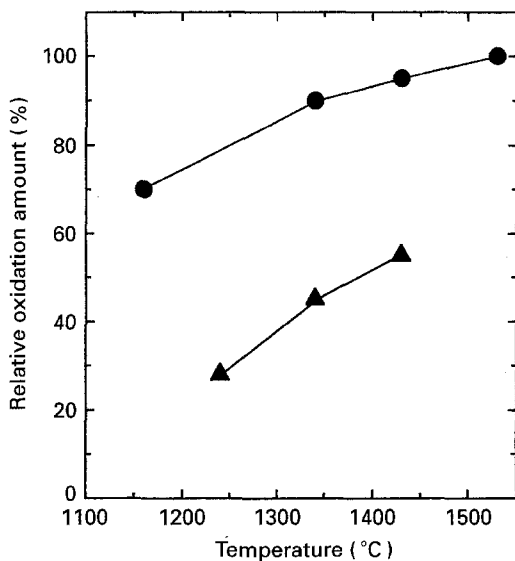*Figure 6* SEM photographs of the fractured surface of (a) oxidized specimen, and (b) sintered specimen.

Figure 7 Comparison of relative oxidation amount of 35 v/o Al content specimen treated by MHH (●) with that of the same composition specimen heated by conventional fast heating (▲).

of electrical resistence of Al powder, which increased the penetration depth as discussed earlier (mass effect). When the 35 v/o Al content specimen oxidized at 1340 °C was cut into halves with a diamond cutter, the specimen treated by MHH showed that the interior was almost oxidized (90 wt % oxidation occurred), but the specimen treated by conventional fast heating showed that only the surface layer was oxidized and the interior was not oxidized and showed a dark gray colour (50 wt % oxidation occurred). This means that for the 35 v/o Al specimen treated by MHH, microwaves penetrated deep inside the specimen and partly oxidized the interior. The total processing time, including oxidation and sintering experiment, was within 1 h. Again, it is shown that microwaves are a very effective method of oxidizing metal powder in metal–

ceramic composites. But for the 35 v/o Al content specimen which was isopressed under 30 000 p.s.i. and the specimen which was isopressed under 20 000 p.s.i., with more than 45 v/o Al content, oxidation took more than 4 h. This probably happened because the flake shaped Al grains connected with one another to form a large Al piece inside the specimen due to the high Al content and the high forming pressure, and premature pore closure near the surface was caused by fast heating in the MHH system. So there exists an optimum Al content and forming pressure of specimen, which can give fast oxidation and sintering.

Fig. 8a is an SEM photograph just on the surface of the 35 v/o Al specimen, which shows a little bit of the large oxidized Al_2O_3 grain. Fig. 8b shows extremely small newly oxidized Al_2O_3 grains in the surface layer, located 2–3 mm below the surface of the 35 v/o Al specimen. The differences in the amount of oxidation between the surface and the surface layer could happen due to fast heating in this MHH system, because the surface of the specimen was initially heated by radiation–convection heat from the SiC and zirconia susceptor. So oxidation started from the surface to inside the specimen.

Fig. 8c shows that a little of the larger oxidized Al_2O_3 grains grew with another oxidized Al_2O_3 grain, or large A-12 Al_2O_3, to become large grains at high temperature. More grain growth occurred from specimens sintered at 1620 °C, Fig. 8d, and the size of some oxidized grains were almost as large as that of A-12 Al_2O_3 grains. The specimen which was sintered at 1645 °C had 73% bulk density and − 4.5% thickness change.

4. Conclusions

1. In order to produce RBAO using microwave energy, powder preparation is a very critical process. Differences in starting powder preparations, i.e. differences of particle size distribution and average
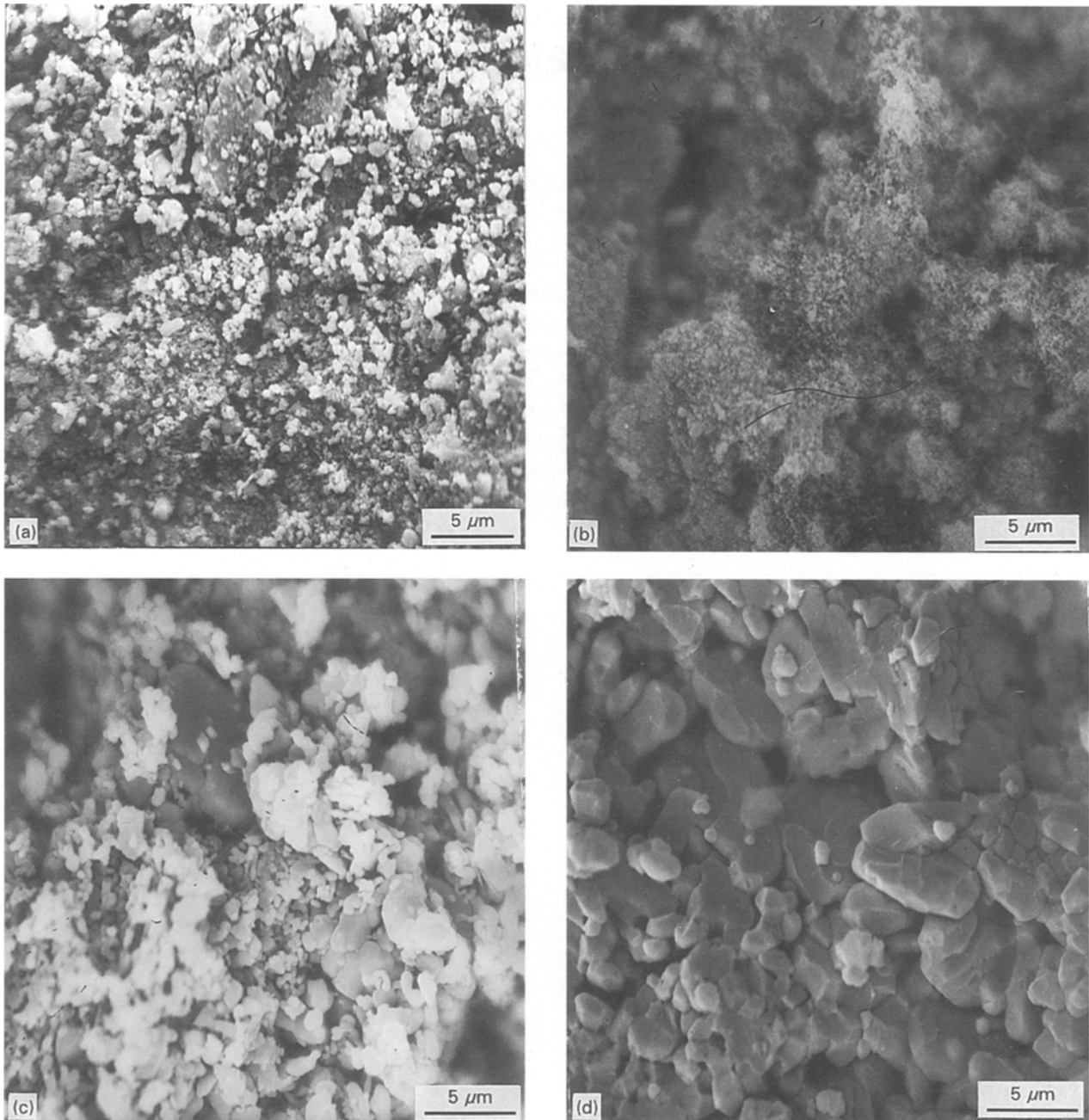
Figure 8 SEM photographs of fracture surface at different temperature for 35 v/o Al content specimen: (a) 1010 °C (on the surface), (b) 1010 °C (surface layer), (c) 1430 °C (surface layer), and (d) 1620 °C (surface layer).

particle size, have large effects on the oxidation and sintering behaviours. These effects are more serious when a microwave oven was used than when a conventional furnace was used.

2. A 35 Al–65 v/o Al_2O_3 powder mixture isopressed under 20 000 p.s.i. was oxidized and sintered within 1 h using a 650 W home-style microwave oven, which greatly reduced energy cost and processing time.

3. It was shown that microwaves are a very effective method for oxidizing Al powder in this metal–ceramic powder mixture. The specimen which was sintered at 1645 °C has a 73% bulk density and − 4.5% thickness change.

Acknowledgement

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